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ASSESSMENT OF WEAR RESISTANCE OF TIN AND TIN ALLOY COATINGS

A Thesis Submitted for Degree of Doctor of Philosophy

by

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ABSTRACT

Tin alloy coatings have traditionally been used as corrosion resistant barriers, due to their inert nature and comprehensive coverage, and have seldom been considered in physically demanding applications, such as wear resistant coatings, owing to misconceptions associated with the soft nature of tin metal.

The alloying of tin with copper has already been shown to significantly increase its mechanical properties, as demonstrated by the adoption of tin-copper alloys for use as bearing materials. Unfortunately, its cyanide plating technology makes tin-copper environmentally unsustainable, whilst the process requires constant regulation and monitoring, and there are disposal costs associated with the cyanide waste products. The tin-nickel alloy, however, can be produced with minimal supervision and its plating process uses less harmful precursors, making it an alternative consideration.

The research documented in this thesis assesses this increase by quantifying the resistance of tin, tin-nickel and tin-copper coatings to removal from sliding wear. As tin is a soft material and behaves dissimilarly to conventional coatings in a sliding wear environment, traditional wear assessment techniques are not appropriate. A novel approach is therefore devised and implemented, and this involves the continually monitoring the effect of damage introduced to the surface of the tin and tin alloy coatings, from an abrading ceramic ball. Using an elemental detection tool, it is possible to analyse wear scars that exhibit progressively depleted coating material, by identifying the underlying substrate material as it becomes exposed. In this way, it is possible to quantify the improvements made to tin from alloying with nickel and copper. The large volume of data acquired from this research is presented in a matrix format to enable simultaneous depiction of multiple parameters, and to allow quick and easy interpretation.

The tin-nickel coating is found to be comparable to tin-copper, in terms of resistance to removal. Despite tin-copper being slightly superior over the range of test conditions used, tin-nickel as been shown to be an environmentally friendly and cost effective alternative coating alloy to tin-copper.

CONTENTS

Page

CHAPTER ONE INTRODUCTION

CHAPTER TWO LITERATURE REVIEW

CHAPTER THREE PRE-TREATMENT OF SUBSTRATE MATERIAL

CHAPTER FOUR DEPOSITION OF TIN, TIN-COPPER AND TIN-NICKEL COATINGS

CHAPTER FIVE CHARACTERISATION OF TIN, TIN-COPPER AND TIN-NICKEL COATINGS

CHAPTER SIX FORMATION OF WEAR SCAR

CHAPTER SEVEN ANALYSIS OF WEAR SCAR

CHAPTER EIGHT DISCUSSION

CHAPTER NINE CONCLUSIONS AND FURTHER WORK

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CHAPTER ONE
INTRODUCTION

1.1 INTRODUCTION

Tin and tin alloys are already widely used in many applications, however, they have not traditionally been considered as wear resistant coating materials. owing to the physical properties of the metal. When compared with other materials, metals and alloys, tin is a soft and malleable metal [1] that is often dismissed as a candidate material for applications requiring hard and robust properties. Of the many tin alloys available, only bronze, which is an alloy of tin and copper, has been adopted for large scale industrial use as a bearing material [2].

The research documented in this thesis investigates the possibility of using tin-nickel coatings in an application not previously widely considered. The tin-nickel coatings are assessed alongside tin coatings, in order to show the difference in wear resistance resulting from the addition of nickel to tin. Tin-copper coatings are also assessed, since bronze has already been proven to be an effective material for wear resistant applications.

The three coatings are evaluated using a novel method, where the degree of coating removal is quantified based on the level of exposed underlying substrate material detected. By assessing tin-nickel alongside tin-copper as well as tin, using the new methodology, it is possible to form a uniform comparison between the three, and the appropriateness of tin-nickel as a wear resistant coating can be measured beside an industrially acceptable benchmark in tin-copper.

1.2 AIMS AND OBJECTIVES

Based on previous experience and research, the mechanical properties of tin, when alloyed with nickel and copper, are significantly augmented. The research documented in this thesis looks at the possibility of using tin-nickel coatings for wear resistance applications. The tin-copper coating, which is also looked at, is a derivation from the alloy bearing material traditionally used in industry. The testing of the two alloys, along with tin, allows the improvement in coating retention from alloy additions to be quantified. It is hoped that the tin-nickel coating performs comparably to the tin-copper coating, and, if this is proven, tin-nickel can be considered as a cost-effective and environmentally viable alternative to tin-copper, since tin-nickel can be easier and consistently produced in the required composition using a non-cyanide based plating bath.

In order to achieve this, the following systematic steps, each one comprising an objective, are taken:

Objective 1:
To prepare substrate coupons for the coating application by adopting an appropriate surface treatment, thereby promoting adhesion between the substrate and coating.

Objective 2:
To apply the tin and tin-alloy coatings to the substrate material, and ensure its uniformity and coverage by a series of characterisations.

Objective 3:
To design and implement a form of wear assessment that appraises the tin and tin-alloy coatings and yields a representative measure of the coating retention.

Objective 4:
To systematically review the performances of the coatings and account for any trends or discrepancies discovered.

1.3 OUTLINE AND LAYOUT OF THESIS

This Chapter introduces the research behind the consideration of tin-nickel coatings as an environmentally friendly and versatile alternative to tin-copper coatings for wear resistant applications. The presentation of this research in this thesis is provided in the form of a structured framework detailing the work conducted at each stage to achieve this end.

Chapter Two of the thesis provides a general literature review of research work carried out on tin and tin alloy coatings, their applications and uses. Reference is also made towards requirements of a wear resistant coating, and the use of tin-copper in bearing applications. This Chapter concludes by highlighting the lack of consideration made towards tin-based materials for wear resistant applications in general.

Prior to deposition of the tin and tin alloy coatings under consideration in this research, it is important to adequately prepare the surface of the substrate material in order to promote adhesion between the two materials. Both a physical and chemical route of achieving this, as well as a novel and quantitative method of determining their effectiveness, are described in Chapter Three

Chapter Four reports on the deposition of tin, tin-nickel and tin-copper coatings onto steel substrates using existing electrochemical methods. The optimum plating conditions, and relationship between plating time and thickness, are determined in order to produce deposits of pre-determined thicknesses.

Chapter Five describes the characterisation of the deposits, which is carried out in order to ensure uniformity in composition, coverage, appearance and thickness.

The methodology behind the combined use of a wear testing rig and Energy Dispersive X-ray analysis, to determine levels of exposed substrate material, is presented in Chapter Six.

Chapter Seven assesses the effectiveness of the three coatings in a sliding wear environment by examination of the wear scar and elemental analysis to quantitatively determine the coating removal.

The findings from the wear testing are discussed in Chapter Eight, and reference is made to certain factors that could influence the degree of coating retention.

The conclusions and further work are presented in Chapter Nine.

CHAPTER TWO

LITERATURE REVIEW

2.1 INTRODUCTION

Prior to describing the practical aspects of this research, it is important to, firstly, define the nature of the coating, and to appreciate its function; this is presented in Section 2.2. Common methods of applying a coating are discussed in Section 2.3. Next, the requirements of a wear resistant coating are examined in Section 2.4 by discussing the existing coatings available for the application, and the current techniques by which the wear resistance property of the coating material is derived. Section 2.5 presents some background information about the intended coating material, tin-nickel, and provides the impetus behind its preference over tin-copper in this research. The Chapter is concluded by a brief summary.

2.2 THE COATING

2.2.1 Purpose of Coatings

A coating can be considered to be a layer of material that has been deposited onto another material. There are many different reasons for applying a coating, most commonly for protective and decorative purposes [1, 3].

Protective coatings

Protective coatings afford a physical barrier to the underlying material from a range of different environments, for example:

- Chemical attack or deterioration such as oxidation, e.g., galvanising of steel with zinc;
- Mechanical damage, e.g., scratch and wear resistant coatings, which are discussed in more detail in Section 2.4;

- Extreme temperatures, e.g., ceramic coatings for protecting metal substrates from heat, and cryogenic jackets for insulating polymers from liquid nitrogen.

Decorative coatings

The coating could also be applied for decorative purposes, usually providing a brighter finish than or a different colour to the original uncoated material. The decorative coating material, therefore, needs to meet the surface requirements of the application, rather than certain mechanical or chemical properties, as in the protective coating. A particular material will appear matte in appearance if its surface topography is rough and uneven. If it is not feasible or practical to modify this surface, consideration could be made to coating with a material that has a smoother surface, which yields a brighter finish. Examples of this are in cutlery and jewellery, where a semi-precious metal, e.g., silver, is applied onto a material such as stainless steel or copper.

Other coatings

Whilst most coatings are applied for protective and decorative purposes, some coatings are applied with other intentions in mind. Some examples are provided below:

1. *Solderable Coatings*. A widely used method of joining two materials together is by soldering, however, the success of a particular joint is strongly dependent on the wetting characteristics and affinity between the solder and materials being soldered. Materials have differing degrees of solderability and solderable coatings are applied to component leads and board pads to promote this, a particular example is the coating of tin onto nickel-iron terminations [4].
2. *Barrier Coatings*. An example is the nickel interlay used in electronic circuit boards to hinder the migration of zinc. Brass, an alloy of zinc and copper, is often used as electrical contact material, due to its good conductivity, and is commonly coated with copper to promote the soldering process. The zinc in the brass readily migrates through the copper coating to the solderable surface, however, zinc is susceptible to oxidation and the presence of its oxides at this surface can have adverse effects on the wettability of the solder to the copper, and, hence, the solder joint. As a result, the nickel interlay is applied between the brass and copper to impair the zinc migration [4].

3. *Conductive Coatings.* An example is the sputtering of gold onto non-conductive samples for scanning electron microscopy (SEM). Samples for viewing with SEM need to be conductive, since an electron beam is used for the analysis and a conductive pathway away from the observation point is required for the electrons. Not all samples are conductive, and specimens that have been sectioned in a resin or are biological, are often coated with a gold or carbon film [5].
4. *Biologically Compatible Coatings.* In the same way that solderable coatings are applied to assist the wetting interaction between the solder and the artefact being soldered, hydroxyapatite coatings are applied to titanium-aluminium-vanadium alloys to promote the acceptability of metallic implants within the human body [6] and polycrystalline calcium titanate films are grown onto titanium-based substrates in order to promote their biocompatibility [7].

2.2.2 Tin and tin alloy coatings

Tin metal has played a significant historical part in the development of the human race, most notably in the form of bronze, when it is alloyed with copper [1, 2, 8].

Tin is found naturally in the form of its oxide ore, cassiterite, and tin producing countries in mostly located in South-East Asia, namely Malaysia, Thailand and Indonesia. Other major tin producers are Nigeria and Bolivia, and, in recent years, Brazil and China have also emerged [1, 3, 8].

As a metal bulk, tin has moderately few uses, compared with, e.g., iron and aluminium, because of its physically soft property, low melting point and relatively high price. Instead, tin is widely used as a coating material, where its thermal and mechanical limitations are less apparent [3, 8].

Tin and tin alloy coating materials have been frequently exploited for centuries. One reason for their early consideration is the low melting point of tin, which could be achieved without modern furnace technology. Previously, the use of tin and tin alloy coatings were restricted to decorative, however, a better understanding of their properties has meant that these materials could be considered for broader uses. Some more modern applications for tin and tin alloy coatings include corrosion resistant coatings and solderable finishes [3, 4, 8].

Tin is used often as a coating applied onto steel, e.g., as tinplate for food packaging, where it acts as a barrier for the steel from corrosion that would otherwise result from contact with the can contents [9], by offering comprehensive coverage and chemical inertness. Another important application is in the electronics industry, where tin has historically been used as the main constituent of solder and solderable coatings, which are applied to electronic board and component finishes to promote the wetting of solder [4, 8]. The advent of the lead-free legislation has meant that the traditional Sn63Pb solder is being replaced by solders with an even higher tin content, some of which (e.g., SnAg and SnAgCu) contain >90weight % tin [10, 11].

Tinplate and electrical finishes are by far the most significant applications for electrotinning due to the versatility of this coating technique, e.g., degree of control over the coating thickness and uniformity in the deposit characteristics. Uses of tin in packaging and electronics industry comprise around 70 percent of the tin usage market. Other uses of tin and tin alloys include decorative or corrosion resistant coatings [1, 3, 8].

Tin coatings can be deposited using either alkaline or acidic electrolytes, and is considered to be one of the easiest metals to be electrodeposited [3, 8, 12, 13]. There are, however, disadvantages to electro-plating in general including the relatively long plating times and the use of materials that are potentially toxic and corrosive. These disadvantages, together with the susceptibility of tin whiskers forming from electrotinned samples, ensure that other tin coating techniques, e.g., hot-tinning, have not been rendered obsolete.

Despite the misconception associating tin and its alloys with weak and soft properties, tin, when alloyed with certain other metals, in the correct proportions, can produce alloys that are significantly harder than tin metal. One such example is tin-copper, which is considered sufficient for use as a common bearing material in industry [2].

2.3 APPLICATION OF TIN AND TIN ALLOY COATINGS

2.3.1 Common Techniques for Applying Metal and Alloy Coatings

There are many different techniques available for coating one material onto another, and the choice is dependent on the nature of the materials under consideration and the application of the final coated material.

Given the diverse range of coating techniques available, nearly any material, even those that are chemically incompatible, can be coated onto another, for example, the coating of nickel-phosphorus and copper coatings onto polymers [14] or application of a polymeric coating onto metallic materials such as polythiophene on zinc alloys [15], ceramic oxide coatings on vanadium alloys [16, 17] and zirconium oxide-nickel composite coatings on stainless steel plates [18].

Regardless of the coating technique, it is always important that, prior to coating deposition, all substrates undergo pre-treatment processes. The objective of these measures is to promote adhesion of the coating by removing surface contamination from the substrate and increasing the available surface area for the coating to adhere to. A study is presented in Chapter Three, where chemical and physical pre-treatment steps are investigated.

Examples of common techniques used in industry for applying coatings of metals and alloys follow, however, electroplating and hot-dipping have been omitted. Since these two techniques have been traditionally used for applying coatings of tin and its alloys, they are presented in further depth in a following section.

Electroless Plating

Electroless deposition is similar to electroplating in that both techniques involve the generation of the coating material from an aqueous solution by reduction of ions.

With electroless plating, however, although the cation reduction is promoted by an agent within the bath, a catalyst is required to initiate the plating process. The component intended for plating upon acts as the catalyst, and the coating is grown from its surface.

Electrons required for the reduction process are provided by either the substrate metal or by the reducing agent in the plating bath, and are accepted by the ions of the coating material. As a result, no external electrical current is required for this coating technique.

Physical Vapour Deposition (PVD)

PVD is a vapourisation coating technique and involves the atomisation of a coating material before its deposition onto the substrate material. The process takes place under low-pressure conditions, in a chamber into which an ionised gas is bled. An electrical current is passed through this gas causing its high-energy ions to bombard a cathode "target" of the coating material. Atoms of this coating material are then dislodged from the surface, vapourised and then deposited onto the intended substrate. Some PVD coatings are in the order of sub-micron, typically producing oxide films of 150-450nm thick [19].

Chemical Vapour Deposition (CVD)

CVD and PVD both involve deposition from a vapour, however, unlike PVD, where the raw materials are in solid form, CVD involves the use of precursors in the gaseous state and is a collective name for the deposition of a solid coating from a gaseous phase. The precursors are used to generate the species to be coated and are passed over the substrate via an inert carrier gas.

Thermal Spraying

Thermal spraying is a technique that involves the combination of heat and velocity, where the coating is produced by the impact of particles onto the substrate. The particles, of the material being coated, are usually, either, in the molten state, or thermally softened. As thermal spraying is a line-of-sight technique, there are restrictions in the number of applications it can be used for.

Nickel-aluminium coatings are applied to steel by thermal spraying to afford protection against carburization, where the carbon content of a steel is increased because of interactions with the environment at elevated temperatures. This is important since the carbon content can greatly influence the mechanical properties of the steel, and a concentration of carbon at the surface results in the formation of a very brittle top layer [20].

Laser Cladding

Laser cladding uses a carbon dioxide or Ni:YAG laser to deposit a coating of a material onto a substrate by introducing an inert gas, such as argon, and the powder form of the coating material, into the laser. This results in the powder material being melted and applied onto the substrate material. In this way, multiple layers can be built up, although care must to taken to control various parameters of the laser cladding process, e.g. a too high beam energy would result in excessive alloying of the coating and substrate materials, leading to difficulty in subsequent layer build up, whilst insufficient energy would result in the incomplete melting of the metal powder and therefore poor wetting and adhesion between the coating and substrate. [21].

2.3.2 Deposition of Tin and Tin Alloy Coatings

A number of techniques can be employed to deposit hard wear resistant coatings, e.g, Chemical Vapour Deposition (CVD), Physical Vapour Deposition (PVD) and thermal spraying [22]. The main problem with some of these techniques is the high temperatures employed, which can result in mismatches in Coefficients of Thermal Expansions (CTEs) and, subsequent crack propagation at the coating-substrate interface.

The method of deposition of a coating material is often determined by the material itself, as well as other issues such as cost. As tin and tin alloy coatings are investigated in this research, traditional techniques employed for applying these are considered and the two main ones, electroplating and hot-dipping, are presented below.

Electroplating

Electroplating can be defined as an operation involving the deposition of a coating upon a substrate electrode by electrolysis, to produce a surface with properties different from those of the substrate material. The technique is one of the most common ways of applying a coating, and involves the transfer of electrons from one electrode to another, making it possible to gradually build up the coating material on the cathode substrate as the material of the anode is depleted.

A typical electrochemical set-up in Figure 2.1.

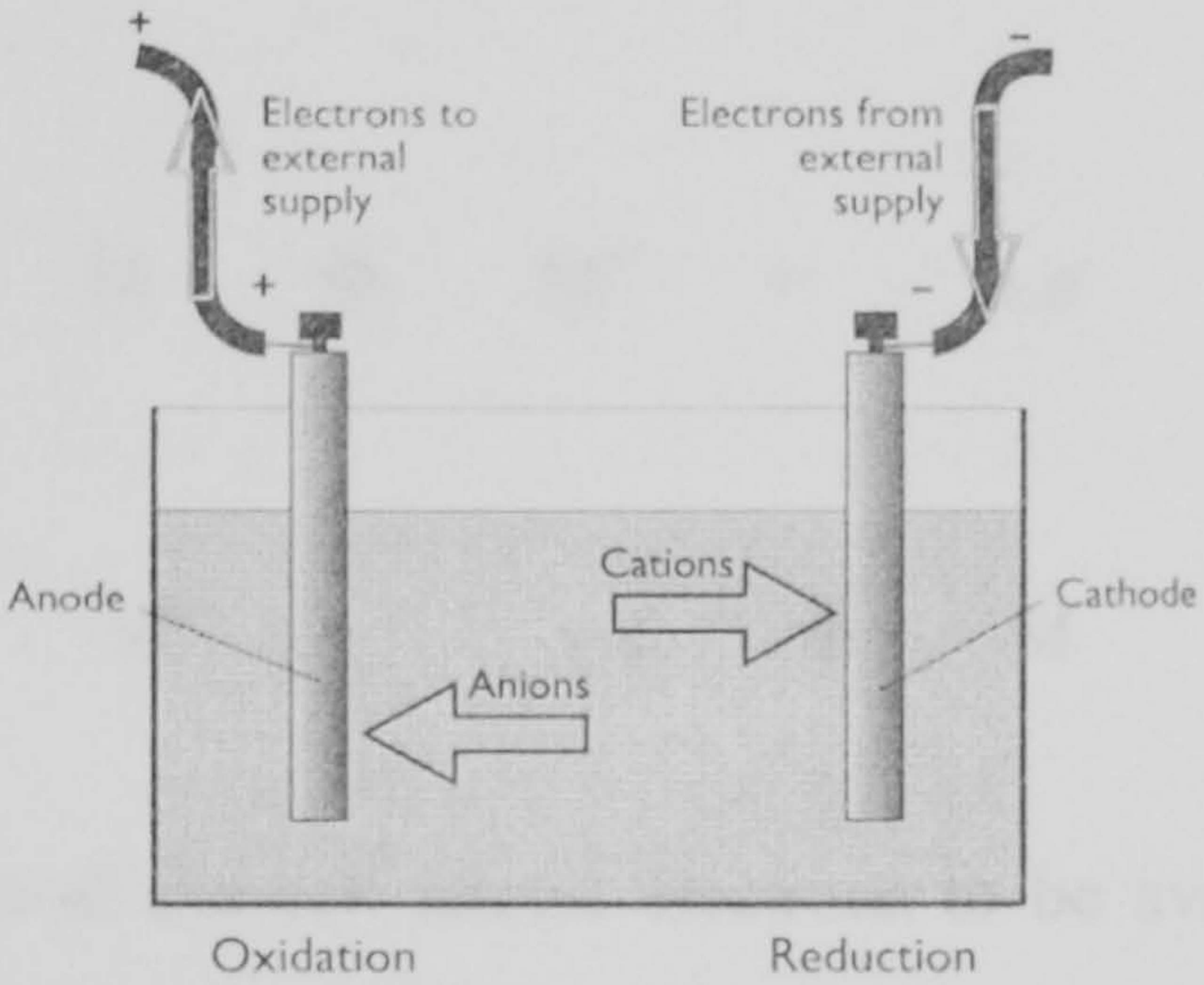

Figure 2.1 Diagram showing flow of electrons and ions in an electrochemical cell [25]

There are several advantages to this method of coating application [23, 24]:

- There is no intermetallic compound formed at the interface between the coating and substrate materials. This intermetallic material is a brittle layer, which can be formed from high temperature process like soldering and hot dipping, that is often considered the weakest part of the coating adhesion, with soldering failures mostly occurring at this zone.
- A uniform structure is produced which can be custom developed through additions to the plating solution, e.g., grain refiners for modifying the grain structure.
- The thickness of the deposited coating material can be easily controlled owing to its linear relationship with coating time, allowing the mass production of coatings of a set thickness consistently.

- Metals with a high melting point can be applied using this method. It is difficult for metals such as nickel, copper and chromium to be coating via hot-dipping.

In theory, deposition occurs when metal atoms leave the anode and lose electrons, becoming M^{+x} (Equation 2.1a), where M corresponds to the metal and x to the number of electrons lost. These positively charged cations are attracted to the negatively charged cathode where they gain electrons and are restored to the metallic state (Equation 2.1b) [8].

Equation 2.1a

$$M \rightarrow M^{x+} + x.e^{-}$$

Equation 2.1b

$$M^{x+} + x.e^{-} \rightarrow M$$

The potential difference of the cell allows electrons to be available at the cathode, giving this electrode a negative charge, whilst the positively charged anode loses electrons when they are released from the metal surface.

The rate at which the cathode and anode gain and lose electrons, respectively, are not strictly related since they are independent reactions. They can, however, influence one another when, for example, the anode reaction proceeds at a faster rate than the cathode reaction, resulting in a surplus of electrons at the anode. In this event, the surplus electrons force the anode potential in a negative direction slowing down the anode reaction. At the same time, the cathode potential is also shifted in a negative direction, which encourages the cathode reaction to speed up. The change in rate of the two electrode reactions in this particular example thus becomes equalised. In this case, dissolution of a metal ion at the anode therefore occurs together with deposition of the metal ion at the cathode, whilst the electrolyte remains unchanged [13], however, the coating constituents can also be generated from the electrolyte.

Hot-dipping

Hot-dipping is generally reserved for coating with low melting point metals such as lead, tin and zinc. The technique involves contact between the substrate and molten tin, and depends largely on the wetting ability of the liquid metal. The wetting ability is determined by the contact angle between the tin and the substrate material – a small contact angle denotes good wetting, shown in the following diagram (Figure 2.2):

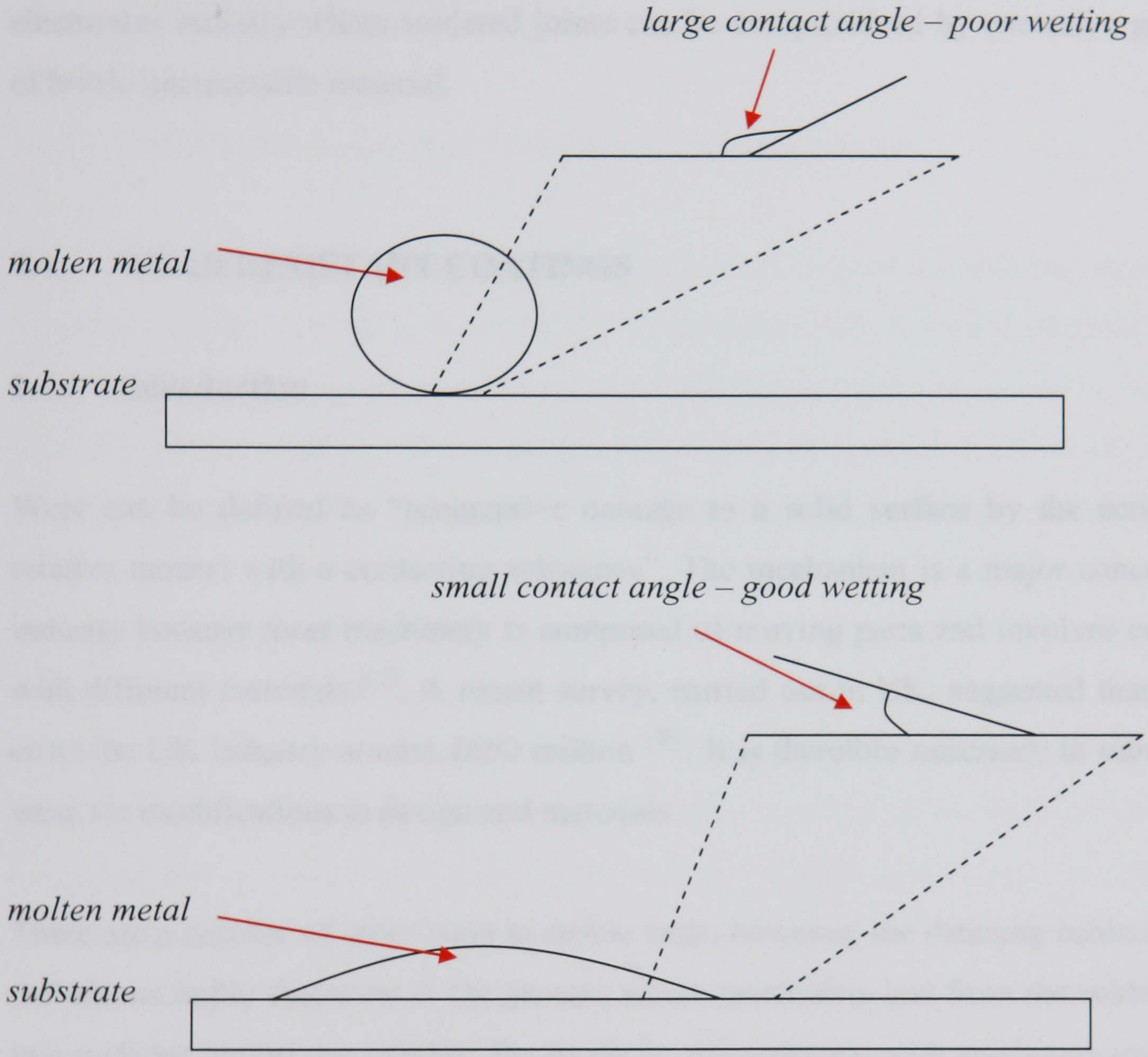

Figure 2.2 – Diagrams of poor and good wetting profiles

For successful hot-dipping, there must be good affinity between the substrate material and the molten metal, and wetting must be relatively quick. Much of this is dependant on adequate substrate preparation which could include chemically pickling and cleaning the substrate to remove surface oxides.

Although hot-dipping is a simple and effective way of coating low melting point metals and alloys, the thickness of the coatings produced with this method is difficult to control. Often, the coating is the thinnest where the sample is first removed from the molten bath, and thickest at the point where the sample is extracted last from the bath, as this is where the molten coating often collects, due to gravitational flow, and solidifies.

Another limitation of hot-dipping is the potential for intermetallic compounds to form at the interface between the coating and substrate. This is of particular concern in the electronics industry where soldered joints can be compromised by excessive growth of brittle intermetallic material.

2.4 WEAR RESISTANT COATINGS

2.4.1 Introduction

Wear can be defined as "progressive damage to a solid surface by the action of relative motion with a contacting substance". The mechanism is a major concern to industry because most machinery is composed of moving parts and involves contact with different materials [22]. A recent survey, carried out in UK, suggested that wear costs the UK industry around £650 million [26]. It is therefore necessary to minimise wear via modifications in design and materials.

There are a number of other ways to define wear, however, the meaning behind most definitions imply that wear is the process where material is lost from the rubbing of two surfaces against one another. For example, moving parts with machinery involves the rubbing between component surfaces, and some form of material loss, however small, is inevitable. Many of these surfaces bear large loads over a small area, and the integrity of the materials at the interacting surfaces is critical to in service operation [22].

An external load that is applied to a material usually results in, either, the material deforming at the surface and near-surface regions, or crack propagation at voids or hairline cracks within the material bulk, resulting in fracture. The effects of both these responses therefore need to be minimised in order to avoid loss in functionality and energy. A secondary consequence of wear is the adverse effect of the debris, generated from the phenomenon, on lubricated or hydro-transport systems [22].

Wear is often associated with friction, however, the relationship between the two is not yet fully understood, and misconceptions, such as, low friction implying low wear and vice versa, are often erroneously assumed [22]. It is important to clarify this at the onset, especially for this research, where relatively soft tin and tin alloy coatings are being assessed, and a high wear rate is expected to result from low friction.

2.4.2 Considerations for Wear Resistant Coating Selection

Since wear is primarily confined to the surface, it is understood that the wear of a particular artefact can be reduced by the introduction of a different material at its surface. History has shown that Romans modified the composition of iron by surface hardening, where carbon from heated bone is diffused into the metal bulk, whilst Vikings incorporated stones onto the edges of their ploughs to resist soil abrasion [22].

A wear resistant material should be sufficiently strong and have a high compressive strength so that the material is not deformed or squeezed out by in-service loads. At the same time, the material should be sufficiently plastic to deform adequately to allow the material tolerance to shock and vibration. In addition, the material needs to be resistant to cracking whilst being able to function adequately under the intended service conditions, e.g. operating temperature, which could influence the mechanical properties of the materials in question. A successful coating generally has a long service life since it is often more expensive to shut-down machinery to replace the part than the cost of re-coating the material [27].

Surface engineering is the study of modifying surface properties of a material, and can be divided into three categories:

1. Application of a separate material as a coating onto the surface of the original material. In this case, there is a defined interface between the coating and substrate materials.

2. Modification of the material surface where a localised compositional change is experienced, e.g., the introduction and diffusion of carbon into iron. Unlike the coating principle above. there is a less well defined interface in this case.
3. Modification of the material surface without changing the composition of the original material, but rather the phase.

As this research is committed to investigating tin and its alloys, the first principle, coating, will be explored. Furthermore, tin is seldom employed as the bulk material for engineering components, therefore consideration will not be made to modifying the surface of tin to improve its wear resistance.

In order for a coating to be successful, it must provide adequate coverage to isolate the substrate from the contact material, and at the same time, exhibit resistance to removal from contact with the foreign material. The substrate, for its part, must be sufficiently robust to support the coating material. The coating and substrate materials should also have a good degree of affinity towards each other, in order for good adhesion between the two, and to prevent in-service removal of the coating via interfacial cracking [22].

The substrate is extremely important as, without it, the coating cannot support any significant load. The substrate confers structural strength on two fronts; it prevents the load bearing coating from flexure under loading and provides lateral support by absorbing tensile and compressive stresses. In order for the substrate to succeed, it is imperative that its bond with the coating is sufficiently sound. Should this bond fail, not only is the effective strength of the coating compromised, heat conduction is impaired. Poor adhesion between the coating and substrate is the most common cause of failures. Ideally the bond should be both strong and continuous. The coating material therefore needs to be applied to a sufficiently cleaned substrate, and this is typically achieved via a combination of shot-blasting, degreasing and pickling.

Another important issue is the thermal expansion of the coating and substrate, especially if the component is being used in a high temperature application. If there are mismatches in the coefficients of thermal expansion between the materials, the coating could delaminate [22]. This is particularly critical when considering the coating technique, as some methods of applying the deposits involve very high temperatures, e.g., CVD and thermal spray. There have been instances after coating where, on cooling back to room temperature, the coating has delaminated due to the contrasting thermal expansion properties.

The consideration of tin and tin alloys in this research would eliminate any high temperature application for the coatings, since the melting point of tin is relatively low. There are advantages, however, for applying a metallic coating, rather than a ceramic coating, over steel:

- The coefficients of thermal expansion for metals and alloys are generally closer to one another than those of ceramics and metals/alloys
- Ceramics are relatively brittle materials and delamination of ceramic coatings has often been attributed to flaws within the ceramic rather than interfacial failure.

2.4.3 Wear Reduction through Lubrication

The concept of lubrication dates back to historical times, e.g., the use of animal fat for early wheel axles around 3,400 years ago [2]. In an environment involving sliding surfaces, reduction of wear results from the presence of a fluid lubricant film that separates the two surfaces. This fluid film lubrication is not always continuously maintained due to factors such as overloading, dislodged particles and irregularities in the surface, which are all inevitable, and contact between the metal surfaces needs to be anticipated. As a result, the surface coating needs to reduce this degree of unavoidable wear. It soon became common understanding that wear between the surfaces could be reduced if they were composed of different materials. Sliding experiments with different metals were carried out and it was discovered that the greatest damage resulted from contact between materials with similar hardness properties. The main reasons are that, on contact without lubrication, local welds could form and the hardness of these welds is usually higher than that of the "parent" materials in question, and this can result in scoring on the coating and substrate. With surfaces of different hardnesses, the damage is usually restricted to the softer material.

A load-bearing coating material would ideally be able to retain a lubricant so that the continuity of the film is maintained between the two surfaces. Although tin and tin alloys are not reported to have low coefficients of friction, it is understood that the chemical nature of tin permits a degree of adhesion with lubricants which compensates for this low value. A lubricating environment allows the build up of a fluid film that imparts load carrying properties [2].

2.4.4 Tin-copper as a wear resistant coating

Soft metals and alloys were initially considered as bearing materials and chariots from the second century AD were understood to have used bronze rings to line the hubs of their wheels. Before 1500 AD, Leonardo da Vinci made reference to the use of antifriction metal that was composed of Cu70Sn30 [2].

Many materials used for bearing applications are based around the softer metals, such as tin and lead, due to the superior ability to embed foreign particles they offer, as a result of their soft properties [28, 29, 30]. By the 20th Century, load-bearing material was being manufactured that consisted of a 50 micron coating of a SnSbCu alloy (also known as "whitemetal") on steel [28]. Around the same time, alloys of SnCuPb and SnAl were also used. In some of these alloys, it was found that, depending on application and requirements, certain properties could be adjusted by the trace additions of elements such as Ni, As, Cd, Cr, In and Be.

The increase in copper content augments the hardness and tensile strength of the alloy, however, this is offset by loss in ductility. In general, the SnCu bronze alloys are still considered the ideal candidate of material family for use in high load applications, and they have a high strength and wear resistance, along with good corrosion resistance [2].

There are, however, environmental implications to using tin and lead based bearing materials. Many of the constituent parts of tin-copper alloys typically contain substances that are hazardous or toxic. For environmental reasons, the lead family of bearing materials is no longer considered [30], whilst several of the tin based bearing alloys contain antimony, which is toxic.

Whilst the use of bulk soft metals and alloys were adequate for simple machinery, the technology developed after the industrial revolution was accompanied by a different level of in service requirements [30]. The soft alloys were found to be squeezed out between the greater forces and loads. This led to the idea of supporting these alloys on stronger backing materials, where the substrate material would confer the integrity of the part, whilst the alloy would address the contact and interaction that was being confined to the surface of the part. The requirement of the bearing material hence became associated with the properties at the surface. Whilst strength is clearly necessary for supporting the loads, the main strength would come from the backing material. The coating should provide protection to the substrate material [2].

The alloy coating must also be inert to the lubricant, since corrosion has been shown to take result in roughening of the surface. For alloys, the preferential attack of a particular phase could lead to overall weakening and deterioration, resulting in compromise in wear resistance. Previous research has already reported on the corrosion resistant properties of tin-copper [31, 32, 33, 34].

2.4.5 Methods for Assessing Wear

There are a number of documented ways that wear resistant coatings can be assessed, for example, pull-off and four-point bend tests [22]:

- The pull-off test involves the measuring force taken to pull away a stud that has been fixed to a coating via an adhesive. It is important that the pulling force is perpendicular to the sample, as any angular deviation would induce a peeling effect. It is not possible to use this test for coatings which have a greater adhesion than the adhesive, since, in these cases, failure would occur within the adhesive and the force measured would be the strength of the adhesive [22].
- The coating adhesion can also be assessed by bending of the substrate-coating assembly to a pre-determined angle in order to promote spalling and cracking of the coating [22].

At the same time, wear is also recognised to be dependant on factors such as temperature, lubricant, and many machines designed for wear testing can yield misleading results unless the materials' properties are all taken into account and the testing is extended over a wide series of tests [2].

It is reported that there are over 300 other different methods for assessing wear resistant coatings, and it is important to use the most appropriate ones for the material in mind [22]. For example, a technique involving thermal treatment, such as those designed to investigate mismatches in thermal expansion coefficients, would be inappropriate for tin and tin alloy deposits.

It is not easy to design a test rig to simulate the exact conditions that a coating undergoes in service. Many of the conditions are inter-related, for example, the thickness of the film between the two surfaces could influence the operating temperature and thus the anticipated lifetime and ability to withstand and carry the load. Failure of the material is usually a slow and gradual process, and seldom sudden. Whilst this can be advantageous, it does, however, mean that detection of the deterioration is difficult [2].

With so many different influences, coupled with microstructural changes in the materials in contact, it is little surprise that a reliable universal wear equation does not exist [35].

It is decided that the testing in this research should introduce a form of damage to the coating material that is representative of in-service wear, and this is elaborated on in further detail in the Chapter Six.

2.5 TIN-NICKEL

The research is committed to investigating tin and tin alloy coatings, and there are a number of tin alloys available for consideration. It is clearly impossible to assess all the main tin alloy systems, due to a number of reasons, such as time constraints and costs, however, environmental implications appear to eliminate many of the major alloys, such as tin-lead, tin-cadmium, tin-antimony and tin-bismuth. A brief appraisal of tin-nickel coatings follows.

Tin-nickel coatings are typically deposited at a Sn65Ni composition, which corresponds to the ratio of the SnNi intermetallic compound. The composition of the tin-nickel appears to remain at this constant ratio regardless of changes to the plating conditions, which negates tedious optimisation of the operating parameters [3, 8].

This alloy is reported to have a significantly higher hardness than tin and good corrosion resistance, which come from the nickel and tin components, respectively, of the coating. Particles of the coating have been reported to break away and act as abrasive particles [36, 37].

Whilst good corrosion resistance is displayed by tin-nickel, it is more noble than steel, and any breach of the coating can lead to corrosion of the exposed underlying steel substrate. The internal stresses can, however, be reduced by optimising the plating conditions, e.g., altering pH towards neutrality, lowering plating temperature) and using special additives, e.g., ammonium chloride. Another potential solution is to plate an interlay of copper or bronze between the steel substrate and tin-nickel coating [8].

The thermal stability of tin-nickel is another issue. Although the alloy does not melt at around 300°C, like some other tin alloys, it will undergo a phase transformation at just above this temperature, thus compromising the coating adhesion to the substrate [8].

The corrosion resistance of the tin-nickel has already been documented, and, if its wear resistance is shown to be comparable to tin-copper, the alloy, boasting a dual resistance to both corrosion and wear, would have clear implications for industry.

2.6 SUMMARY

Although much work has been conducted on the application and utilisation of tin and tin alloy coatings, most of the current uses appear to be confined to corrosion resistance, where alloys, such as tin-zinc, seem to excel over other alloys. Another area where tin and tin alloy coatings appear to be considered for is as solderable coatings for the electronics industry. Again, this is attributed to its high performance in this aspect, which is expected, since the main constituent of solder is tin. With the lead-free legislation being implemented and enforced in the electronics industry, the new lead-free solders that are being considered as substitutes for the traditional Sn-Pb eutectic have an even higher tin content.

Despite the popularity of tin and tin alloy coatings for corrosion resistance and solderability, there appears to be little work conducted on the utilisation of the said coatings in wear resistance applications, except for tin-copper. Instead, the current literature appears to be punctuated by quotes of hardness measurements, as though hardness implies wear resistance. Although the two are evidently related, it is incorrect to assume that, just because a material is harder, it is also more wear resistant by default [35].

It is possible that this could be attributed to the common misconception that, since tin is a relatively soft metal, tin alloys are also generally soft. Some tin alloys are indeed very soft, to the extent that they would be inadequate for wear resistant applications, however, other coatings, such as tin-nickel, are significantly harder and the appropriateness of these tin alloys as wear resistant coatings is assessed in this research. Another misconception is that wear resistant coatings should be extremely hard, in order to withstand the operating environment, however, using less hard coatings could help reduce the amount of wear, by introducing a lubricating effect to the system and, relaxing stress through plastic deformation.

Desirable wear testing results, when compared with tin-copper, along with the documented corrosion resistance properties of the deposits, could mean that tin-nickel can be considered for applications requiring both physical and chemical durability.

CHAPTER THREE

PRE-TREATMENT OF SUBSTRATE MATERIAL

3.1 INTRODUCTION

The coating of a substrate is a process, which may involve a number of steps. Due consideration must be given to the mandatory step of substrate preparation, prior to any coating, which is referred to as the "pre-treatment" step.

Pre-treating the surface of a substrate introduces scratches and pits into the material, thereby increasing the surface area and providing a "key" for adhesion of a coating. In addition, the process also removes surface species such as oxide films, giving a surface that is free of contamination, which is essential for good adhesion to a coating. Coating failures are often associated with poor pre-treatment, therefore it is important to have the correct pre-treatment for any given substrate material.

In general, substrates can be supplied by a variety of industrial sources, and, as such, the nature of a supplied substrate material surface cannot be assured. It is therefore prudent to pre-treat any substrate prior to further investigation both to remove surface contaminants and to increase the surface area. There are two methods of pre-treating the "as-received" substrate surfaces to achieve an increase in surface area, namely:

1. A chemical method;
2. A mechanical method.

By subjecting the mild steel substrates, prior to the electrochemical application of tin or tin alloy coatings, to one of these methods and evaluating the exact nature of the resulting surfaces of the pre-treated substrate material, using scanning electron microscopy, any difficulties in the reproducibility of industrially supplied samples are overcome.

The steel substrates, which are subjected to the chemical or mechanical pre-treatment techniques, are analysed to identify the optimum treatment for a given material that yields the greatest increase in surface area. Optimising any pre-treatment steps prior to coating is key.

3.1.1 Pre-treatment via Chemical methods

Pre-treatment of material surfaces via chemical reaction involves the immersion of the material into either an acidic or alkaline bath. The etching solutions react with the material, as well as its surface oxides, sulphides, etc., to either solubilise them or to produce salts that are soluble [38].

Chemical pre-treatment is often considered economical when compared to mechanical abrasion, and the loss of material is usually less. The main disadvantages to this chemical route is the toxicity or corrosiveness of the solutions used, and the increased after-corrosion tendencies of the pre-treated material [38]. An example of chemical pre-treatment is the use of hydrochloric acid on iron [39].

Hydrochloric acid is considered to be a relatively strong pre-treatment agent, very effective, even at room temperature. Sulphuric acid, although is cheaper and, for this reason, often preferred, may require higher temperatures. Furthermore, in the pre-treatment of iron or steel, dissolution of the iron oxide is much faster with hydrochloric acid than with sulphuric acid [40].

3.1.2 Pre-treatment via Mechanical methods

The use of mechanical methods for pre-treatment can involve abrasive blasting, where solid material such as sand or grit is propelled at high speeds onto the material being treated, causing removal of the surface contaminant, as well as some of the treated material.

It is understood that, whilst such mechanical methods are generally effective, they tend to be more expensive than chemical methods because of equipment use, and the methods can also remove more material [38].

Usually sharp-edged abrasive material is used for the blasting, as these are more effective at abrading the surfaces. It is important to ensure that the abrasive material is clean, since contamination can potentially leave dirt on the surface that is being treated.

3.2 METHODOLOGY

In the application of the chemical pre-treatment technique in this study, the use of an acidic route is considered, given both the documented effectiveness and availability of the required precursors [12, 41, 42].

In the application of the mechanical pre-treatment technique, the use of sand or grit blasting is not, however, adopted for the pre-treatment step due to the high associated costs. Instead, physical grinding with SiC abrasive papers is considered as a cheaper and simpler method [43] compared with sand or grit blasting which uses large volumes of the abrasive material and specialised apparatus.

3.2.1 Chemical Etching

Increases to the surface area of the substrate by chemical means are a result of preferential etching of the substrate in an acidic environment, leading to surface pitting and texturing. The standard etchant used for steel is composed of a mixture of distilled water and hydrochloric acid (HCl) in equal proportions. The steel substrates are immersed in the HCl solution for 30 seconds [12, 41, 42].

3.2.2 Physical Grinding

In order to introduce a roughened texture to the substrate surfaces, use of metallographic grinding papers was considered [43]. These abrasive papers consist of many individual silicon carbide (SiC) particles held onto backing paper by a cementing resin (Figure 3.1). The papers themselves are mounted onto a Struers TegraPol grinding machine (Figure 3.2), where they are rotated at 240 rpm.

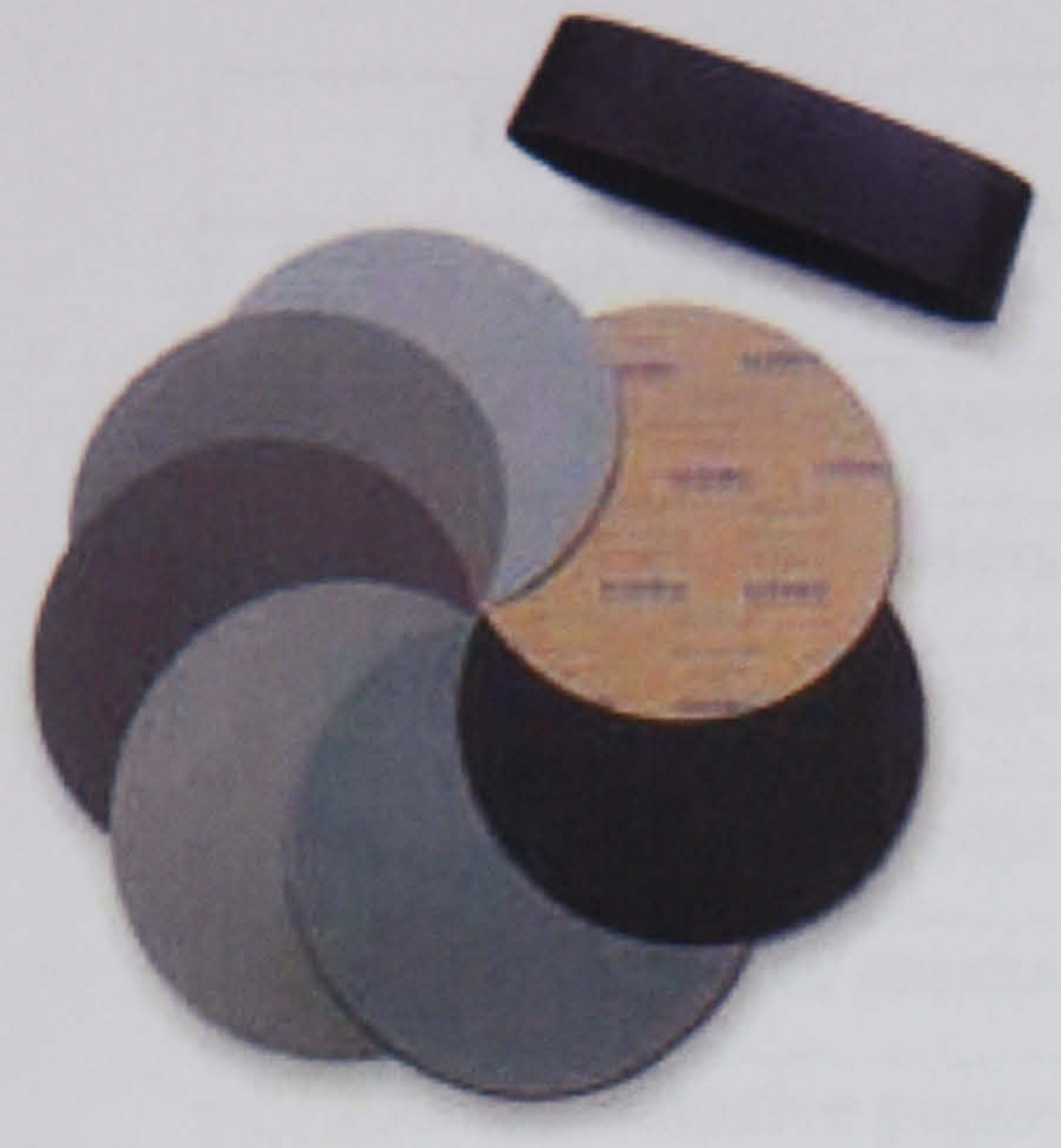

Figure 3.1 – An assortment of

Figure 3.2 – The Struers TegraPol

During a typical grinding process, the sample is physically forced by hand against these rotating papers, allowing the SiC particles to gradually abrade the surface of the material [43]. By introducing the substrate surface to these particles, the surface is subjected to multiple point stresses that result in the gradual removal of substrate material and the introduction of many minute scratches on the substrate surface, thereby increasing the surface area of the substrate [44].

Through moving the substrate, as it is ground, an array of random scratches is produced, thus providing a "key" surface for the initialisation of the coating process, which is critical in achieving good adhesion with the intended coating.

The SiC abrasive papers are divided into different grades, and the extent of damage resulting from the grinding is determined by the size of the SiC particles. The P-number (an industrially recognised notation) is used to grade the abrasive paper and higher P-numbers denote finer grades (Table 3.1).

Description	Average Size of Abrasive Particles / µm
P60 SiC abrasive papers	269
P120 SiC abrasive papers	127
P180 SiC abrasive papers	78
P320 SiC abrasive papers	46
P400 SiC abrasive papers	35
P600 SiC abrasive papers	26
P1200 SiC abrasive papers	15

Table 3.1 – Table showing size of SiC particles in abrasive papers used

The substrate material was ground using P60, P120, P180, P320, P400, P600 and P1200 papers, and yielded different appearances in the surface finish, which are examined and reported in the Results Section.

3.3 ANALYTICAL METHODS FOR DETERMINING EFFECTIVENESS OF PRE-TREATMENTS

3.3.1 Scanning Electron Microscopy (SEM)

The SEM used in this research is a Topcon SM300 (Figure 3.3), which allows the capture of micrographs via a digital imaging system.

The discovery of X-rays in 1912, and the evaluation of its shorter wavelength, in the range 0.1-100 Angstroms (0.00001-0.1 microns), which enabled the limitations of the optical microscope to be overcome [45], proved to be an essential step in the evolution of SEM [46]. Through these advances, the SEM has now become an established analytical technique used for high magnification observation.

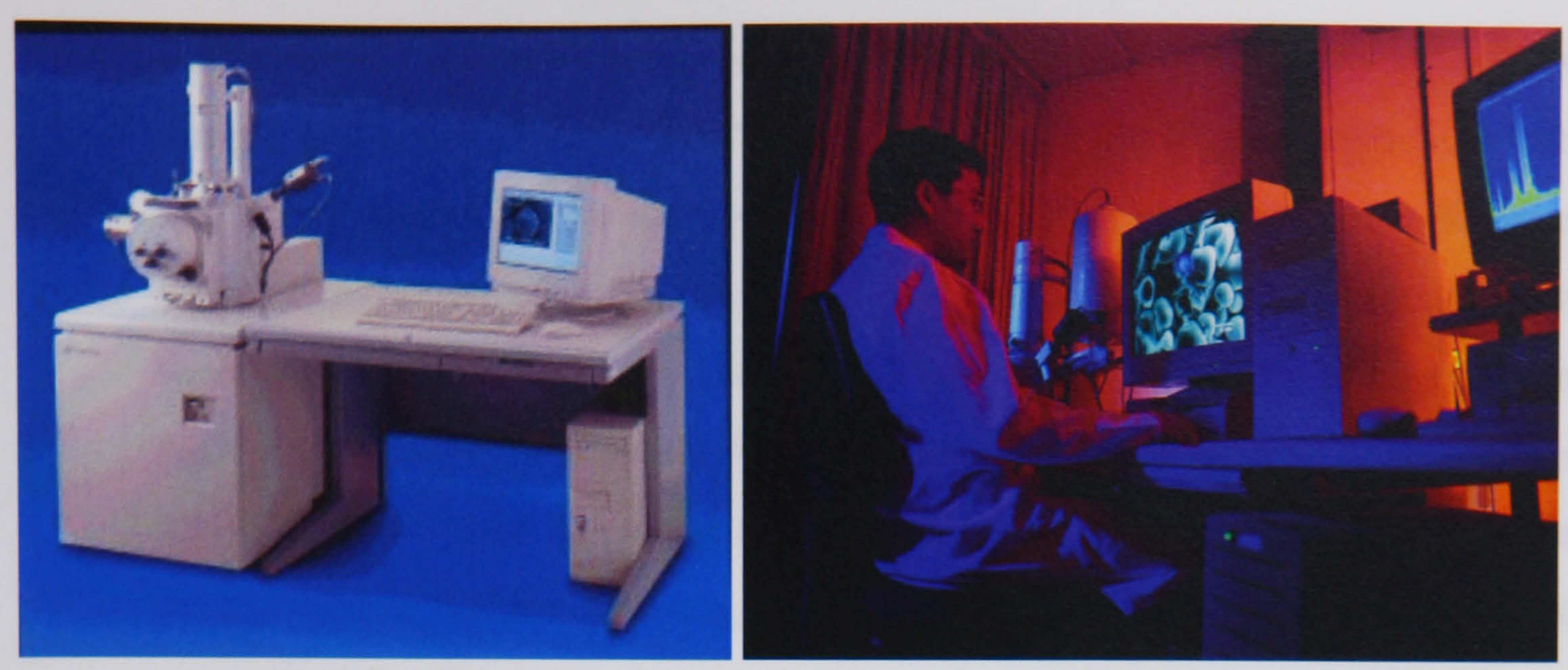

Figure 3.3 – The Topcon SM300 (left) and in operation (right)

The operation involves a fine electron beam striking the sample being viewed, with the electrons generated from a current being passed through a hairpin shaped tungsten filament, which is heated (Figure 3.4). The filament gradually depletes as the tungsten is evaporated off and eventually fractures at the tip. Filament life is dependent on its operating conditions, with poor vacuum and a high beam voltage being the main causes of filament failure [47], since a partial vacuum promotes oxidation of the filament surface, and a high operating voltage removes the tungsten electrons quicker.

The bombardment of electrons onto the specimen surface generates signals, resulting from the interaction between the beam electrons and the sample, which are collected and interpreted into data that can in turn be utilised to produce an image of the sample surface (Figure 3.4). Three species of interest are produced when the electron beam hits the sample (Figure 3.5), amongst them, two types of electrons, generated from the interaction, are particularly relevant to the characterisation:

- Secondary electrons are released from the sample being viewed as a result of interactions between the beam electrons and the electrons in the sample. These produce an image where the contrast is determined by surface topography. In most cases, high altitude areas appear light, making this viewing mode best for surface analysis of coatings. A rough surface would generate secondary electrons that offer a high degree of contrast; hence, this technique is primarily used for surface analysis;

- Backscattered electrons are produced when the beam of electrons strikes the sample and some of these are "slingshotted" back out by the interaction with the atoms' nuclei of the sample material. Different materials have different nuclei sizes so the characteristics of backscattered electrons are dependent on the material with which they interact. In this way, observation of a sample in backscattered mode allows the interpretation between elemental compositions to be made. Unlike the secondary electron viewing mode, contrast in the backscattered electron viewing mode is determined by the relative atomic mass (RAM) of the sample constituents, where a light area corresponds to a high RAM area; e.g., a multiphase material gives a wide contrast range. This backscattered electron mode is usually reserved for samples that are cross-sectioned since these specimens are mostly flat, from the metallographic polishing (giving poor topographical contrast in secondary electron mode).
- As well as secondary and backscattered electrons, x-rays are also generated from the interaction. Each material has a characteristic x-ray series at particular energies, and, by detecting these, it is possible to evaluate the materials present. The Energy Dispersive X-ray analytical technique is described in further detail later.

The scanning of the electron beam across the specimen surface can be done simultaneously with a cathode ray tube in order to impose an image of the specimen onto the surface of the display screen [48].

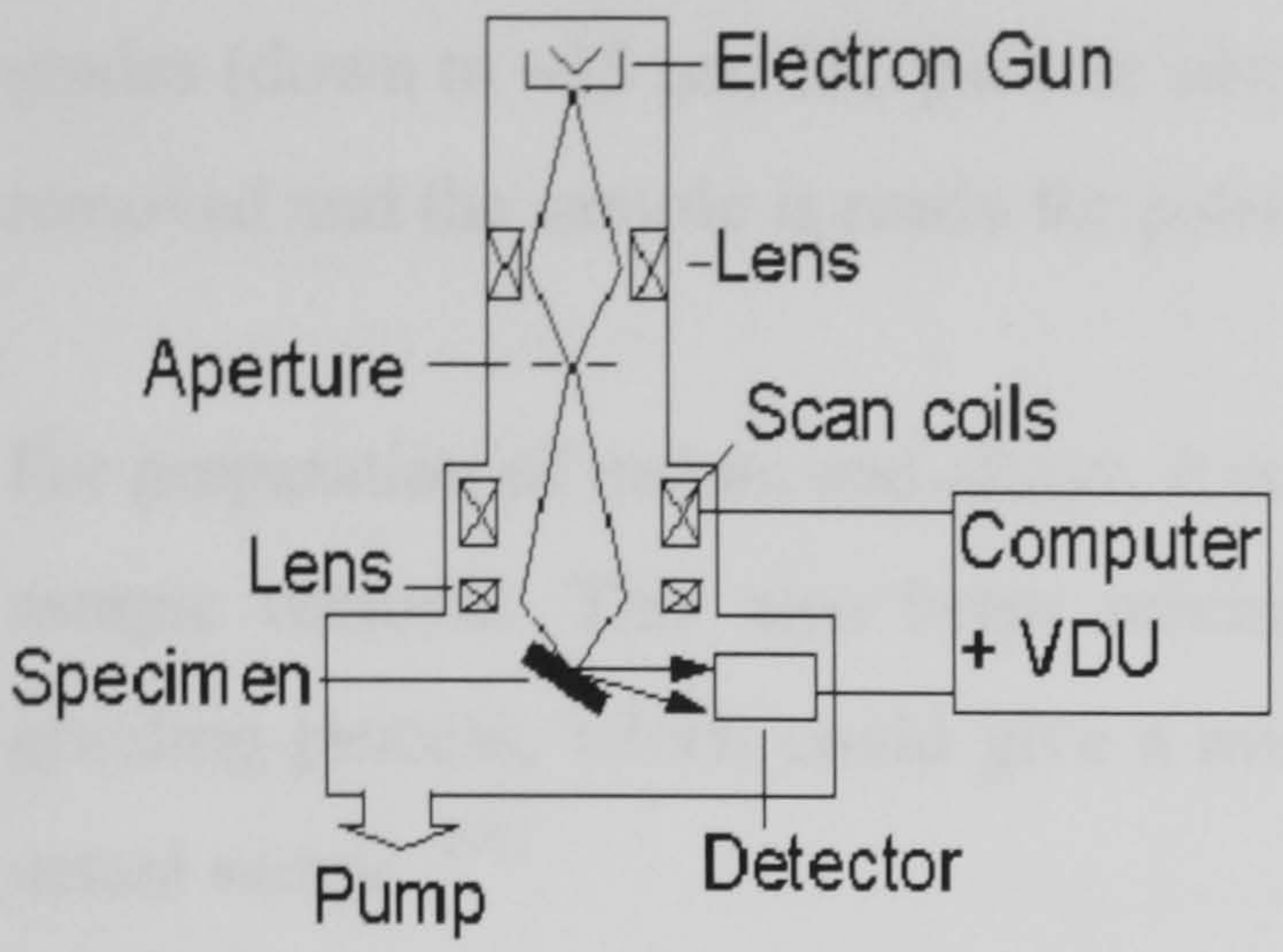

Figure 3.4 – Schematic drawing showing the electron column, the deflection system and the electron detectors [48]

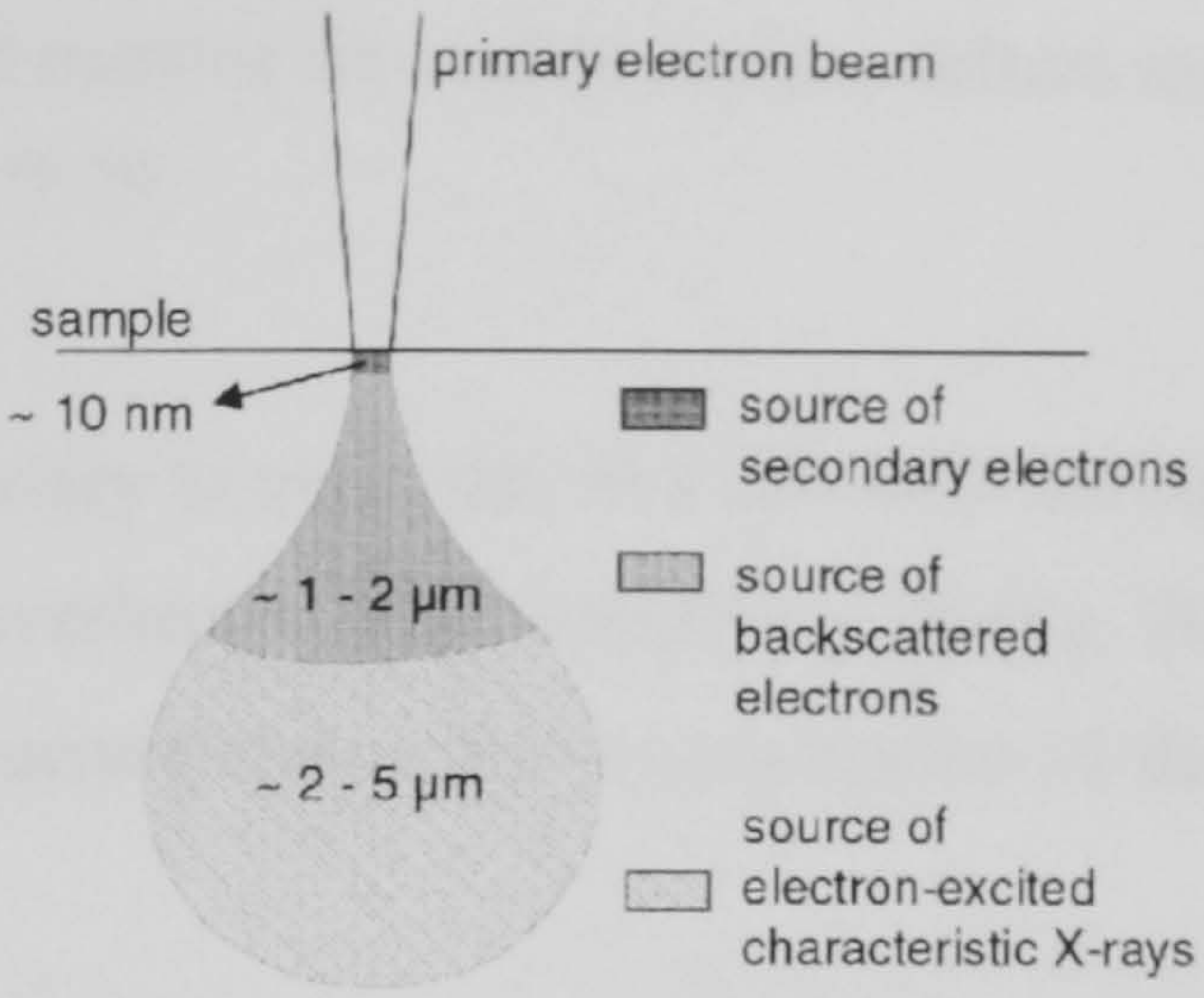

Figure 3.5 – Diagram illustrating the generation of electrons and x-rays from the interaction between the electron beam and sample [5]

Surface analysis, using SEM techniques for surface scanning, can pick up defects such as cracking in the substrate and/or poor coating coverage. It often requires the use of cross-sectional analysis, however, to determine a coating thickness or to identify "hidden" defects, such as porosity, inconsistent coating thickness and interfacial cracking. Cross-sectional analysis is described in the following section. Analyses of samples in both the surface and cross-sectional views therefore complement each other and afford a greater understanding of the specimen being examined.

3.3.2 Metallographic preparation

The primary metallographic stage involves the encapsulating of the ground steel samples in the desired geometric plane within an epoxy resin, and once the resin has polymerised (or cured) the sample becomes permanently suspended within the solidified mix.

The secondary stage involves cutting the encapsulated sample near the point of intended analysis, and then grinding/polishing the face of the sample to a mirror finish. The sample face is first receded to the point of analysis by abrading with silicon carbide (SiC) abrasive papers. Coarse grit papers (from a maximum of ~269 μm SiC particle size) are used initially, progressively followed by a series of finer grades (down to ~15 μm SiC particle size) until most of the visible surface defects are removed and the sample is ready for polishing [49, 50].

For preparation of metals and alloys, it is necessary to use water as a lubricant during sample removal. This also helps minimise overheating and tempering during the grinding process, which could give a microstructure that is not representative of the actual sample [51].

The polishing stage involves the use of fine diamond suspensions on a set of polishing cloths. Like the grinding, the polishing also involves the use of progressively finer abrasives until all the scratches are removed. Smoothing of the scratches at this stage may arise from either removal of material in small volumes (i.e., erosion), or melting of the top atomic layers of the sample to give an amorphous surface [52]. In this way, a relatively flat and smooth surface is achieved. The metallographic preparation process is illustrated schematically in Figure 3.6.

SEM analysis requires a conductive sample, which is achieved by coating with a few atomic layers of gold in a sputtering instrument. Failure to achieve this, adversely affects the imaging of the sample with a poorly prepared or non-sputtered sample being characterised by an unstable image or by excessive contrast at some points, which is sometimes referred to as "charging".

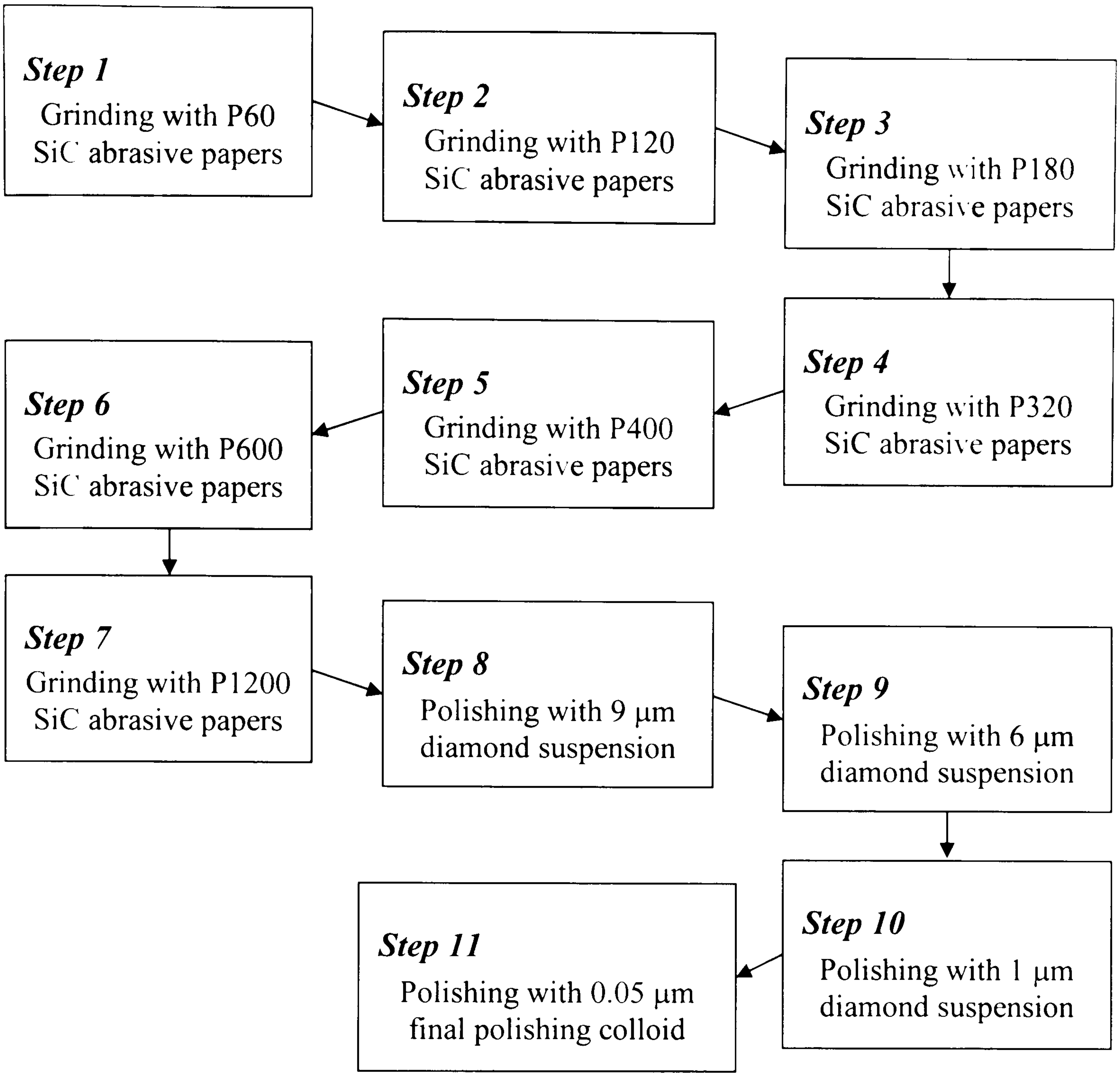

Figure 3.6 – The metallographic route used for sample preparation

3.3.3 Surface area evaluation

As there is no documented study on the quantified effectiveness of different grades of SiC abrasive papers, a novel method based on visual examination of cross-sectioned samples that have been pre-treated is devised and implemented [43]. The method is used to also assess the surface area increase resulting from the chemical etching in order to determine the most effective form of steel pre-treatment.

Image analysis software is used to quantify the increases in total available surface area, for a coating to adhere to, with respect to the pre-treatment used. Micrographs of cross-sectioned pre-treated substrates are examined with the software. In a typical cross-section through a pre-treated substrate, the profile of the steel substrate surface is located adjacent to the resin as seen in Figure 3.7, which has been captured using SEM in backscattered electron mode. The contrast in this mode of viewing is determined by relative atomic mass (RAM), where the material with the higher RAM appears lighter. The substrate material is therefore shown as the grey phase, whilst the carbonaceous resin is shown as the dark phase.

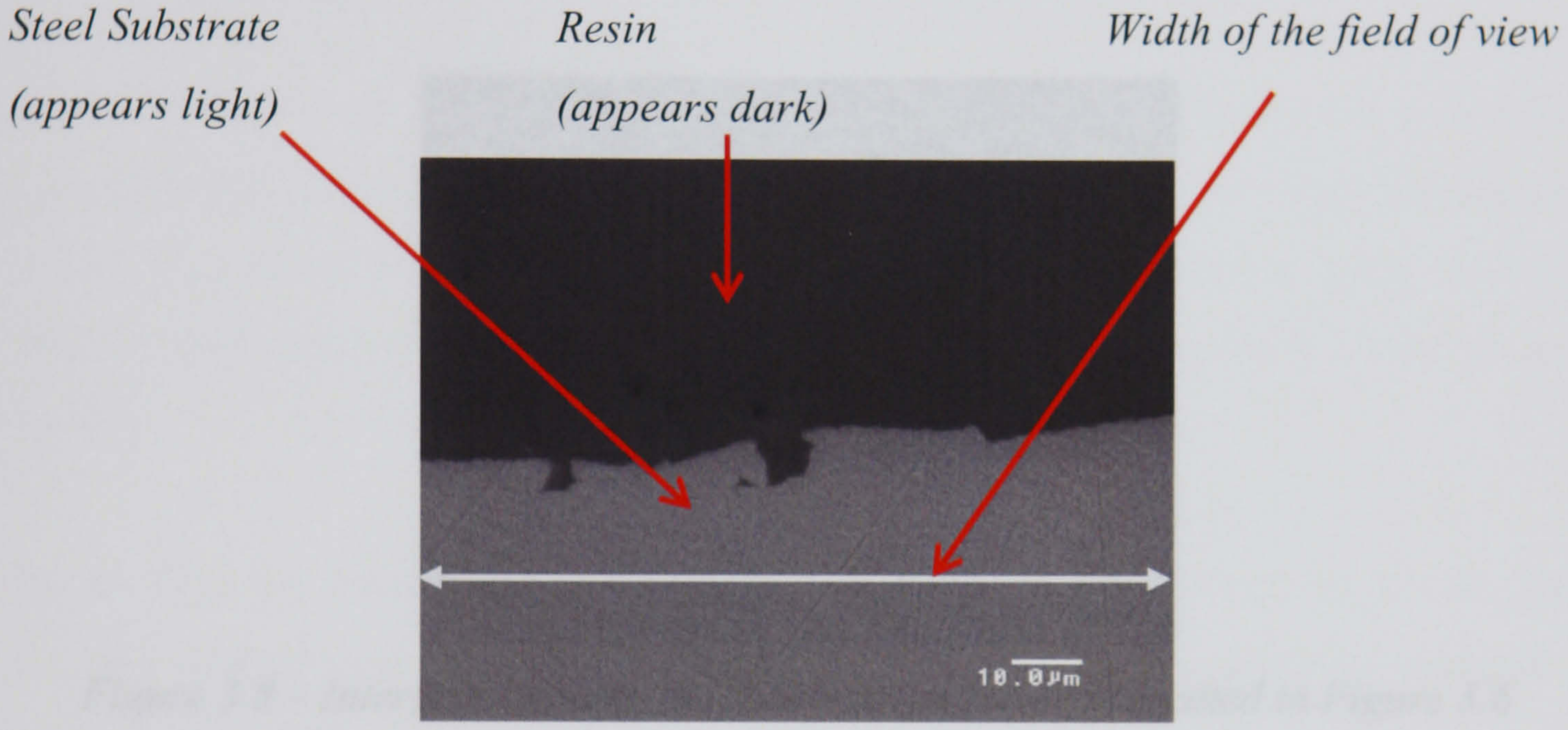

Figure 3.7 – Typical cross-sectional view of prepared substrate surface

The surface area of the substrate material is determined by examination of several fields of view taken of its cross-section at 1000x magnification. Using the scale bar, in the bottom right hand corner, it is possible to deduce that the width of the field is 110 µm. In Figure 3.7, this length is represented by the white line that has been drawn from edge to edge.

For a perfectly flat sample, the length of the interface on the screen would be 110 microns; hence, the area of this perfectly flat surface in one single field of view is the square of the length of the interface, i.e., 110 µm x 110 µm = 12100 µm^2.

In practice, however, surfaces are seldom perfectly flat, and the pre-treated samples investigated in this research are significantly scratched and pitted, giving the profile an uneven appearance at SEM magnifications. The interfaces between the resin and the substrate in twenty-five micrographs, for a given substrate and pre-treatment stage, are measured with imaging software, SigmaScan Pro 5.0, supplied by Clecom Software Specialists. This software is capable of tracing a line between two areas of different contrasts and can be used to measure the interface between the substrate and the resin from an image of the cross-sectioned sample.

The rougher and larger the surface area of the sample, the longer is the interface. This is illustrated in Figure 3.8, where the red line is a trace of the substrate-resin interface presented in Figure 3.7.

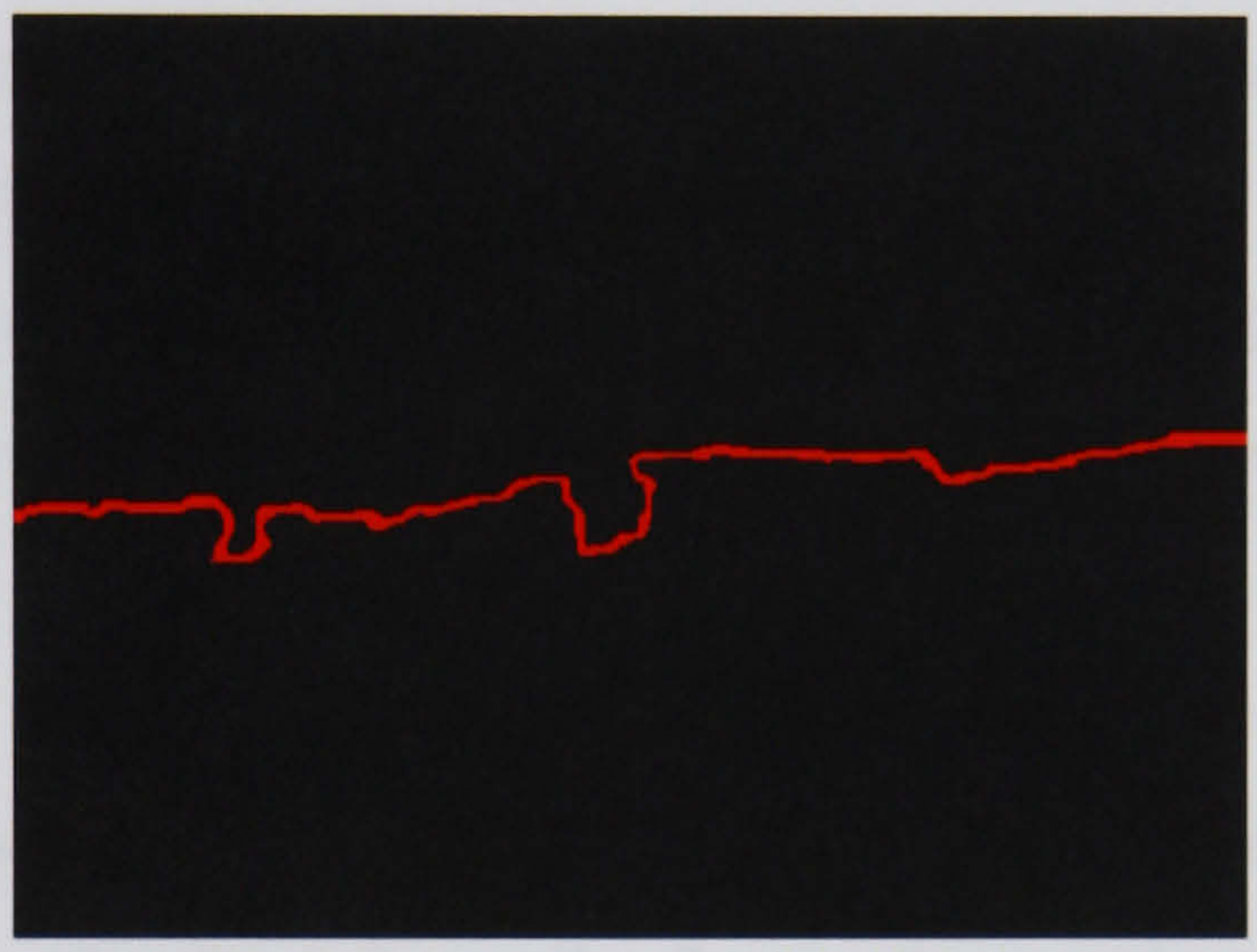

Figure 3.8 – Interface between the substrate and resin presented in Figure 3.6

As mentioned earlier, the length of this line is measured in microns and then squared to give a theoretical surface area for a given material and pre-treatment. Once this value for a control sample (as-received sample that has not undergone any pre-treatment) is determined, the effectiveness of a particular pre-treatment can be calculated by dividing the surface area for a pre-treated substrate by the corresponding value for the control sample to yield a percentage surface area increase from the control state to the specific pre-treatment state.

The evaluation of a "percentage surface area increase over a control sample" is a measure of how a particular pre-treatment method has improved the surface of a given substrate material from its "as-received" state. Whist this is a fairly good indication of the effectiveness of different pre-treatments, these values could be rendered misleading by control substrates that are already quite rough prior to any pre-treatment, particularly as the supplied substrate surface finish could vary between different sources. In such cases, an otherwise considered effective pre-treatment could be undermined because, if a control substrate is already relatively rough, the percentage surface area increase resulting from any surface preparation process is going to be low regardless of the practical effectiveness. To account for a range of different control substrate finishes, and to ensure consistency, surface area increases are accompanied by corresponding data derived from surface area increases over a hypothetically flat surface. The reason for adopting this approach is because it is a large surface area, rather than a large surface area increase, that is the main factor affecting good coating retention and adhesion.

The parameter "percentage surface area increase over a hypothetically flat surface" is therefore also determined with a slight modification to the previous calculation. Although a perfect surface is not attainable, however, polishing with diamond abrasive and alumina suspension can produce surfaces that approach a near perfect surface.

By dividing the surface area data, evaluated for each pre-treatment, by 12100 μm^2, i.e., the surface area of a hypothetically flat surface, it is possible to evaluate a measure of surface area increase over a perfectly flat surface.

3.4 RESULTS

3.4.1 Chemical Etching

Following etching, the relatively smooth finishes of the steel substrates become tarnished and textured. The dull appearance following the etching is consistent with the introduction of greater surface topography on the metal since light is being reflected at a larger range of angles. A smooth surface appears bright because most of the light is reflected at approximately the same angle.

SEM characterisation

The appearance and texture of the etched sample is evident upon visual inspection and using optical microscopy, while more detailed information illustrating an effect of chemical attack on the substrate is provided by SEM analysis. Surface analysis of the etched steel samples using SEM reveal that the surface area is dramatically altered, as illustrated in Figure 3.9a. Figure 3.9b corresponds to a cross-section of an etched mild steel substrate.

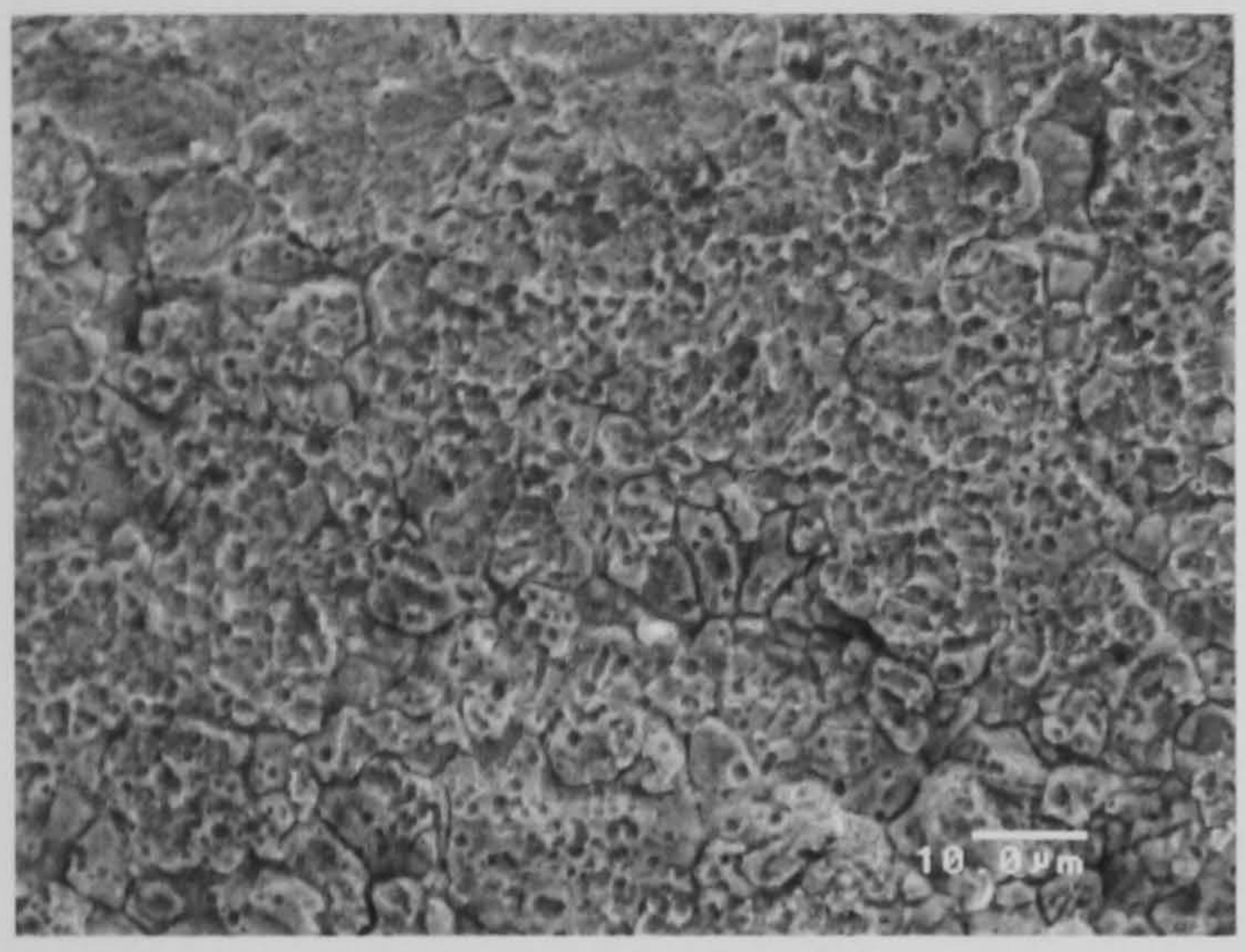

Figure 3.9a – Etched steel surface

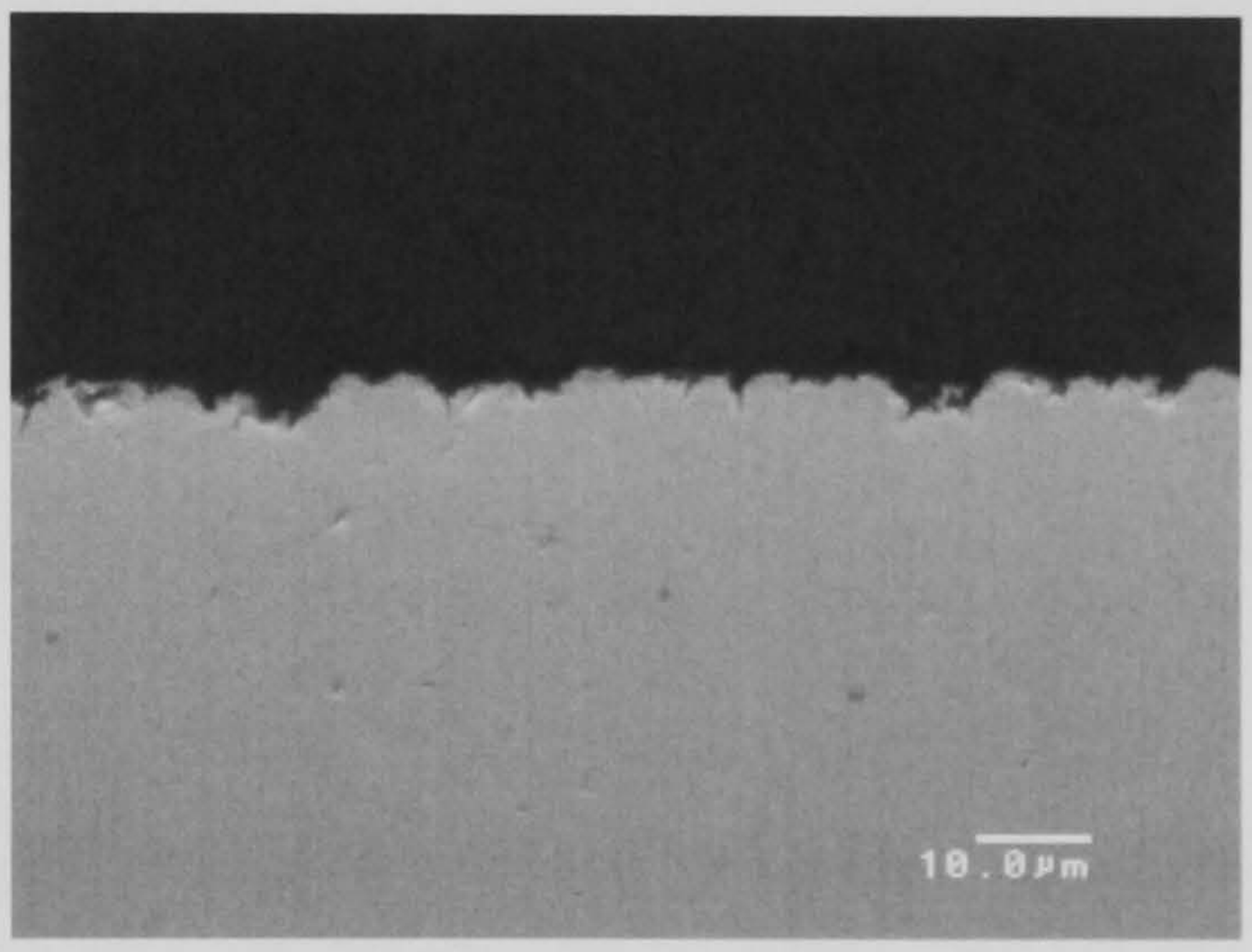

Figure 3.9b – Etched steel section

The cross-sectional analysis provides further information, e.g., on the depth of the pits and the extent at which the acid has textured the surface.

Surface area measurements

The steel substrates are chemically etched, and their respective surface area and associated standard deviation (S.D.) are evaluated with the steps below. Also included are 95% confidence interval values, using the equation below. The use of confidence limits, specifically at the 95% level, is due to the level of use in modern applied practice, according to Zar 1984.

$$\text{Confidence Interval} = \text{mean} \pm 1.96 \times \left(\text{S.D.} / \left[\sqrt{\text{(number of readings)}} \right] \right)$$

- The average theoretical surface area, determined using the method described in Section 3.3.3, of unetched control samples of steel is 14,000 μm^2 (S.D. = 800)

- The average theoretical surface area of samples of steel that have been etched is 19,500 μm^2 (S.D. = 1000)
- In order to determine the surface area increase from a control sample to an etched sample, the value of the etched sample is divided by 14.000. The resulting value, representing the increase in surface area, is 39.3 % (95% confidence limits: 34.6 – 45.6)
- The increase over a hypothetically flat sample is calculated by dividing the value of the etched sample by 12100 μm^2 (surface area of a hypothetically flat surface as determined in Section 3.3.3) and this value is evaluated to be 61.6 % (95% confidence limits: 58.5 – 64.7)

3.4.2 Physical Grinding

Physical pre-treatment by grinding with SiC abrasive papers produces different surface topographies, which are apparent to the naked eye and different surface textures detectable by touch.

SEM characterisation

Surface and cross-sectional SEM analysis of the ground samples were recorded at x1000 magnifications in order to establish effects of the abrasion using different grades of SiC abrasive papers.

Figures 3.10 – 3.17 are micrographs taken of the steel substrates. For each grade of SiC paper used, an SEM image of the resulting surface (a) is presented together with the corresponding cross-sectioned micrograph (b).

Unground metal substrate – control

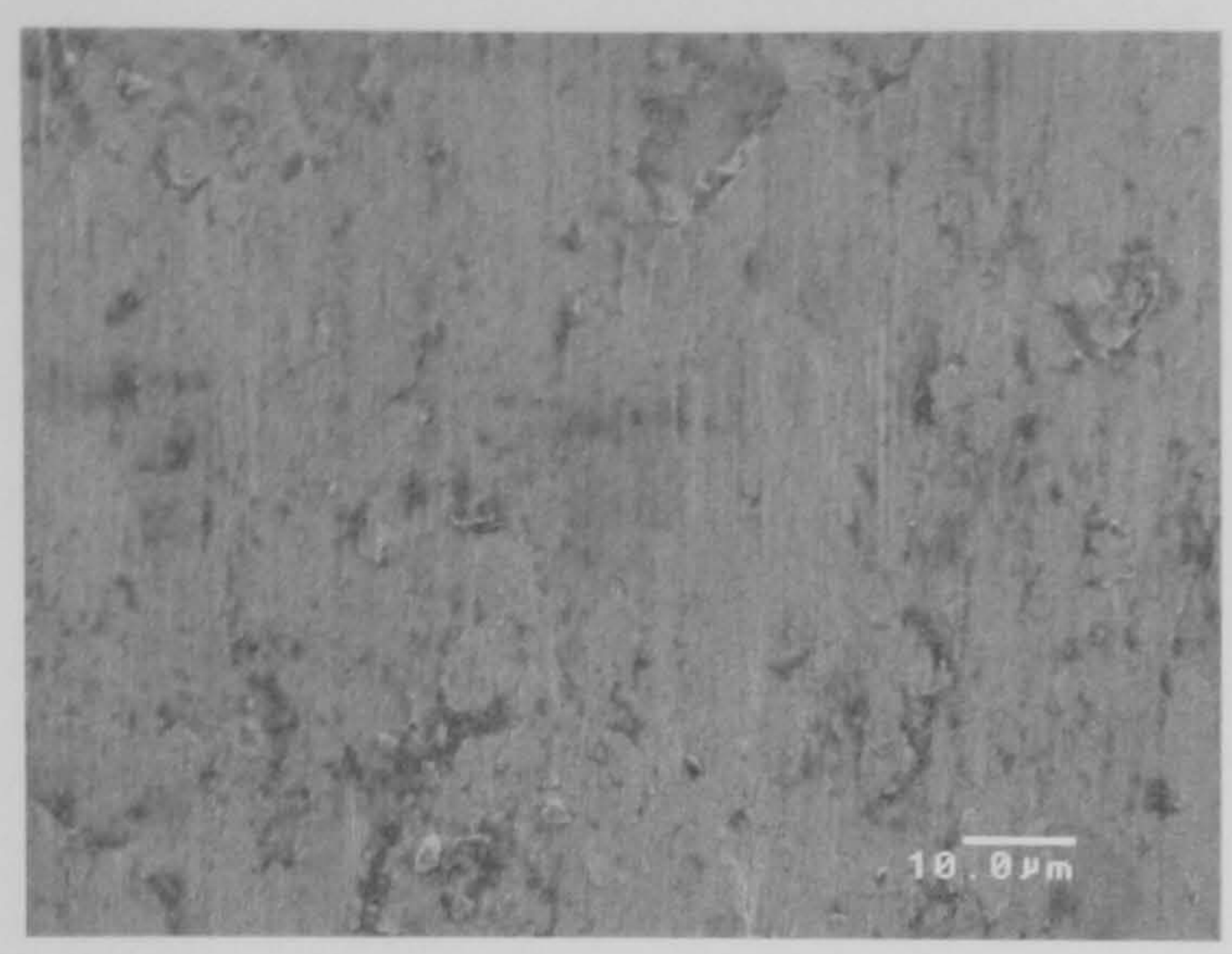

Figure 3.10a – Surface analysis

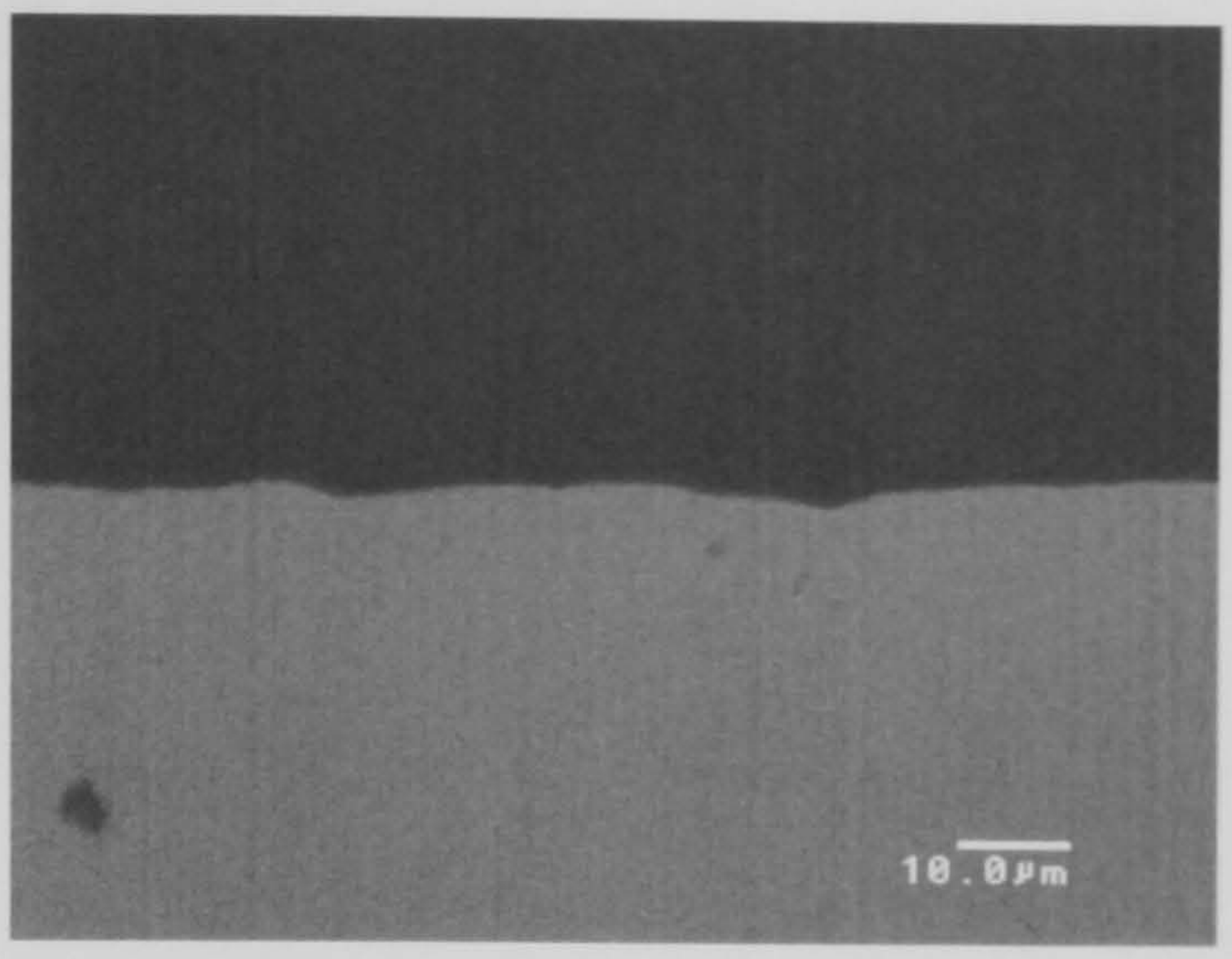

Figure 3.10b – Cross-sectioned view

P60 Grit Size

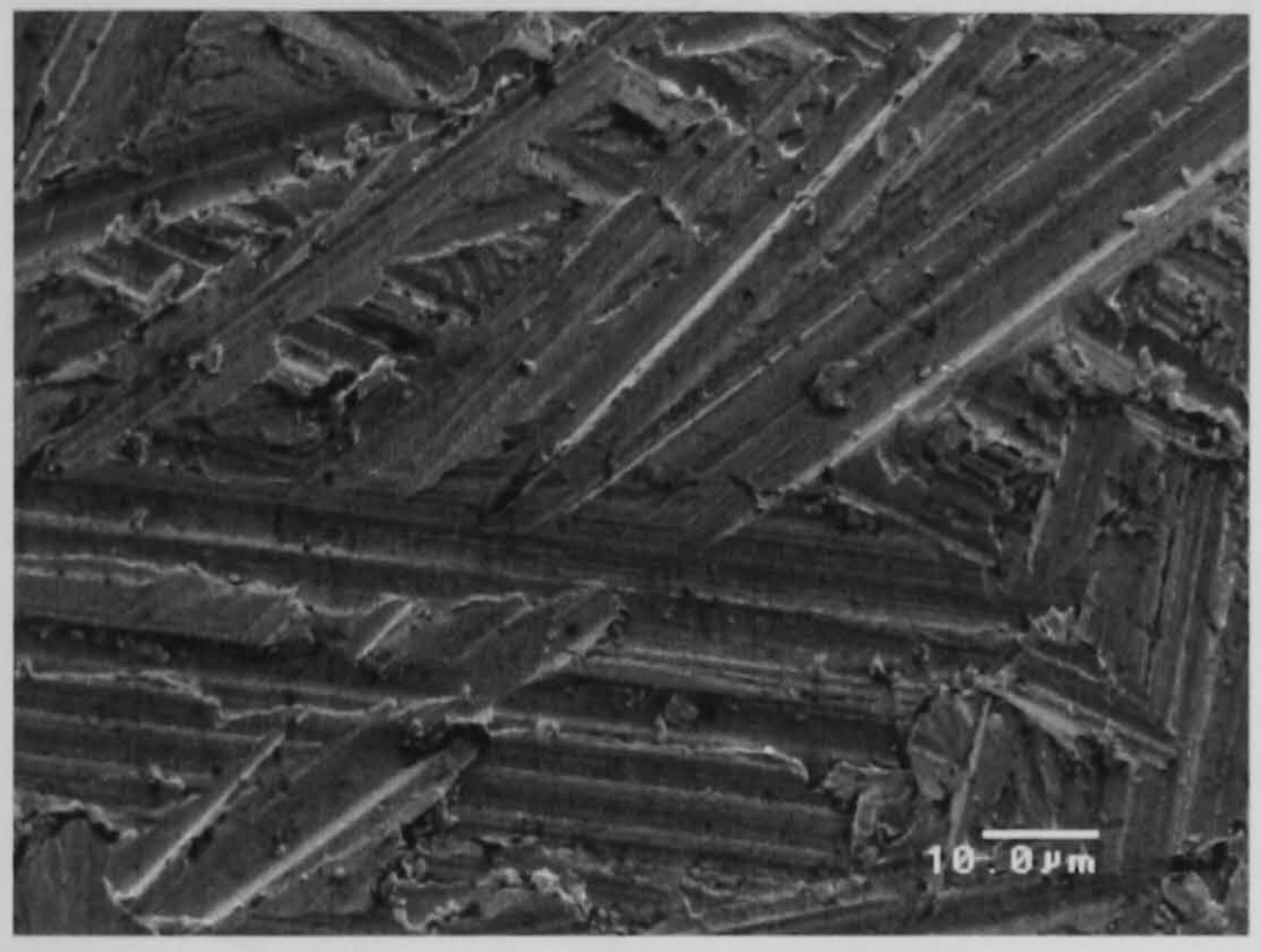

Figure 3.11a – Surface analysis

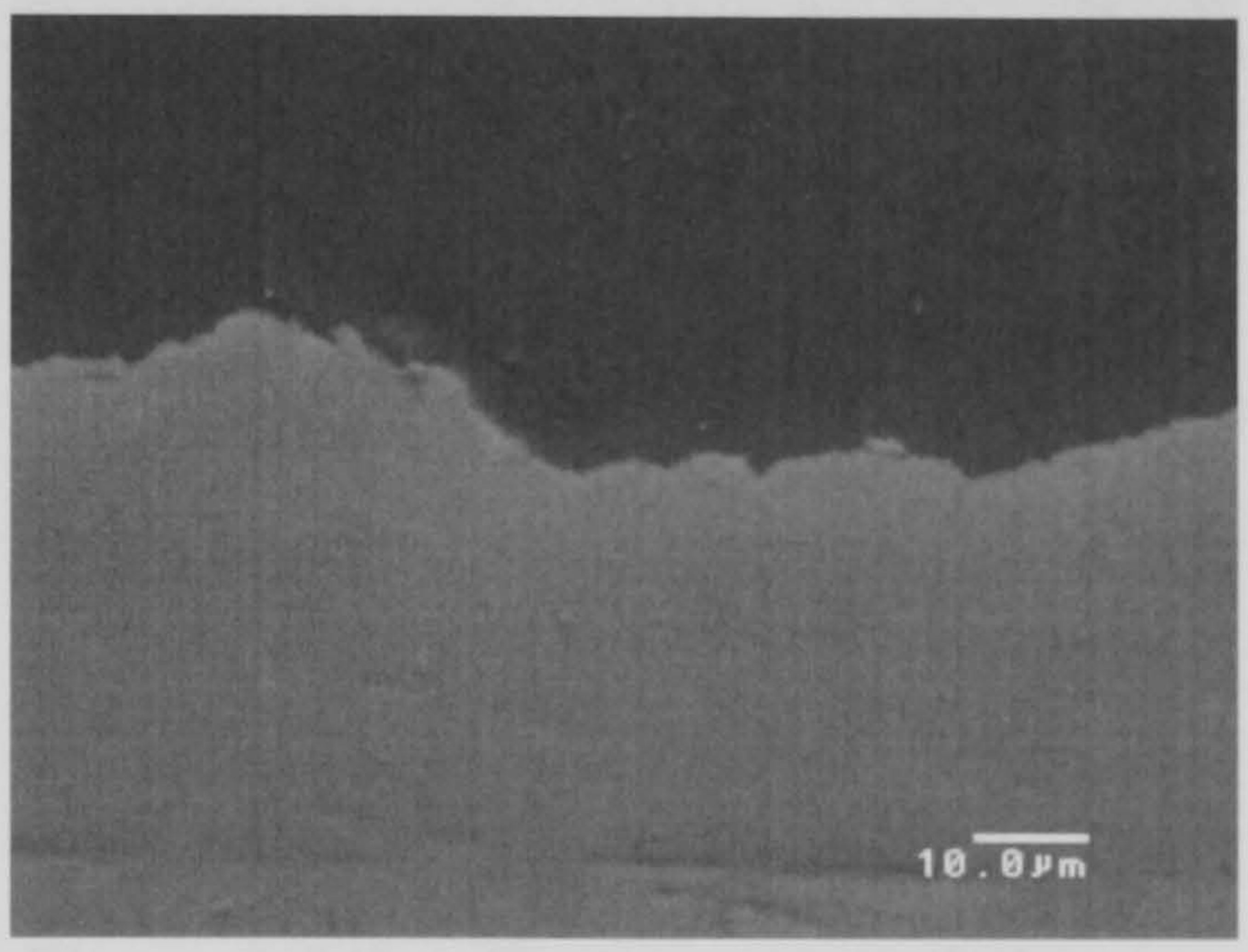

Figure 3.11b – Cross-sectioned view

P120 Grit Size

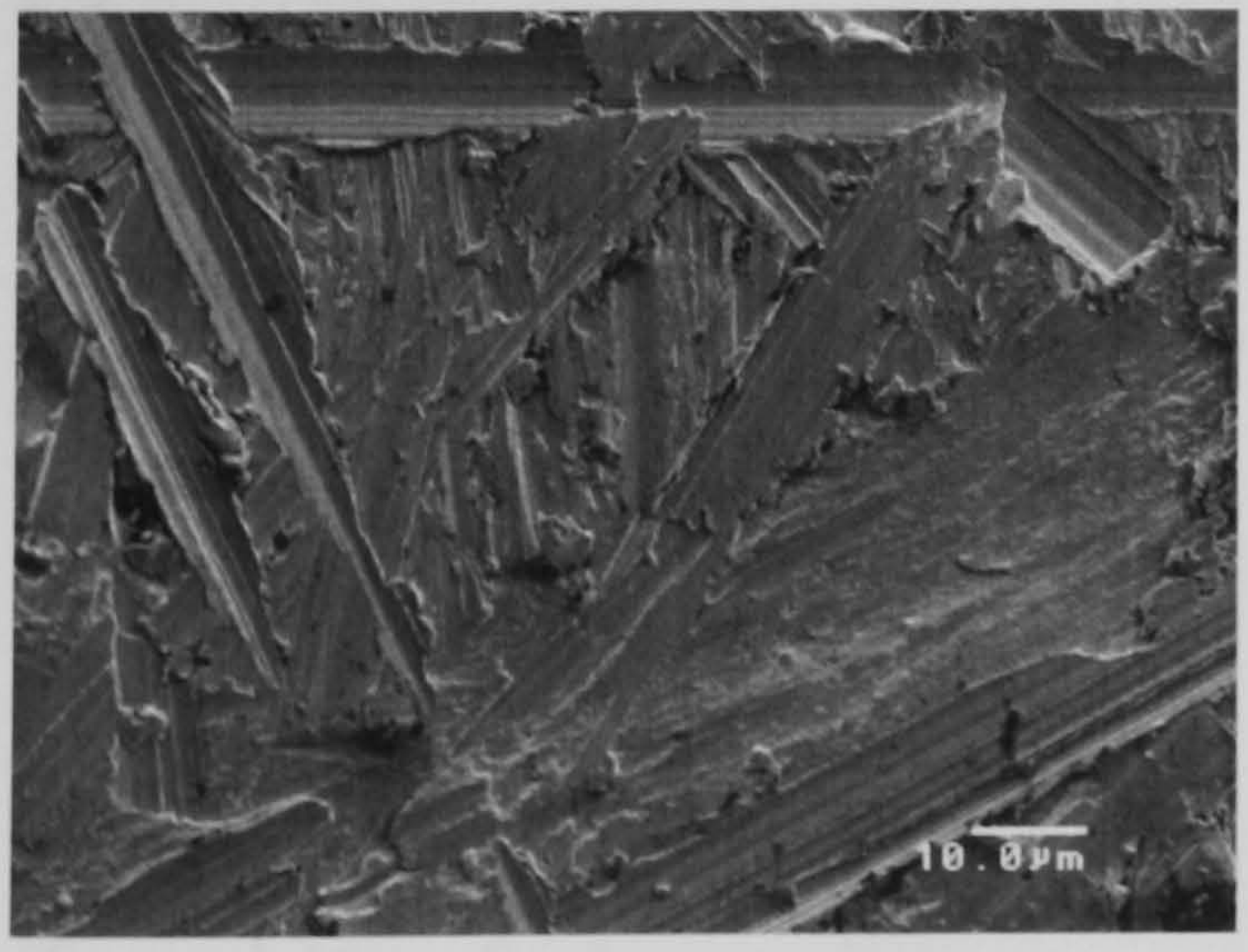

Figure 3.12a – Surface analysis

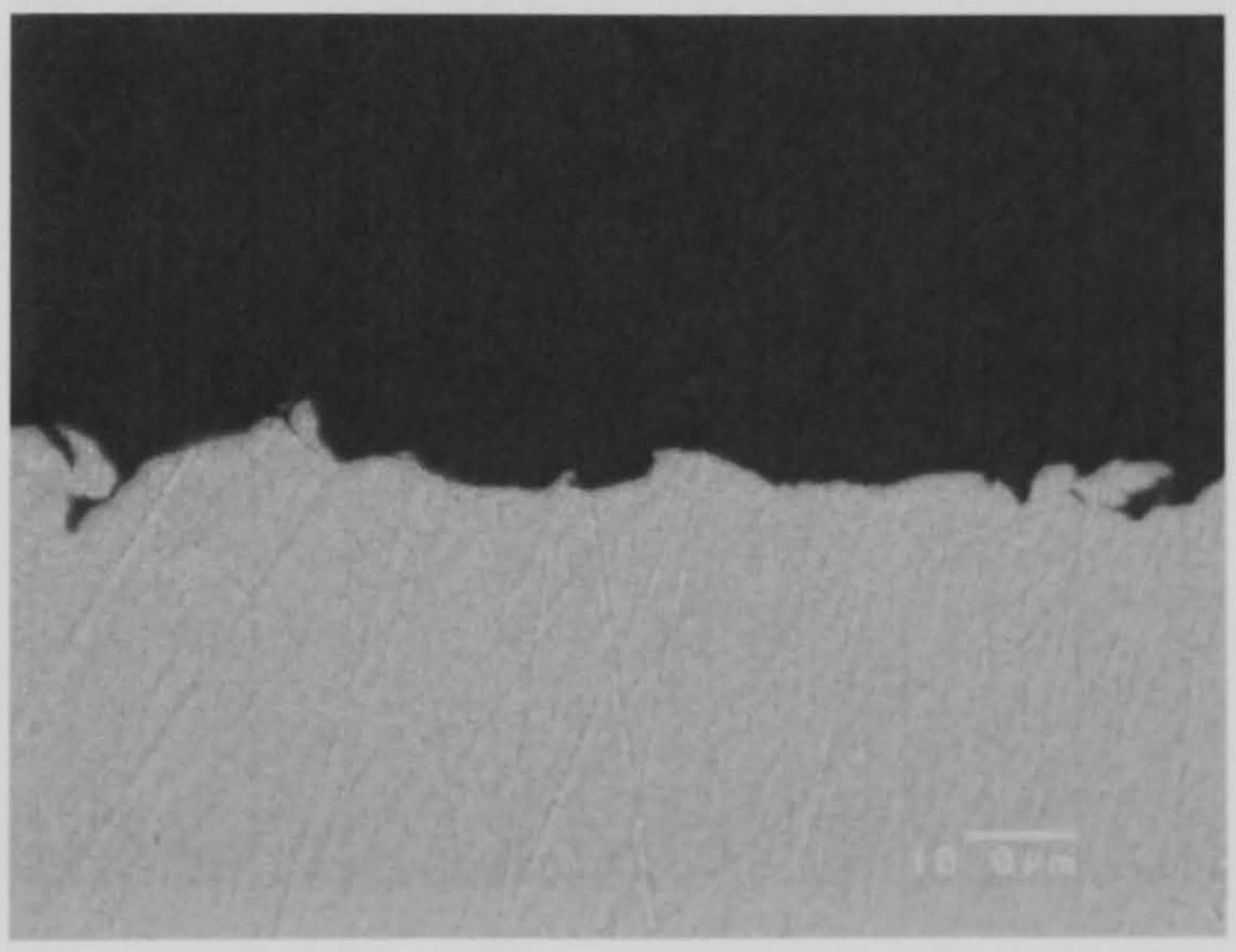

Figure 3.12b – Cross-sectioned view

P180 Grit Size

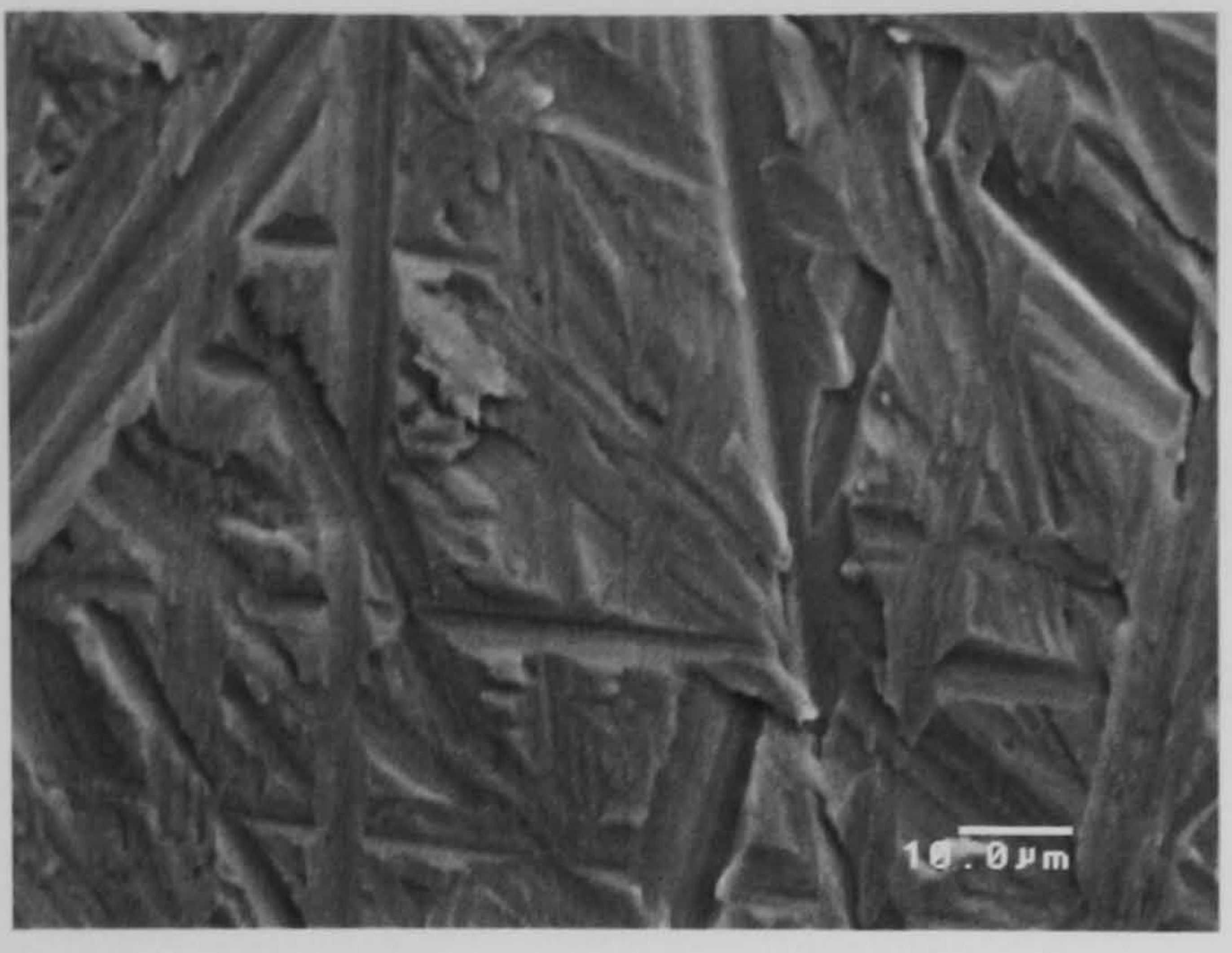

Figure 3.13a – Surface analysis

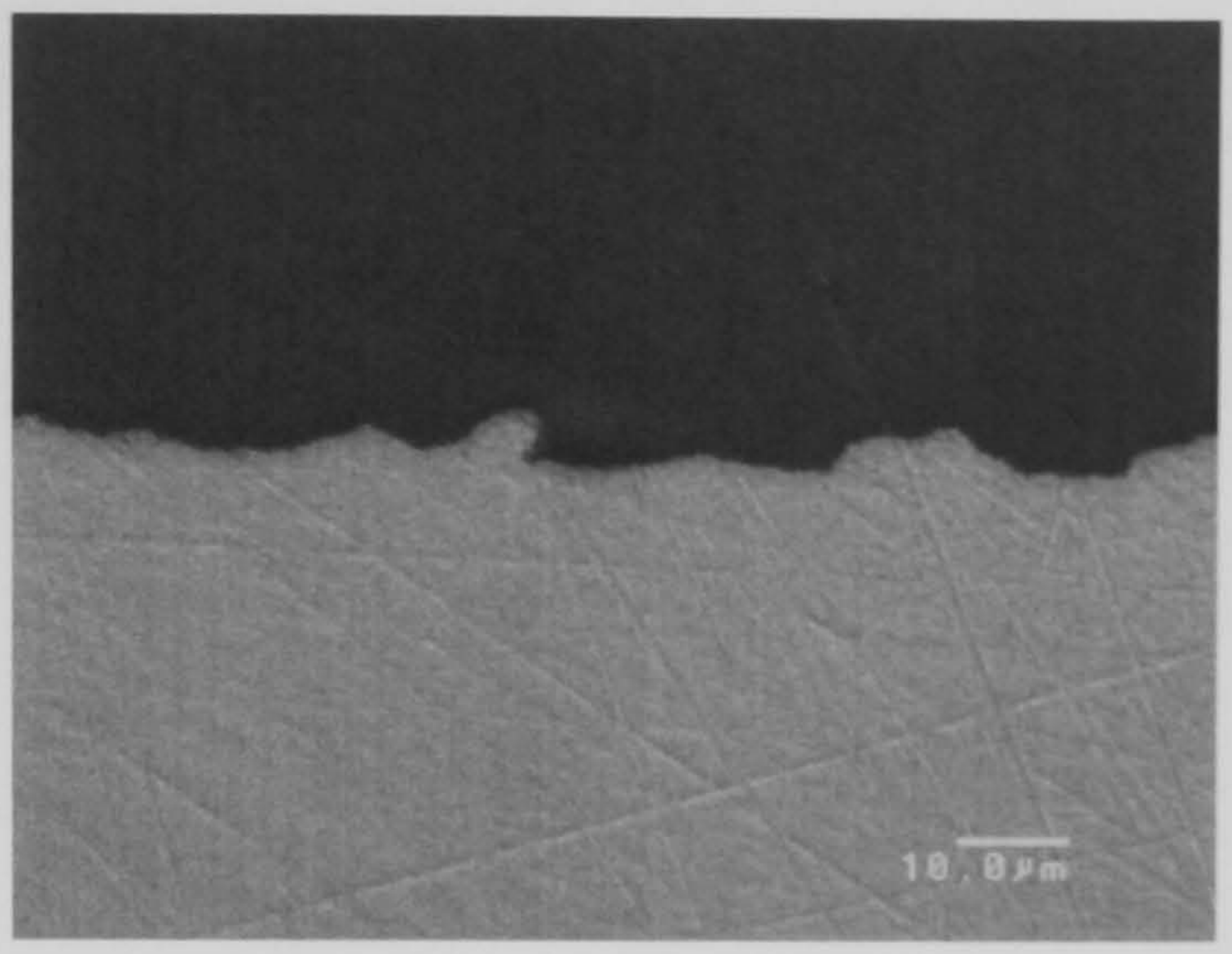

Figure 3.13b – Cross-sectioned view

P320 Grit Size

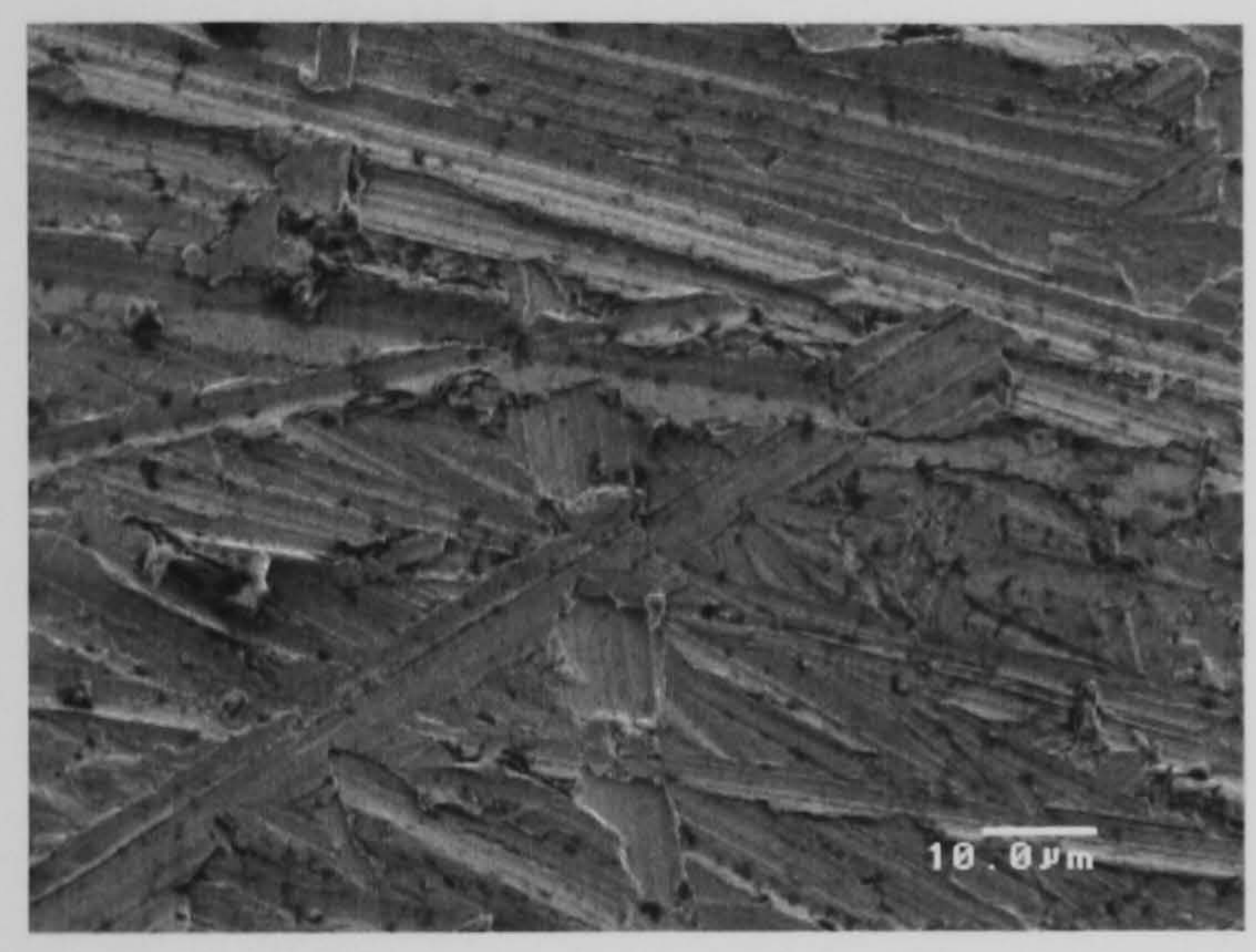

Figure 3.14a – Surface analysis

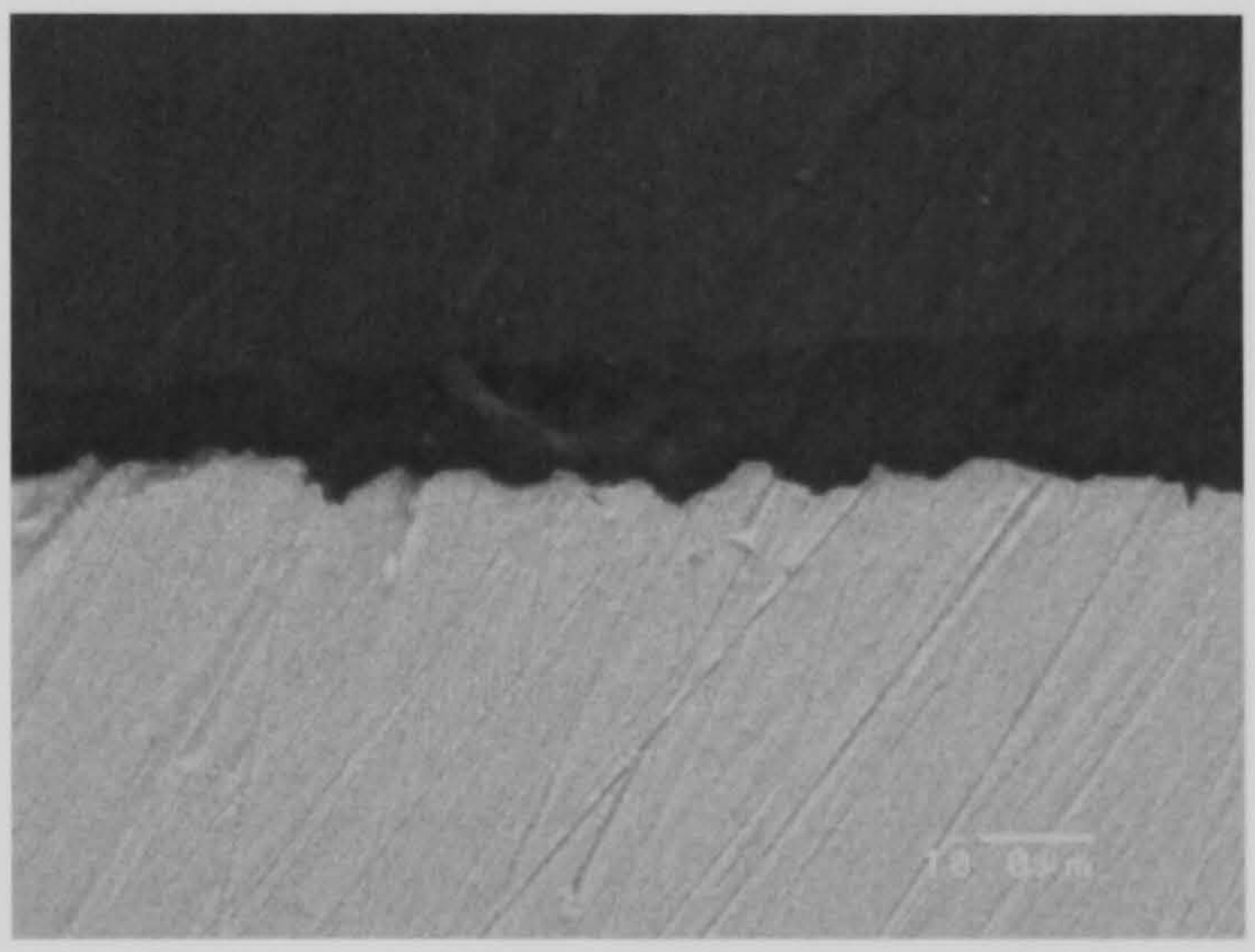

Figure 3.14b – Cross-sectioned view

P400 Grit Size

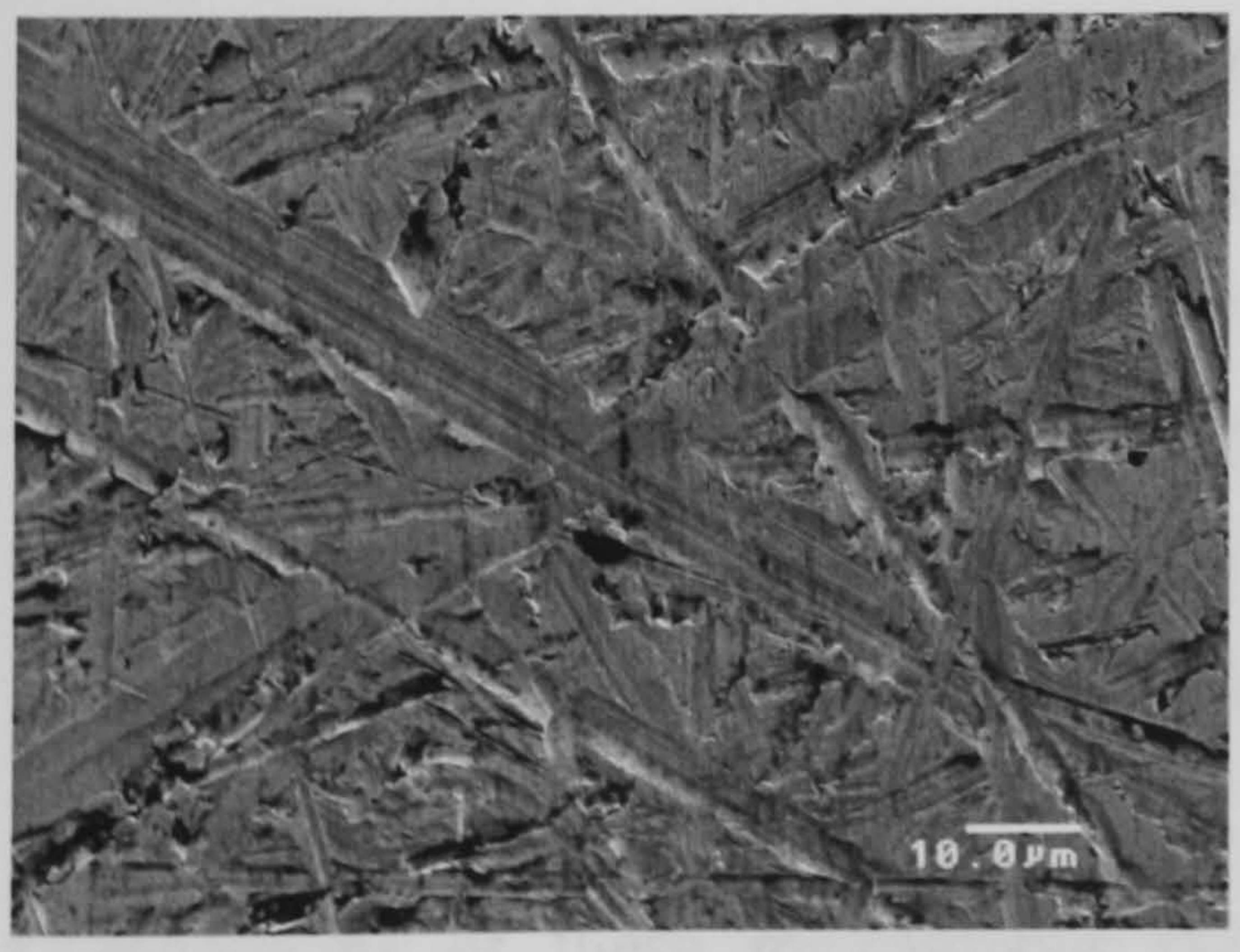

Figure 3.15a – Surface analysis

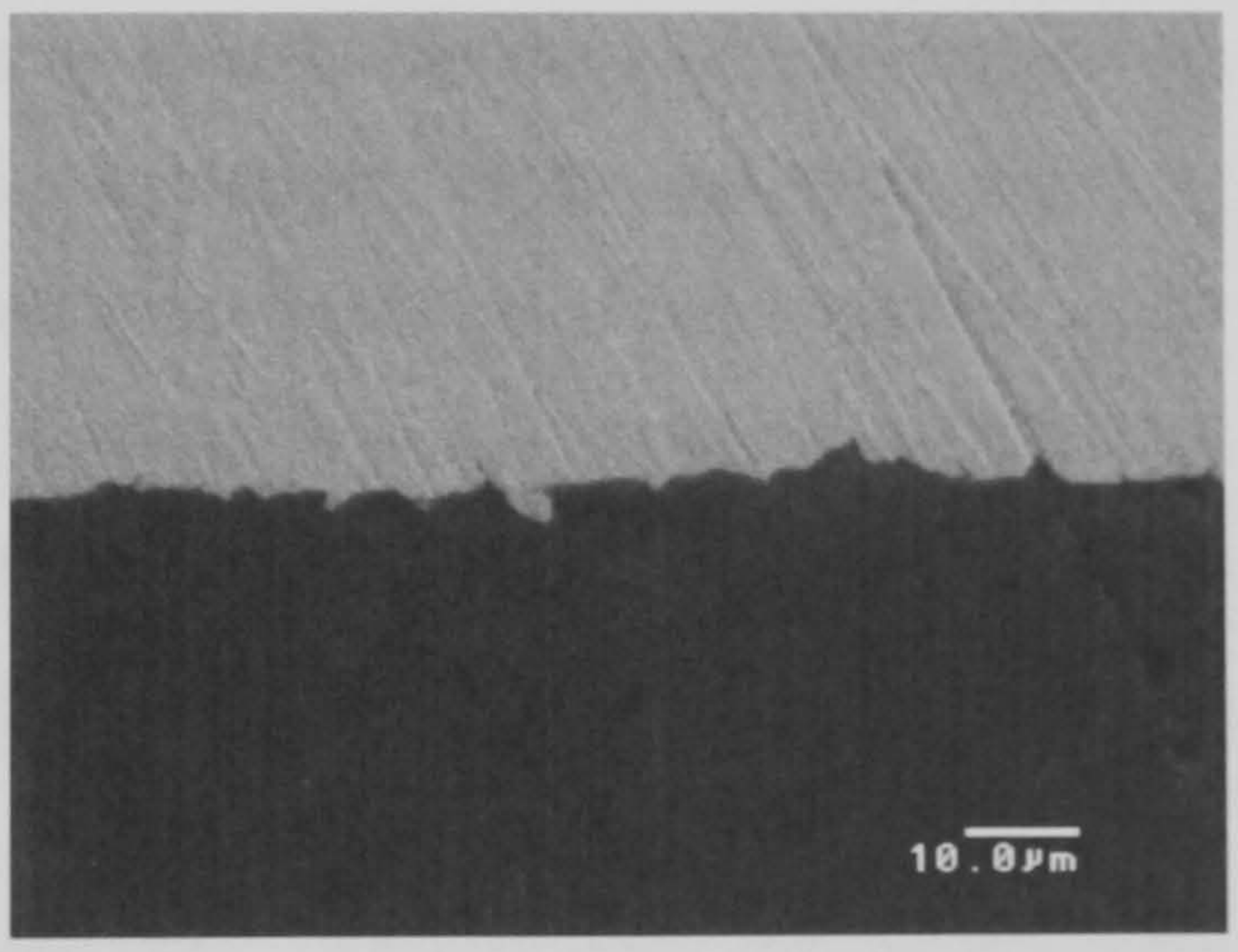

Figure 3.15b – Cross-sectioned view

P600 Grit Size

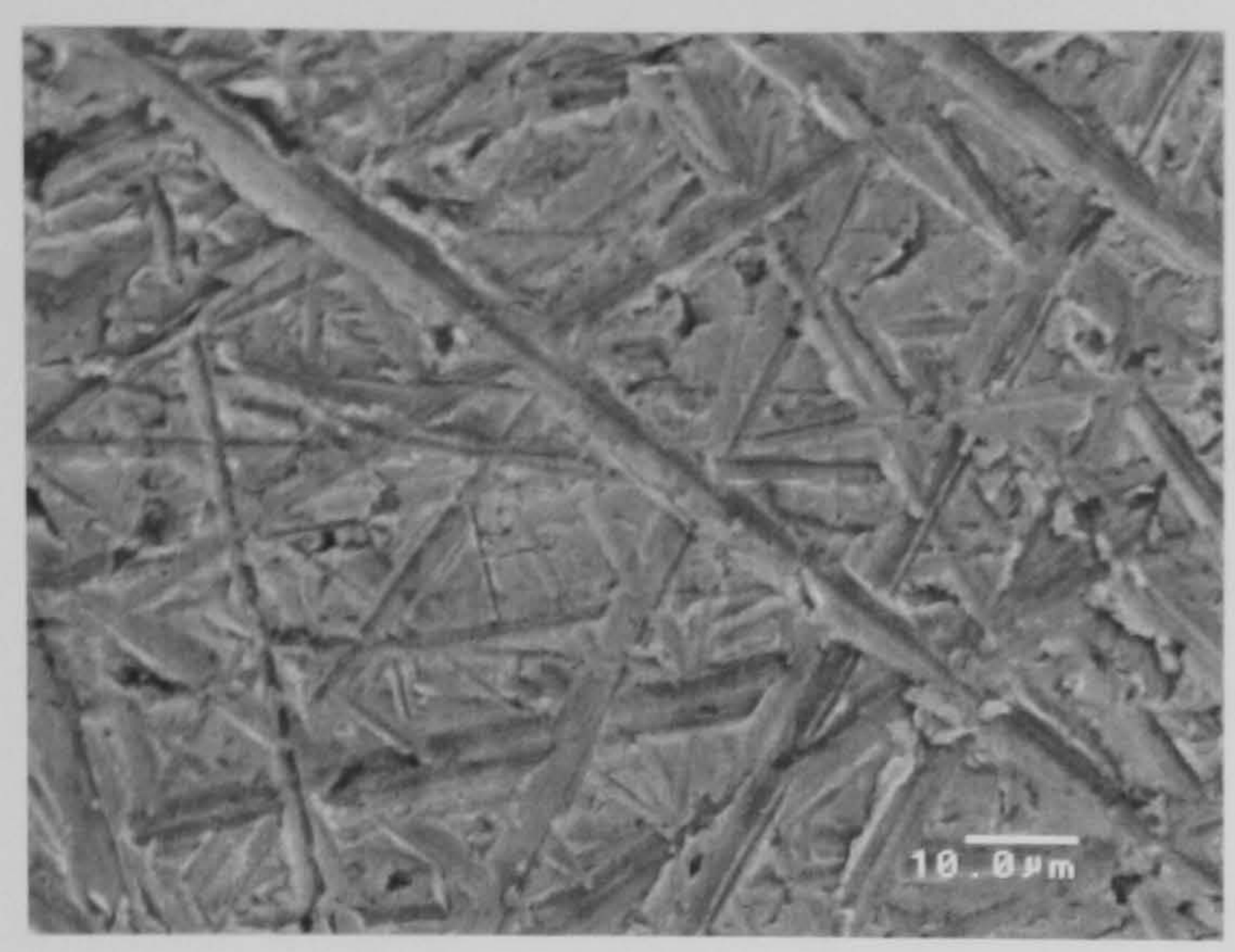

Figure 3.16a – Surface analysis

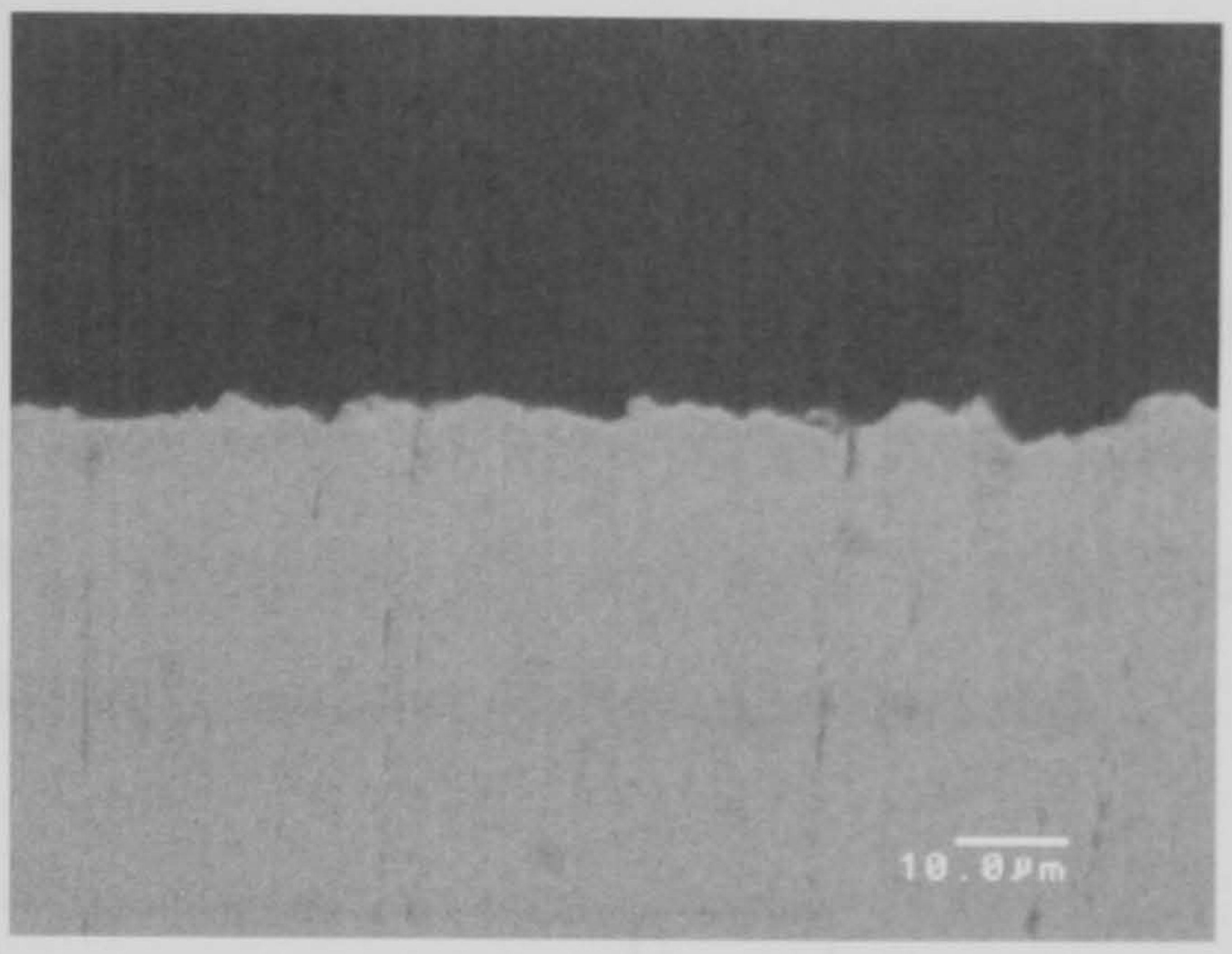

Figure 3.16b – Cross-sectioned view

P1200 Grit Size

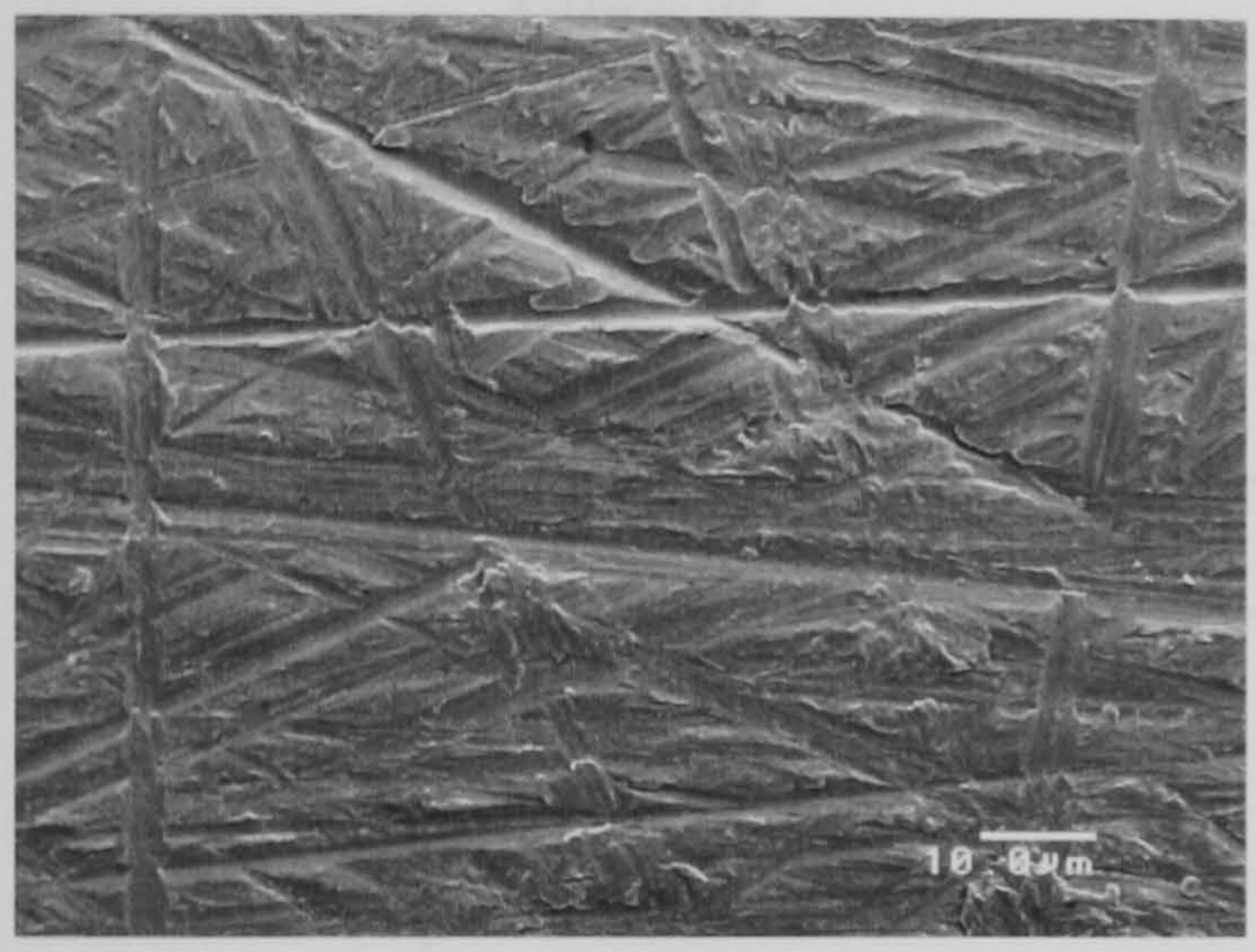

Figure 3.17a – Surface analysis

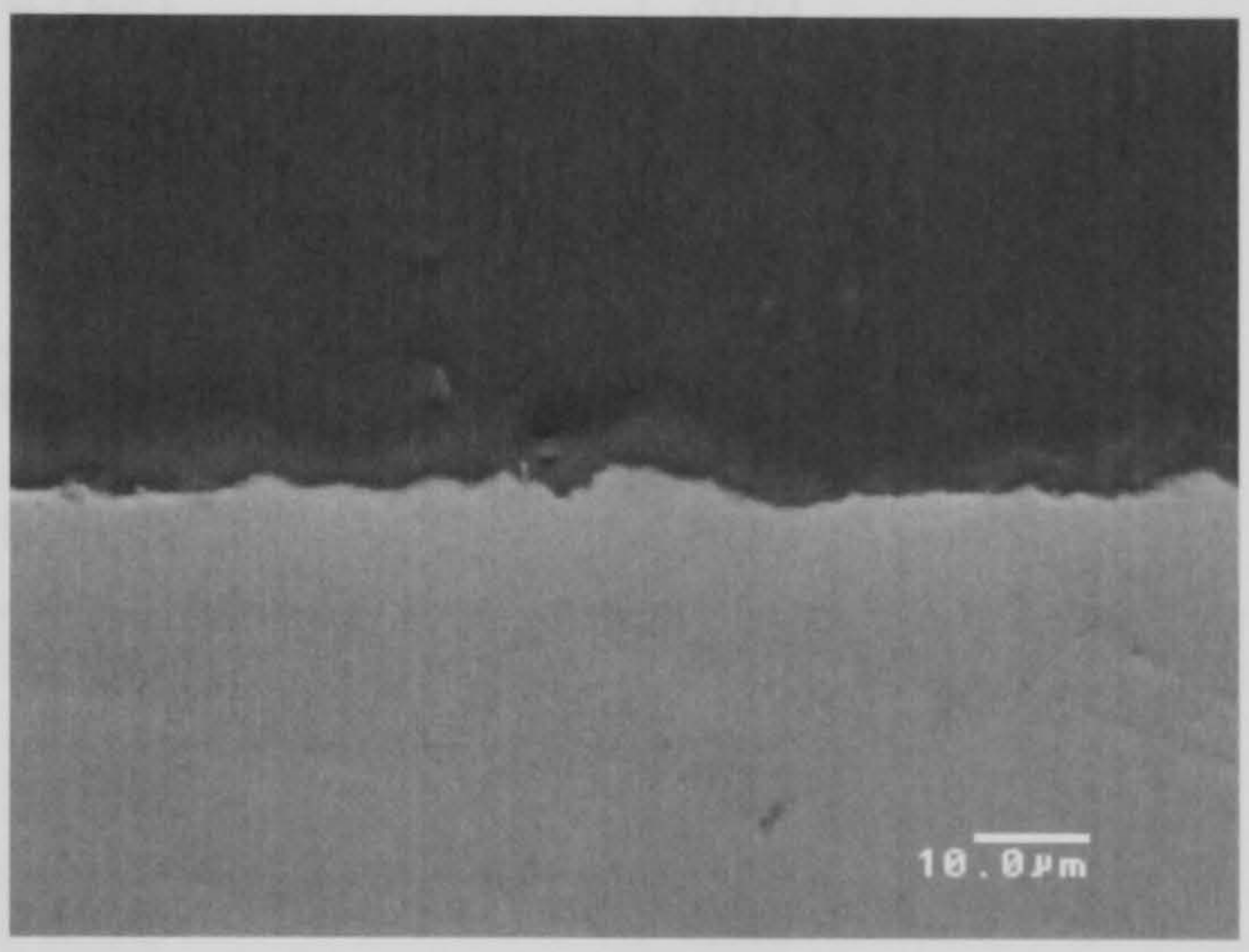

Figure 3.17b – Cross-sectioned view

As the P-number of the abrasive paper increases, the finer are the SiC particles used in the paper, and this is reflected in the number of scratches in the SEM images and the damage to the substrate surfaces. The surface topography of the sample prepared by the coarse SiC grade (Figure 3.10a) is very different from that of the finest SiC grade (Figure 3.17a), with average scratch widths for these two extremes being 10 microns and 2 microns respectively. Another observation is the presence of an increase in the number of the finer scratches per unit area as the P-number of the SiC paper increases.

Comparisons of these micrographs (Figures 3.11 - 3.17) with the micrographs illustrating the effects of chemical etching (Figure 3.9) show that, unlike the pitting caused by the etchant, the increase to the surface area is a result of deep recesses, mechanically produced by the abrasive SiC particles.

Surface area measurements

Surface area measurements were made following the pre-treatment of steel using different grades of SiC papers. For each of the grinding grades, the mean theoretical surface areas were calculated from twenty-five fields of view taken from cross-sections. The results are shown in Table 3.2, where the grit size used to yield the largest surface area was found to be the P120 grade, and this is highlighted in red.

SiC Grade	Average Theoretical Surface Area / μm^2	S.D.
Control	14,000	*800*
P60	15,800	*900*
P120	17,400	*900*
P180	16,300	*700*
P320	16,100	*900*
P400	15,500	*500*
P600	15,000	*700*
P1200	14,800	*800*

Table 3.2 – Mean surface area measurements for each grade of abrasive paper used

The data for each grit size are divided by the values for the control sample thereby giving the percentage increase in surface area for each of the ground samples with respect to the control sample (i.e., a measure of surface area change from an "as-received" substrate when using a particular grit size). The resulting percentage surface area increases and 95% confidence limits, are shown in Table 3.3, and the grit sizes that provide the greatest increase are highlighted in red.

SiC Grade	Average % Surface Area increase	95% Confidence Limits
P60	13.1	*8.4 - 17.9*
P120	25.4	*19.8 – 29.4*
P180	16.8	*12.6 – 21.2*
P320	15.3	*10.8 – 20.0*
P400	10.8	*7.2 – 14.4*
P600	7.3	*3.3 – 11.4*
P1200	6.3	*2.1 – 10.6*

Table 3.3 – Mean surface area increases resulting from preparation using SiC papers

It is recognised that a large increase in surface area may not necessarily mean a large resulting surface area, since the latter figure is dependent on the initial surface area of the "as-received" sample. Comparison of surface area increasing techniques between different materials can be moderated by assessing the surface area increases against a standard. Using the data shown in Tables 3.2 & 3.3, the parameter "percentage surface area increase over a hypothetically flat surface" is evaluated and given in Table 3.4. Also included in this Table are confidence limits calculated to 95% certainty.

SiC Grade	Average % Surface Area increase over a Hypothetically flat area	95% Confidence Limits
Control	15.4	*13.1 – 17.7*
P60	30.5	*27.6 – 33.4*
P120	43.7	*41.1 – 46.4*
P180	34.8	*32.6 – 37.1*
P320	33.1	*30.4 – 35.7*
P400	27.8	*26.2 – 29.4*
P600	23.8	*21.5 – 26.0*
P1200	22.6	*20.2 – 25.1*

Table 3.4 – Average surface area increases over a flat surface for each grit size

The data in Table 3.4 are graphically illustrated in Figure 3.18 and demonstrate that the optimal surface area increase results occur from grinding using the P120 grade grit size.

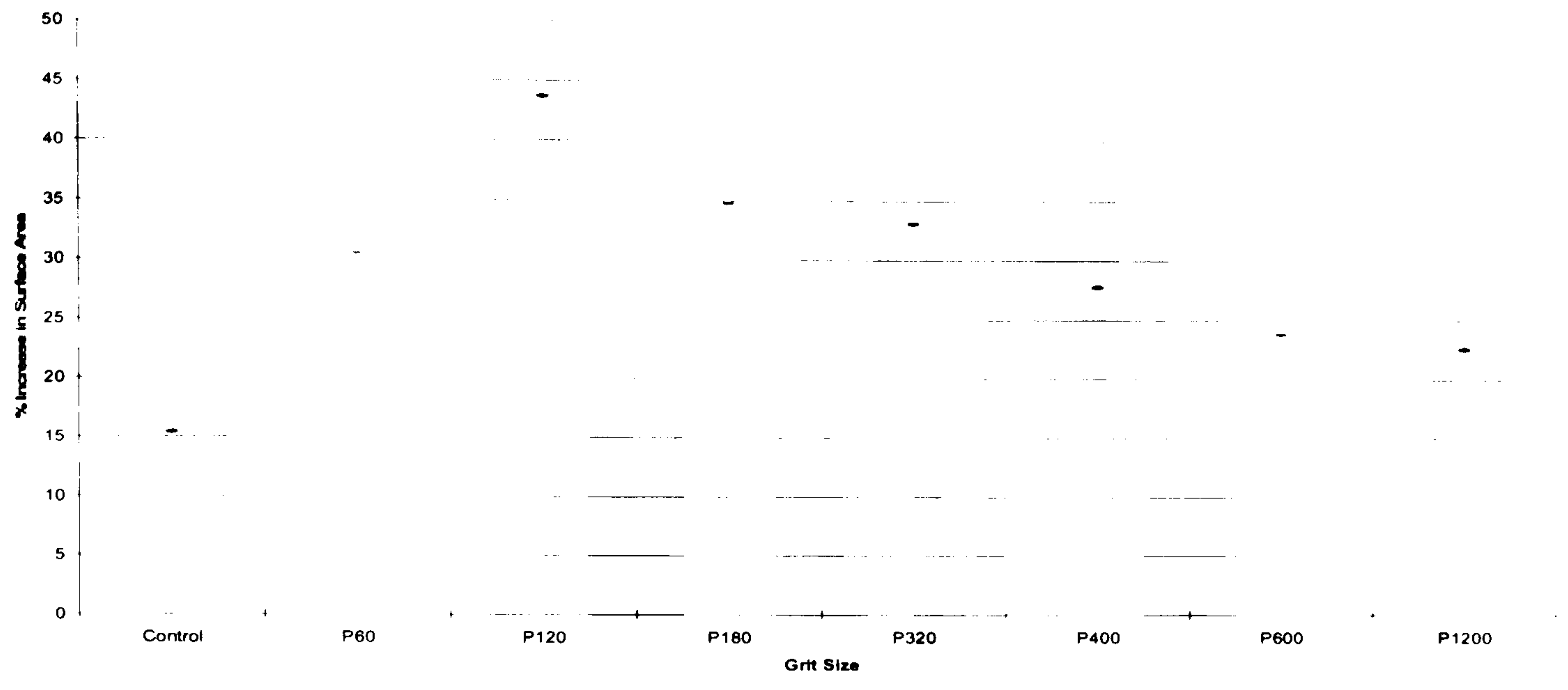

Figure 3.18 - Graph Showing Effect of Grit Size on Surface Area Increase over a Hypothetically Flat Surface for Stainless Steel

The results illustrate the effect of each grinding grade on the % surface area change for the steel substrates studied and suggest that the coarsest and the finest grades were not the most effective, with the highest percentage surface area increases occurring between the two extremes.

A possible explanation for this is that the largest grit size (P60) did not produce enough scratches per unit area to increase the surface area whilst the finest grit (P1200) did not produce scratches that were deep enough; the middle grades produced a good mix of deep scratches, which could account for the higher incidence per unit area.

3.5 CONCLUSIONS

A method for the determination of surface area by a combination of cross-sectional analysis with SEM and image analysis software is devised and implemented [43].

Surface area increases in steel by chemical etching are the result of surface texturing characterised by the introduction of surface pitting. Immersion into the appropriate acid solution produces a large surface area increase (~ 60%).

Surface pre-treatment of steel substrates by grinding using SiC abrasive metallographic papers was carried out. Surface area increases by physical grinding are the result of surface texturing characterised by the introduction of scratches and recesses. The largest surface area increase for steel (~44%) was achieved using the P120 grit size.

Both physical grinding and chemical etching significantly increases the surface area of steel material, although chemical pre-treatment is found to be slightly more effective. The information acquired from the surface area studies conducted and reported on in this Chapter is adopted for use when considering the pre-treatment of steel substrate materials prior to coating with tin and tin alloys.

CHAPTER FOUR

DEPOSITION OF TIN, TIN-COPPER AND TIN-NICKEL COATINGS

4.1 INTRODUCTION

4.1.1 The Case for Electroplating

Prior to assessing the wear resistance of a coating, it is important to describe the method of application. Although a large number of techniques are available for producing various coatings of metals and alloys, the choice of coating technique in this research can be narrowed down by the fact the coating materials are already pre-selected as tin, tin-nickel and tin-copper. Whilst much work has been previously conducted on using several different techniques of applying these coatings, including using some of the techniques described in Chapter Two, coatings of tin and its alloys have traditionally been applied by electroplating and hot-dipping, as they have been shown to be cheaper and quicker than other methods, e.g., electroless plating and PVD.

Electroplating and hot-dipping both have their advantages and disadvantages, and the most appropriate technique for applying tin and tin alloy coatings in this research is the one whose disadvantages are least significant. For electroplating, the formation of whiskers issue is a major issue in the electronics industry, but has negligible impact on wear studies since any growths at the surface will be removed on contact with the counter surface. The main disadvantage of hot-dipping, lack of thickness control, however, is a potential problem for this research because one of the parameters intended for investigation is the effect of increasing thickness, which requires production of samples with pre-set coating thicknesses. If performance is to be heavily dependant on thickness, it is clear that control over the coating thickness is necessary.

It is understandable that different coating thicknesses and types will influence their wear resistant characteristics, so it is critical that the coating process produces uniform samples to minimise margins of error when these samples are assessed in the next chapter. This can only serve to confer better understanding of the correlation between the thickness and wear resistant properties of each of the three coatings investigated.

As a result of the above consideration, electroplating has been selected as the technique for applying tin and tin alloy deposits in this research.

4.1.2 Electroplating Tin Alloy Coatings

An alloy can be defined as a material that is composed of two or more elements, where at least one of which is a metal. There are a number of ways to produce an alloy, and alloys were historically made by melting the constituent parts and combining them whilst at least one of the major ones were in molten form, thereby either melting or dissolving the minor additions. Another method is by diffusion, which involves electroplating the constituent metals separately before they are interfused on application of heat. The heat is not entirely necessary as some metals tend to interfuse at the interface to form an intermetallic layer over time, however this could take in the order of years.

Whilst electroplating has been selected as the most appropriate method for applying the deposits in this research, it is not as widely used in industry for coating alloys. The main reasons for this are that there are few electroplated alloys that are considered to be superior to pure metal deposits, and, more importantly, the conditions used for plating alloys require more stringent controlling than the metal plating processes. Alloy plating requires, not only that two or more metals are co-deposited, the process must deposit the constituent metals in the correct ratio. The deposition ratio is usually affected by a number of parameters such as temperature, pH, current density and composition of the plating bath.

Another consideration is that each metal has a deposition potential, and a more noble metal will be preferentially deposited at expense of the less noble metal. As a result, metals that have deposition potential values close together (e.g., within 200 mV) are easier to co-deposit than metals that have contrasting values.

Tin alloys, in general, are easier to plate than most other alloys, and several generalisations have been assumed in this research when optimising conditions for the alloy deposition process:

- An increase in the proportion of the more noble metal being deposited is usually a result of an increase in agitation and temperature.
- An increase in the proportion of the less noble metal being deposited is usually a result of an increase in current density.

The work presented in this chapter documents the deposition of the coatings using existing electroplating techniques and formulae. The coatings produced by the methods documented in this Chapter are subsequently characterised in the next Chapter.

4.2 HULL CELL TESTING: DETERMINATION OF PLATING CONDITIONS

The research documented in this thesis involves tin and tin alloy coatings that are applied via electrodeposition. Under favourable conditions, it is possible to simultaneously deposit metals onto a cathode, and the resulting alloys are usually comparable to those formed by thermal methods.

4.2.1 Experimental Technique and Methodology

Before any electroplating takes place, the current for driving the deposition process needs to be established, and this figure is calculated by the following equation:

$$\text{Current Density (A.dm}^{-2}\text{) x Area to be plated (dm}^{2}\text{) = Current (A)}$$

Only by knowing current density and the area to be plated can the electroplating current be evaluated.

Substrate material, in the form of 40 mm x 22 mm steel wear test coupons, are coated. The area to be plated can be simply calculated from the dimensions, as illustrated in Figure 4.1.

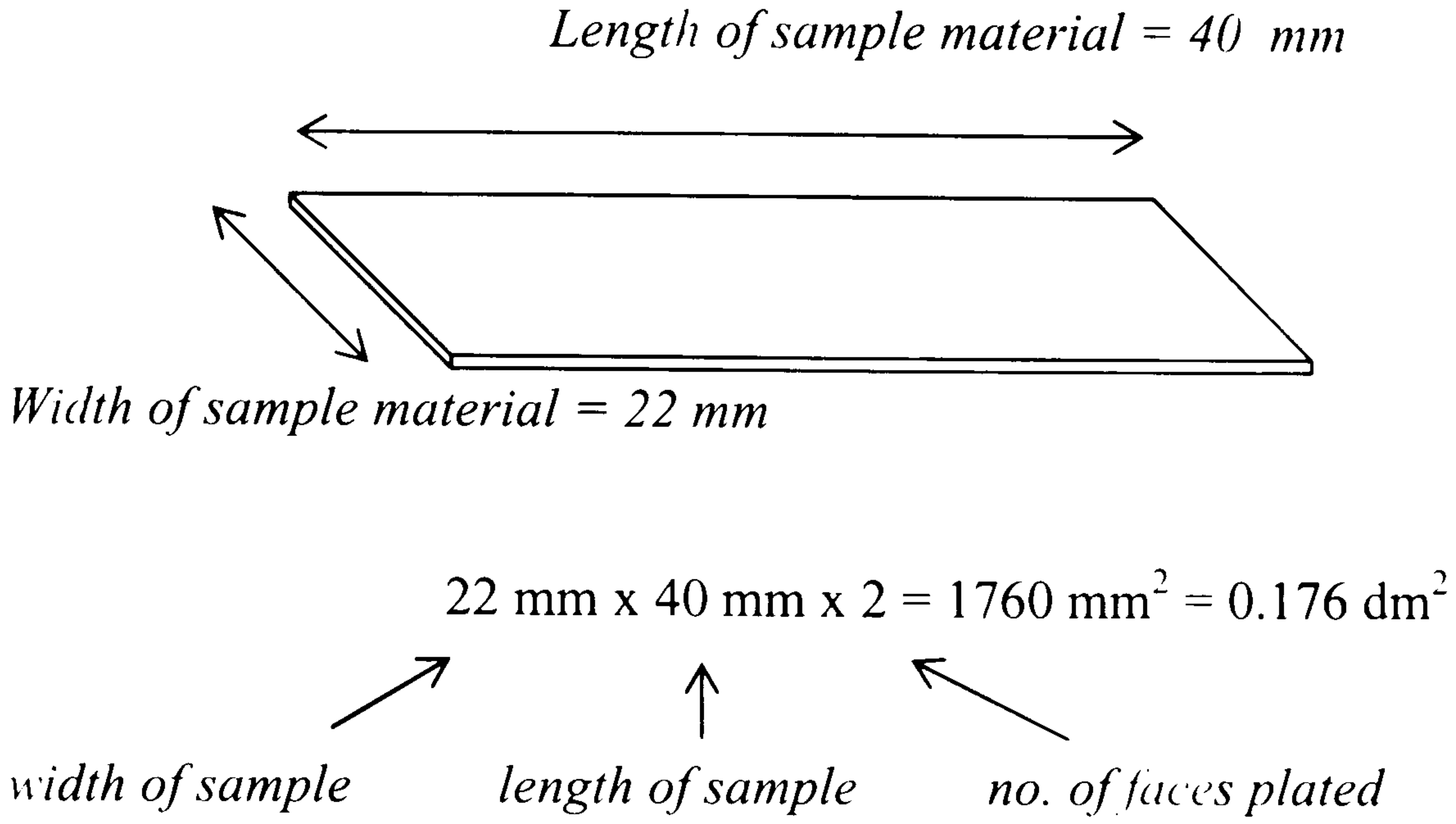

Figure 4.1 – diagram showing area intended for plating for wear test coupon

The evaluation of current density requires the use of the Hull Cell Test, which is an industrially recognised method for determining these values and is extensively used to assess the effect of additives to a plating solution or plating quality over a wide current density range. Due to the variable anode-cathode distance, it is possible to see the extent of plating as the current density changes; the distance between the electrodes at a given point is indirectly proportional to the current density at the same point.

The Hull Cell, illustrated by Figure 4.2, is composed of a trapezoid box and the slanting face, EFGH, is represented by the cathode, whilst a stainless steel sheet anode is placed at face ABCD. The cell is filled with electrolyte and a current is passed through the two electrodes placed at both ends of the cell.

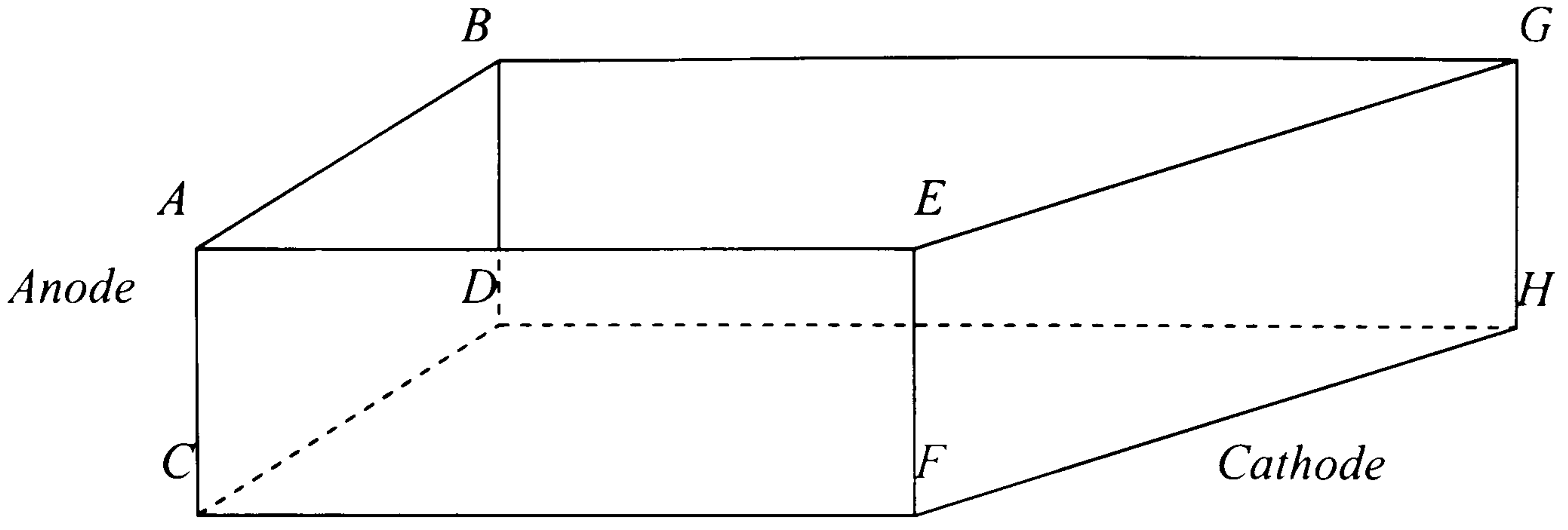

Figure 4.2 – Simplified diagram of a Hull Cell

In this way, reduction at the cathode, a 100 mm wide sheet, referred to as the Hull Cell panel, occurs across a range of current densities from the low end (distance BD-GH) to the high (distance AC-EF).

In order to achieve a fairly uniform coating deposit, an optimum current density for this particular electroplating application needs to be determined. The Hull Cell allows for such a plating distance over an applied range, and the resulting finishes over this range are then analysed to establish the most appropriate plating current. At high current densities, coatings can exhibit "burning" and is often scored as a result of the mass evolution of hydrogen. At the lower current density end of the scale, there is often insufficient current for adequate plating and in between these two extremes is a zone of satisfactory plating. The greater area this zone covers, the greater the current density range over which good quality plating can occur.

The quality of the plating over the current density range also depends on the electrolyte; uniform stirring of the solution is required to promote mass transport of the species. To determine the optimum current density, the Hull Cell was run at 2 Amps. According to Faraday's Laws of Electrolysis, the higher the current the shorter the plating times, however, using greater currents yield a smaller range of current densities where acceptable plating can be seen.

Using Table 4.1 below, it is possible for the boundaries of these zones to be identified with respect to the current densities by corresponding with Figure 4.3, which is a graphical diagram of the Hull Cell panel [12].

Current / Amps	**Current density / Amps per Square Decimetre (ASD)**													
	Position on Hull Cell Panel													
	a	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*	*k*	*l*	*m*	*n*
2	10	8	6	4	3	2.5	2	1.5	1	0.8	0.6	0.4	0.2	0.1
3	15	12	9	6	4.5	3.75	3	2.25	1.5	1.2	0.9	0.6	0.3	0.15
5	25	20	15	10	7.5	6.25	5	3.75	2.5	2.0	1.5	1.0	0.5	0.25

Table 4.1 – Current density positions on Hull Cell Panel at 2,3 & 5 Amps

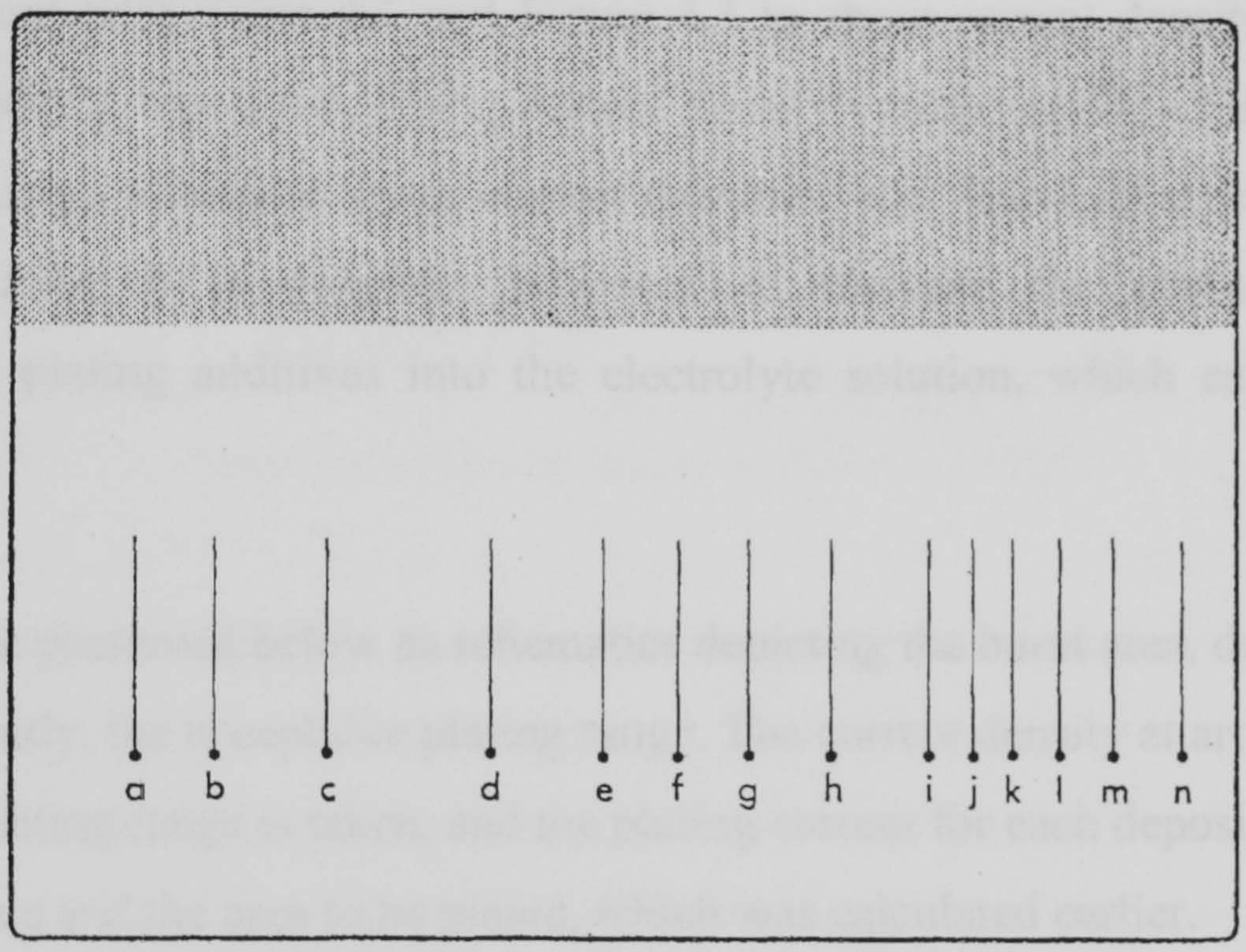

Figure 4.3 – Diagram of a Hull Cell Panel showing differing current densities at marked locations [12]

Operating at greater current densities also produces a higher level of gas evolution, large quantities of which are often detrimental to the quality of the deposit. Gas evolution at the electrodes, however, is necessary and can be used as a measure of the efficiency of the current [53].

The next section presents the Hull Cell test results for each of the three coatings, and the subsequent determination of their respective optimum current densities. Once these values have been derived, evaluation of the electroplating currents for tin, tin-nickel and tin-copper is possible.

4.2.2 Results

In order to determine the optimum working current density for use in this research, for each of the three coatings, Hull Cell testing was conducted at 2 Amps on brass cathode specimens.

In all cases, the Hull Tests produced, on the brass test panels, poor coating coverage at low current density, characterised by dull deposits (on the right side), and burnt areas at high current density, caused by excessive gas evolution (on the left side). Between these two areas is the zone of acceptable deposition and this location is shown by a red arrow in the photographs. For each coating, the locations of the three zones are cross-referenced with Table 4.1 and Figure 4.3 to show current densities that yield acceptable coating deposition. Using current density values outside of this range can lead to little or no plating at lower current densities, and "burning" defects at higher current densities. It is possible, however, to increase the plating range by incorporating plating additives into the electrolyte solution, which can reduce the "burnt" zone.

The results are presented below as schematics depicting the burnt area, dull plate, and, more importantly, the acceptable plating range. The current density at around the mid-point of the plating range is taken, and the plating current for each deposit is evaluated using this value and the area to be plated, which was calculated earlier.

Tin coating

The tin deposits were electroplated using a proprietary plating bath (BT-200, as supplied by Rohm and Haas Company). A schematic of the corresponding Hull Cell results, using 2 Amps, is presented below (Figure 4.4).

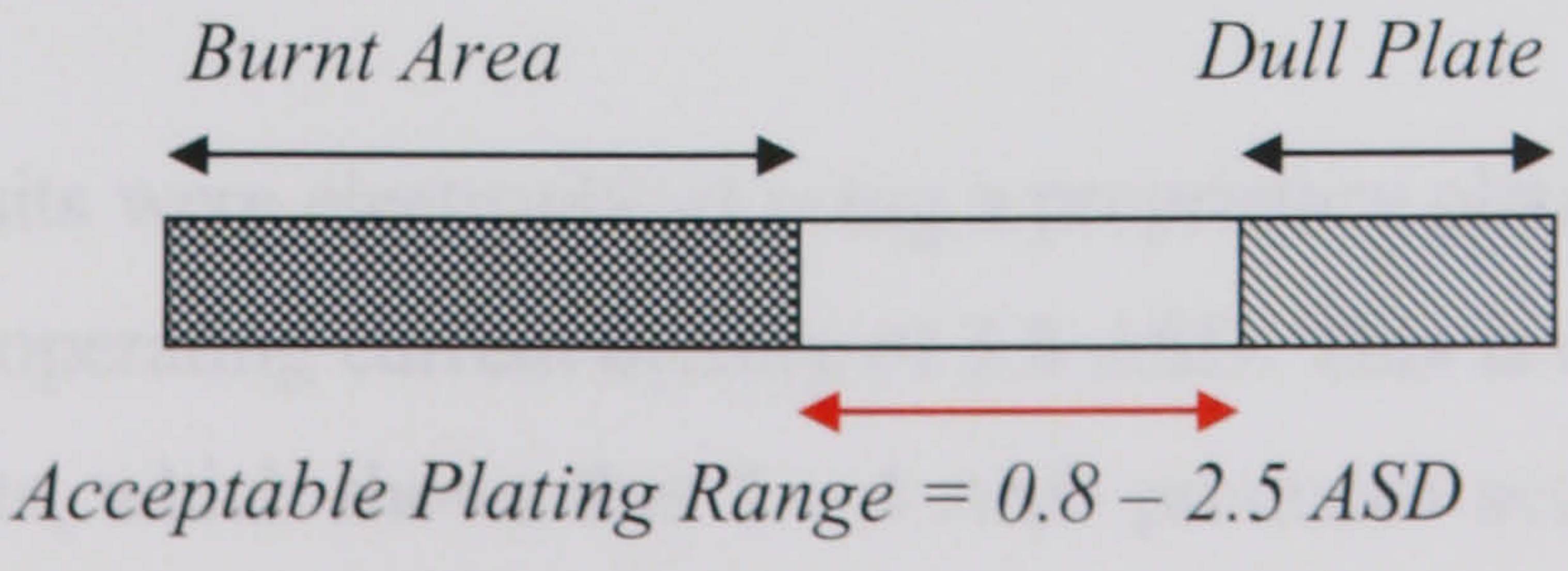

Figure 4.4 – Hull Cell schematic for tin coating at 2 Amps

From the Hull Cell experiments, it was found that 2-10 ASD produced acceptable tin deposits. From these results, it was decided that 7 ASD should be used for the tin plating, and using the area dimensions calculated previously, the applied current required for the satisfactory deposition of a tin coating was calculated as:

$$7\ \text{A.dm}^{-2} \times 0.176\ \text{dm}^{2} = 1.23\ \text{A}$$

Tin-Nickel Coating

The tin-nickel plating bath was formulated to instructions presented in Bowden 1991 [33], and a schematic of the corresponding Hull Cell results, using 2 Amps, is presented below (Figure 4.5).

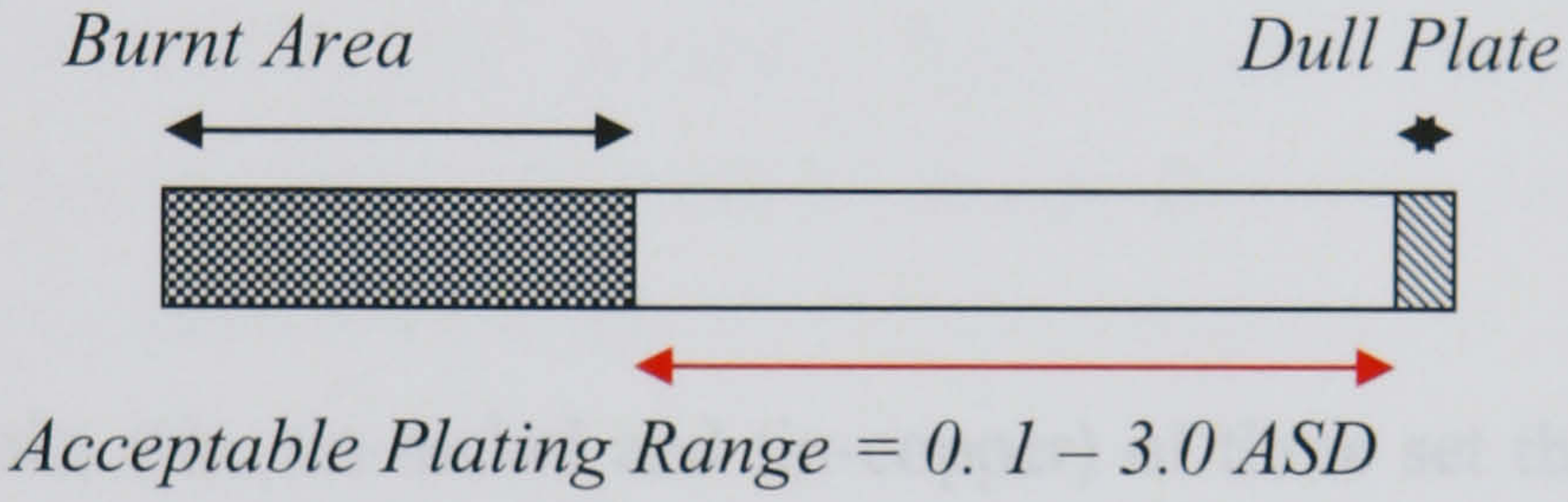

Figure 4.5 – Hull Cell schematic for tin-nickel coating at 2 Amps

Bowden states that the optimum current density for using this tin-nickel bath is 2.6 ASD and this is confirmed with the Hull Cell experiments, which shows that 0.1 – 3.0 ASD produced acceptable tin-nickel deposits. Using the 2.6 ASD and the area dimensions calculated previously, the applied current required deposition of a tin-nickel coating was calculated as:

$$2.6\ \text{A.dm}^{-2} \times 0.176\ \text{dm}^{2} = 0.46\ \text{A}$$

Tin-Copper Coating

The tin-copper deposits were electroplated using a proprietary plating bath [54], which had a recommended operating current density of 3.8 ASD. This is confirmed with the Hull Cell experiments, which shows that 2 – 4 ASD produced acceptable tin-copper deposits (Figure 4.6).

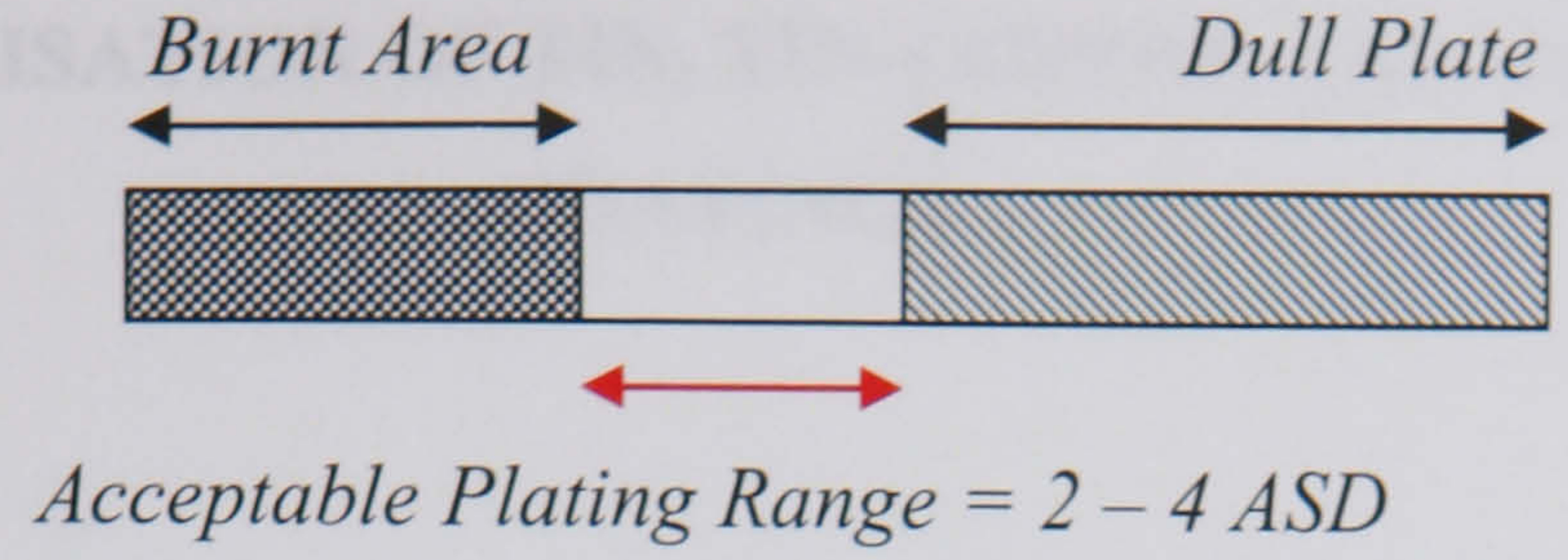

Figure 4.6 – Hull Cell schematic for tin-copper coating at 2 Amps

Using the 3.8 ASD and the area dimensions calculated previously, the applied current required deposition of a tin-copper coating was calculated as:

$$3.8\ \mathrm{A.dm^{-2}} \times 0.176\ \mathrm{dm^{2}} = 0.67\ \mathrm{A}$$

4.3 SUMMARY

Three different deposits (tin, tin-nickel and tin-copper) of three set thicknesses (2, 5 and 10 microns) are successfully applied onto the appropriately sized wear testing steel coupons using existing electroplating solutions and techniques. The use of the Hull Cell enables plating conditions to be optimised and the deposit of an acceptable coating.

The test coupons are ready for wear testing, and a sample is taken from each batch for characterisation, to ensure complete coating coverage, and uniformity in composition and thickness. The characterisation methodology and results are presented in the next Chapter.

CHAPTER FIVE
CHARACTERISATION OF TIN, TIN-COPPER AND TIN-NICKEL COATINGS

5.1 INTRODUCTION

It is necessary to stress the importance of characterisation of the deposits applied, since, regardless of the coating technique used, a coating that is poorly adhered, or a set of coatings that differ despite being produced with identical conditions, will yield poor results. Using a combination of analytical techniques, it is possible to confirm deposition of complete coating coverage, and uniformity in composition and thickness. This is important for the generation of consistent results from the subsequent stages of testing and analysis. This chapter describes a set of characterisation techniques, which are used to ensure that the coatings tested are consistent and any variation is controlled.

Following the deposition of the tin and tin alloy coatings, it is important to characterise the deposits to ensure that all coatings produced have complete coverage and uniform topography, are of the intended thickness, and of the correct composition. The intention is to show that there are minimal variations between samples from the same batch of wear test coupons.

The characterisation is carried out on three counts:

- The surface of the coating is examined by Scanning Electron Microscopy (SEM) to inspect the degree of coverage and observe whether or not surface defects are present.
- The thickness of the coating is determined by cross-sectional analysis of the coating using SEM. This part of the characterisation establishes the relationship between the coating thickness and plating time. Using this relationship, it is possible to generate pre-determined coating thicknesses

- The coating is analysed using Energy Dispersive X-ray (EDX), which provides information on the elemental composition of the deposit.

5.2 SURFACE APPEARANCE FROM SEM

5.2.1 Experimental Technique and Methodology

The surface characterisation of the electrodeposits is achieved with Scanning Electron Microscopy (SEM), which is described in Chapter Three. No sample preparation was necessary and the specimens were examined in the "as-plated" state.

5.2.2 Results

Tin Coating

Examination of the tin deposit with SEM revealed a relatively smooth and uniform coverage, as illustrated in Figure 5.1a. Only at a higher magnification, Figure 5.1b, was it possible to reveal detailed topographical information.

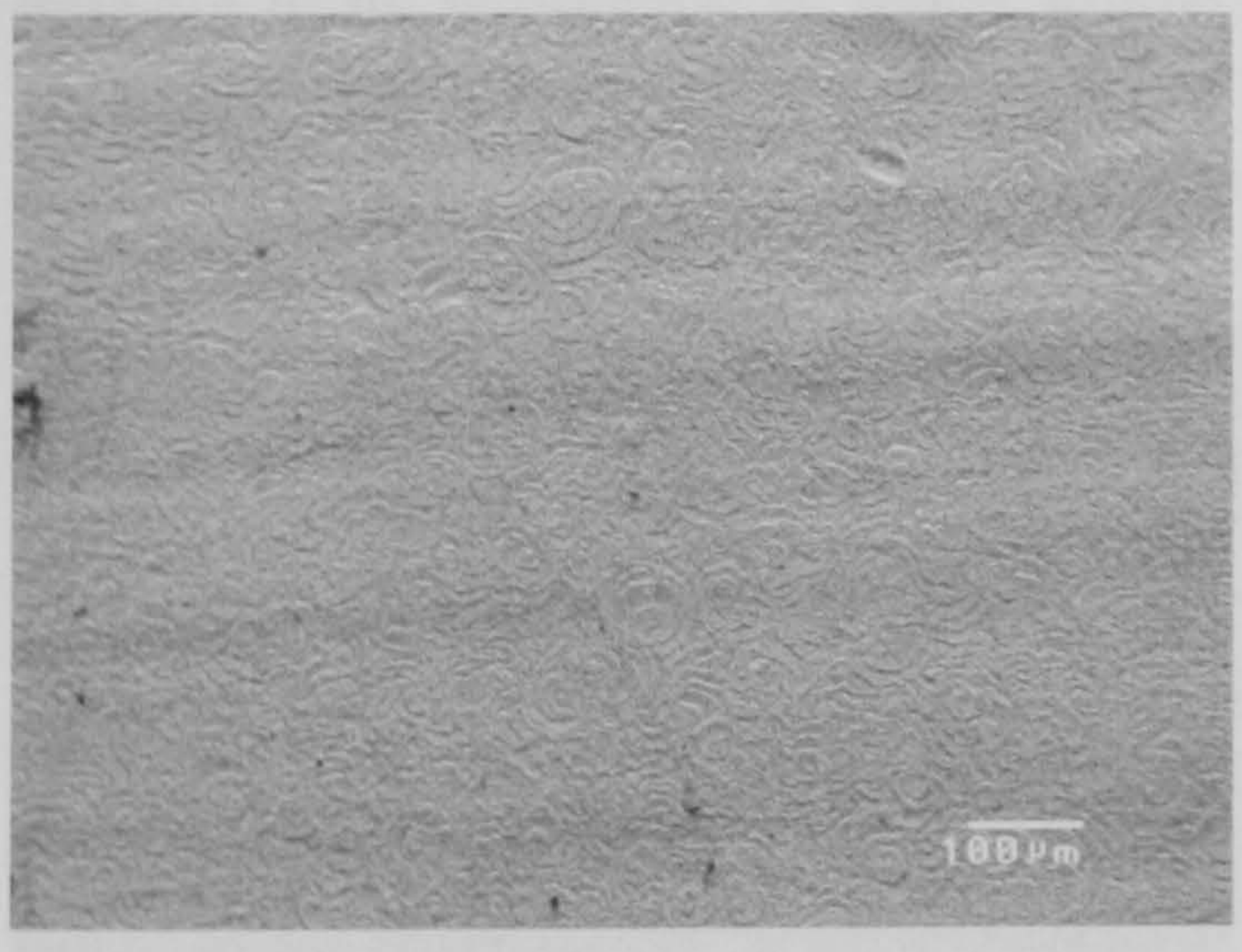

Figure 5.1a – surface of Sn deposit

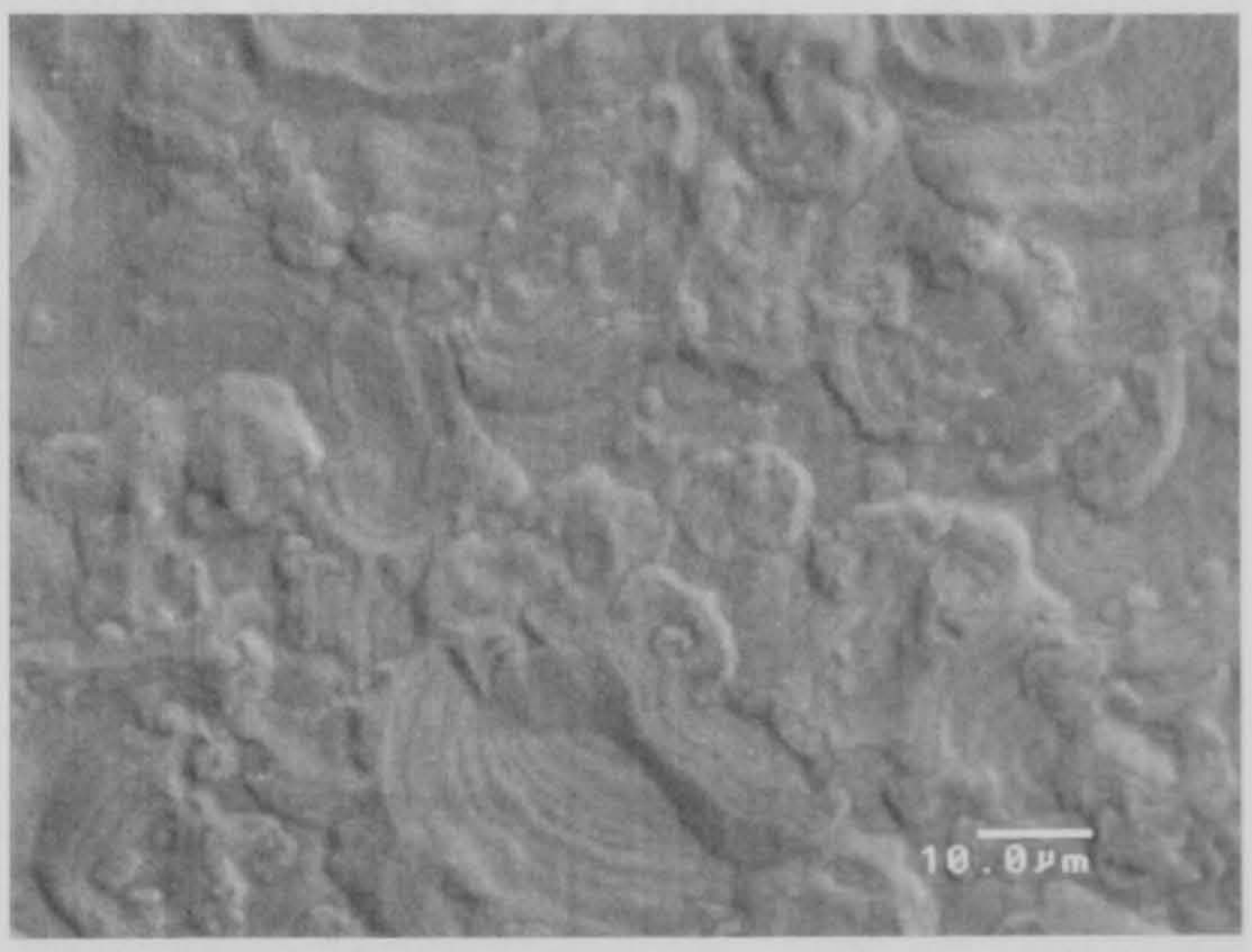

Figure 5.1b – surface of Sn deposit

Tin-Nickel Coating

At low magnifications, the texture of the tin-nickel deposit (Figure 5.2a) appears to be seemingly rougher than tin. Examination at higher magnifications (Figure 5.2b) appears to show that the tin-nickel alloy coating is composed of small grains, around 2-6 microns in diameter.

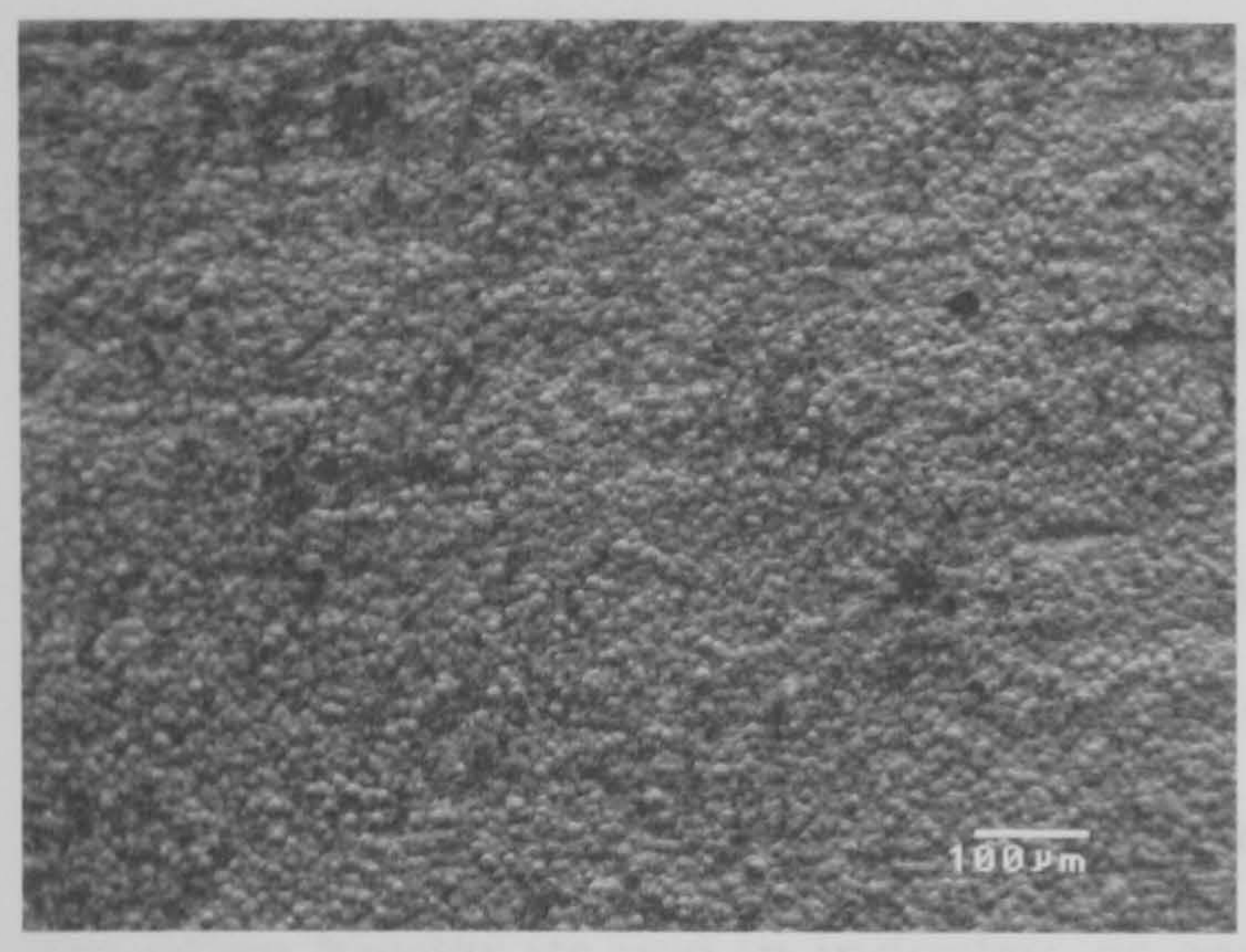

Figure 5.2a – surface of Sn-Ni deposit

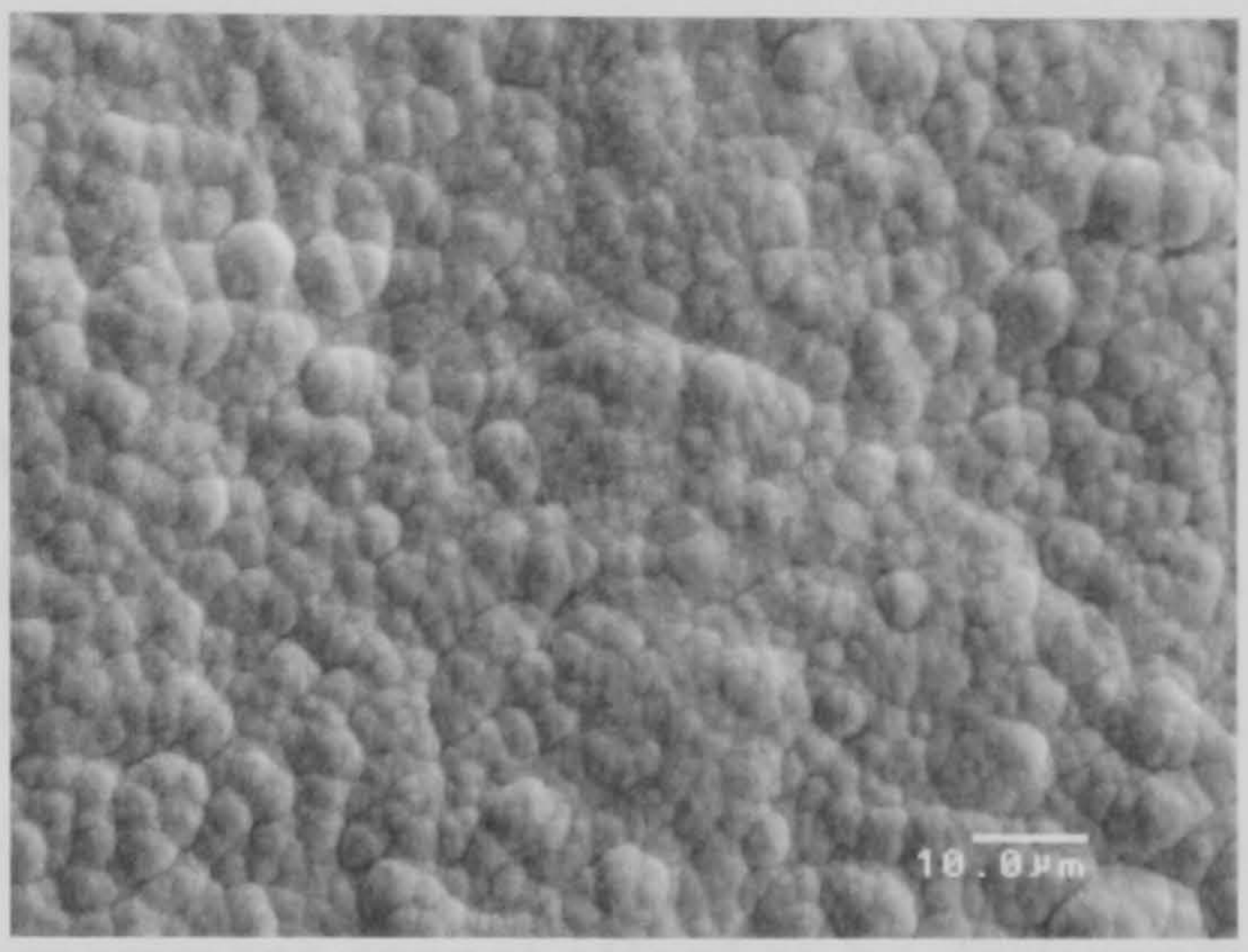

Figure 5.2b – surface of Sn-Ni deposit

Tin-Copper Coating

The tin-copper deposit surface appears very smooth and uniform at low magnifications (Figure 5.3a). On inspection at higher magnifications, the surface appears to be composed of many grains measuring around 5-15 microns in diameter (Figure 5.3b).

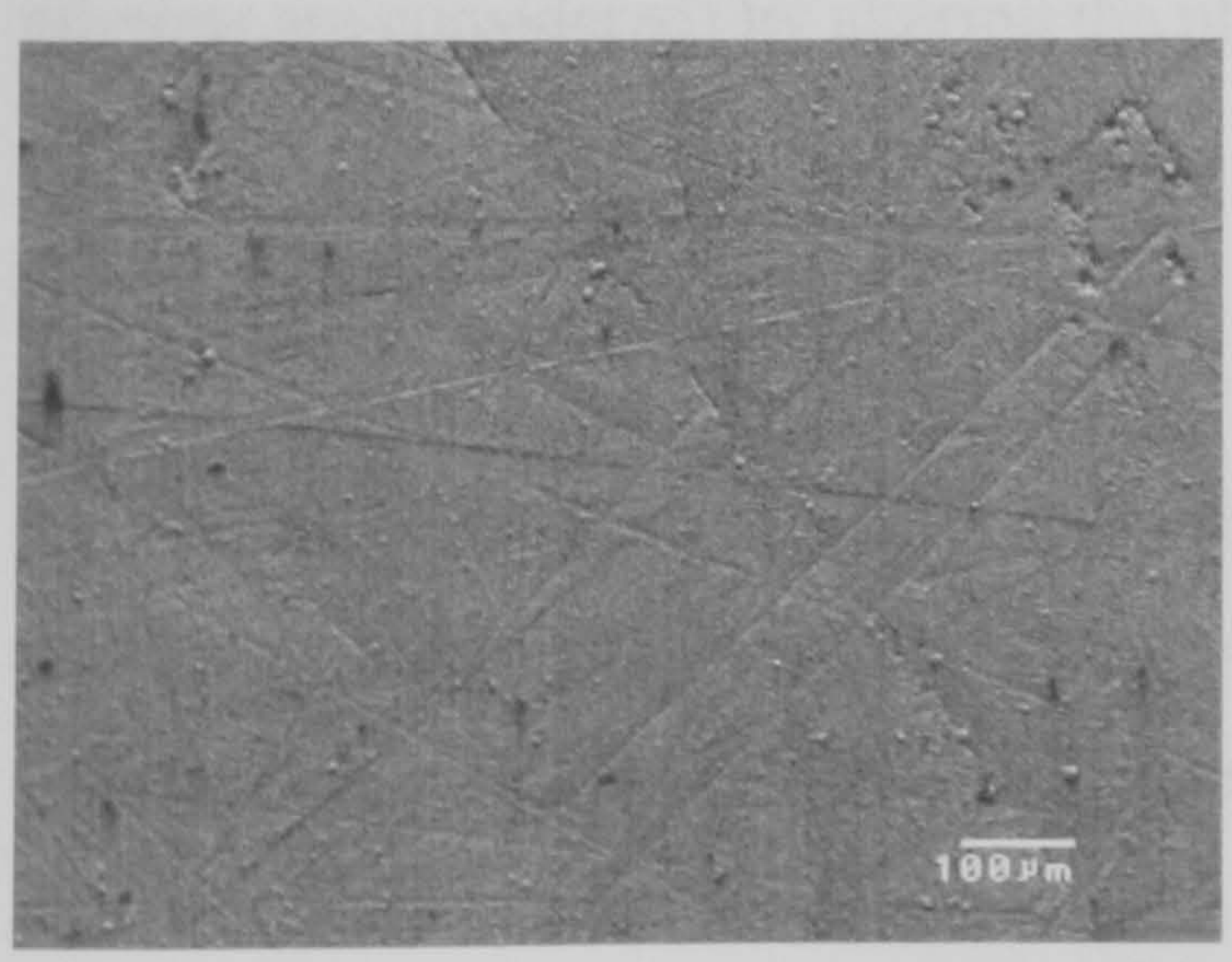

Figure 5.3a – surface of Sn-Cu deposit

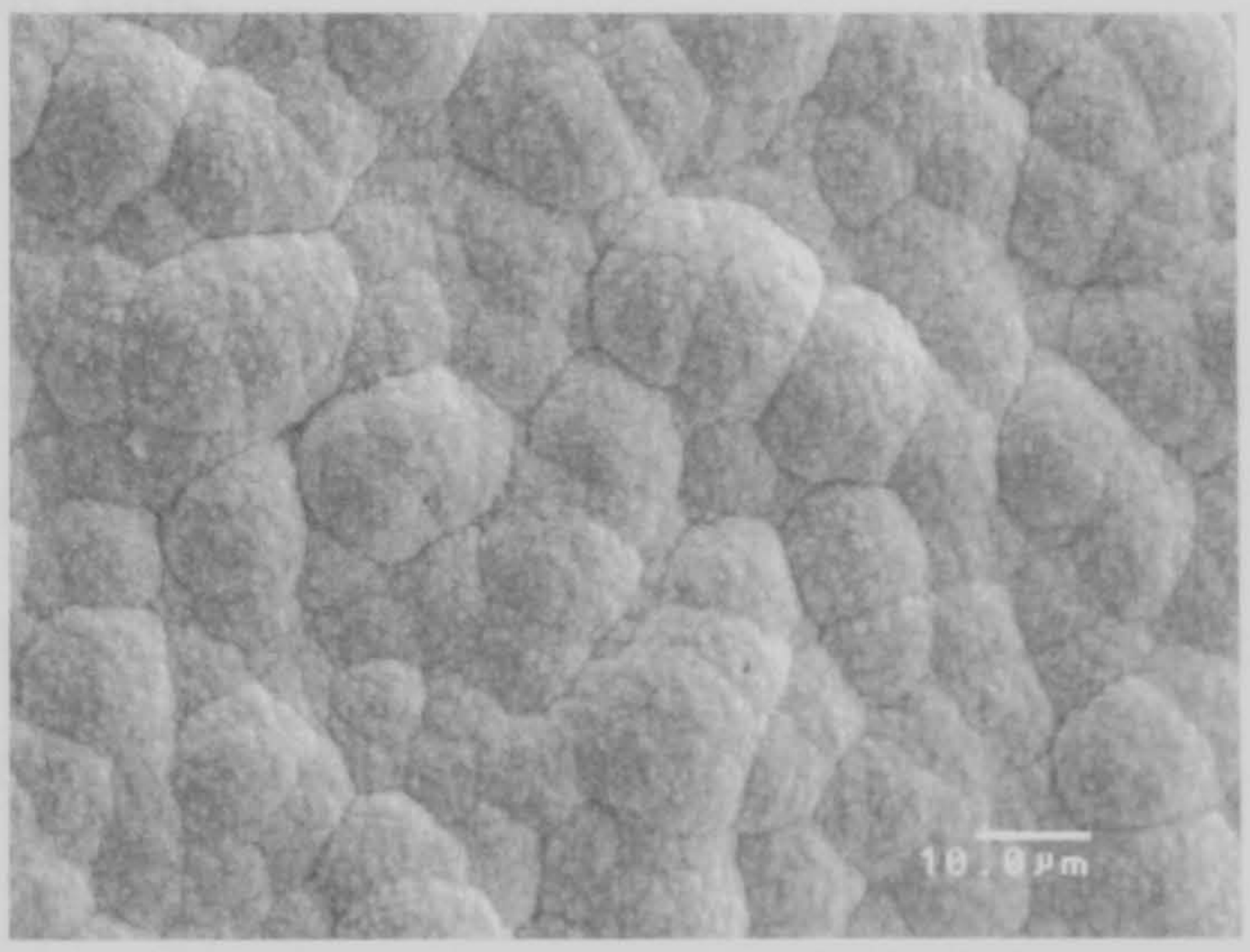

Figure 5.3b – surface of Sn-Cu deposit

5.3 COATING THICKNESS FROM MICRO-SECTIONING AND SEM

5.3.1 Experimental Techniques and Methodology

In order to assess the thickness of the plated tin and tin alloy deposits the plated samples examined with SEM in the sectioned state. Thus coatings produced in this Chapter are observed with SEM in both the surface and cross-sectional plane. Whilst the electron microscopy of a specimen surface involves the simple loading of the sample into the SEM chamber, the micro-sectioning, also known as metallographic preparation, makes this mode of examination more time consuming and labour intensive. What SEM observation of coatings in the micro-sectioned state provides is the security and certainty of viewing an entire plane where the substrate and coating interface is clearly defined. The technique is obviously a destructive technique, which can often hinder its use in industry, as some specimens cannot afford to be destroyed; however, samples in this research are not thus restricted. The microsectioning and metallographic preparation is decribed in Chapter Three.

Samples plated for different durations are firstly sectioned to establish the deposit thickness as a function of plating time. From this, a relationship between plating duration and coating thickness is determined. Consequently, it is possible to plate to pre-determined thicknesses (in this research coating thicknesses of 2, 5 and 10 microns are considered) by altering the plating time.

5.3.2 Results

As well as ascertaining the thickness values from cross-sectional measurements, the theoretical relationship between plating time and thickness was also evaluated from Faraday's equation, and the two sets of findings were compared.

Faraday's Equation is:

$$Q = F.Eq$$

Where,

Q = current [A] x plating time [s];

F = Faraday's Constant = 96490 [A.s/g]

Eq = mass of deposit [g] / (RAM of coating / no. electrons exchanged)

Tin Coating

According to the thicknesses measured from the sections:

- plating for 60 seconds yielded a thickness of 2.9 microns
- plating for 90 seconds yielded a thickness of 4.4 microns
- plating for 120 seconds yielded a thickness of 5.8 microns
- the relationship is therefore (where t = time and T = thickness):

$$t_{Sn} \sim 20 \times T_{Sn} \text{ (i.e., 20 seconds per micron)}$$

Using Faraday's Equation,

i = 1.23 A (determined by Hull Cell)

F = 96490 A.secs/g (Constant)

Eq needs to be calculated from Mass, which is evaluated from the density equation:

ρ = Mass / Volume

ρ tin = 7.28 g/cm^3

RAM$_{Sn}$ = 118.69

No. of e$^-$ = 2

Volume = platable area of substrate x thickness of deposit

= 17.6 cm^2 x 1 micron = 0.00176 cm^3

Mass = Density x Volume

= 7.28 g/cm^3 x 0.00176 cm^3 = 0.0128128 g

Eq = mass / (RAM / no. electrons exchanged)

= 0.0128128 g / (118.69 / 2) = 0.0002159 g

Therefore,

t = F.Eq / i

= (96490 A.secs/g x 0.0002159 g) / 1.23 A = 17 secs

The theoretical plating time for 1 micron of 17 seconds is slightly less than the practical time of 20 seconds. This slight discrepancy can be attributed to no plating solution and setup being 100% efficient.

The plating durations are thus evaluated for the following thicknesses:

- 40 seconds ➔ 2 microns
- 1 minute 40 seconds ➔ 5 microns
- 3 minutes 20 seconds ➔ 10 microns

Tin-Nickel Coating

According to the thicknesses measured from the sections:

- plating for 2 minutes yielded a thickness of 1.2 microns
- plating for 5 minutes yielded a thickness of 2.7 microns
- plating for 10 minutes yielded a thickness of 5.2 microns
- the relationship is therefore (where t = time and T = thickness):

$$t_{SnNi} \sim 110 \times T_{SnNi} \text{ (i.e., 110 seconds per micron)}$$

Using Faraday's Equation,

i = 0.46 A (determined by Hull Cell)

F = 96490 A.secs/g (Constant)

Eq needs to be calculated from Mass, which is evaluated from the density equation:

ρ = Mass / Volume

ρ SnNi = (65/100).ρSn + (35/100).ρNi

= (0.65 x 7.28 g/cm^3) + (0.35 x 8.90 g/cm^3) = 7.847 g cm^3

RAM_{SnNi} = (65/100).RAM_{Sn} + (35/100).RAM_{Ni}

= (0.65 x 118.69) + (0.35 x 58.69) = 97.69

No. of e^- = 2

Volume = platable area of substrate x thickness of deposit

= 17.6 cm^2 x 1 micron = 0.00176 cm^3

Mass = Density x Volume

= 7.847 g cm^3 x 0.00176 cm^3 = 0.01381072 g

Eq = mass / (RAM / no. electrons exchanged)

= 0.01381072 g / (97.69 / 2) = 0.0002827 g

Therefore,

t = F.Eq / i

= (96490 A.secs/g x 0.0002827 g) / 0.46 A = 59 secs

The theoretical plating time for 1 micron of 59 seconds is just over half the practical time of 110 seconds. This discrepancy can be attributed to a low efficiency in the plating process, which evolves a high amount of hydrogen.

The plating durations are thus evaluated for the following thicknesses:

- 3 minutes 40 seconds ➔ 2 microns
- 9 minutes 10 seconds ➔ 5 microns
- 18 minutes 20 seconds ➔ 10 microns

Tin-Copper Coating

According to the thicknesses measured from the sections:

- plating for 60 seconds yielded a thickness of 1.0 microns
- plating for 90 seconds yielded a thickness of 1.5 microns
- plating for 120 seconds yielded a thickness of 2.0 microns
- the relationship is therefore (where t = time and T = thickness):

$t_{SnCu} \sim 60 \times T_{SnCu}$ (i.e., 60 seconds per micron)

Using Faraday's Equation,

i = 0.67 A (determined by Hull Cell)

F = 96490 A.secs/g (Constant)

Eq needs to be calculated from Mass, which is evaluated from the density equation:

ρ = Mass / Volume

ρ SnCu = (15/100).ρSn + (85/100).ρCu

(0.15 x 7.28 g cm^3) + (0.85 x 8.96 g cm^3) = 8.708 g cm^3

RAM_{SnCu} = $(15/100).RAM_{Sn} + (85/100).RAM_{Cu}$

= $(0.15 \times 118.69) + (0.85 \times 63.546) = 71.8176$

No. of e^- = 2

Volume = platable area of substrate x thickness of deposit

= $17.6\ cm^2 \times 1\ micron = 0.00176\ cm^3$

Mass = Density x Volume

= $8.708\ g/cm^3 \times 0.00176\ cm^3 = 0.01532608\ g$

Eq = mass / (RAM / no. electrons exchanged)

= $0.01532608\ g / (71.8176 / 2) = 0.0004268\ g$

Therefore,

t = F.Eq / i

= $(96490\ A.secs/g \times 0.0004268\ g) / 0.67\ A = 61\ secs$

The theoretical plating time for 1 micron of 61 seconds is close to the practical time of 60 seconds. One reason for this is because cyanide baths are particularly efficient and produce less hydrogen.

The plating durations are thus evaluated for the following thicknesses:

- 2 minutes ➔ 2 microns
- 5 minutes ➔ 5 microns
- 10 minutes ➔ 10 microns

Figure 5.4a – 5.4c are SEM micrographs showing microsectioned examples of these three thicknesses being obtained for SnCu.

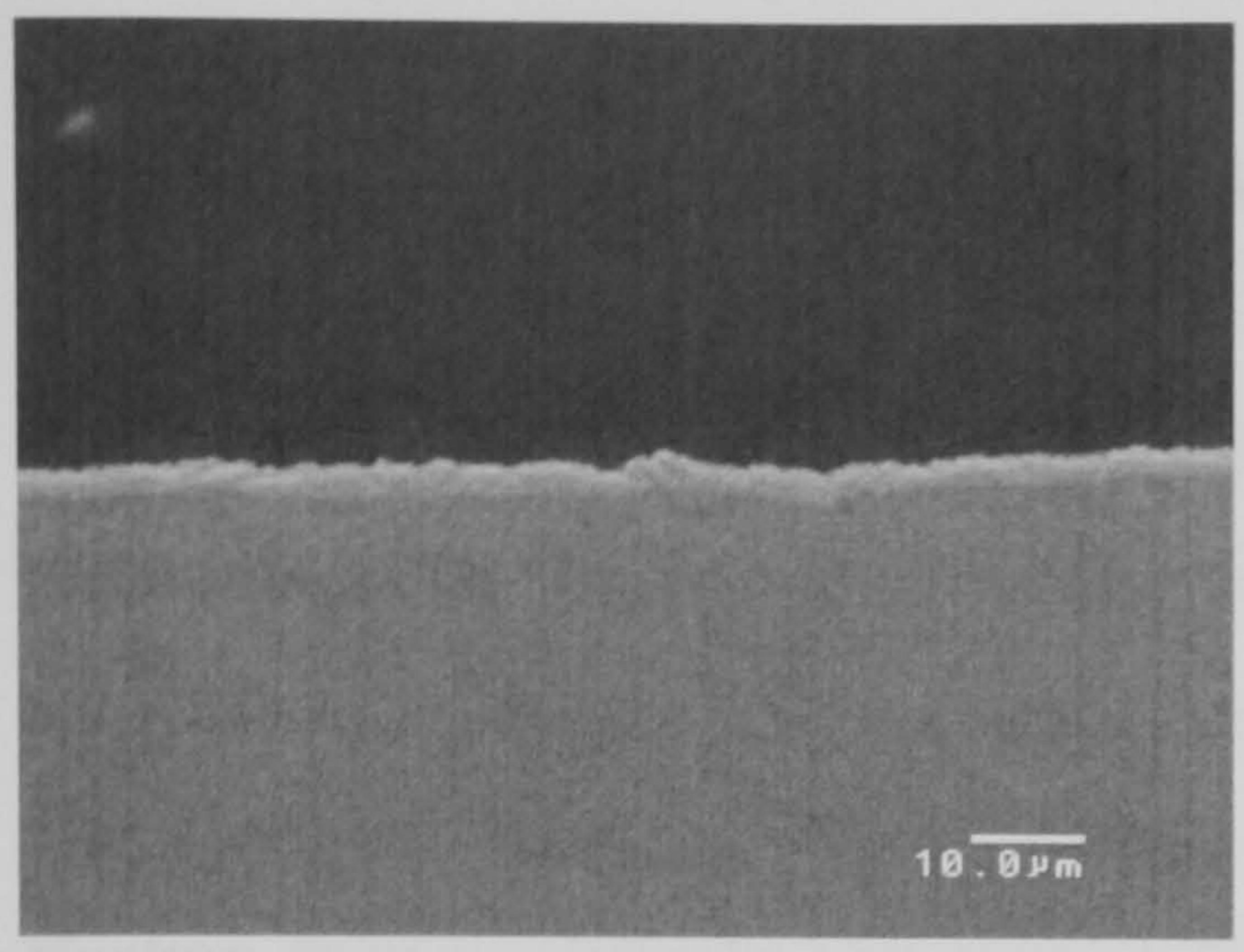

Figure 5.4a – section of 2 µm deposit

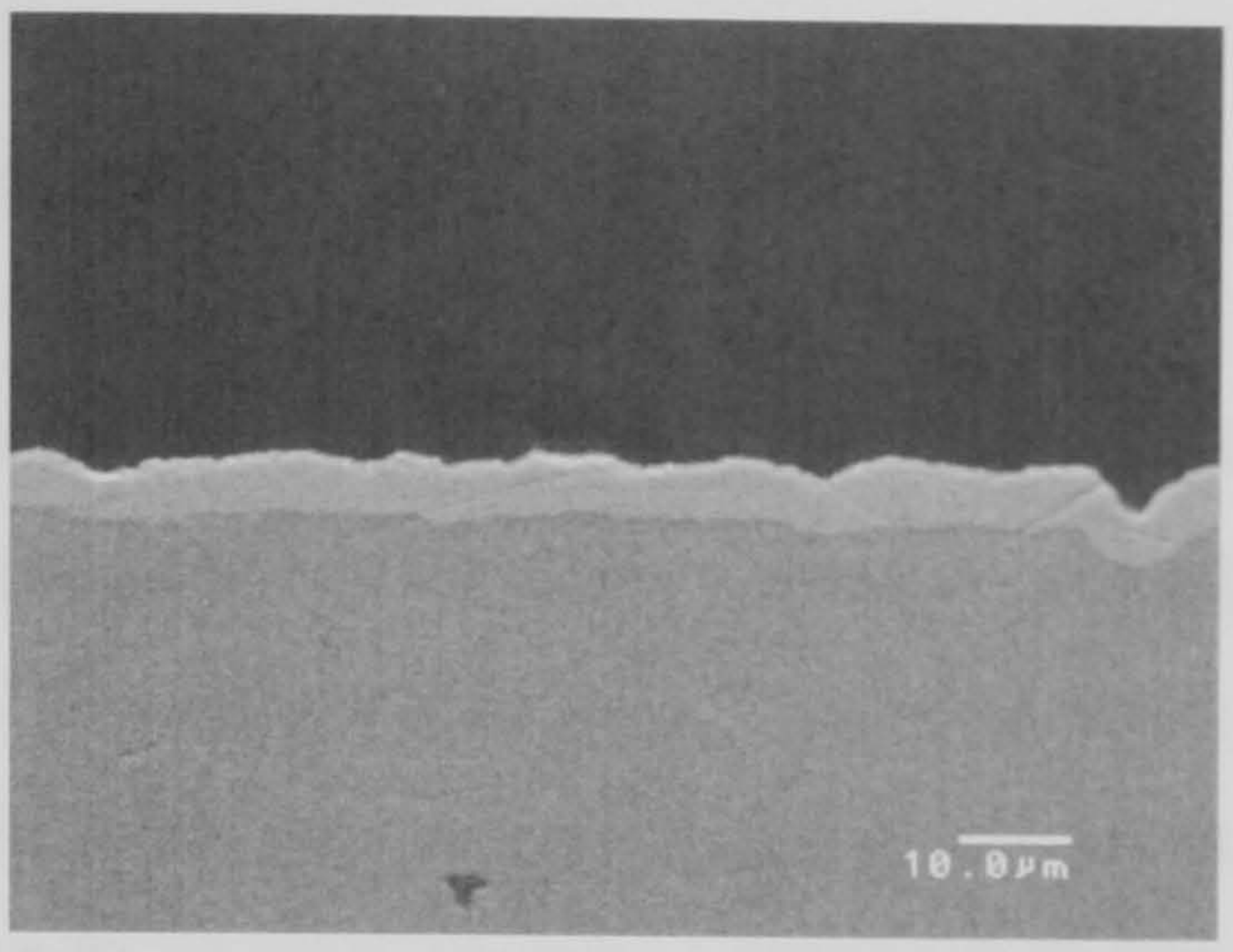

Figure 5.4b – section of 5 µm deposit

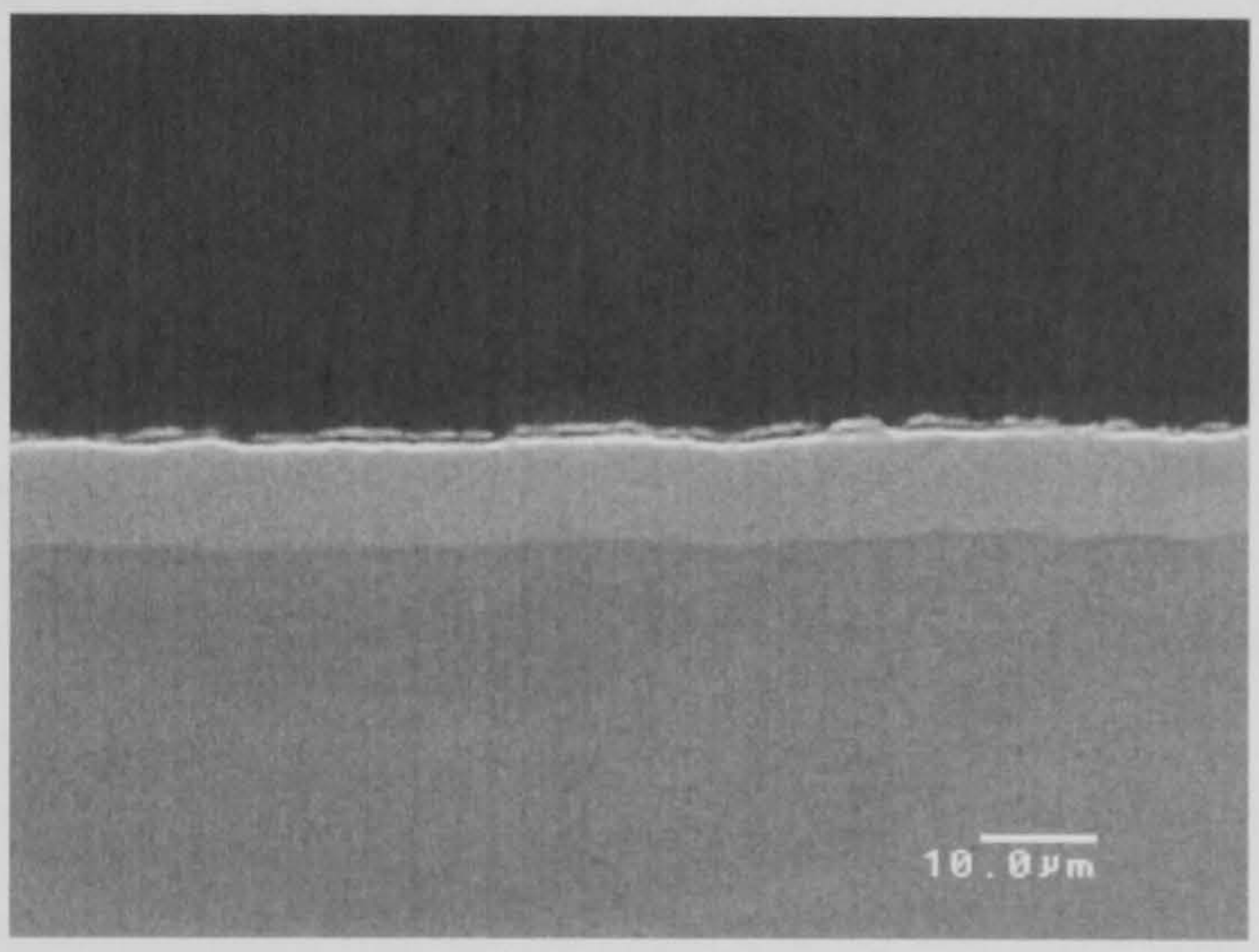

Figure 5.4c – section of 10 µm deposit

Coatings of tin, tin-copper and tin-nickel are thus deposited at these three thicknesses.

5.4 COATING COMPOSITION FROM EDX

As well as confirming the thicknesses of the plated tin and tin-alloy deposits, it is also important evaluate the composition, since different ratios of constituent elements can greatly affect the properties of an alloy.

The method used to determine the compositions is Energy Dispersive X-ray (EDX), which is often used in conjunction with SEM.

The aim of this section is to report on whether or the materials plated correspond to their respective compositions cited in the literature research.

5.4.1 Experimental Techniques and Methodology

The Energy Dispersive X-ray (EDX) detector uses x-rays, which are photons of electromagnetic radiation generated by the interaction between the electron beam and the specimen during SEM analysis (Figure 3.5), to determine elemental information. The electron beam causes excitation at the point of interaction and removes an electron from a relatively low energy shell, with an electron from a higher shell then filling the gap vacated by this ionisation. The x-rays that are emitted through this ionisation are characteristic of the individual element present at the point of impact. The energy or wavelength, and the number of x-rays are detected, and, from this, compositional information of the sample can be determined. The resulting spectrum, usually displays one or more signature peaks of the element(s) present, which correspond to the different shells of a particular element, in a trace of counts versus wavelength [55]. The higher the number of counts of a particular element in a spectrum, the more of the element is present.

EDX is a useful technique for determining unknown constituents in materials and their relative concentrations within the material. Using this technique, it is possible to, initially confirm the metals present in the plated deposits, and then to quantify the ratios between the identified metals.

For each plated coating, an EDX spectrum is acquired over a large area of the surface, in order to firstly identify the elements present. The peak heights in each spectrum are then analysed with the INCA computer software, supplied by Oxford Instruments, to determine the counts for each element. From this data, the weight percent of the elements present are calculated with respect to each other.

5.4.2 Results

Tin Coating

Analysis of the tin surface with the INCA EDX system yields a spectrum (Figure 5.5) showing peaks that correspond to the position of the tin series, indicating high counts of tin only. The positions of the iron peaks have been marked, and there is no evidence of the latter metal detected, indicating that there were no areas of exposed steel present from the positions analysed, thus confirming complete coverage.

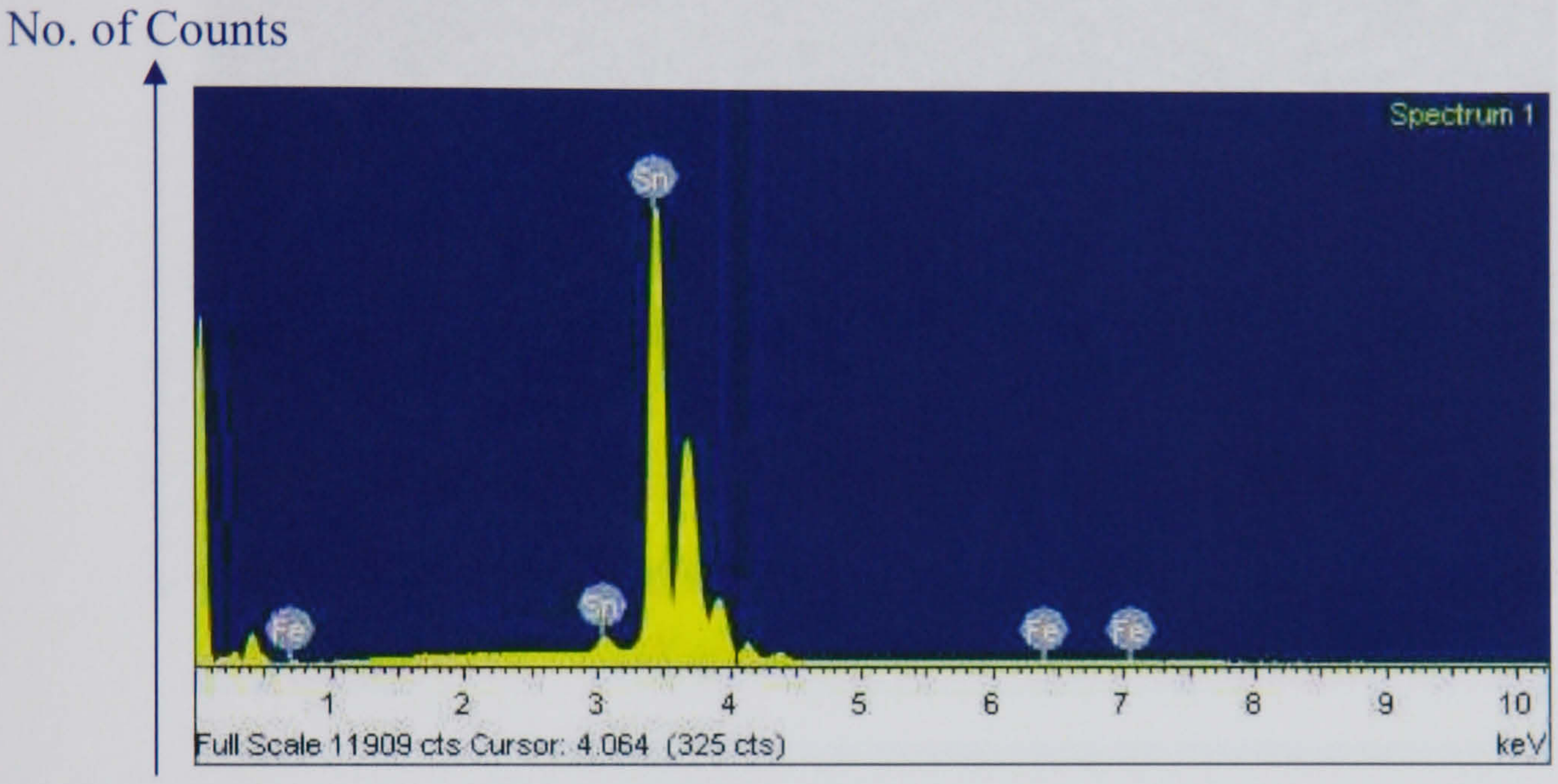

Figure 5.5 – EDX spectrum of tin deposit surface

The results from the qualitative analysis are consistent with a quantitative account of the peak positions and heights, and Table 5.1 shows the results from calculations based on tin and iron.

Element	Weight %
Sn	99.96
Fe	0.04

Table 5.1 – Elemental composition of deposit with respect to iron

Tin-Nickel Coating

Analysis of the tin-nickel surface with the INCA EDX system yields a spectrum (Figure 5.6) showing high counts of tin from the tin series and a smaller set of peaks that correspond to the nickel series. The positions of the iron peaks have been marked, and there is no evidence of the latter metal detected, indicating that there were no areas of exposed steel present from the positions analysed.

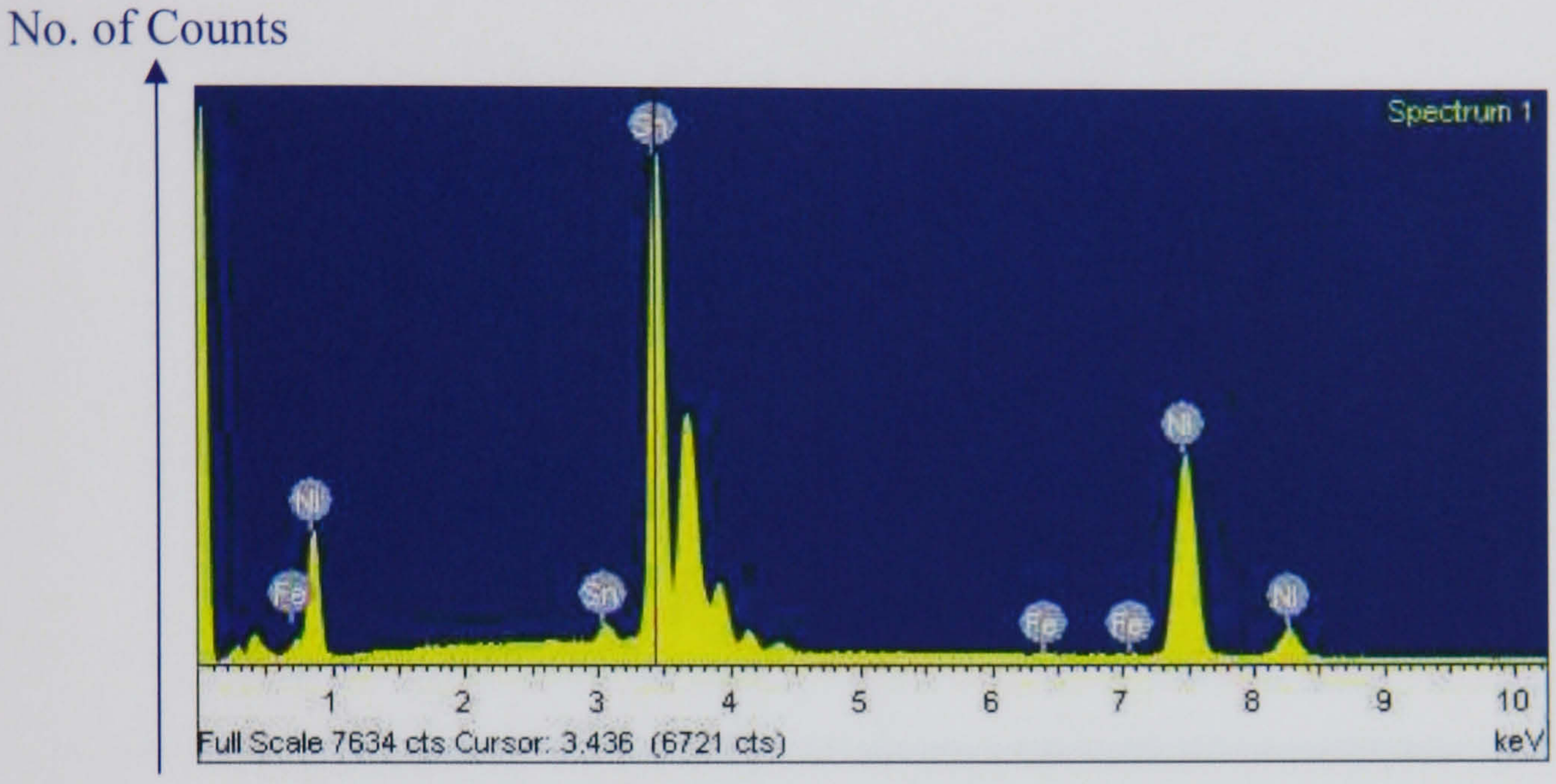

Figure 5.6 – EDX spectrum of tin-nickel deposit surface

The results from the qualitative analysis are consistent with a quantitative account of the peak positions and heights, and Table 5.2 shows the results from calculations based on tin, nickel and iron.

Element	Weight %
Sn	63.67
Ni	36.13
Fe	0.21

Table 5.2 – Elemental composition of deposit with respect to iron

Tin-Copper Coating

Analysis of the tin-copper surface with the INCA EDX system yields a spectrum (Figure 5.7) showing high counts from the copper series and a smaller set of peaks that correspond to the tin series. The positions of the iron peaks have been marked, and there is no evidence of the latter metal detected, indicating that there were no areas of exposed steel present from the positions analysed.

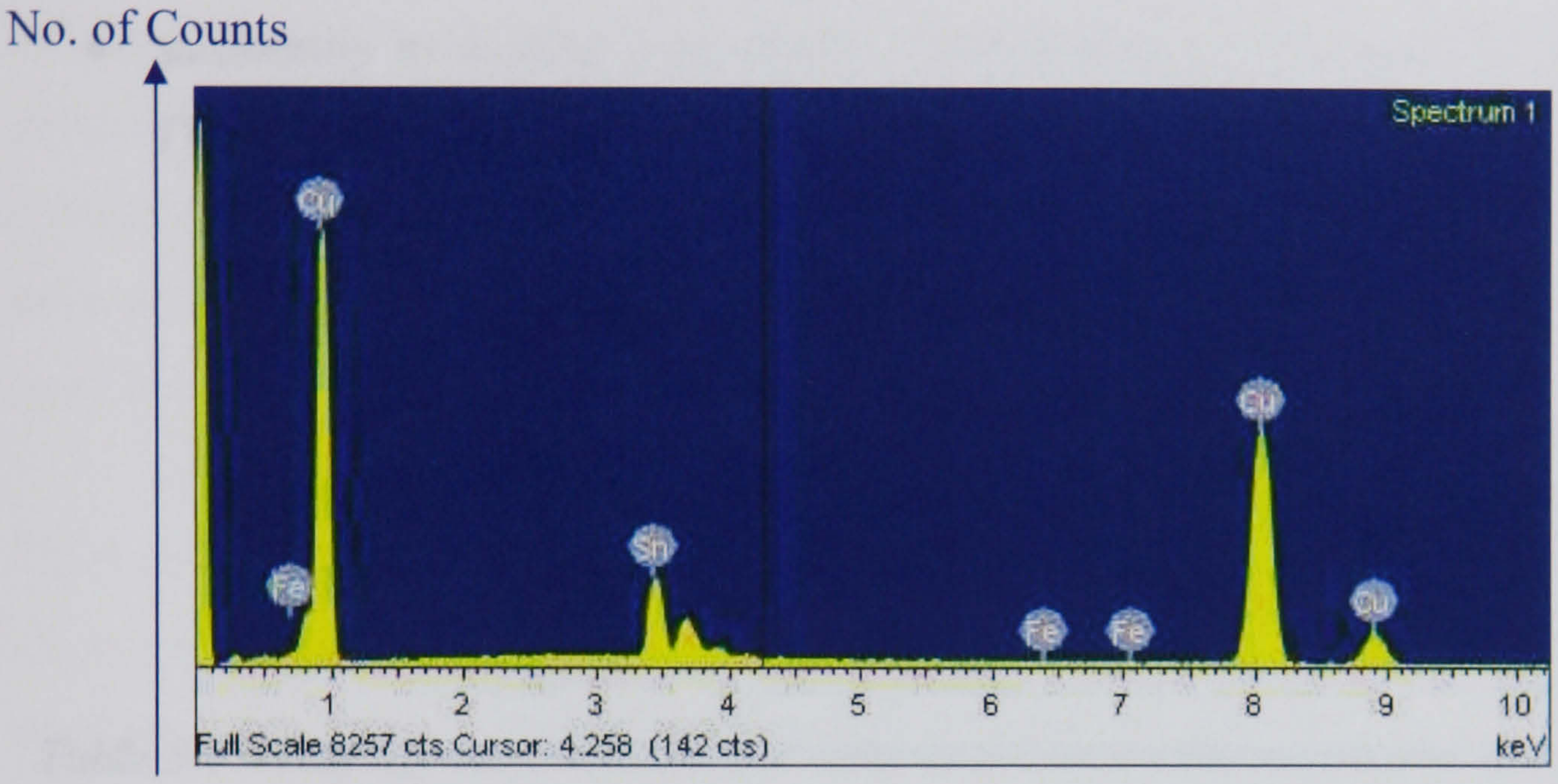

Figure 5.7 – EDX spectrum of tin-copper deposit surface

The results from the qualitative analysis are consistent with a quantitative account of the peak positions and heights, and Table 5.3 shows the results from calculations based on tin, copper and iron.

Element	Weight %
Sn	17.49
Cu	82.47
Fe	0.03

Table 5.3 – Elemental composition of deposit with respect to iron

5.5 SUMMARY

Using a combination of analytical techniques, it is possible to confirm:

- deposition of complete coating coverage, from examination of the coating surface with SEM
- uniformity in coating thickness, for a given plating duration, from examination of micro-sections taken of coating with SEM (Table 5.4)
- uniformity in coating composition, from analysis of the coating with EDX (Table 5.5)

Coating	**Plating times / secs**		
	2 µm	**5 µm**	**10 µm**
Sn	40	100	200
SnNi	220	550	1100
SnCu	120	300	600

Table 5.4 – Plating times required for achieving certain thicknesses for the deposits

Coating	**Elemental composition / wt %**			
	Sn	**Ni**	**Cu**	**Fe**
Sn	100.0	-	-	0.0
SnNi	63.7	36.1	-	0.2
SnCu	17.5	-	82.5	0.0

Table 5.5 – Elemental composition of three deposits

The characterisation stage is essential for the generation of consistent results from the next stages of testing and analysis. The findings documented in this Chapter provides assurances that erratic coating deposition can be eliminated as a potential cause of any discrepancies that may be revealed from results generated from testing of the coatings.

The wear testing and subsequent analysis of the resulting wear scars are reported on in the next Chapters.

CHAPTER SIX

FORMATION OF WEAR SCAR

6.1 INTRODUCTION

It is necessary to investigate the wear resistance of the coatings produced because of the importance of this property in engineering applications. The degree of wear in an engineering material is often overlooked despite being responsible for costs related to maintenance, repair and replacement, and financial losses associated with subsequently diminished efficiency or productivity. Wear is therefore an important consideration when selecting appropriate coating materials.

There are studies that have been conducted on the corrosion resistance properties of tin, tin-nickel and tin-copper, and the findings reveal that they outperform many other materials. The protection these coatings can afford against corrosion mean that they have been adopted for industrial use.

Past wear resistance studies of these three materials, however, have been confined mainly to tin-copper, which is considered to be sufficiently appropriate for use as a bearing material. As the method for assessing wear resistance in this research is novel, it is important to use it for assessing tin-copper, an alloy that has been adopted as a bearing material. This would enable tin and tin-nickel to be assessed alongside and compared with tin-copper.

Chapters Three to Five provide detailed accounts of how coatings of tin, tin-nickel and tin-copper were deposited onto steel wear test coupons at set thicknesses, and a description of the characterisation of these coatings using a variety of analytical methods. The assessment of the wear resistance of the coatings deposited on the steel coupons follows, and this Chapter commences with a discussion of the decision to adopt a novel method for assessing the property, and then describing fully the methodology. The results yielded from the new test methodology are presented in the next Chapter along with any trends and findings revealed.

6.2 DEVELOPMENT OF NOVEL ASSESSMENT APPROACH

6.2.1 Limitations to Current Methods

Although coatings can be assessed in a number of ways, including pull-off tests for adhesion and four-point bend tests for inducing coating delamination [22], wear resistance is best determined by introducing a form of deformation of the coating material that is representative of in-service wear.

Using apparatus such as the reciprocating scratch test or rotary abrasive wheel, the coating is worn away and wear resistance is usually assessed by measuring the coefficient of friction or by weight loss of the material [22, 65, 57, 58, 59].

Whilst the introduction of deformation to the coating has been maintained for this research, both the evaluating of the friction coefficient and material weight loss have not been considered for the following reasons:

- The effectiveness of soft coatings is due to the solid lubrication properties they offer via reduction of friction. Measuring of this reduction in friction coefficient may provide some indication of when the coating has been breached, but it does not give any quantitative indication of the degree of coating depletion.
- It is felt that mass loss figures could be misleading. Some studies have used mass loss measurements to directly quantify wear, and concluded that a coating with 50% less mass loss will lead to service life doubling [28]. Whilst mass loss is indicative of the depletion of the coating, it does not identify the exact areas where the substrate is susceptible to removal. Rather, the assumption is that a uniform amount of coating is being removed per unit of surface area. In reality, the locations of highest coating depletion are dictated by factors such as the substrate topography and uniformity of the coating.

Indeed, some existing techniques are far from comprehensive and reliable, e.g., the relationship between wear rate and normal load can be erratic, with the wear rate fluctuating independently of the load applied [60].

A coating that offers protection to the underlying substrate is only performing its role while it is still adhered, particularly if it is also conferring corrosion resistant properties. Figure 6.1 demonstrates a scenario where uniform coating depletion over a wide area is often mistaken as a greater concern than coating removal at a concentrated point. Figure 6.1a is the original 10 micron coating, whilst Figure 6.1b is the same coating after being eroded to less than half the original thickness. Whilst measuring the mass loss would indicate that that over 50% of the coating has been removed, the coating appears to maintain its protective barrier over the substrate, albeit with less material than from the onset. Figure 6.1c is the 10 micron coating after it has been damaged and the micro-section reveals evidence of a breach in the coating where the underlying substrate is exposed. Evaluating the mass loss would yield a value than would erroneously suggest that the latter case was less of a concern.

It is therefore decided that the retention of the coating is to be assessed in this research and the continual monitoring of the removal of the coating is carried out by inspection of the wear scar surface. The use of a surface sensitive analytical technique, namely EDX, is considered for the examination of elemental composition in the wear scar location, enabling the ratio between detected coating and substrate material to be evaluated [61]. The amount of exposed substrate material is more indicative of coating retention than weight loss, since failure of mechanical parts is usually due to breach of the wear resistant coating, and not its progressive depletion, which is merely a cause of the breach.

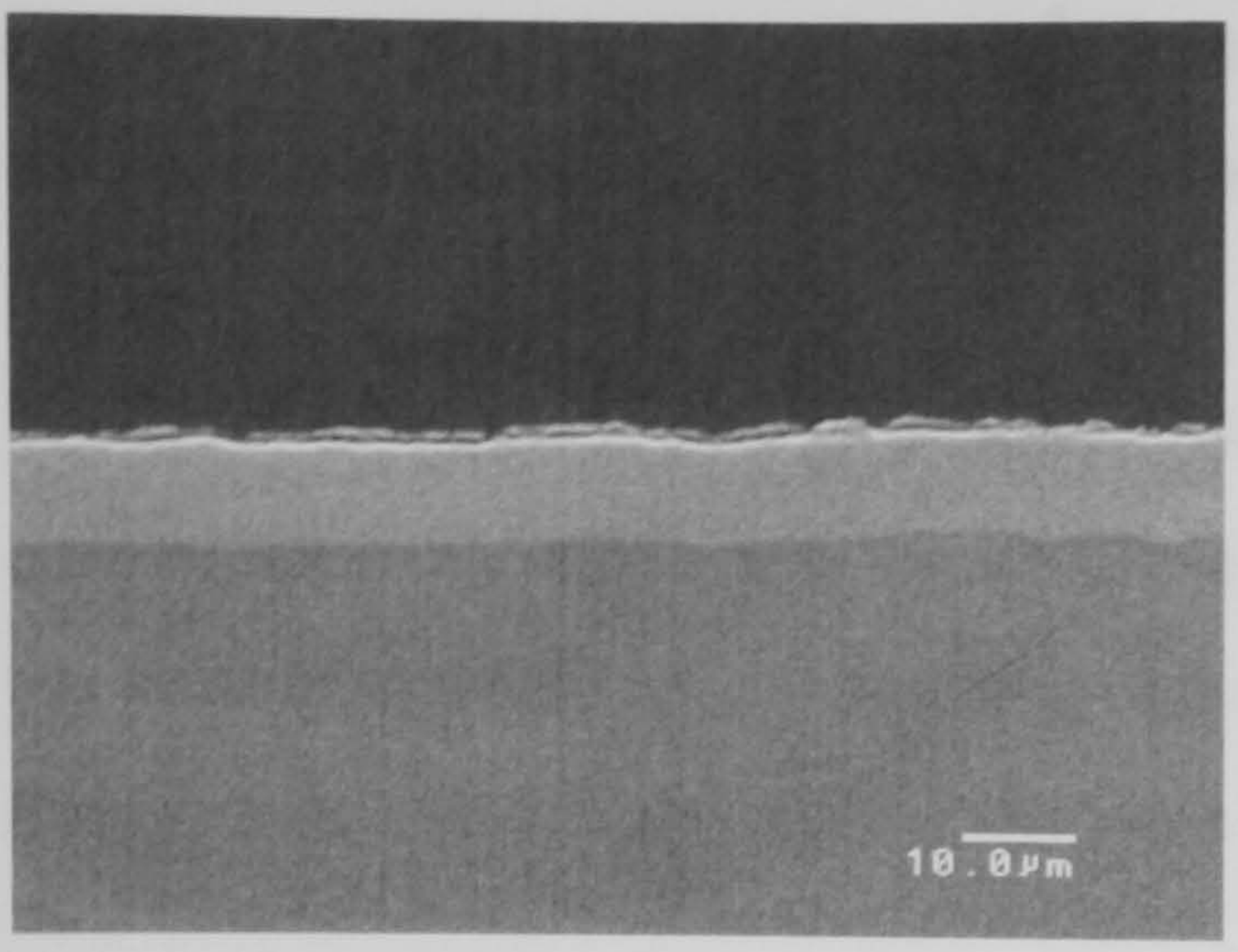

Figure 6.1a – Original 10 µm coating

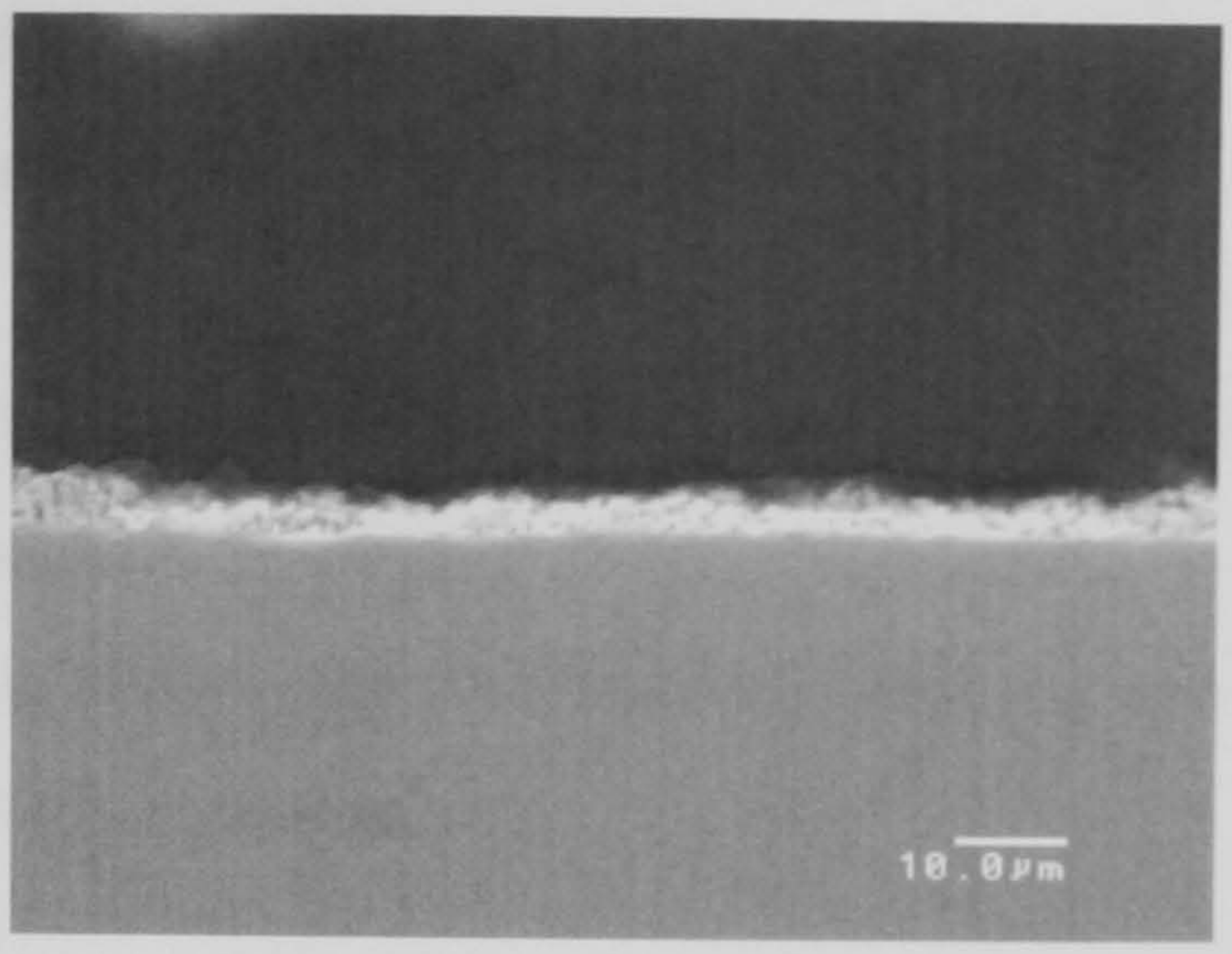

Figure 6.1b – Coating eroded to ~4 µm

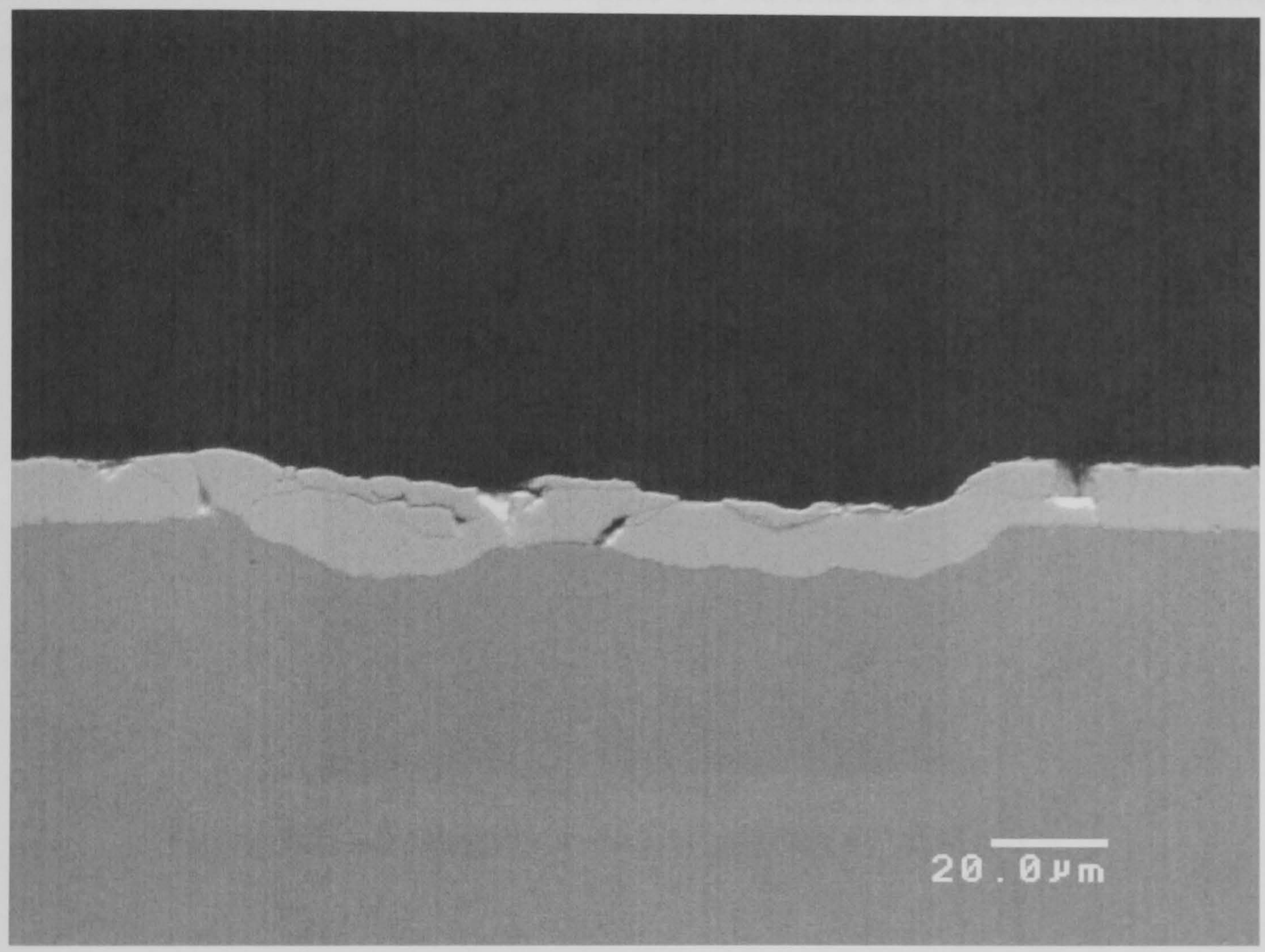

Figure 6.1c – Underlying substrate material exposed by coating breach

6.2.2 New Method: Exposed Substrate Determination from EDX

These resulting wear scars are examined using SEM and EDX in order to determine the extent of damage introduced by contact with the sliding ceramic ball. This is achieved by measuring the amount of detectable iron within the wear scar [61]. As established in the Characterisation Chapter, the amount of iron detected for 0 hour samples is negligible; therefore, any iron detected within the wear scar will be from the underlying steel substrate, which has been exposed by removal of the coating.

The level of exposed iron is therefore used as a measure for assessing the degree of coating removal, and hence, the wear resistance of the deposit. A high iron content in the wear scar would imply that large areas of underlying steel has been exposed and therefore denote that the coating has been mostly removed.

EDX is used to evaluate the approximate level of exposed iron by acquiring from a rectangular area within the wear scar. Figure 6.2 illustrates the purple rectangle drawn within the wear scar, designating the area where the EDX acquisition is to take place [61].

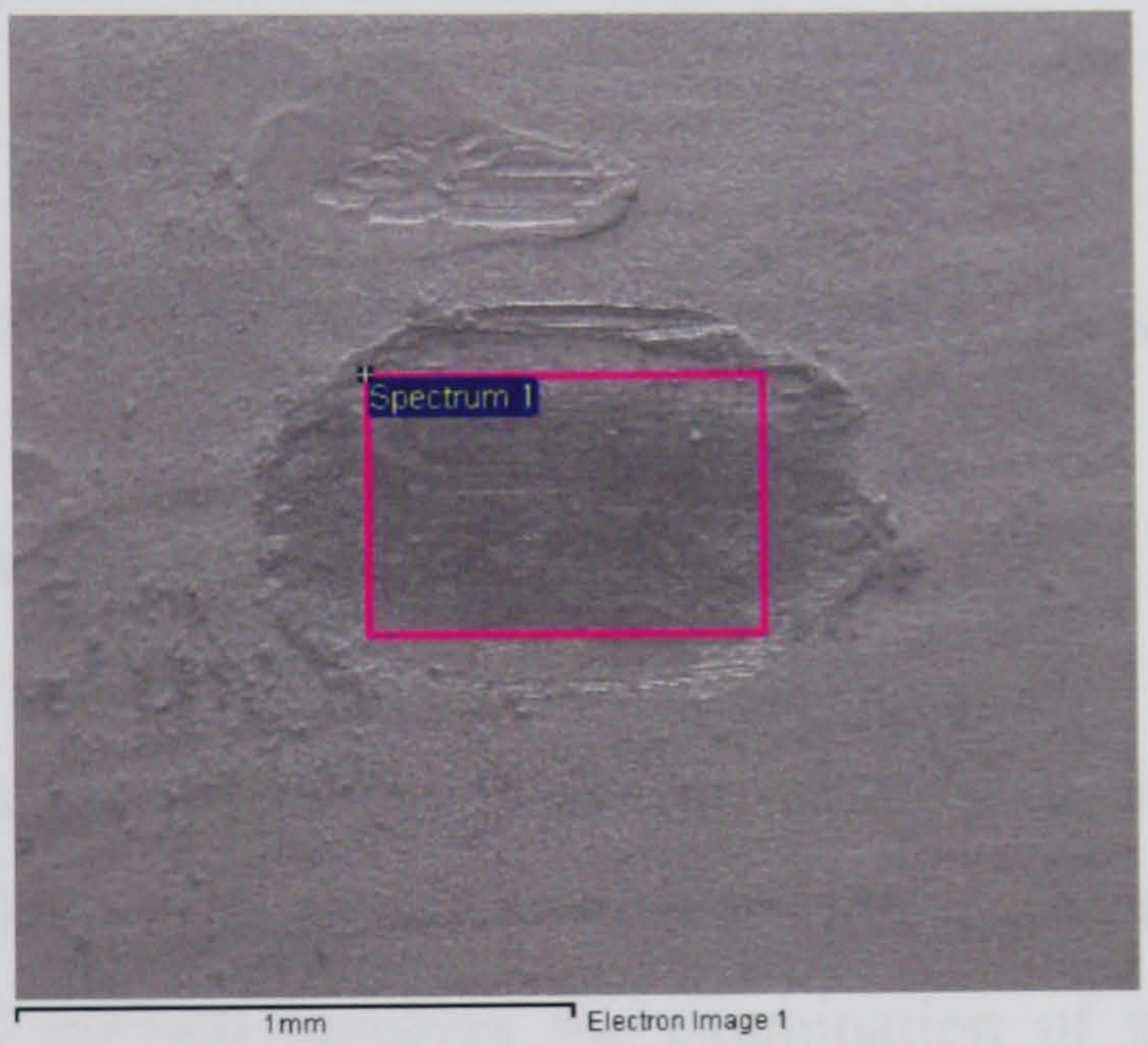

Figure 6.2 – Area within wear scar selected for EDX analysis

The iron content detected is presented as a weight percentage, and recorded with reference to the coating material, coating thickness, load used and the duration of the wear test [61].

For the benefit of presentation and data analysis, the degree of coating removal has been separated into five different categories:

- Negligible: 0 – 20 wt % Fe detected
- Moderate: 20 – 40 wt % Fe detected
- Significant: 40 – 60 wt % Fe detected
- Severe: 60 – 80 wt % Fe detected
- Failure: 80 – 100 wt % Fe detected

The categorisation of the results allows the full results to be tabulated in the form of a matrix, where an individual cell corresponds to a certain set of test parameters, are shaded with respect the degree of coating removal, with a darker shade denoting more iron detected. This is presented in the next Chapter.

6.3 INTRODUCING THE WEAR SCAR TO COATING SURFACE

6.3.1 Requirements and Restrictions

With the analytical aspect of the methodology established, it is then necessary to consider the method by which the wear scars are introduced to the coating surface. Since the SEM/EDX method involves the examination of small areas which are within the field of view of the SEM, it is important that similar sized areas of damage are being introduced to the test coupons.

As the technique is novel, it is important to maximise the amount of information obtained by testing to as many parameters as possible. Past research has often focussed on wear as a function of time, whilst other studies have studied the relationship with increasing load. Using time and load, along with the ability to consistently produce deposits of pre-determined thicknesses, the coating deterioration was quantified with respect to increasing load, thickness and testing duration.

In carrying out testing to the above three parameters. a number of restrictions needed to be accommodated. Firstly. the industrial working day dictated a maximum test duration of eight hours, which meant that a method for inducing total coating failure within this time limit was required. The time restriction then impinged on the appropriate test load used. since a maximum test load for yielding complete coating removal after eight hours was required. The most flexible parameter was the thickness of the coating deposit, since the required thickness could be achieved by the necessary variation in electroplating time.

6.3.2 TE70 Microfriction Machine

It was decided that the wear scar in this research is introduced to the coating surfaces from sliding abrasion with a silicon nitride ball mounted on a TE70 microfriction machine, which uses a reciprocating ball-on-plate contact configuration (Figure 6.3). Although the apparatus is theoretically capable of assessing friction force, via a graph plotter, the machine is used in this research as a means for introducing controlled damage to the surface of the test specimens, in the form of wear scars.

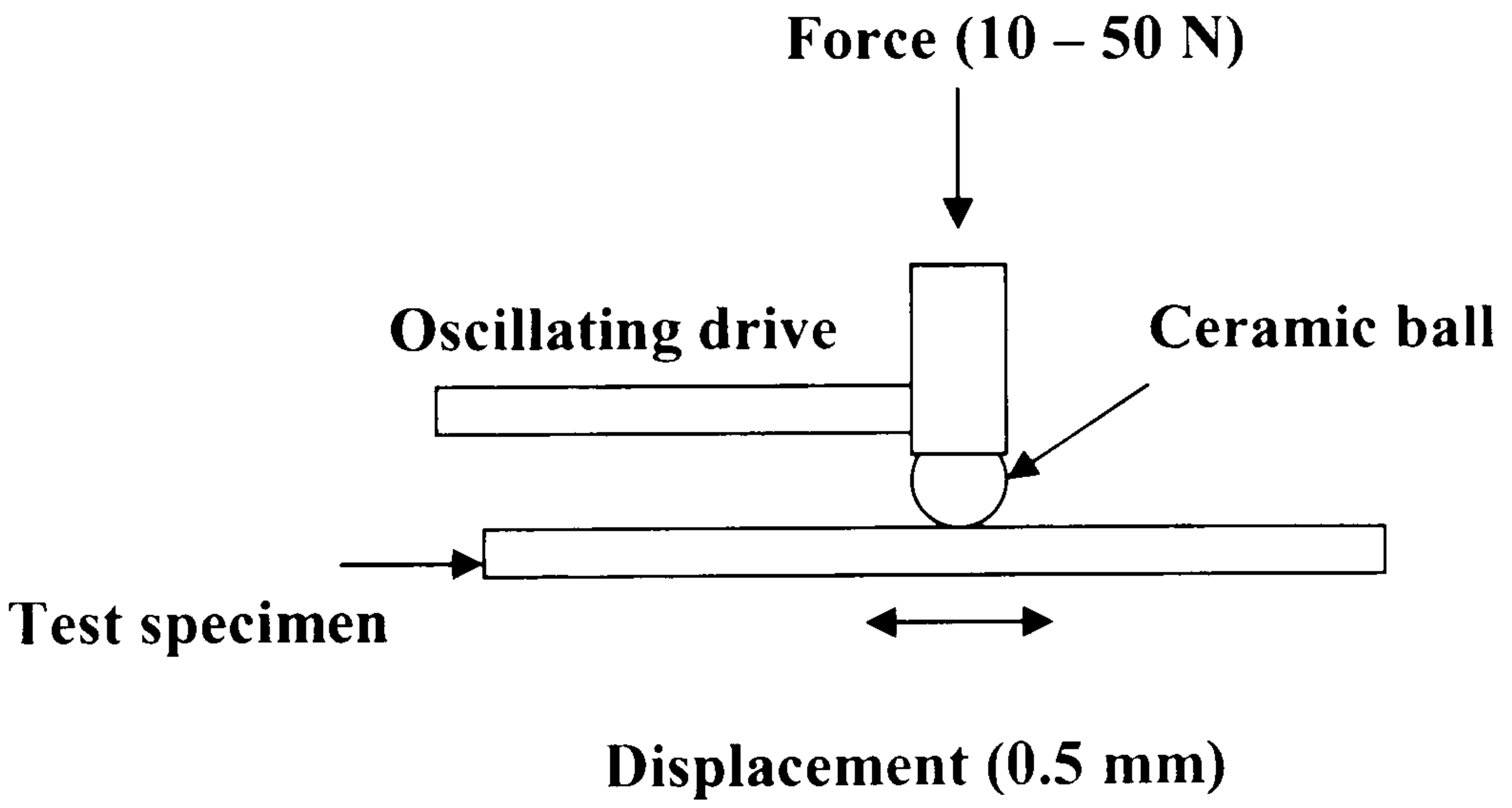

Figure 6.3 – Schematic of TE70 machine setup used for wear testing

The setup allows the adjustment of testing load on a holder located directly above the housing for the ceramic ball. The holder itself has a weight of 10 N, and has a capacity of a further 40 N, providing a total maximum load of 50 N. In this way, it is possible to pre-determine the normal load as well as the wear duration.

A silicon nitride ball is considered over a steel one because past studies have shown the ceramic to be extremely durable and more wear resistant. Since the condition and geometry of the counter surface is critical, with some tests specifying periodic inspection to ensure there is no damage, a new surface of the ball is used for each individual test to ensure consistency. The ball is released by loosening the ball holder cap, which is then re-tightened once the ball has been adjusted.

The wear test coupons, plated by the electrochemical techniques described in Chapter Four, are fixed in the sample holder of the TE70 machine via two nuts. The sample holder is then screwed to the TE70 unit below the oscillating arm, which houses the ceramic ball and to which the load is applied.

In order to reduce the influence of third party materials in the wear process, the surfaces of both the surfaces of the ceramic ball and wear test coupons are cleaned with acetone prior to each test. The importance of clean surfaces have been stressed in previous studies conducted on the influence of contamination on bearing service life and function [62].

The TE70 setup does allow for lubrication during the wear testing, and past research on different lubricants have been conducted on this apparatus. Lubrication is not, however, considered in this research because there is still much to understand about the effect of certain additives in lubricants on materials during a wear test, and variables such as oxidation and corrosion would complicate the wear scar formation. Furthermore, it is felt that, even if lubrication was present, extreme service conditions would still inevitably generate a degree of dry sliding occasionally [28]. An example is high temperature as a result of the sliding causing any lubricant to deplete through oxidisation or degradation [63]. Whilst temperature causes a decrease in lubricant viscosity, water content in the lubricant increases viscosity, promotes corrosion and bacterial growth [29]. Hence, a lubricated system would require constant monitoring of the lubricant.

The resulting wear scar is next analysed to assess the amount of exposed substrate detected, and the results are presented in the next Chapter.

6.4 SUMMARY

There are certain limitations to current methods for monitoring wear, for example, measuring mass loss of a coating places the emphasis on amount of coating removed. Whilst this may be indicative of the rate of coating deterioration, it is not easy to ascertain the degree of underlying substrate material that has been exposed from the coating removal. A worn coating could continue to provide protection as long its integrity and coverage has not been breached, however, the same coating could potentially be compromised prior to service if a defect is present that runs from the surface of the coating through to the substrate.

A novel method of assessing wear scars is developed where an area of the scar is examined with EDX to provide compositional information at the location. In this way, it is possible to analyse wear scars introduced to the surfaces of tin, tin-nickel and tin-copper deposits to determine how much, if any, steel is exposed over a range of test loads and durations.

The technique allows the difference in wear resistance between tin, tin-nickel and tin-copper to be measured quantitatively. In particular, it also allows tin-nickel to be directly compared with tin-copper, and determine if tin-nickel coatings could be an environmentally friendly alternative to tin-copper coatings.

CHAPTER SEVEN
ANALYSIS OF WEAR SCAR

7.1 INTRODUCTION

The wear testing methodology described in Chapter Six is implemented to yield a series of wear scars on the coating deposits tested. The wear scars are examined individually with SEM/EDX and the results are presented in this Chapter.

The data is firstly categorised by individual coating, to establish the fundamental trends, i.e., the effects of increasing testing duration, testing load and coating thickness.

The coatings are then compared with each other by, first, assessing the level of substrate exposure as testing time elapses, and then by referencing the amount of time taken for a given deposit to reach specific thresholds of coating removal.

7.2 RESULTS: INDIVIDUAL COATINGS

The results allow the effect of certain test conditions on the degree of coating removal to be identified, namely:

- time: the effect of increasing wear test duration
- load: the effect of increasing the force applied to the coating surface via the ceramic ball
- coating thickness: the effect of increasing the thickness of the tin or tin alloy deposited

For each coating assessed, it is therefore possible to present the findings in six different ways:

- Effect of increasing load with respect to increasing coating thickness
- Effect of increasing coating thickness with respect to increasing test duration
- Effect of increasing test duration with respect to increasing load
- Effect of increasing coating thickness with respect to load
- Effect of increasing test duration with respect to coating thickness
- Effect of increasing load with respect to test duration

7.2.1 Tin Coating

Effect of increasing load with respect to increasing coating thickness

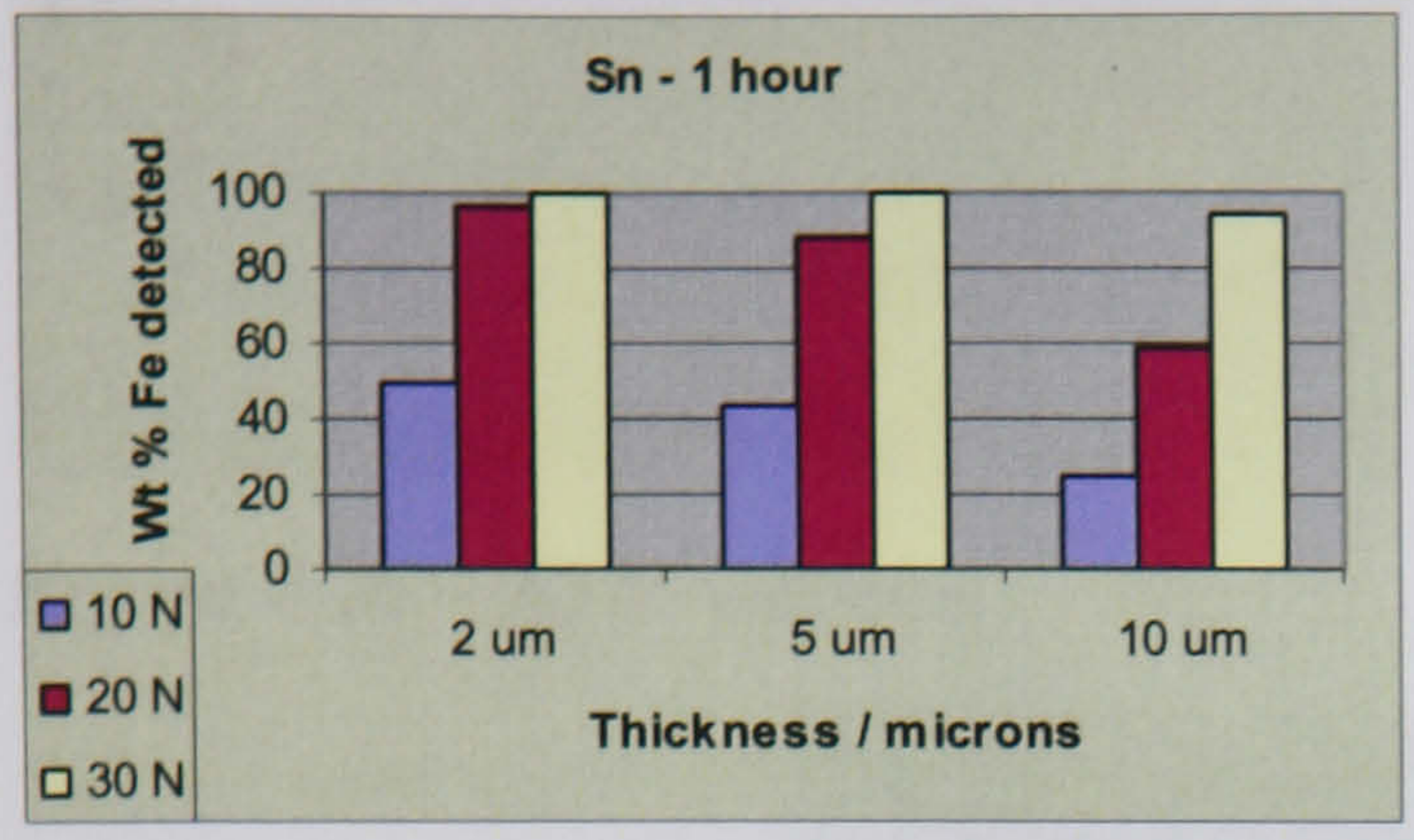

Figure 7.1a – 1 hour test duration

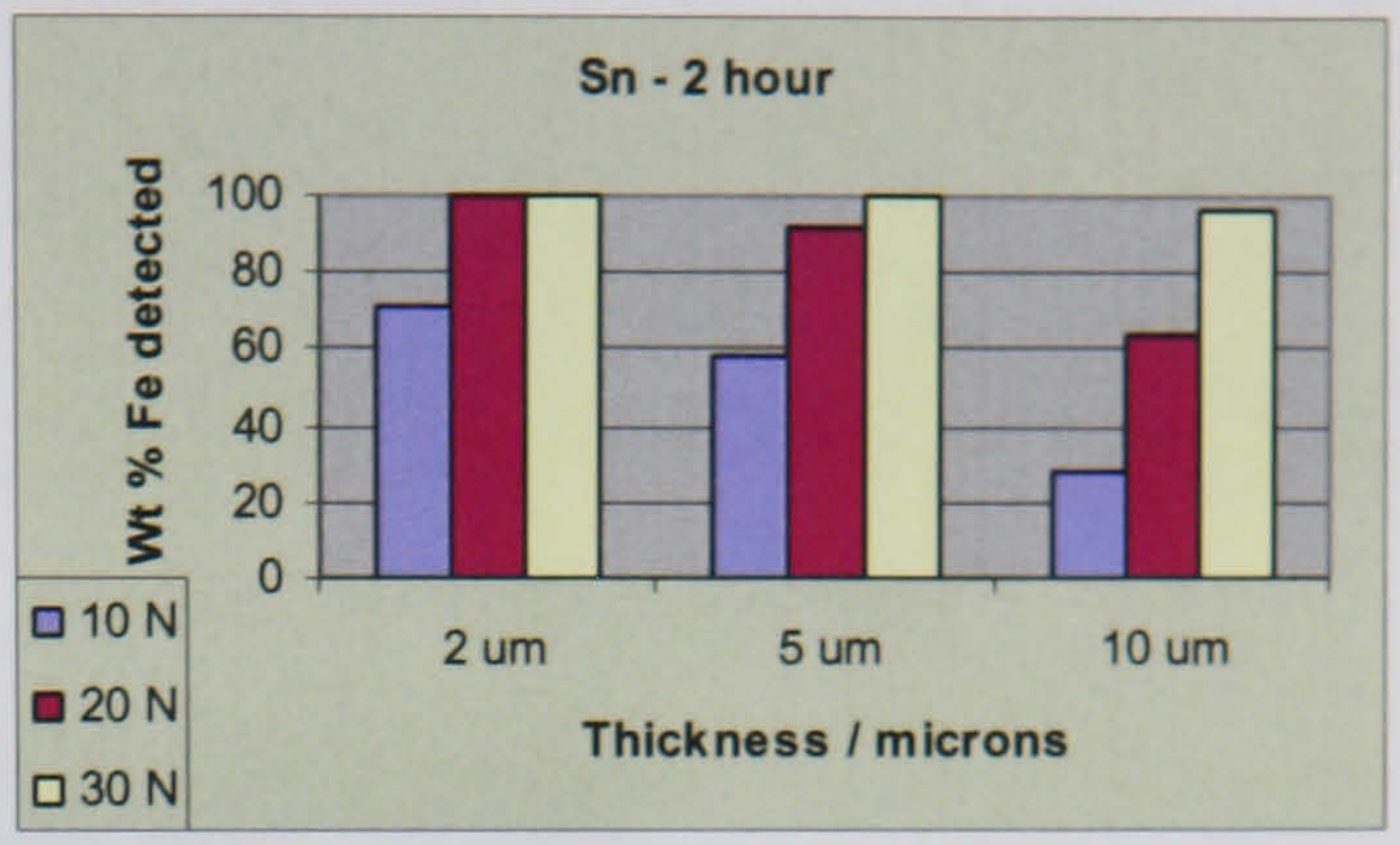

Figure 7.1b – 2 hour test duration

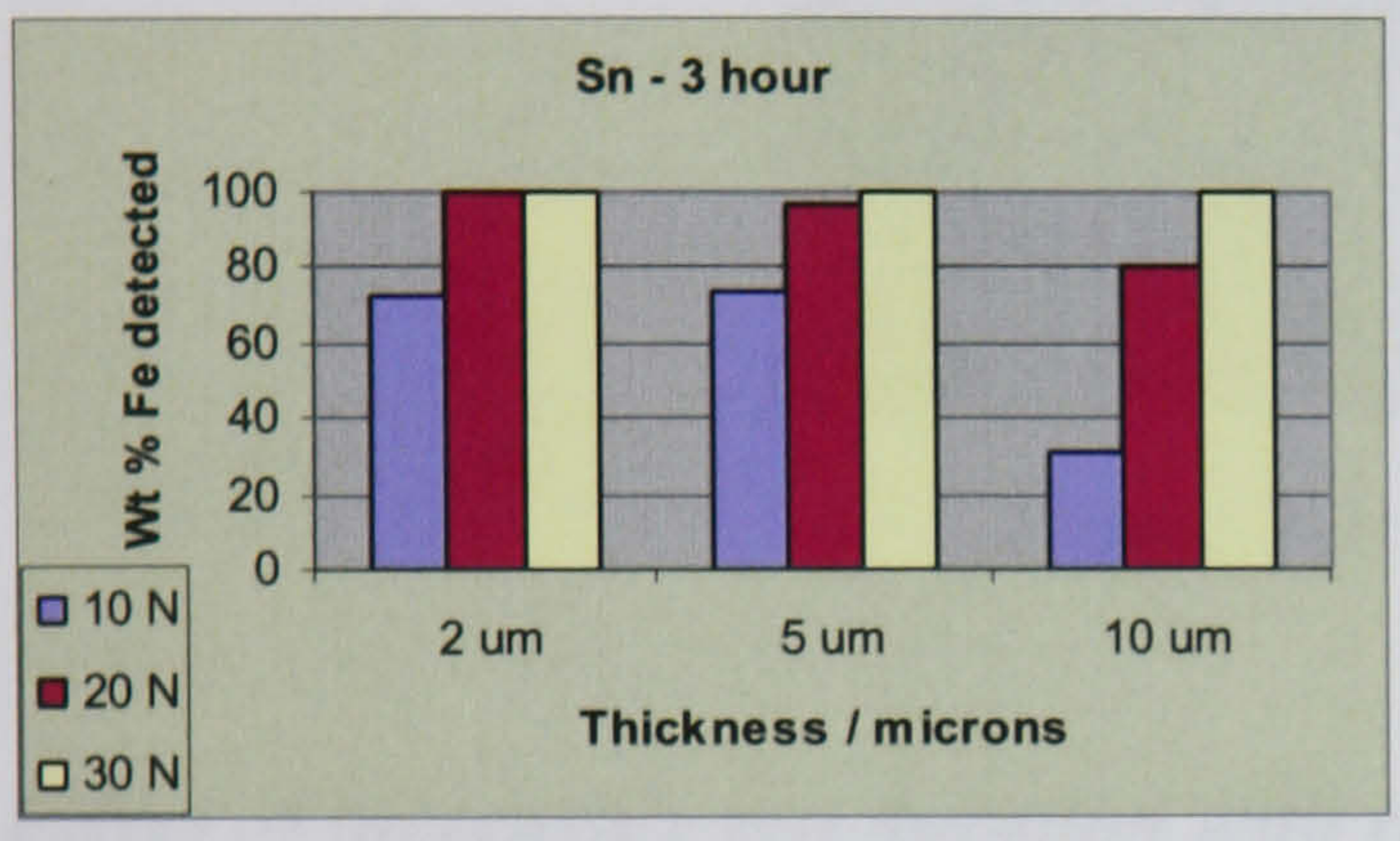

Figure 7.1c – 3 hour test duration

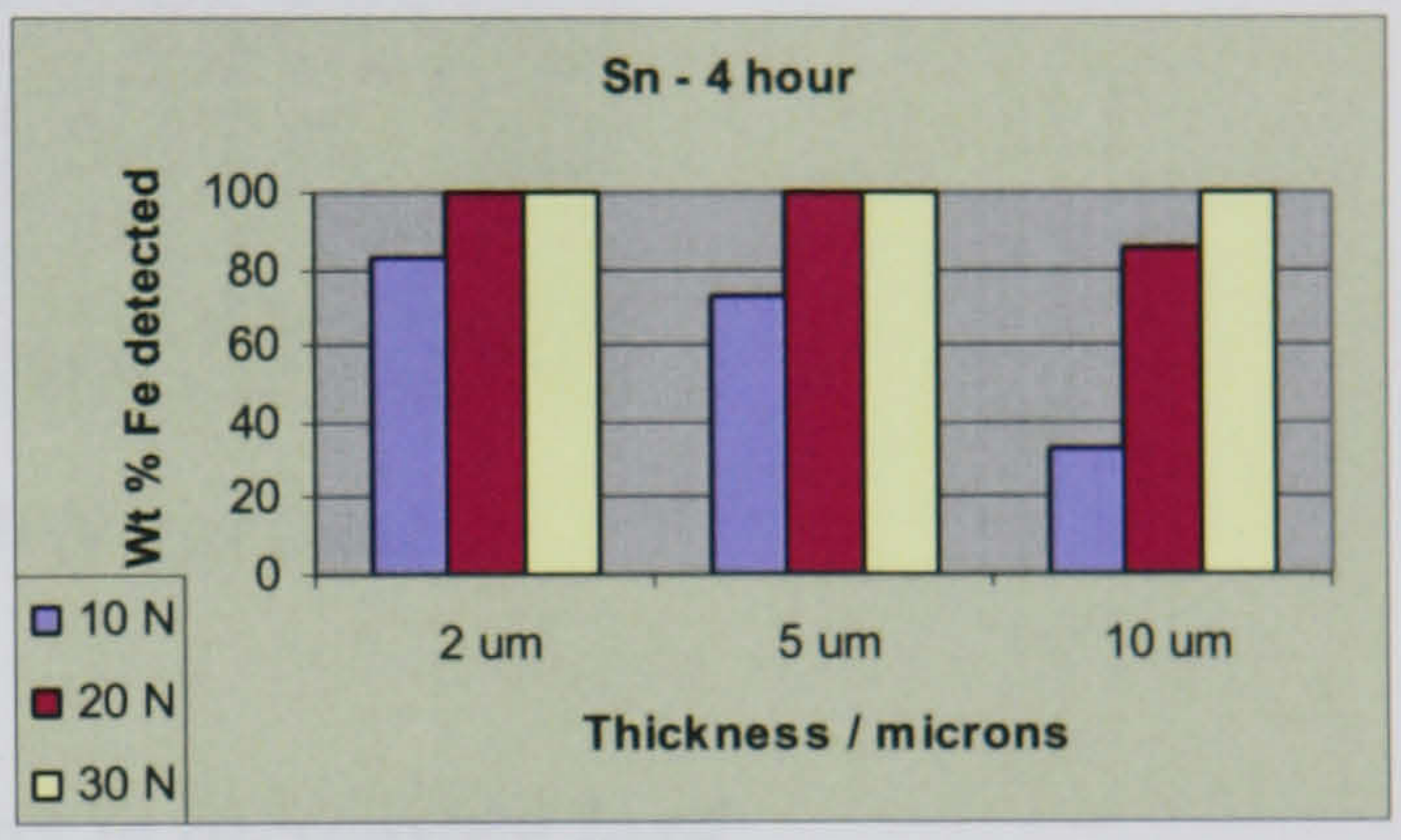

Figure 7.1d – 4 hour test duration

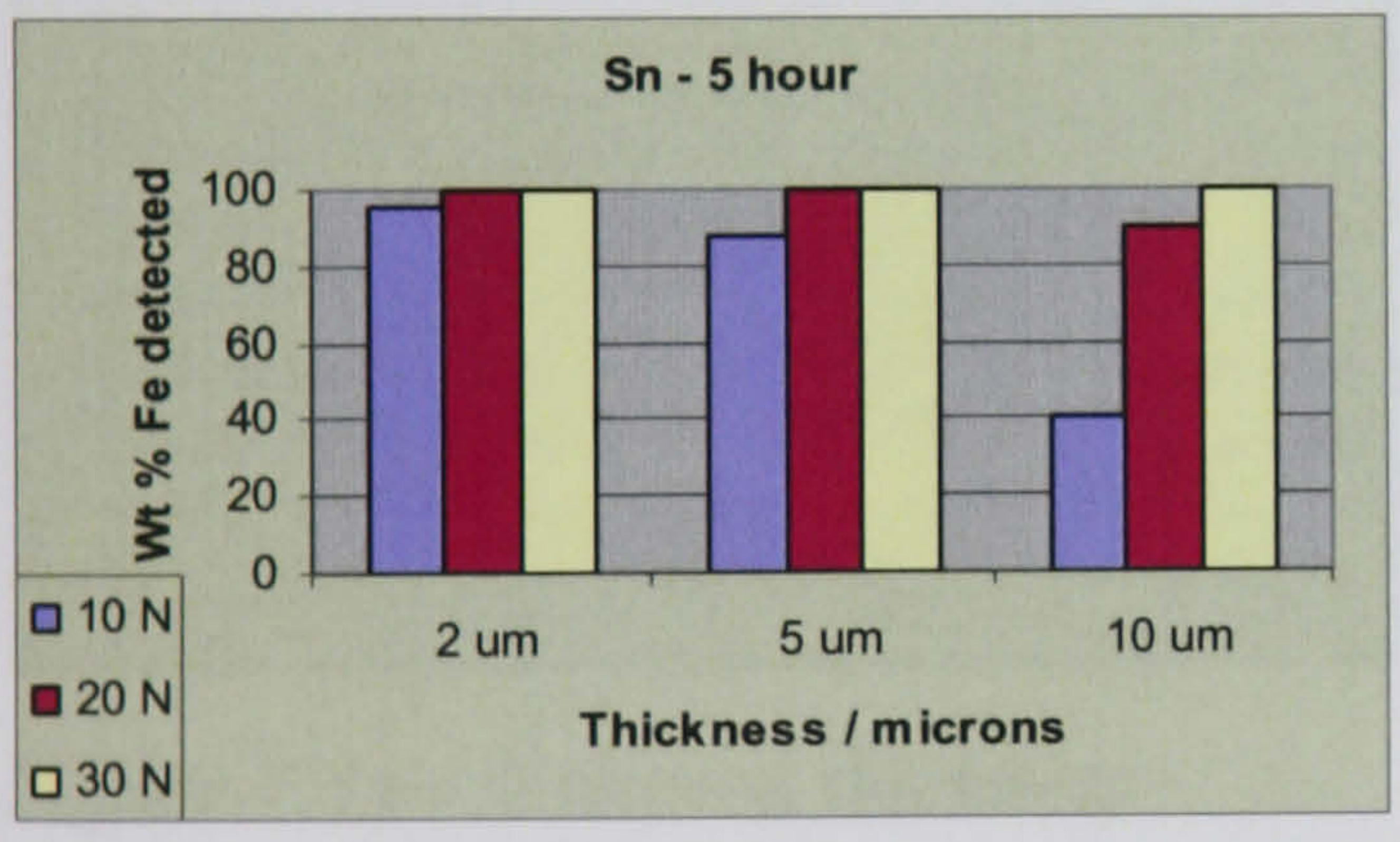

Figure 7.1e – 5 hour test duration

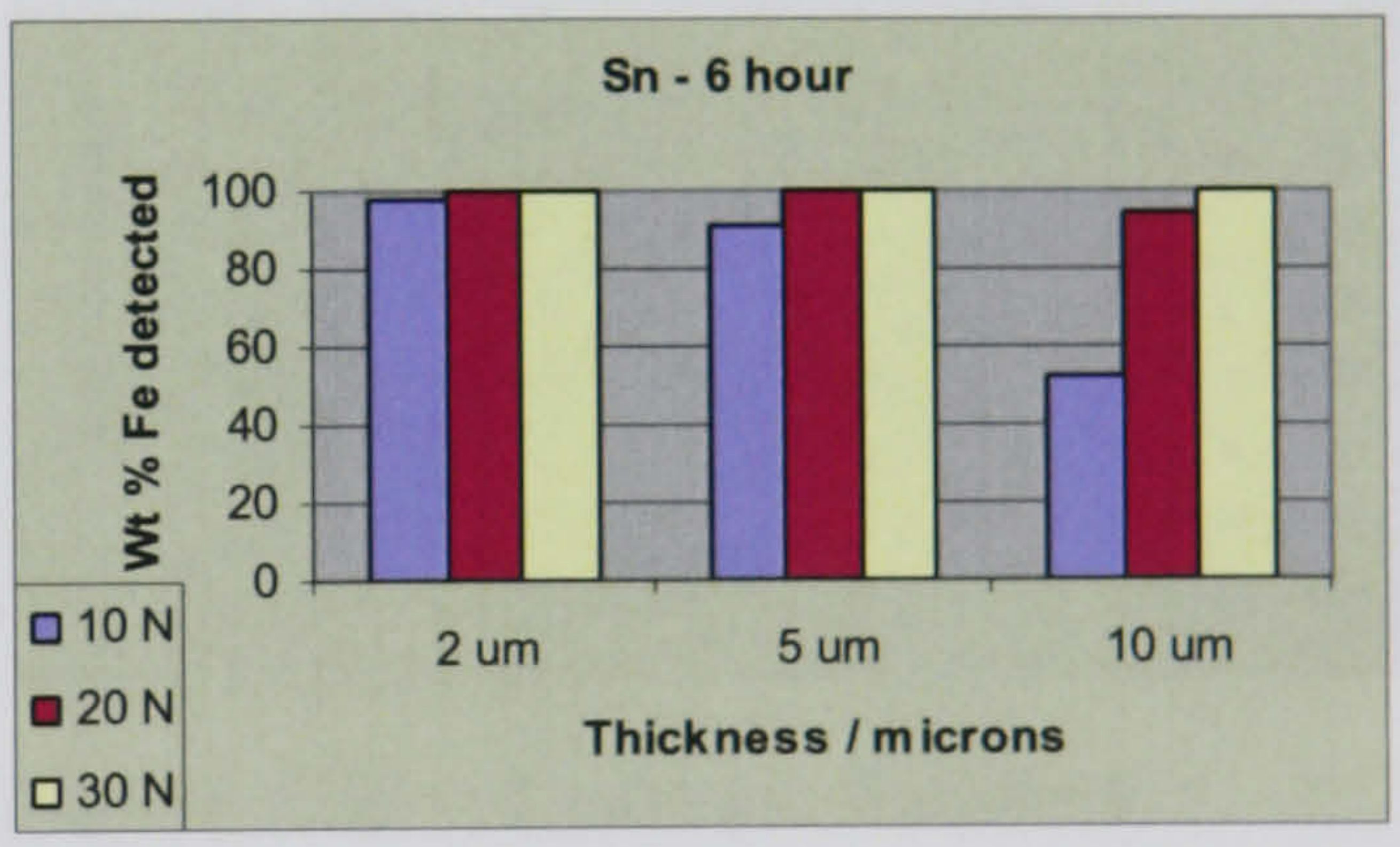

Figure 7.1f – 6 hour test duration

Figure 7.1g – 7 hour test duration

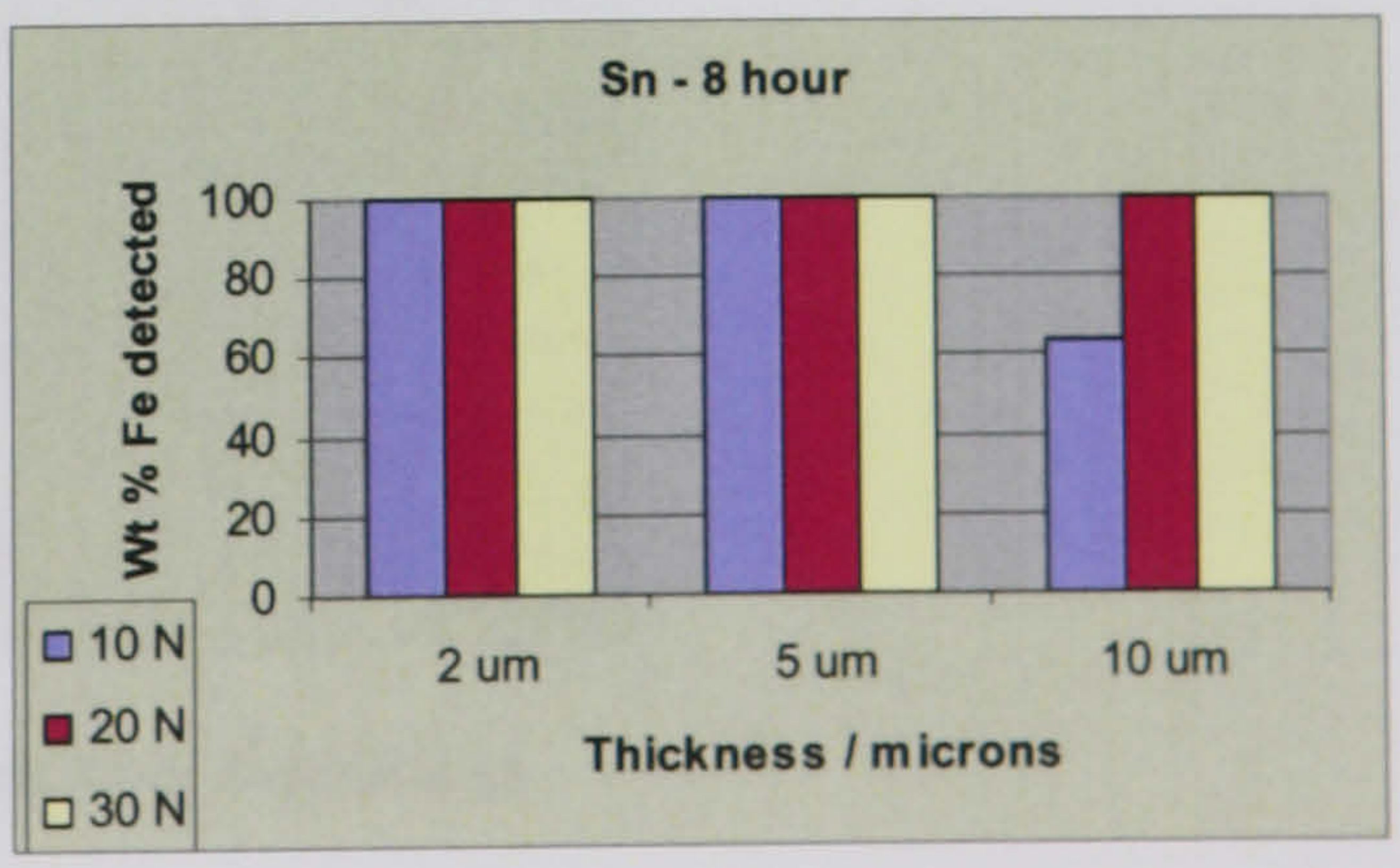

Figure 7.1h – 8 hour test duration

Effect of increasing coating thickness with respect to increasing test duration

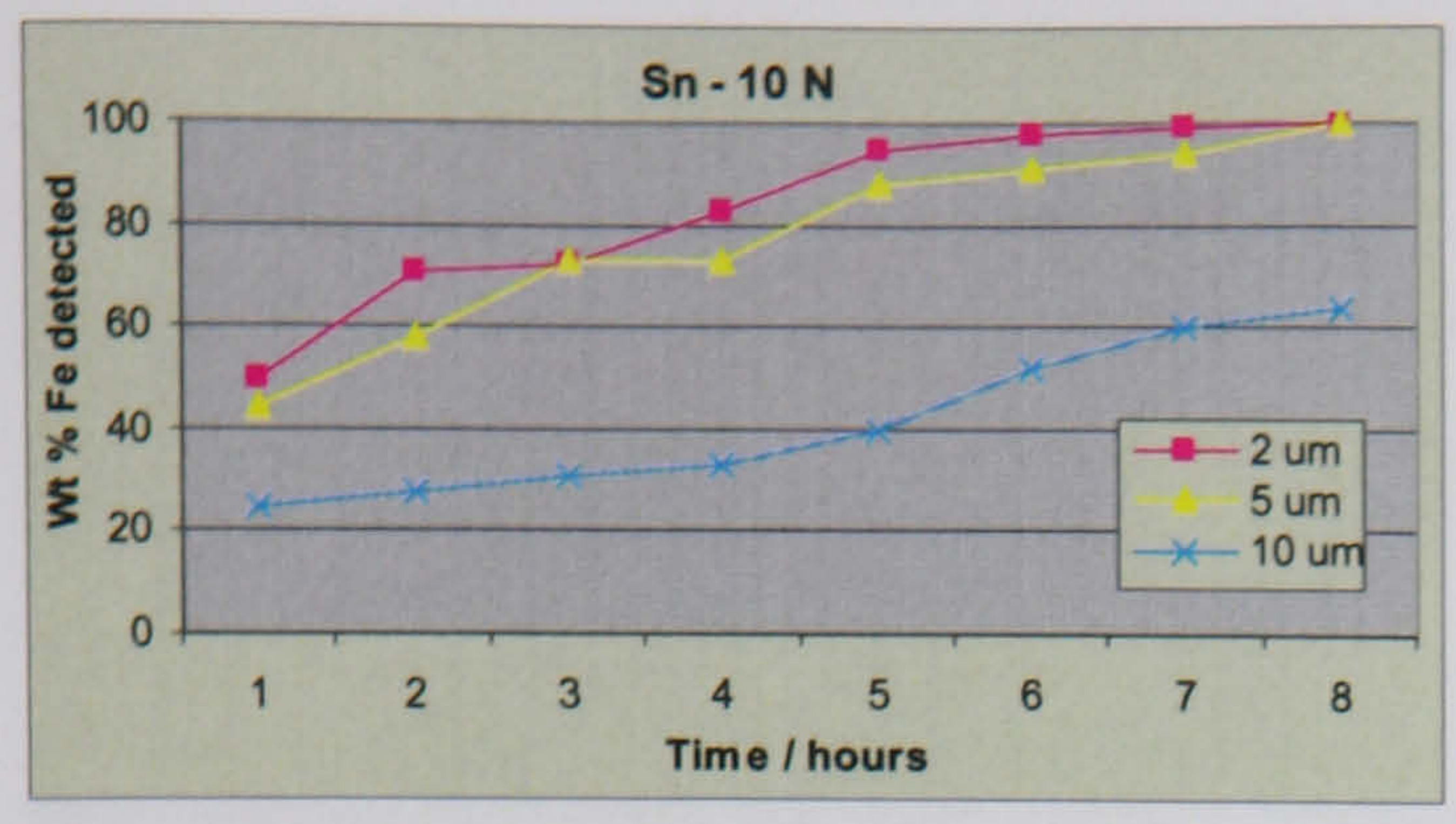

Figure 7.2a – 10 N test load

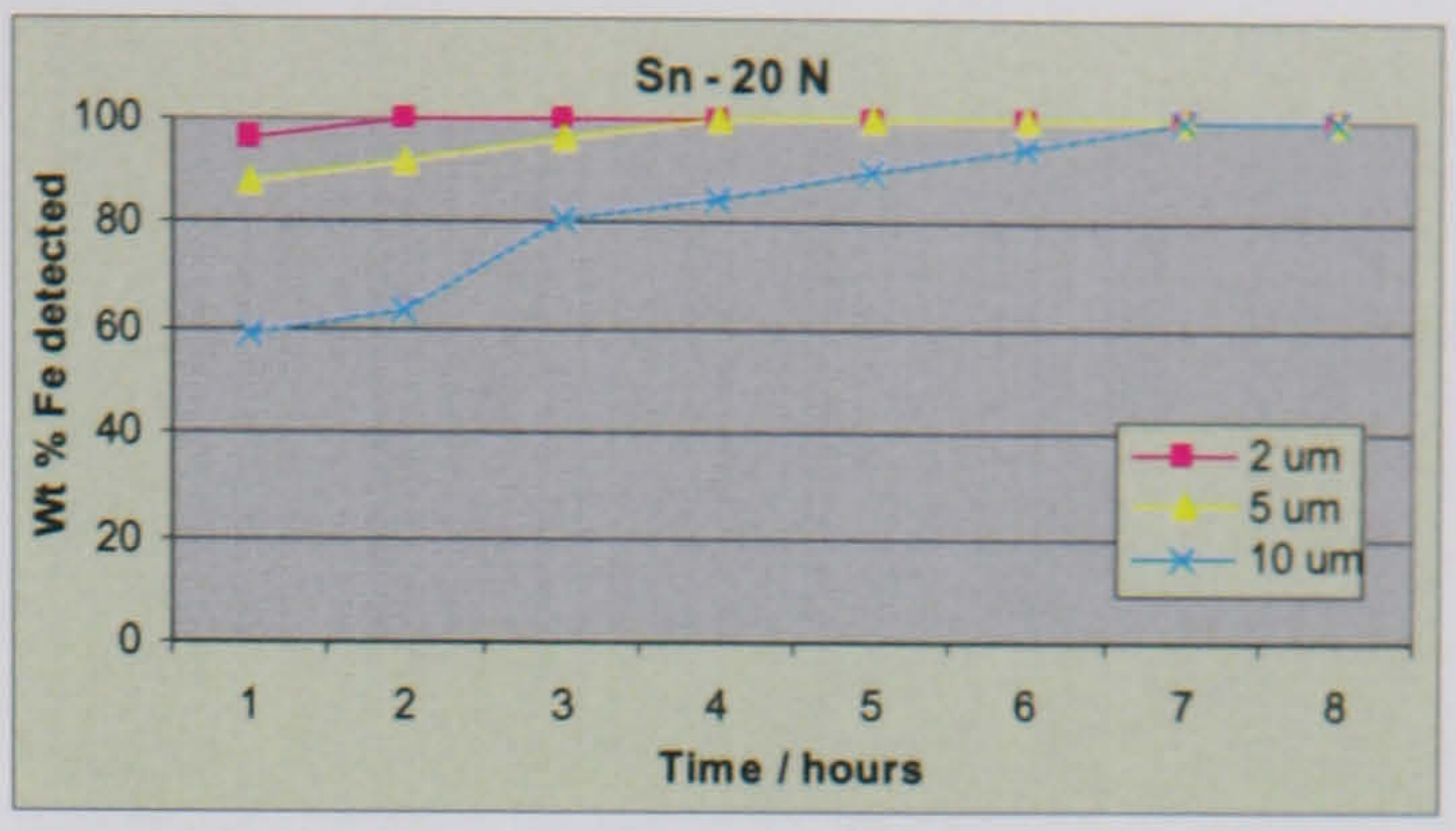

Figure 7.2b – 20 N test load

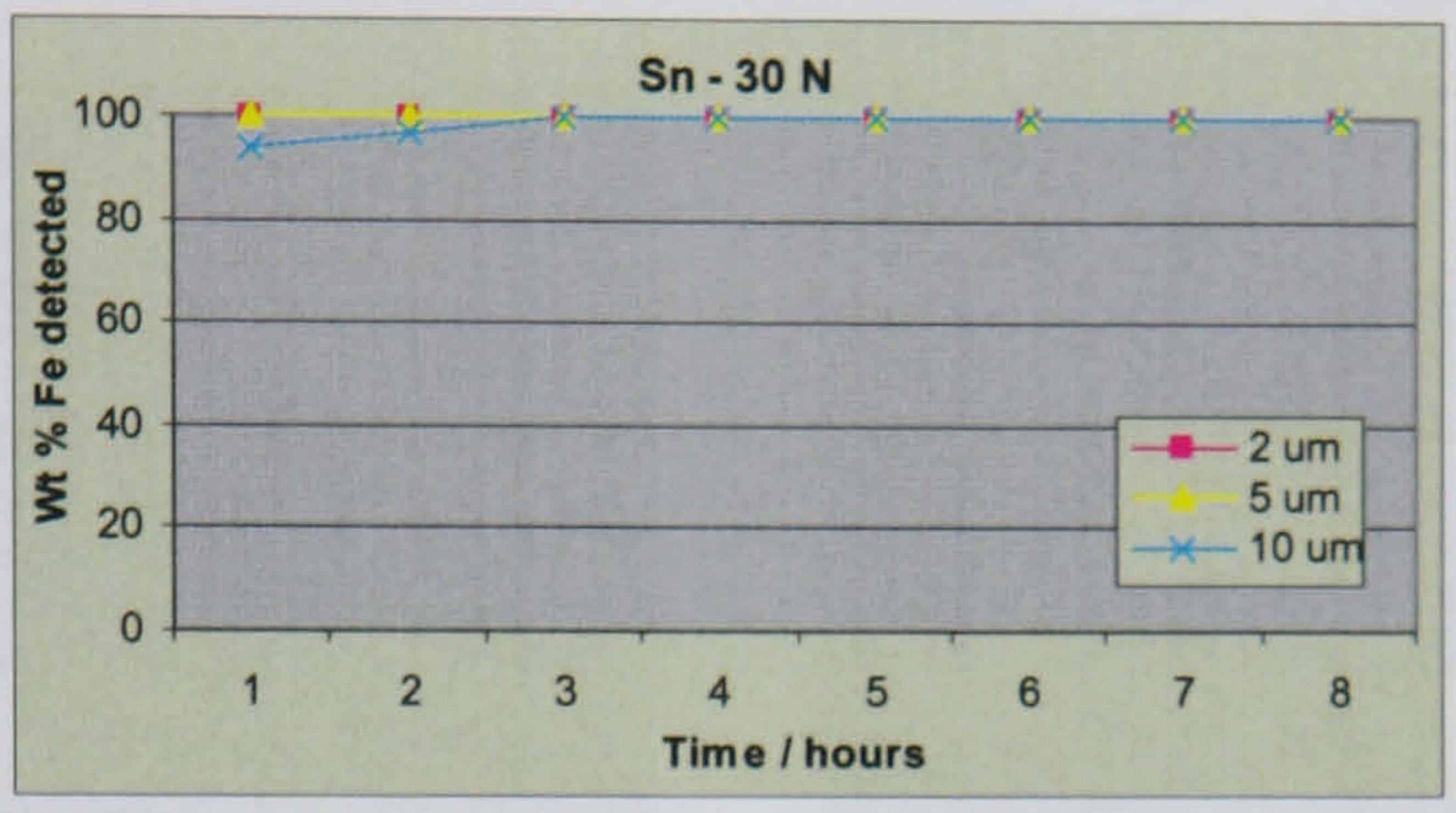

Figure 7.2c – 30 N test load

Effect of increasing test duration with respect to increasing load

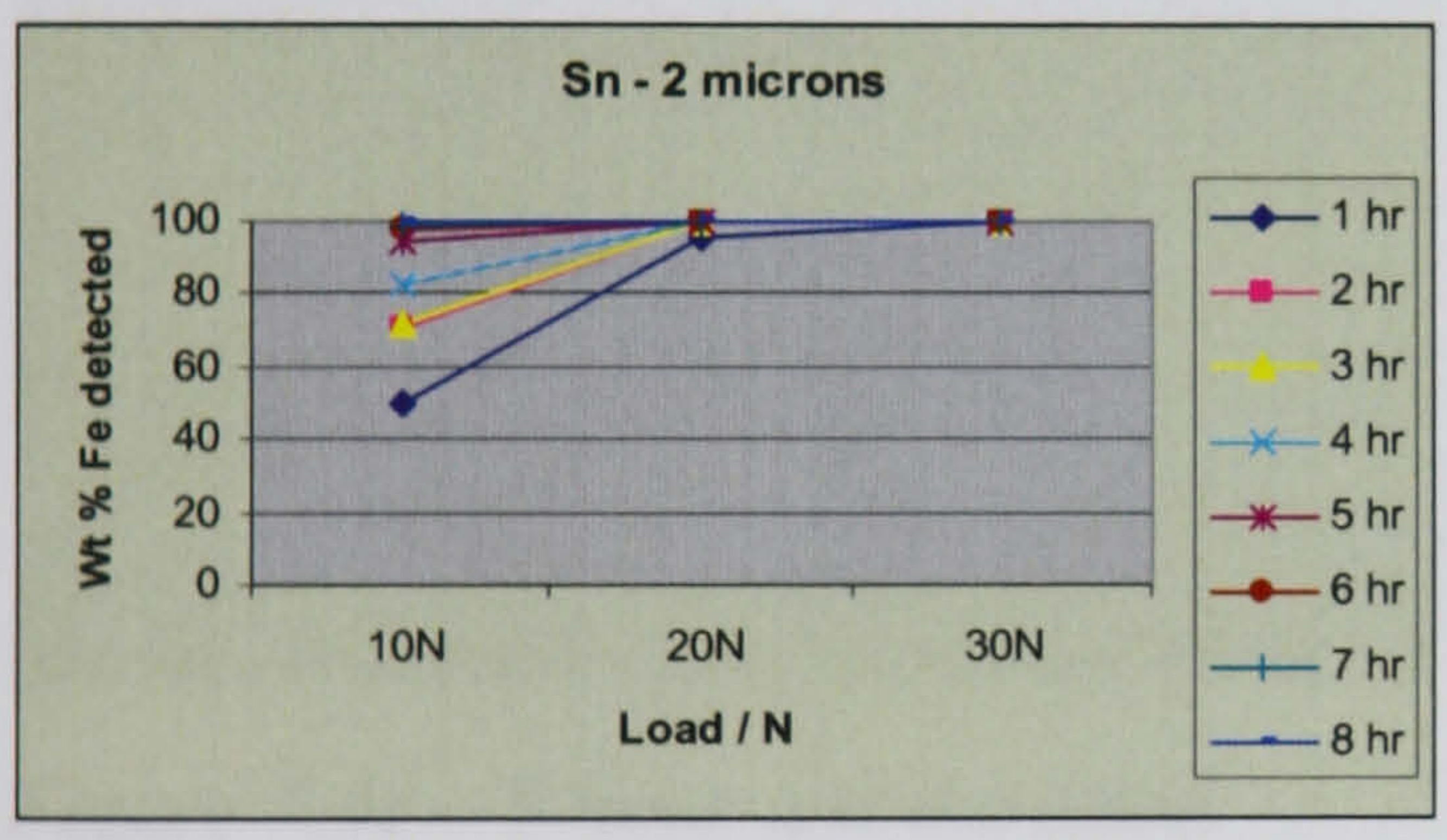

Figure 7.3a – 2 micron thickness

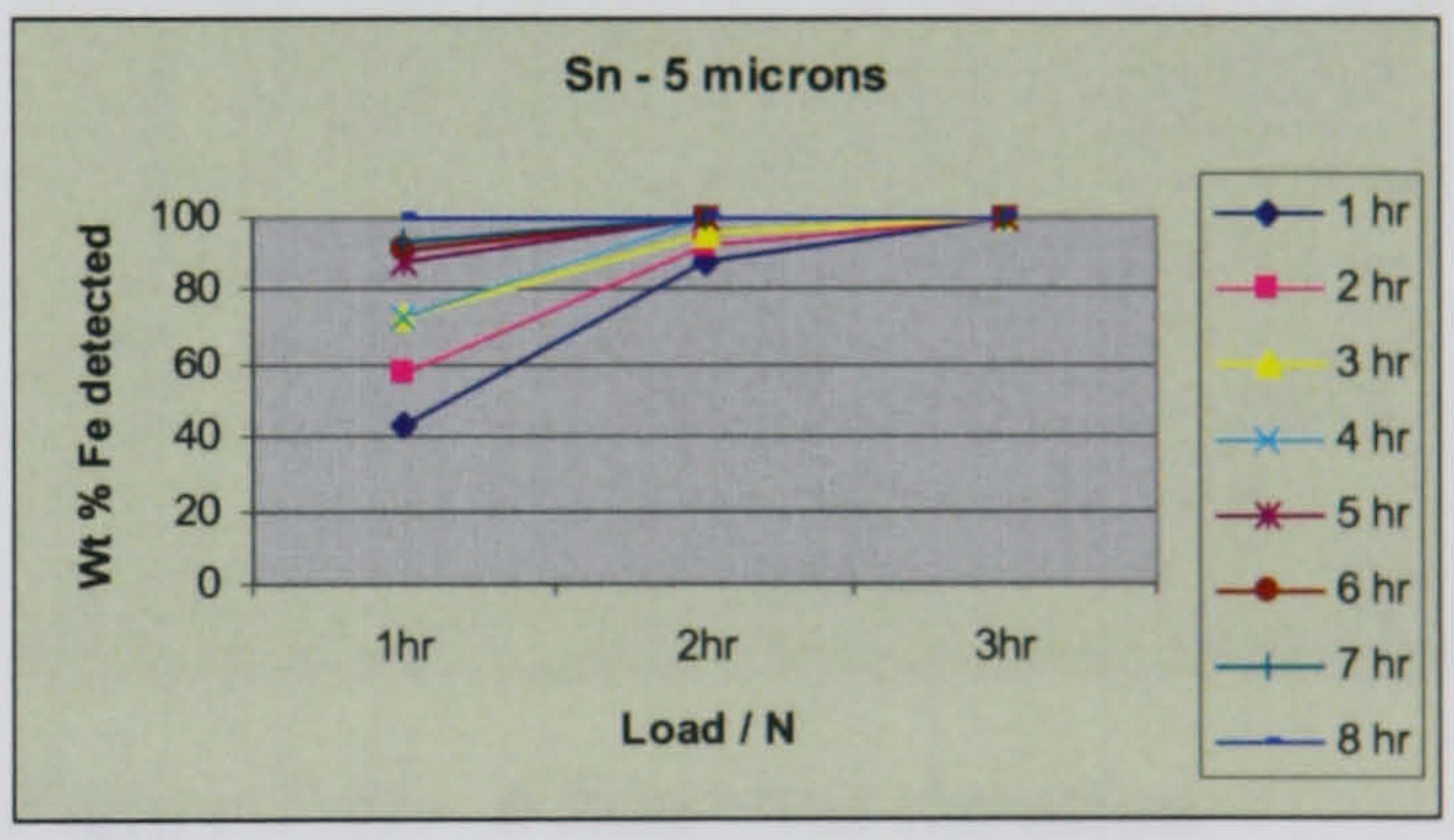

Figure 7.3b – 5 micron thickness

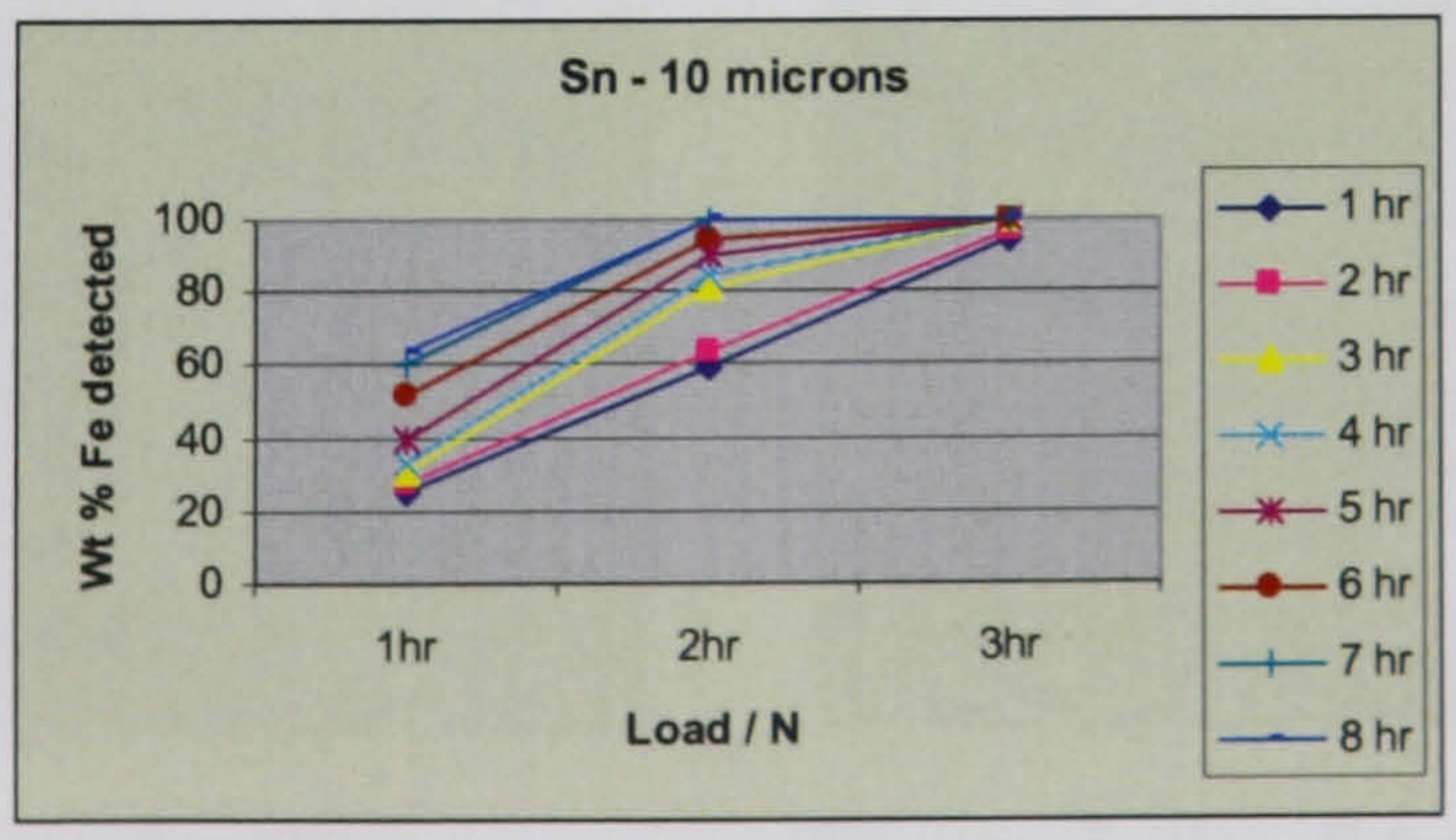

Figure 7.3c – 10 micron thickness

Effect of increasing coating thickness with respect to load

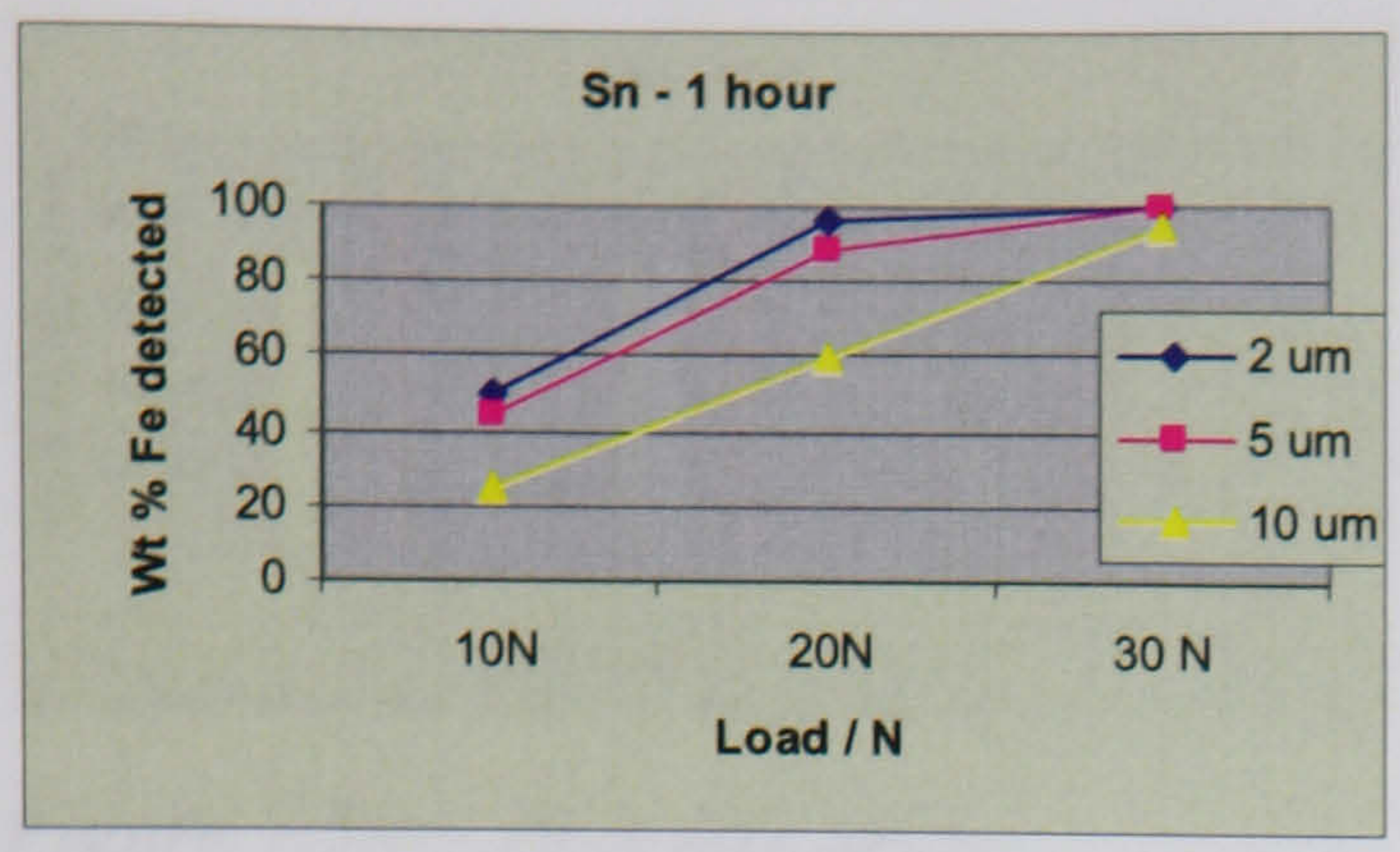

Figure 7.4a – 1 hour test duration

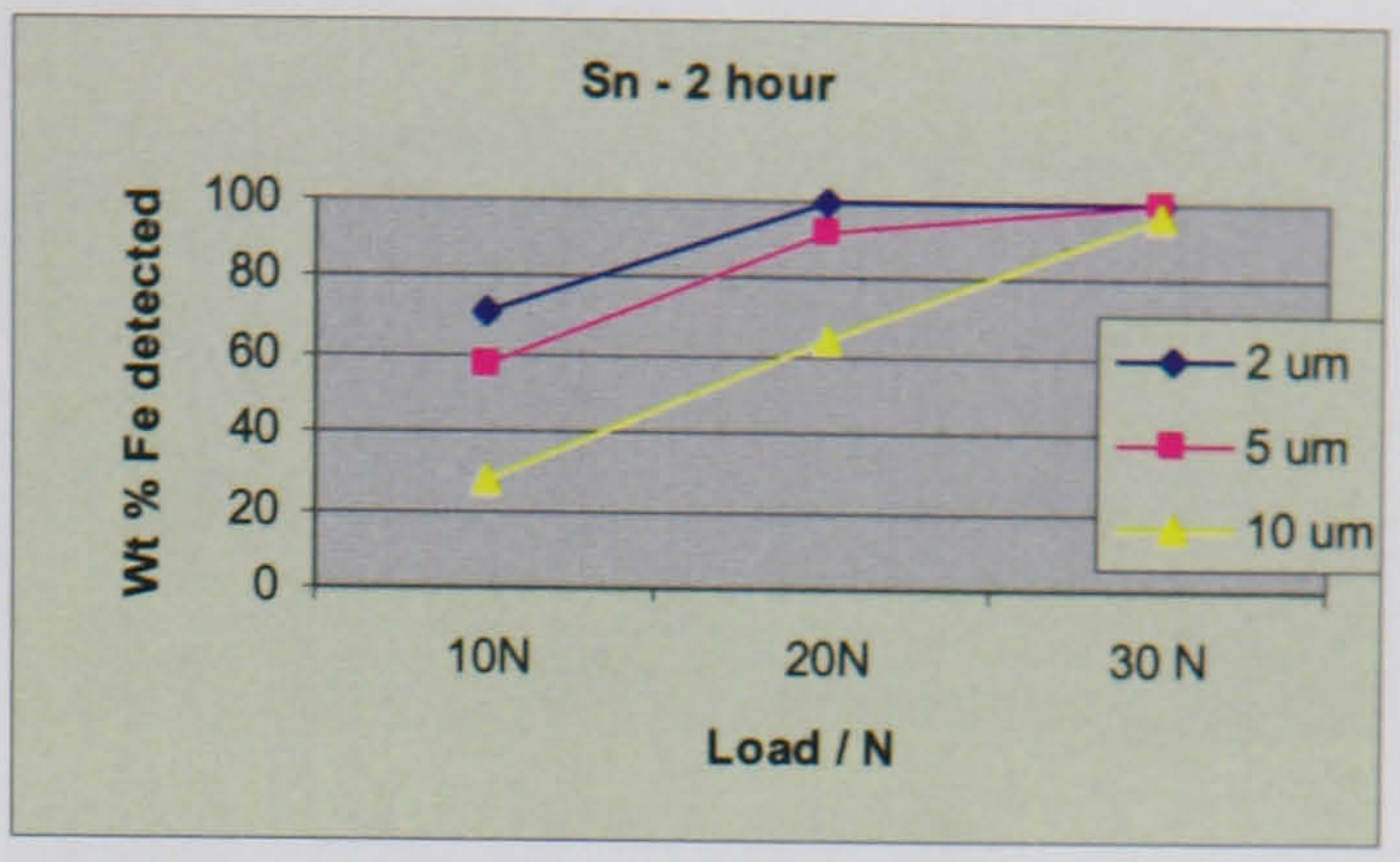

Figure 7.4b – 2 hour test duration

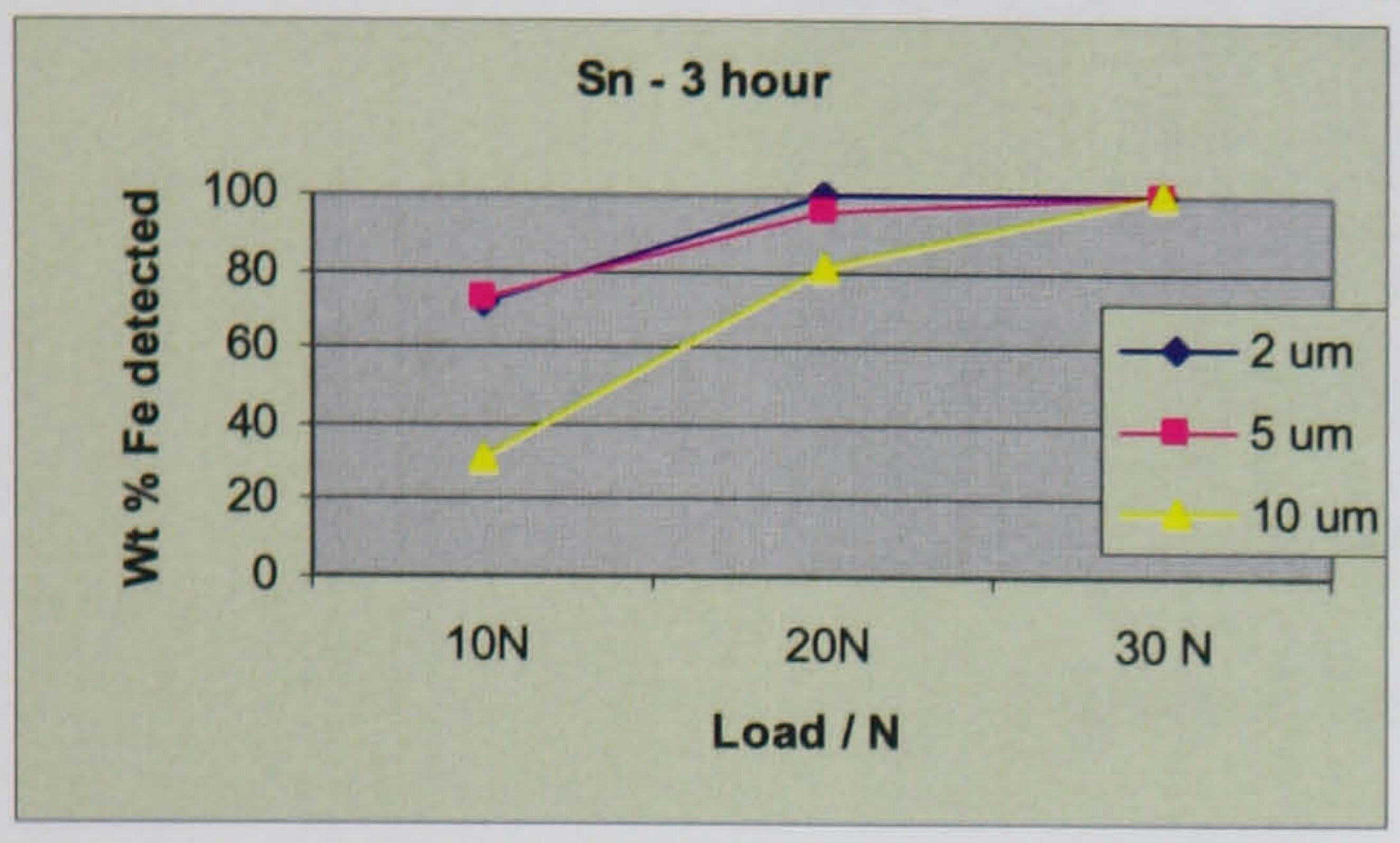

Figure 7.4c – 3 hour test duration

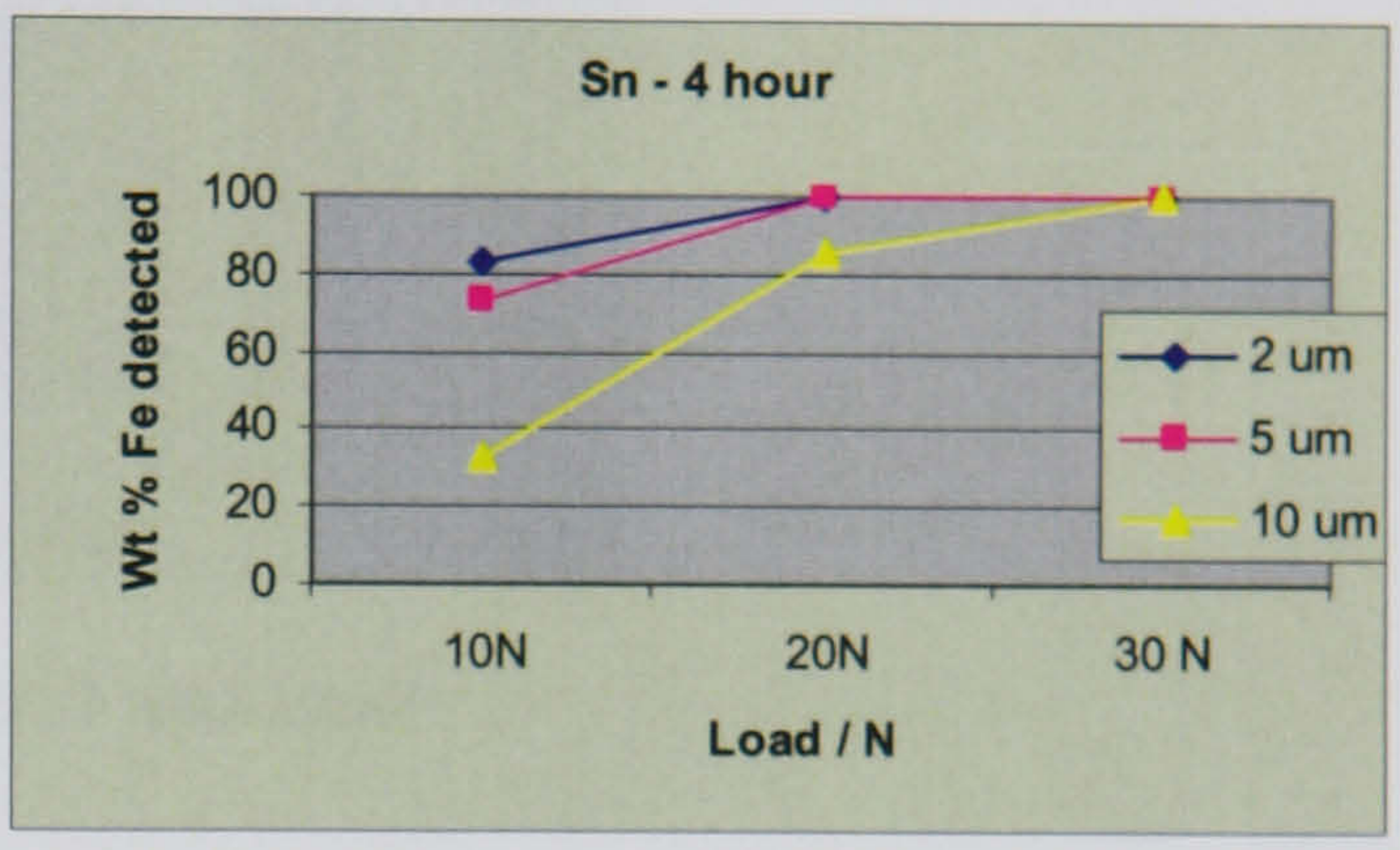

Figure 7.4d – 4 hour test duration

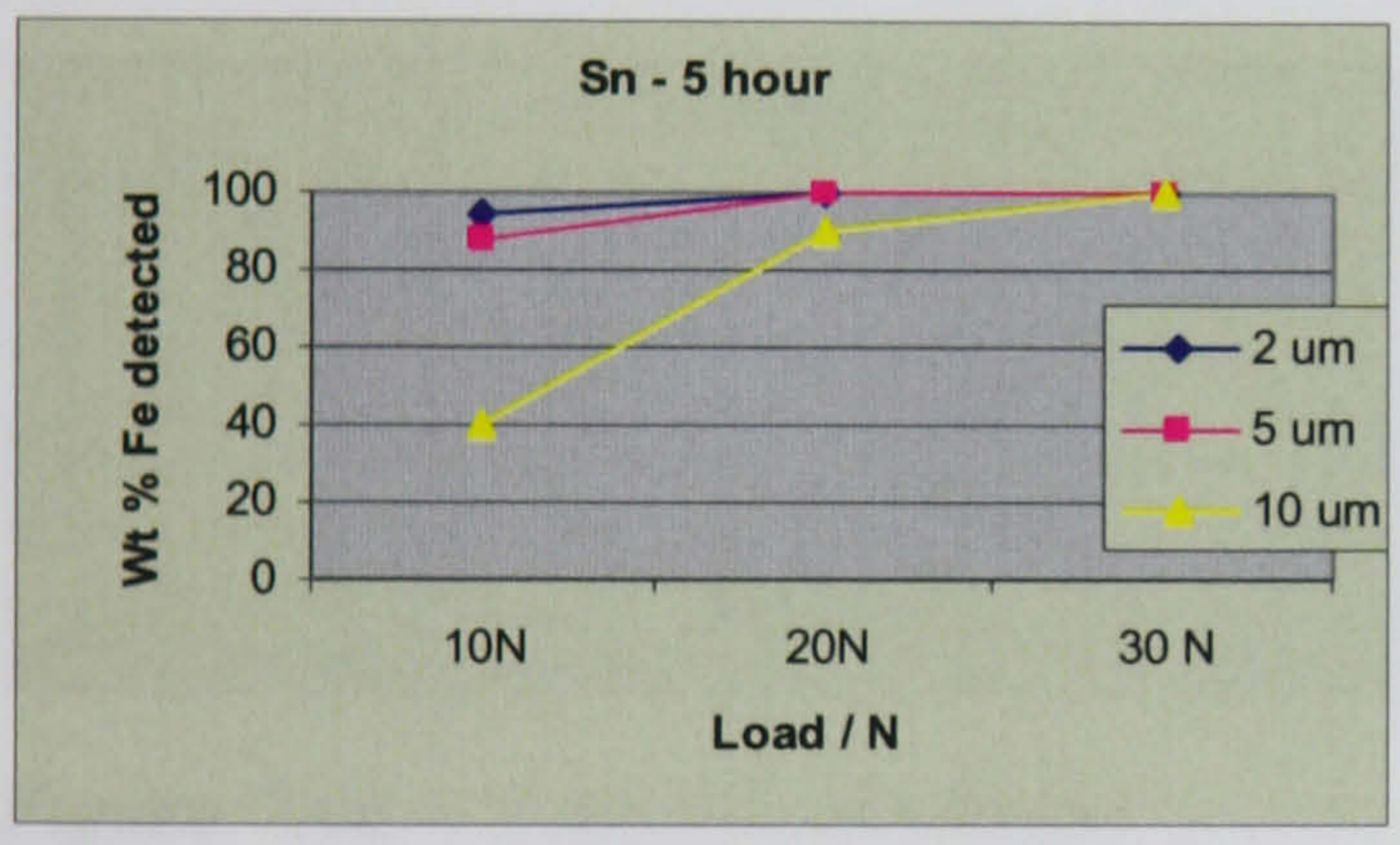

Figure 7.4e – 5 hour test duration

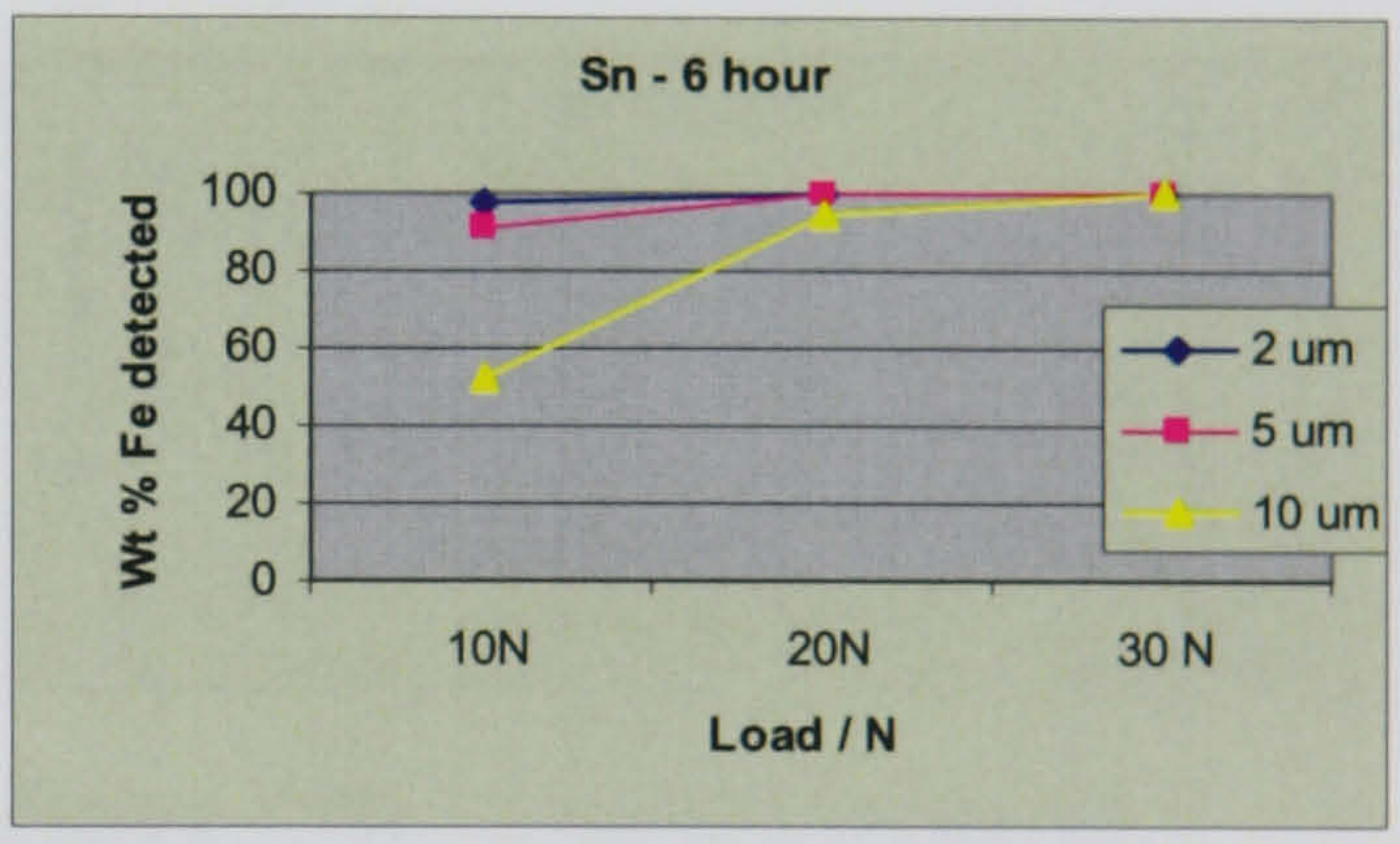

Figure 7.4f – 6 hour test duration

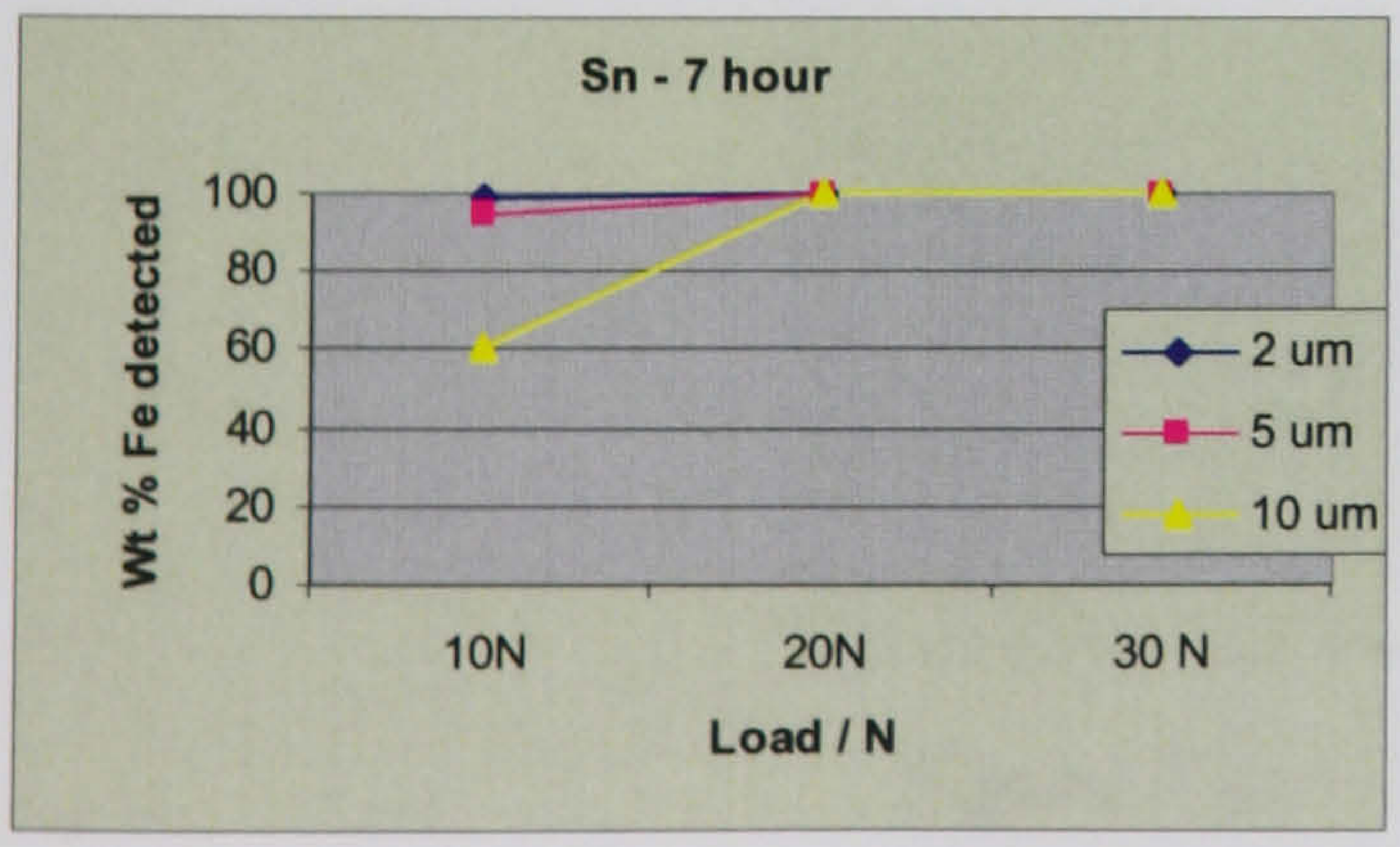

Figure 7.4g – 7 hour test duration

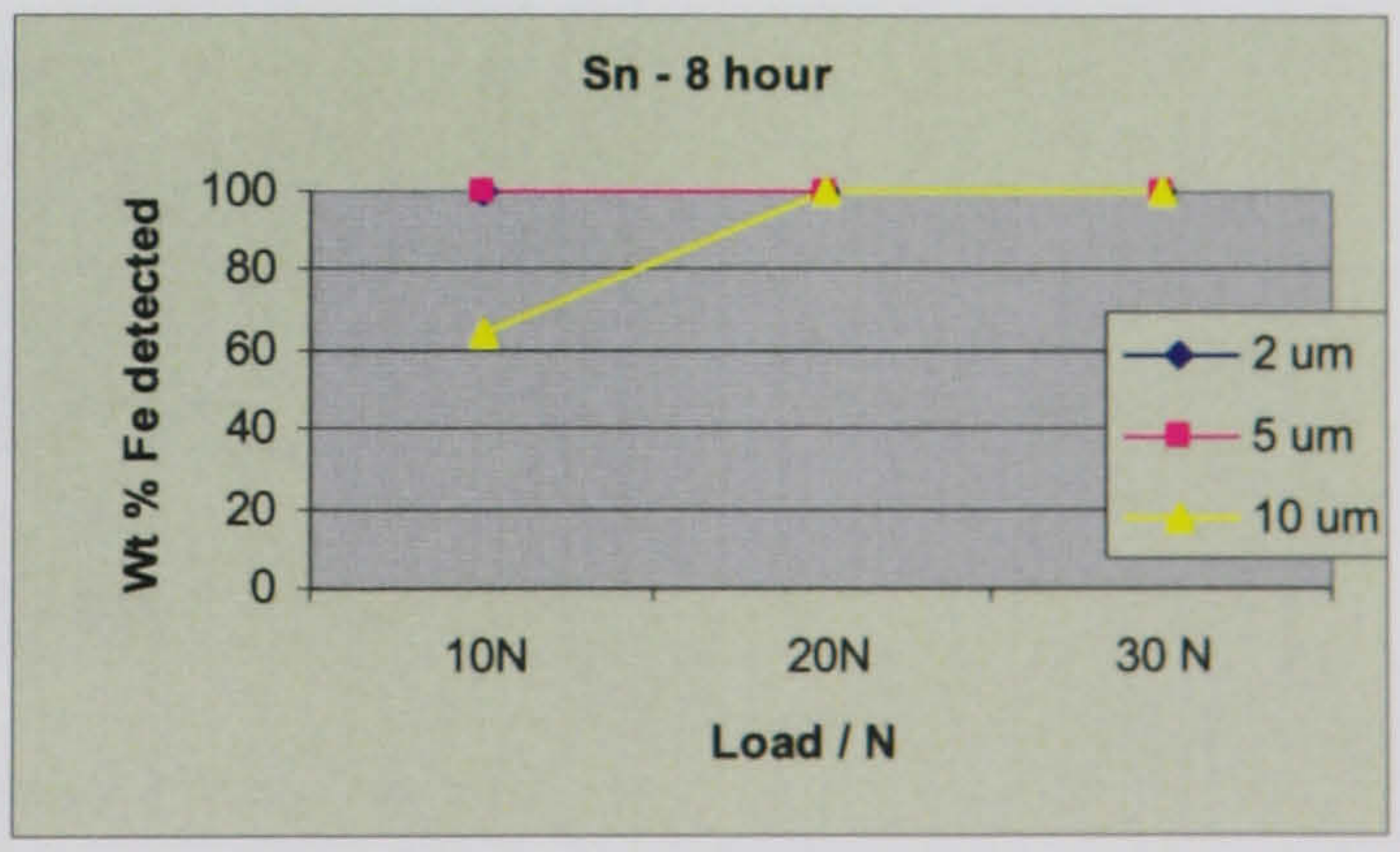

Figure 7.4h – 8 hour test duration

Effect of increasing test duration with respect to coating thickness

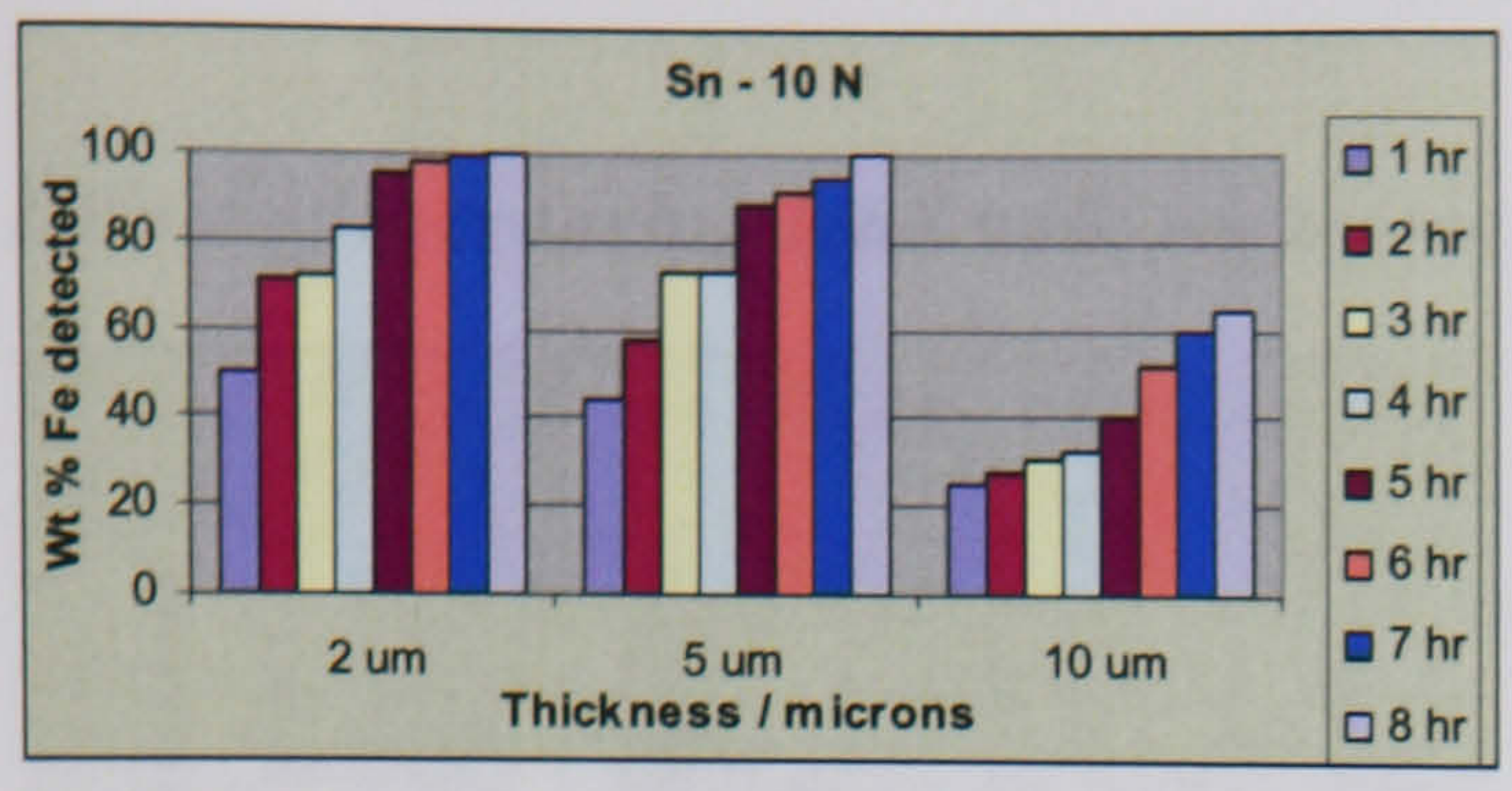

Figure 7.5a – 10 N test load

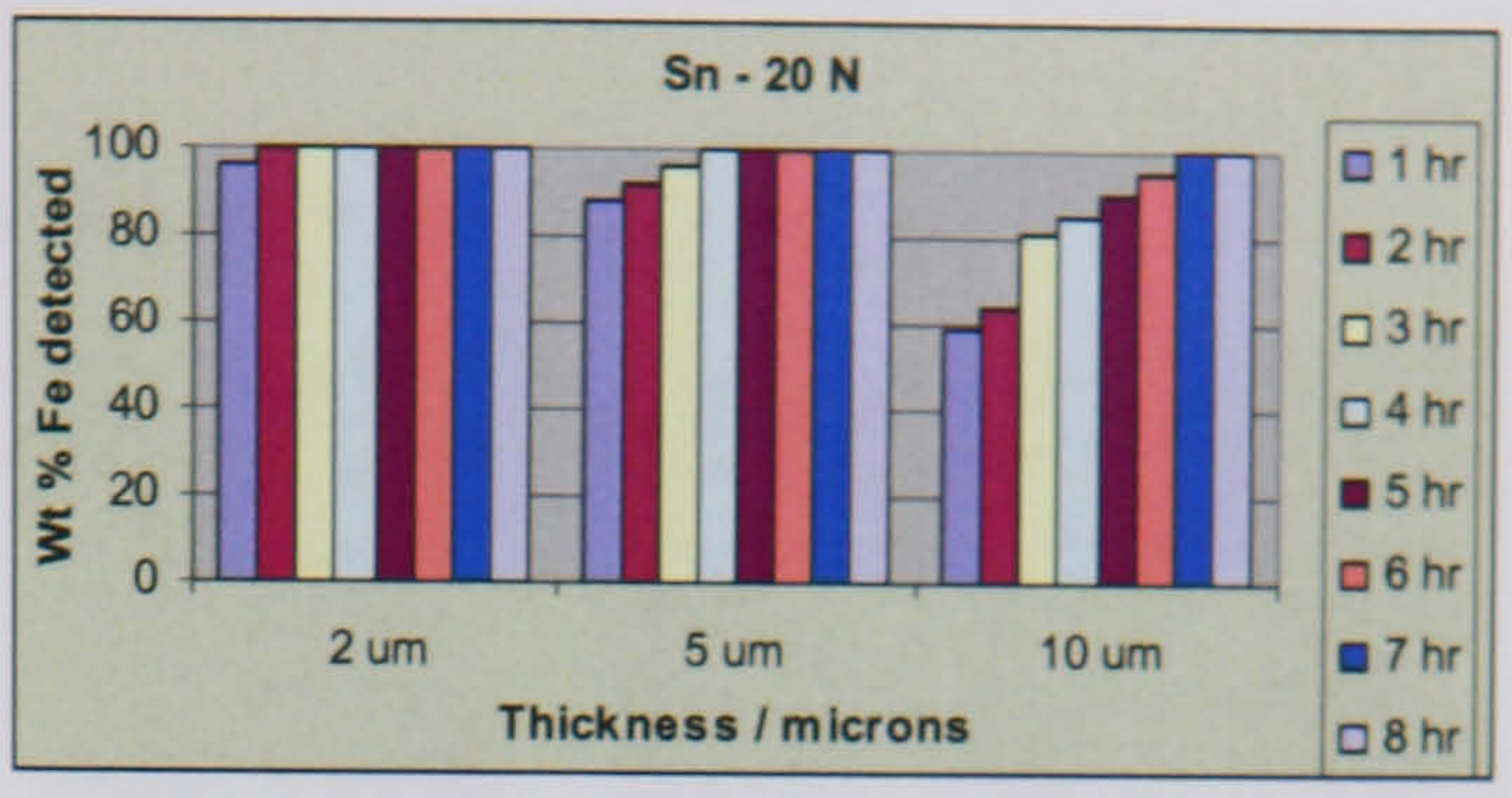

Figure 7.5b – 20 N test load

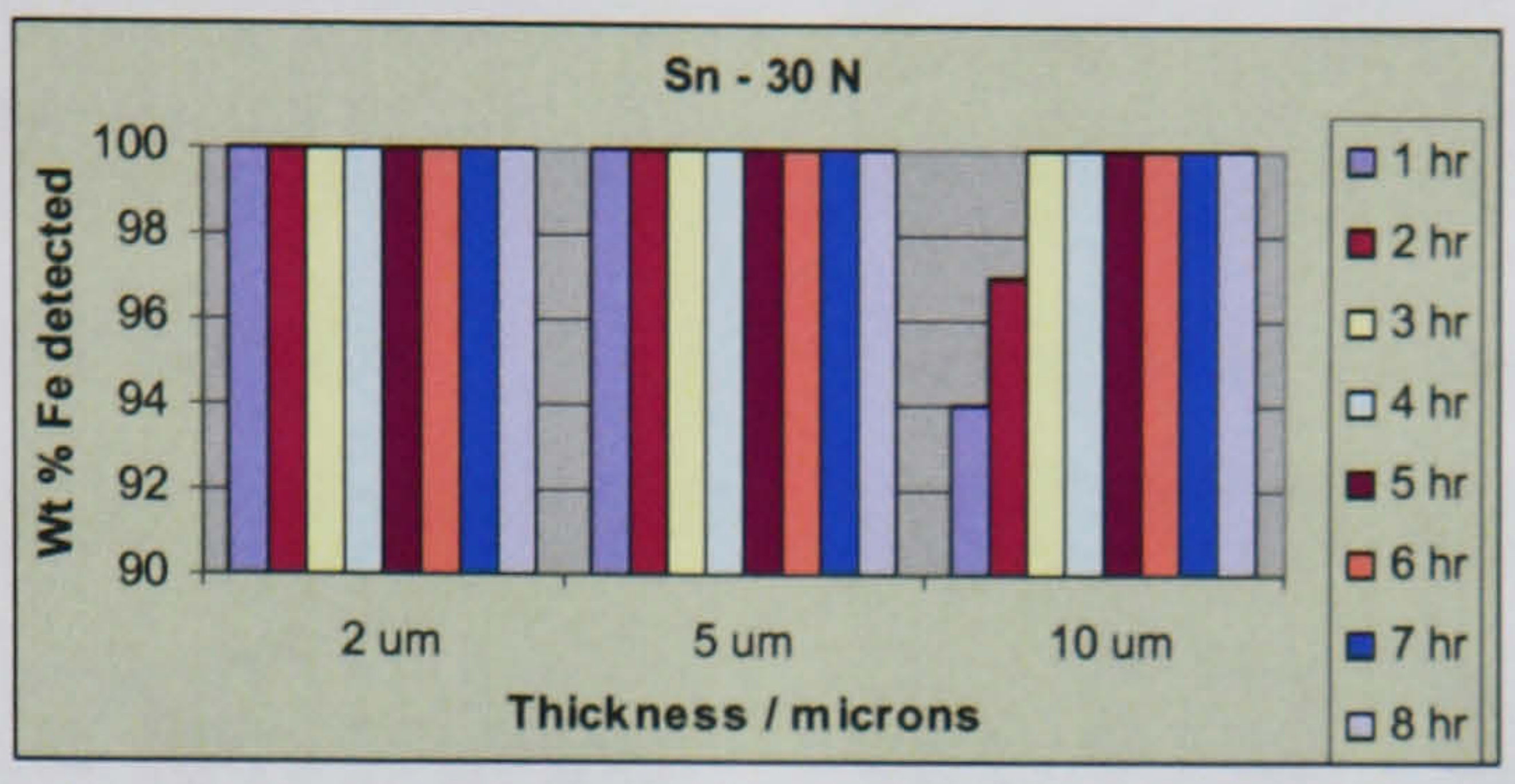

Figure 7.5c – 30 N test load

Effect of increasing load with respect to test duration

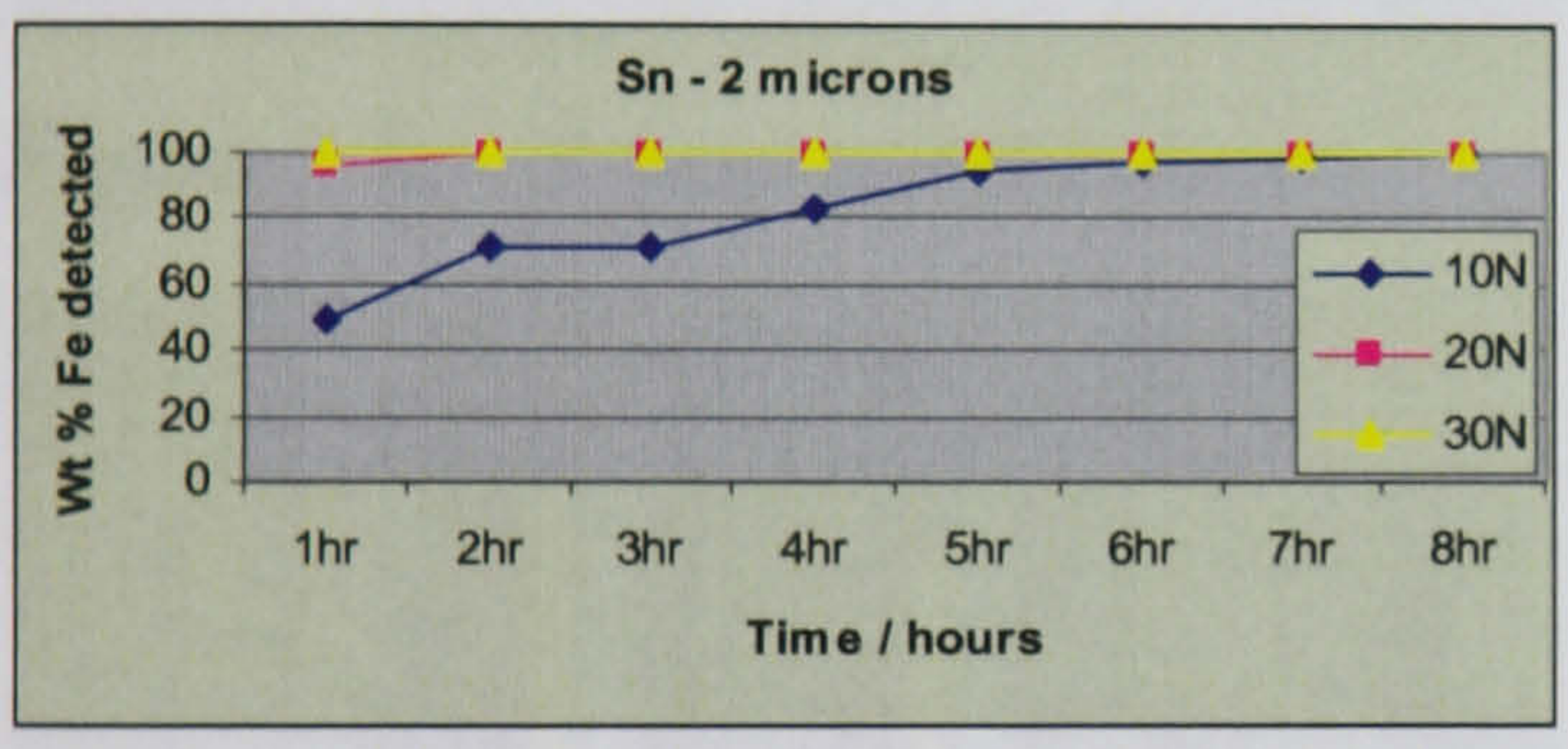

Figure 7.6a – 2 micron thickness

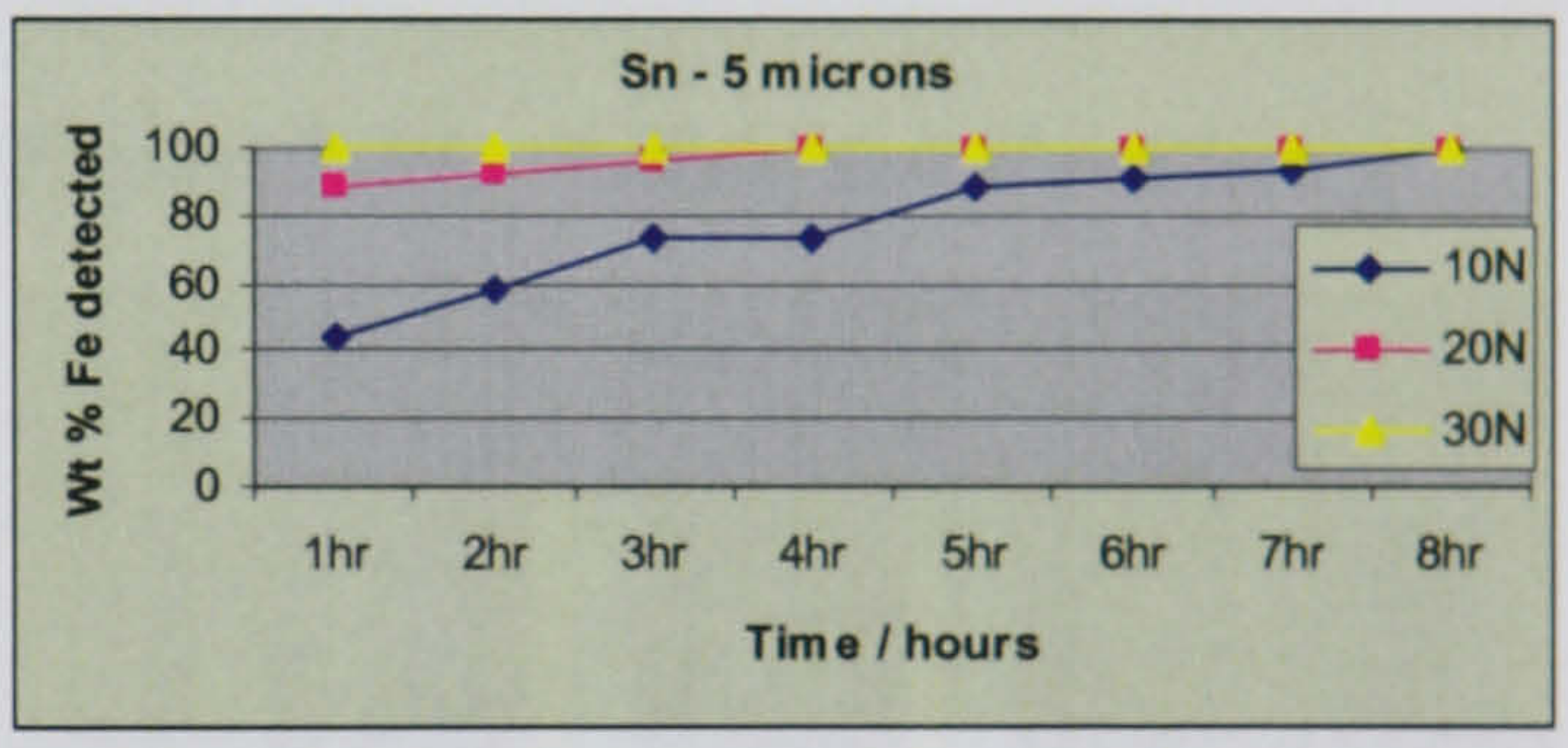

Figure 7.6b – 5 micron thickness

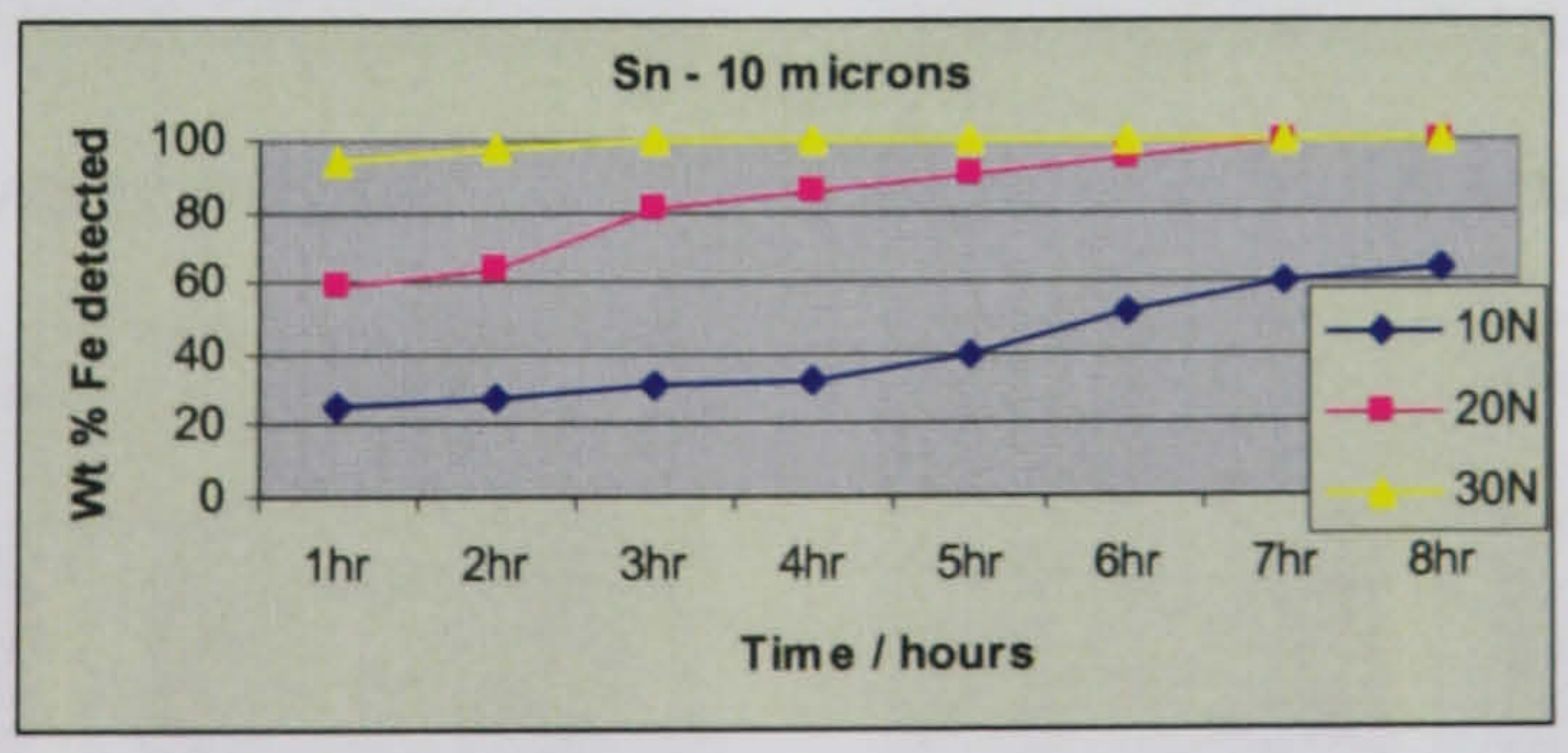

Figure 7.6c – 10 micron thickness

7.2.2 Tin-Nickel Coating

Effect of increasing load with respect to increasing coating thickness

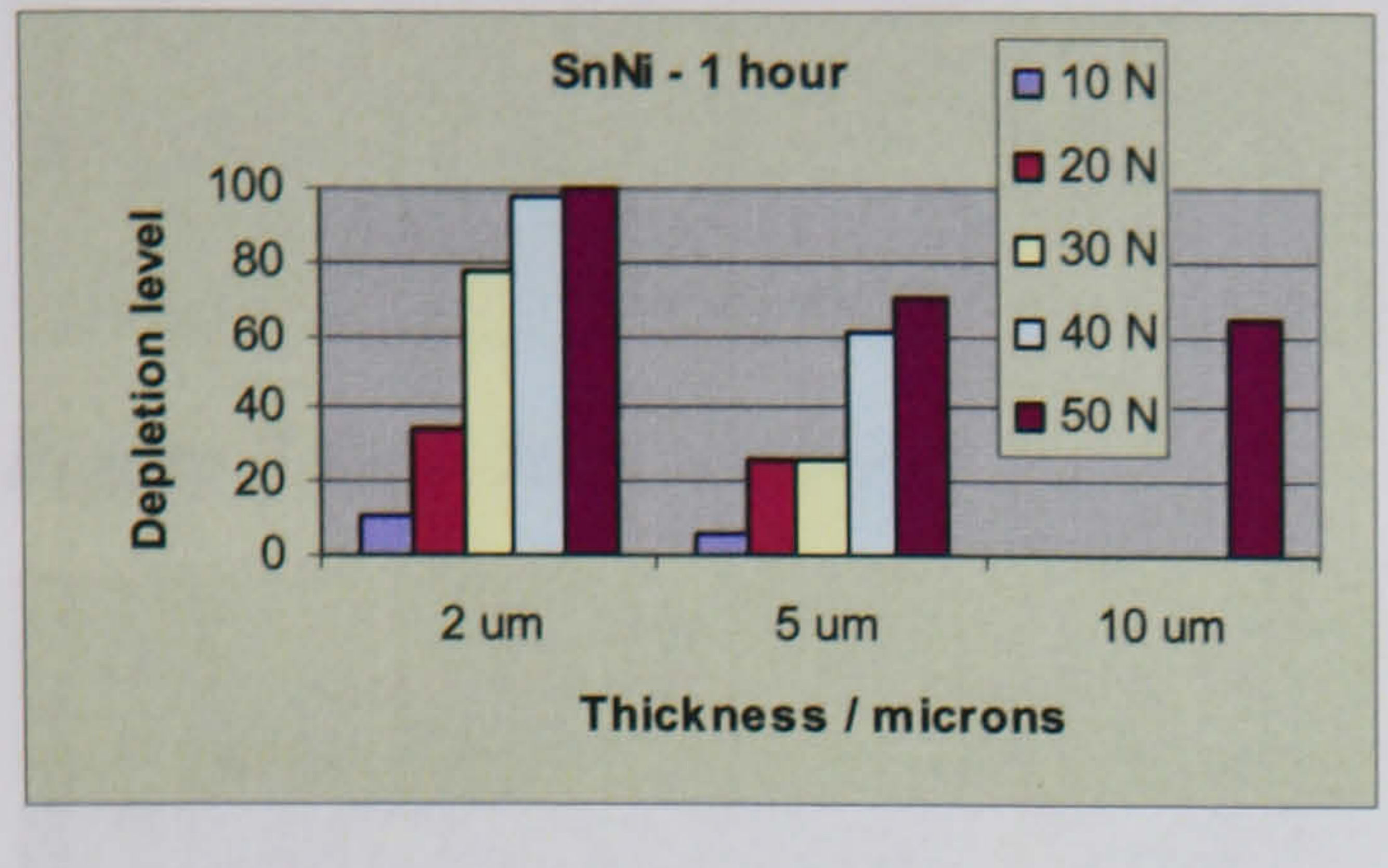

Figure 7.7a – 1 hour test duration

Figure 7.7b – 2 hour test duration

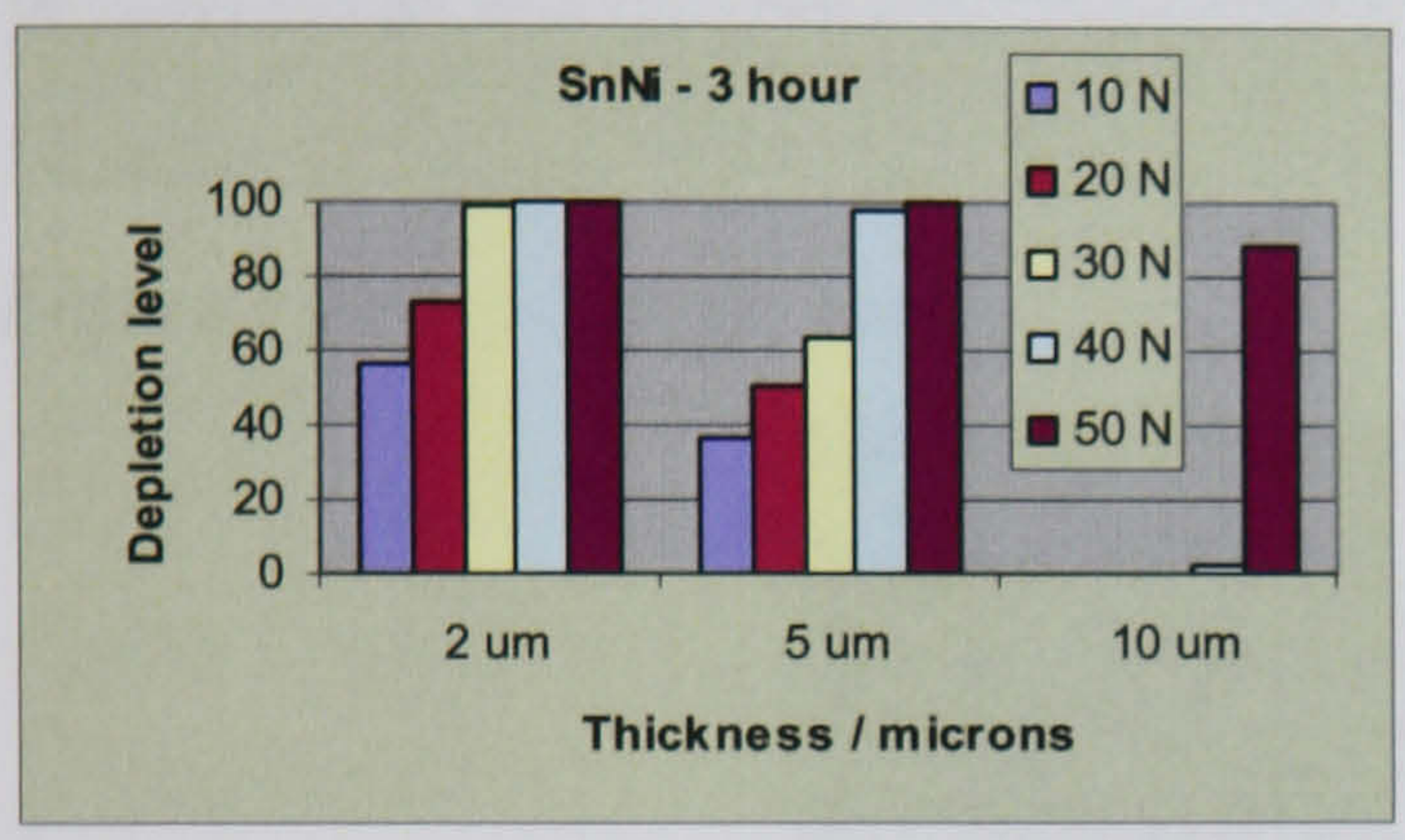

Figure 7.7c – 3 hour test duration

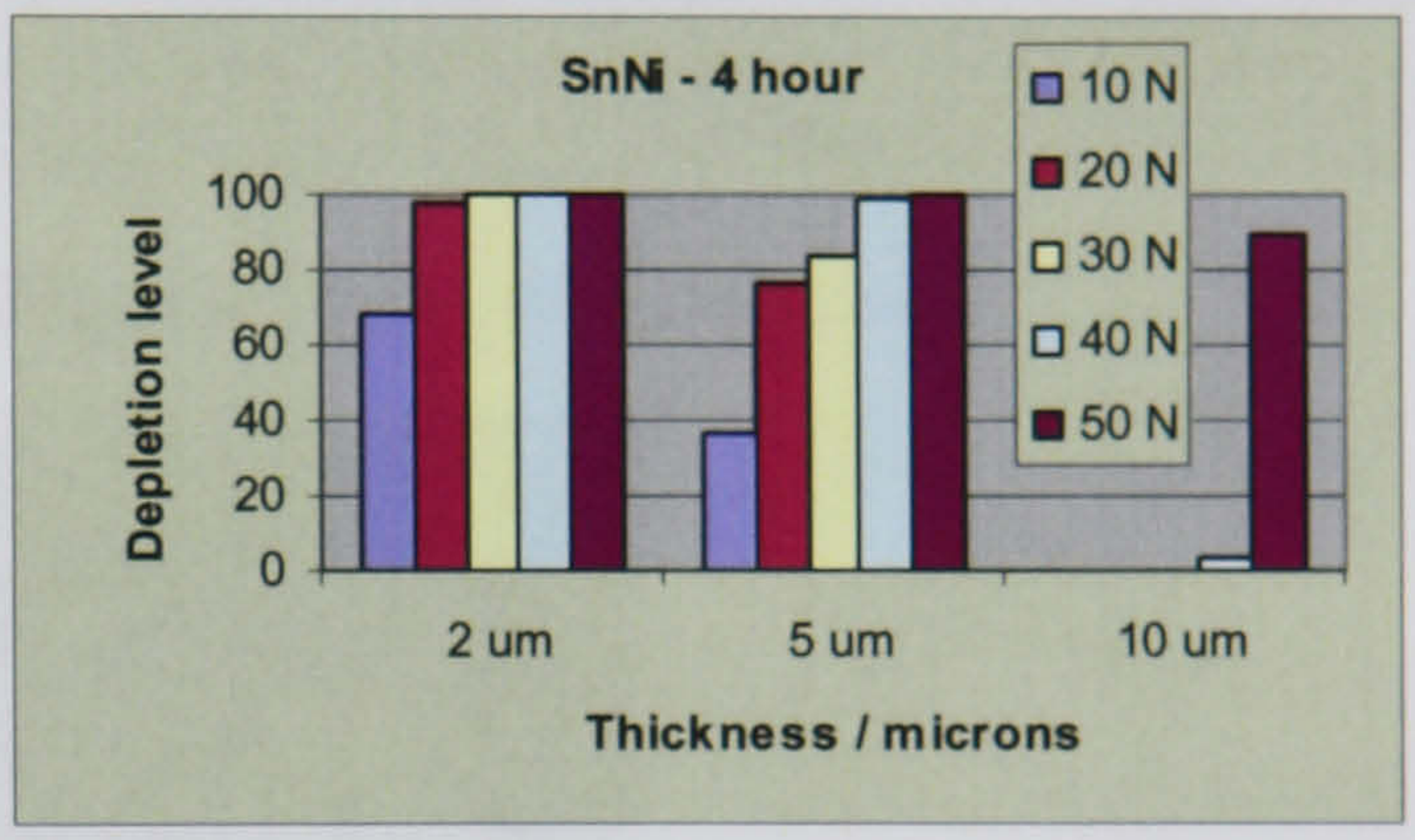

Figure 7.7d – 4 hour test duration

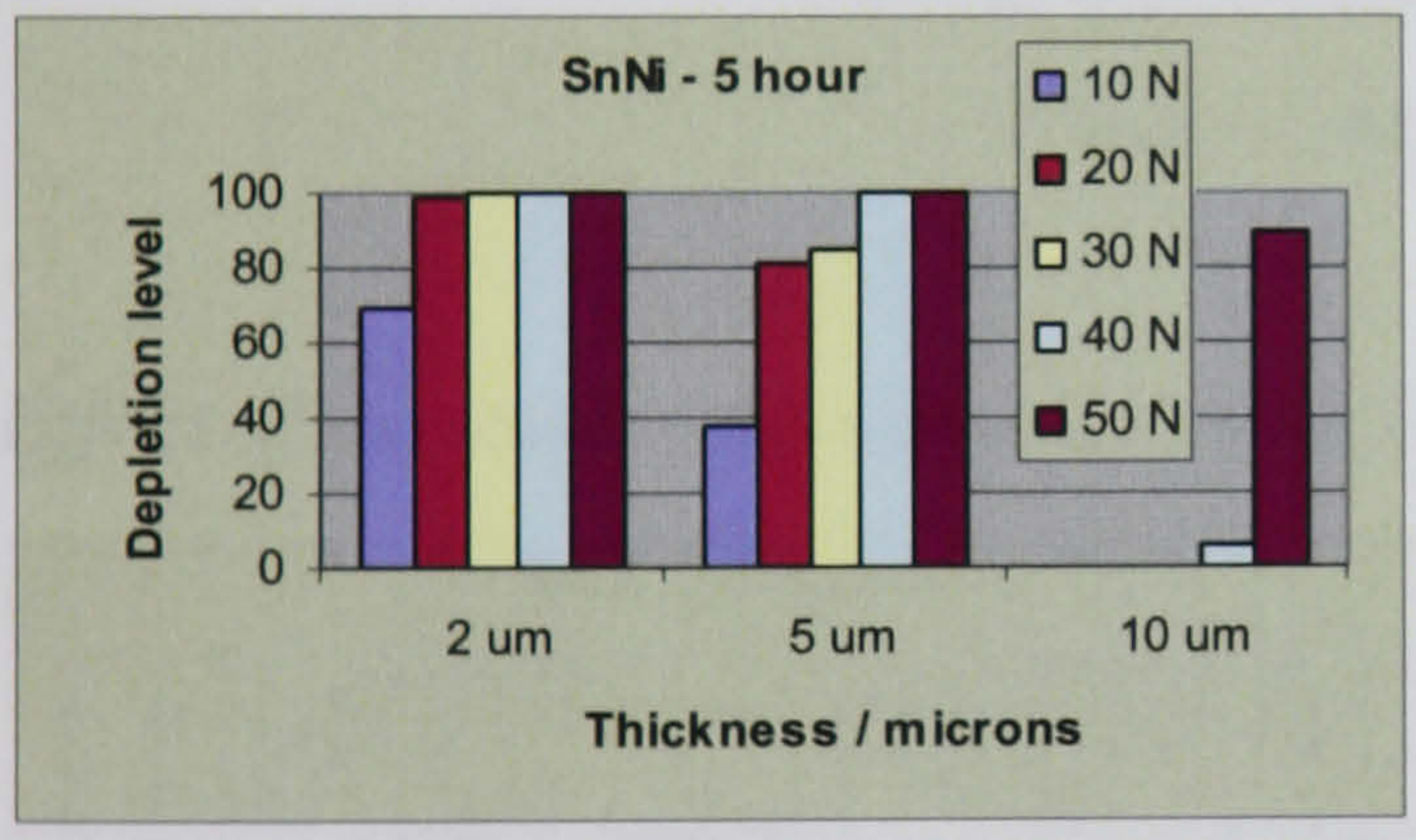

Figure 7.7e – 5 hour test duration

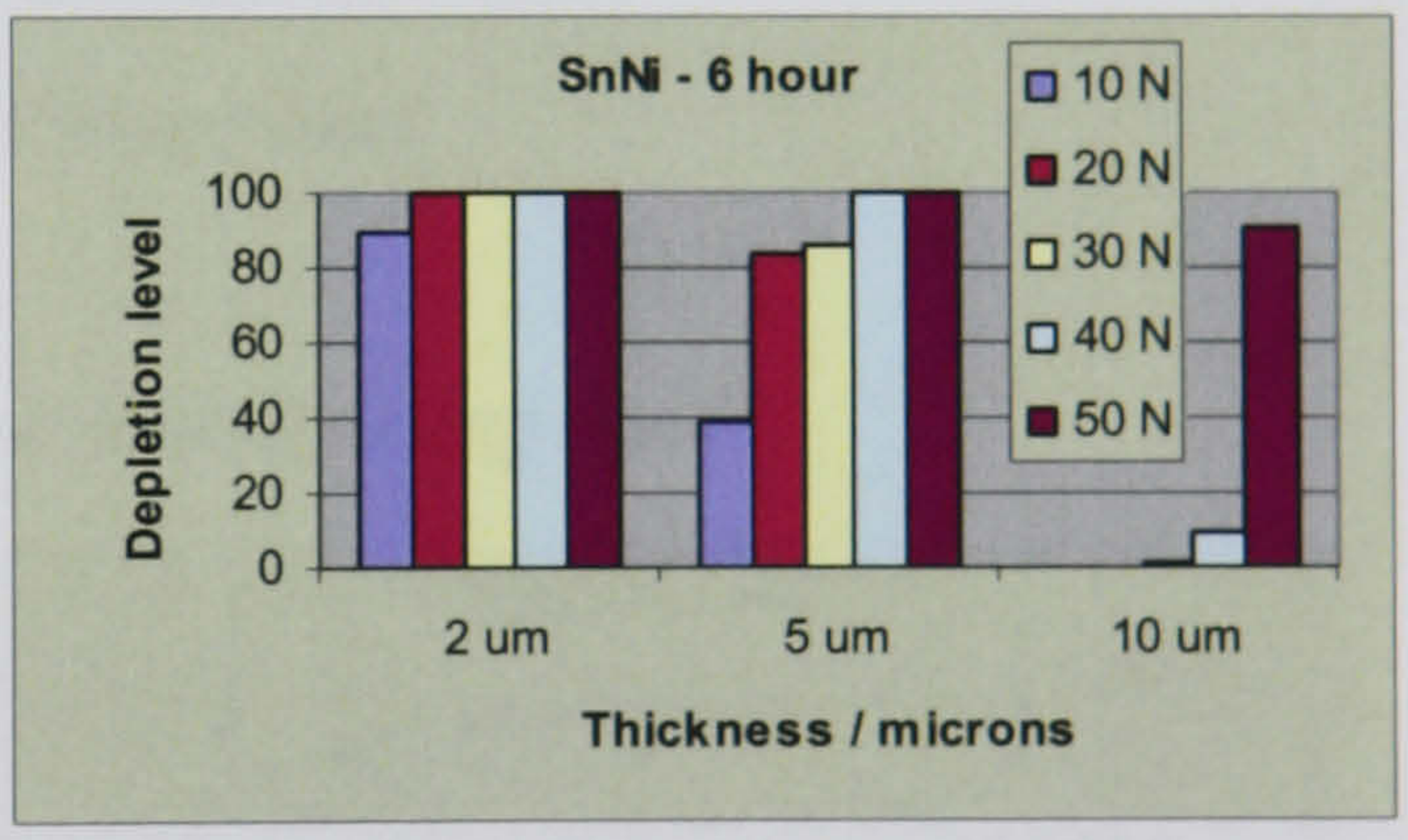

Figure 7.7f – 6 hour test duration

Figure 7.7g – 7 hour test duration

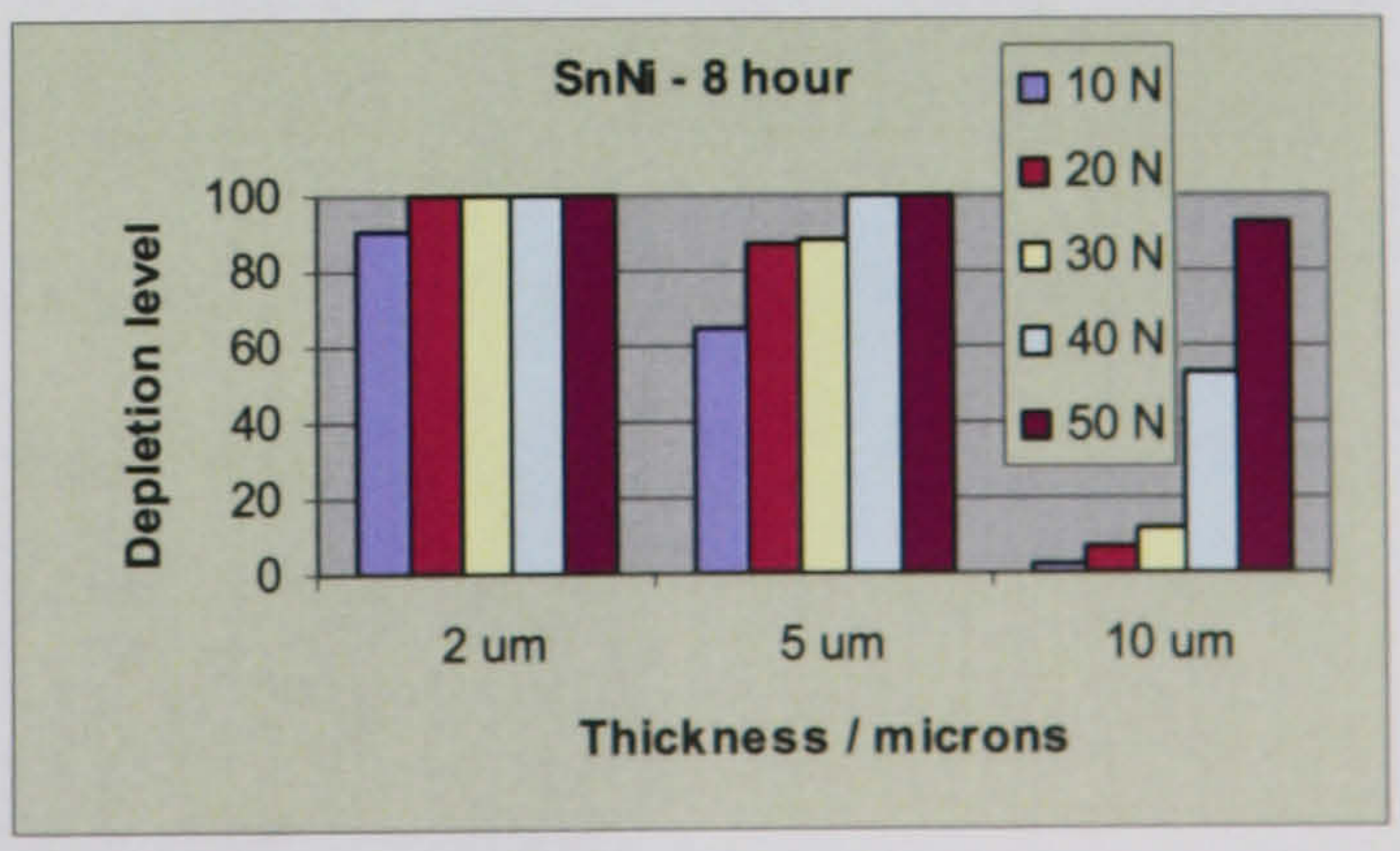

Figure 7.7h – 8 hour test duration

Effect of increasing coating thickness with respect to increasing test duration

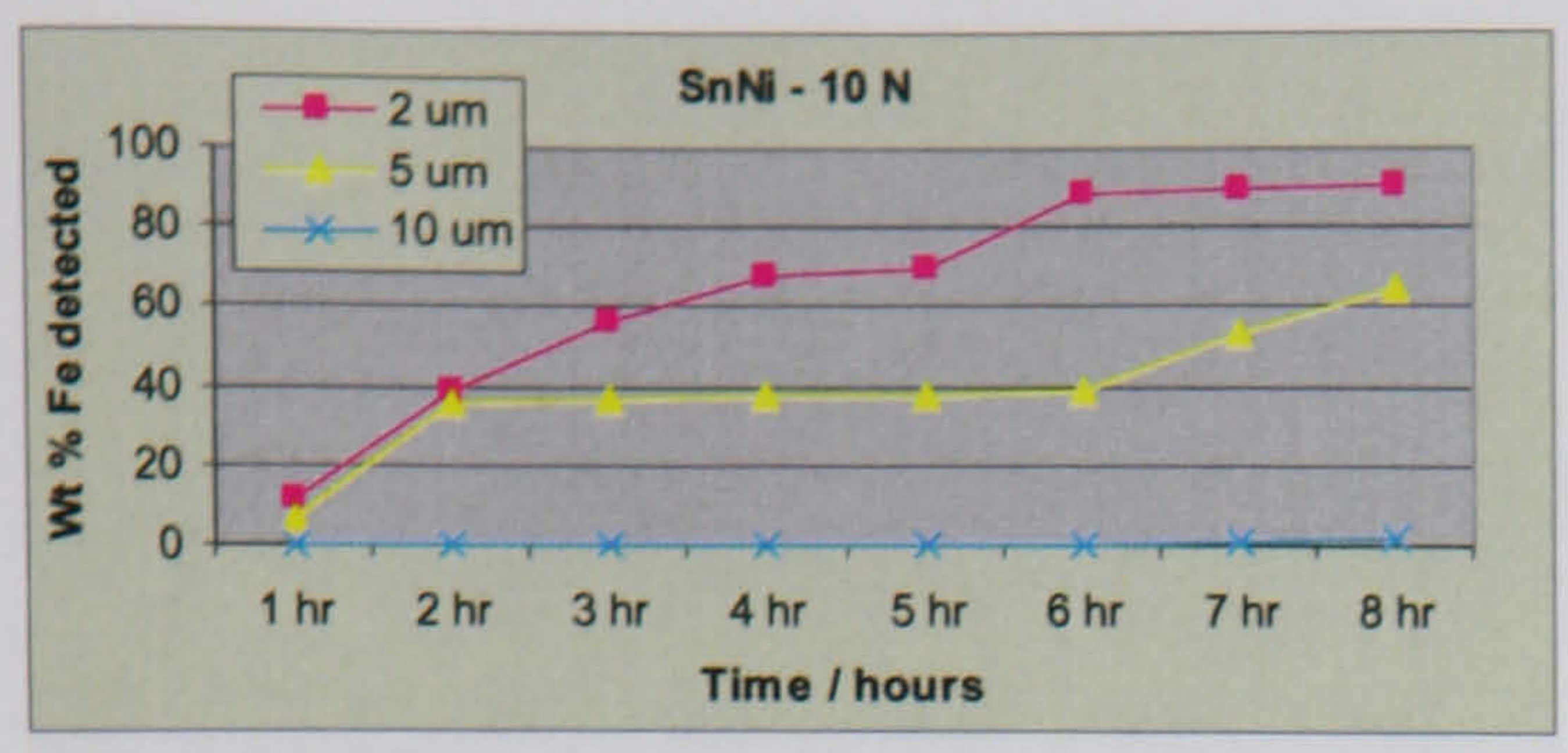

Figure 7.8a – 10 N test load

Figure 7.8b – 20 N test load

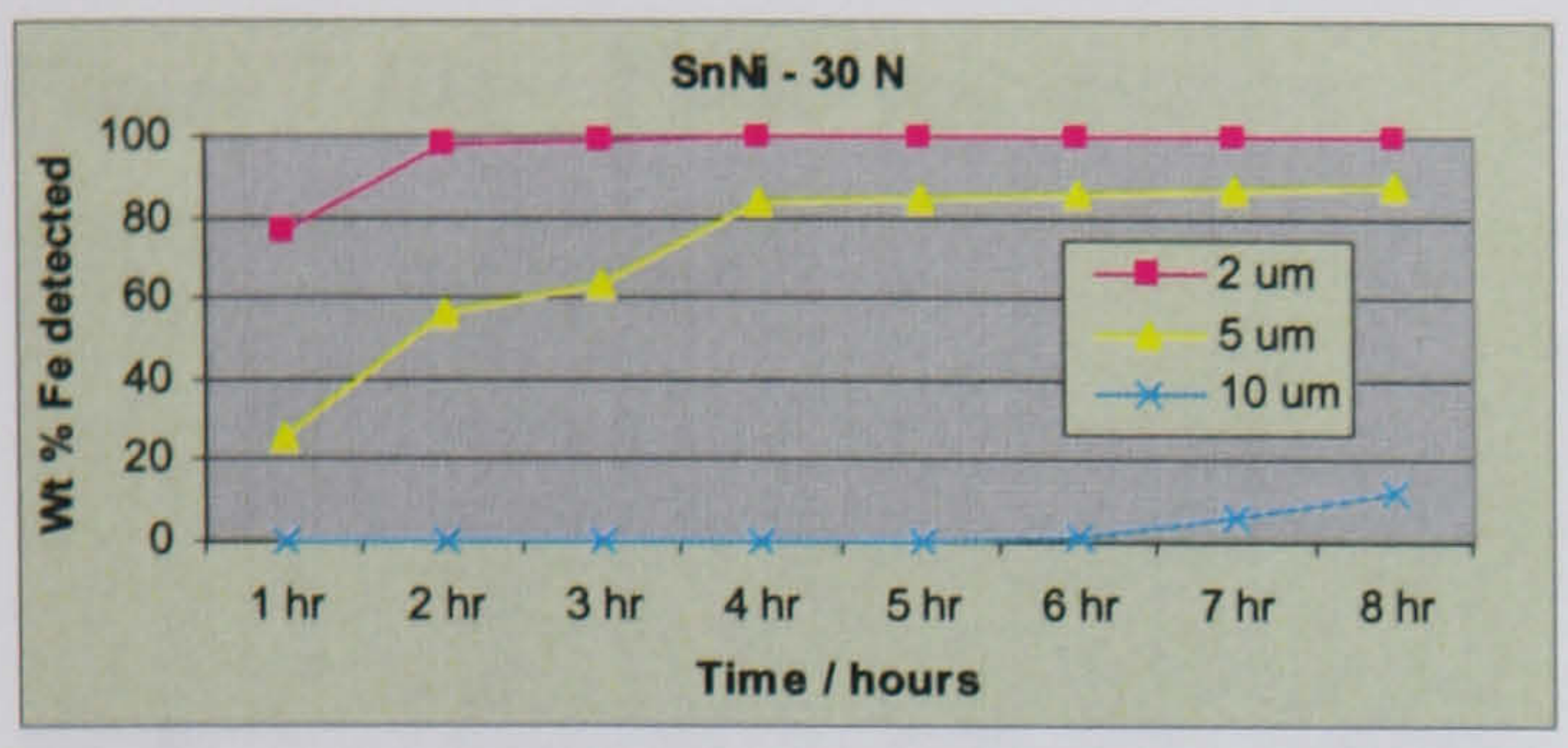

Figure 7.8c – 30 N test load

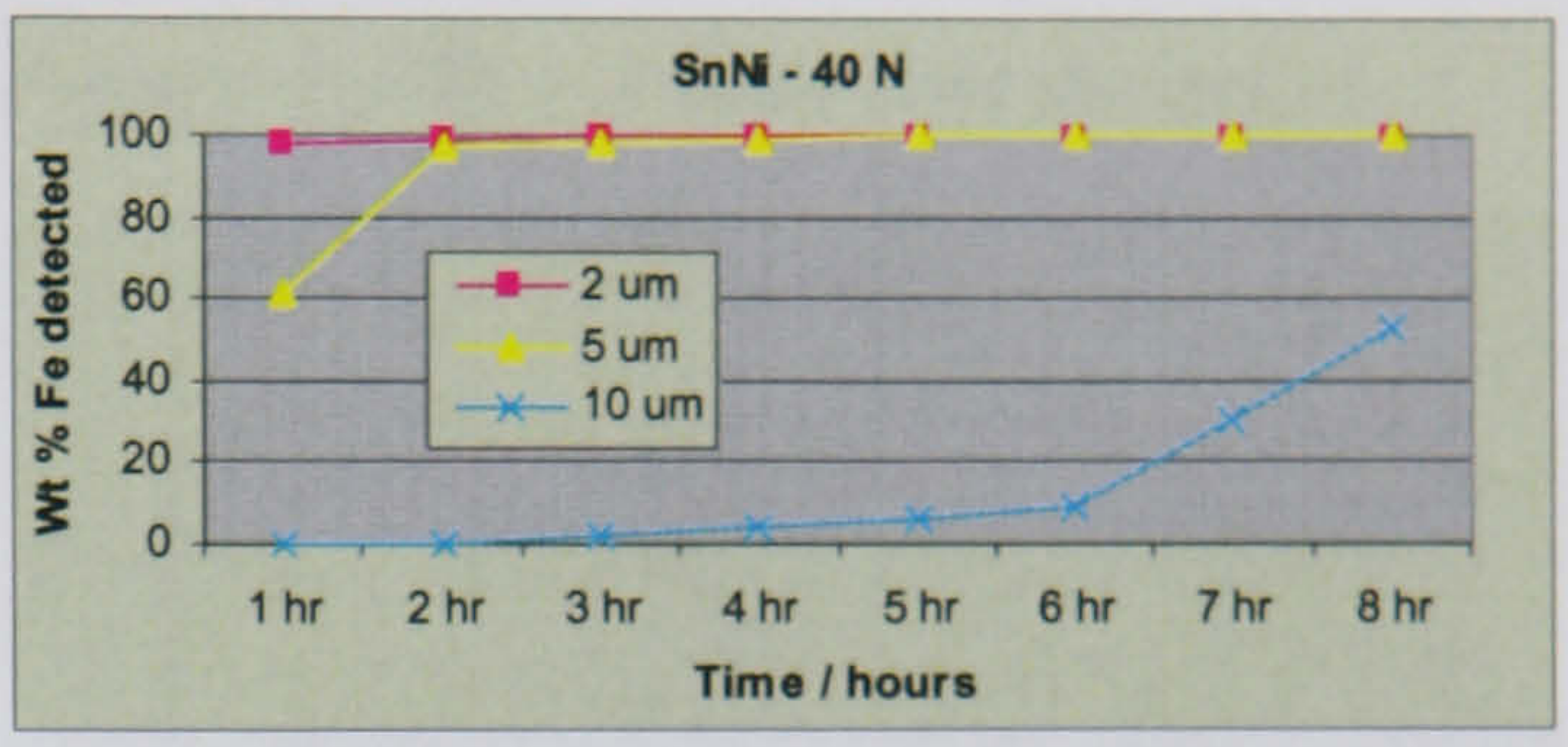

Figure 7.8d – 40 N test load

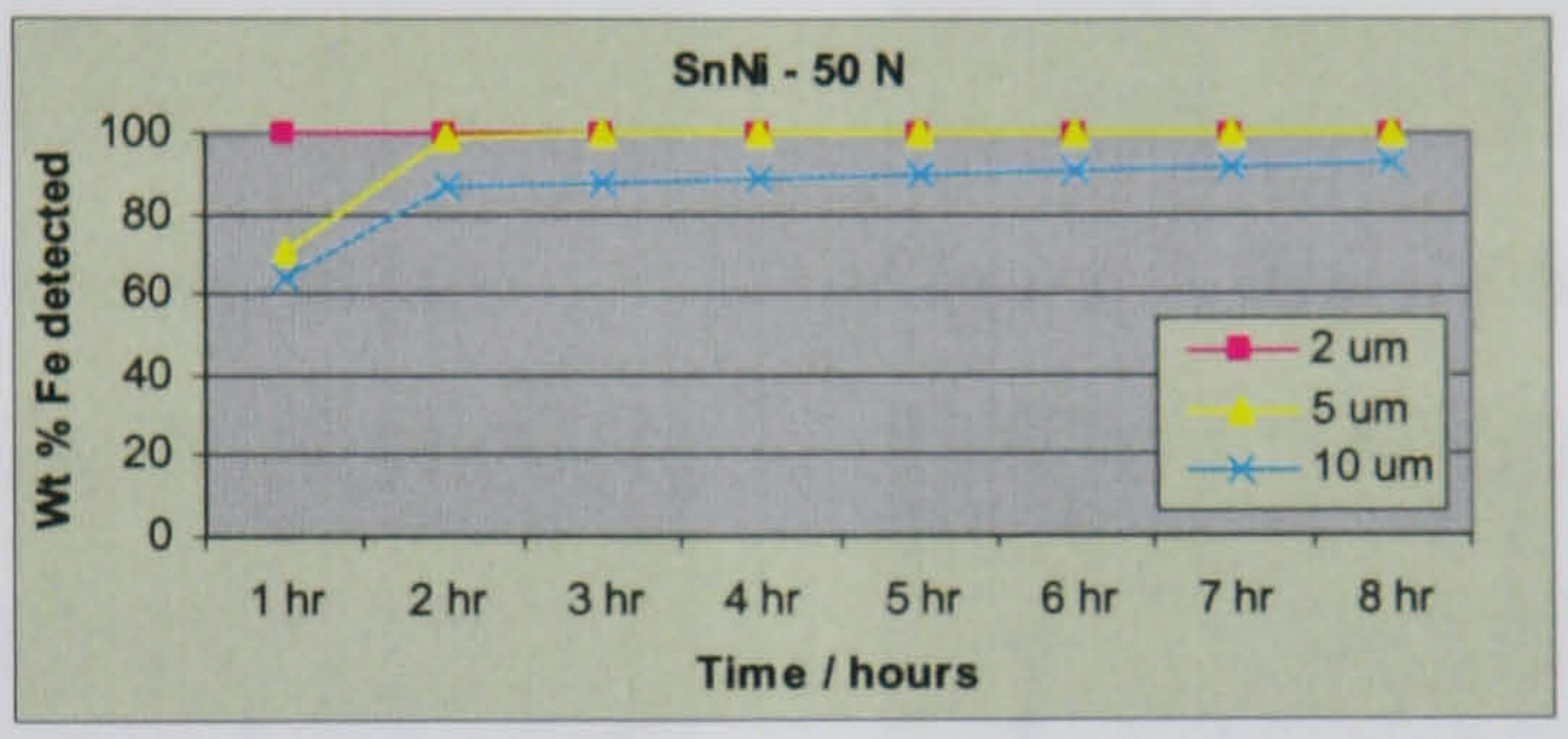

Figure 7.8e – 50 N test load

Effect of increasing test duration with respect to increasing load

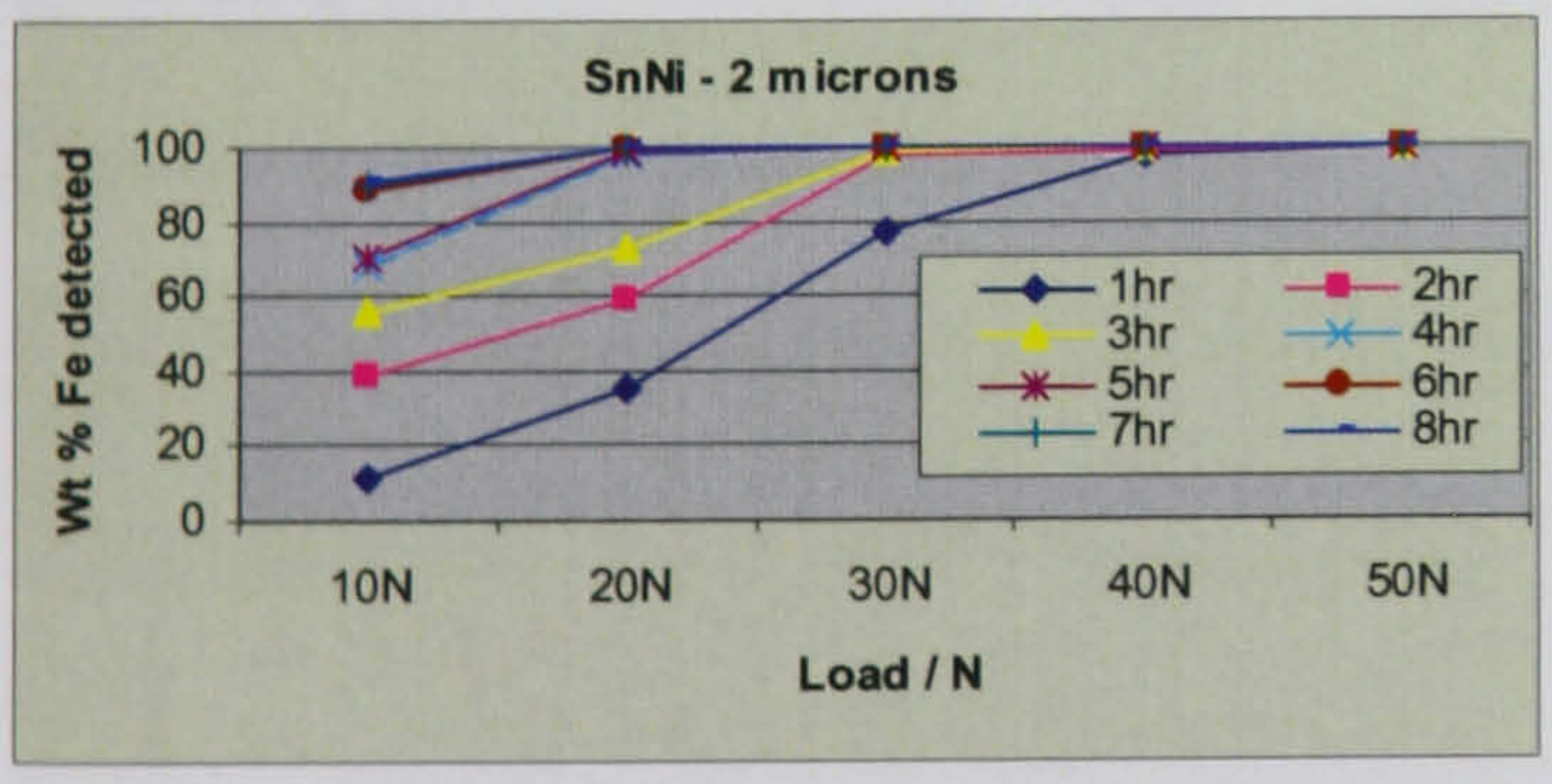

Figure 7.9a – 2 micron thickness

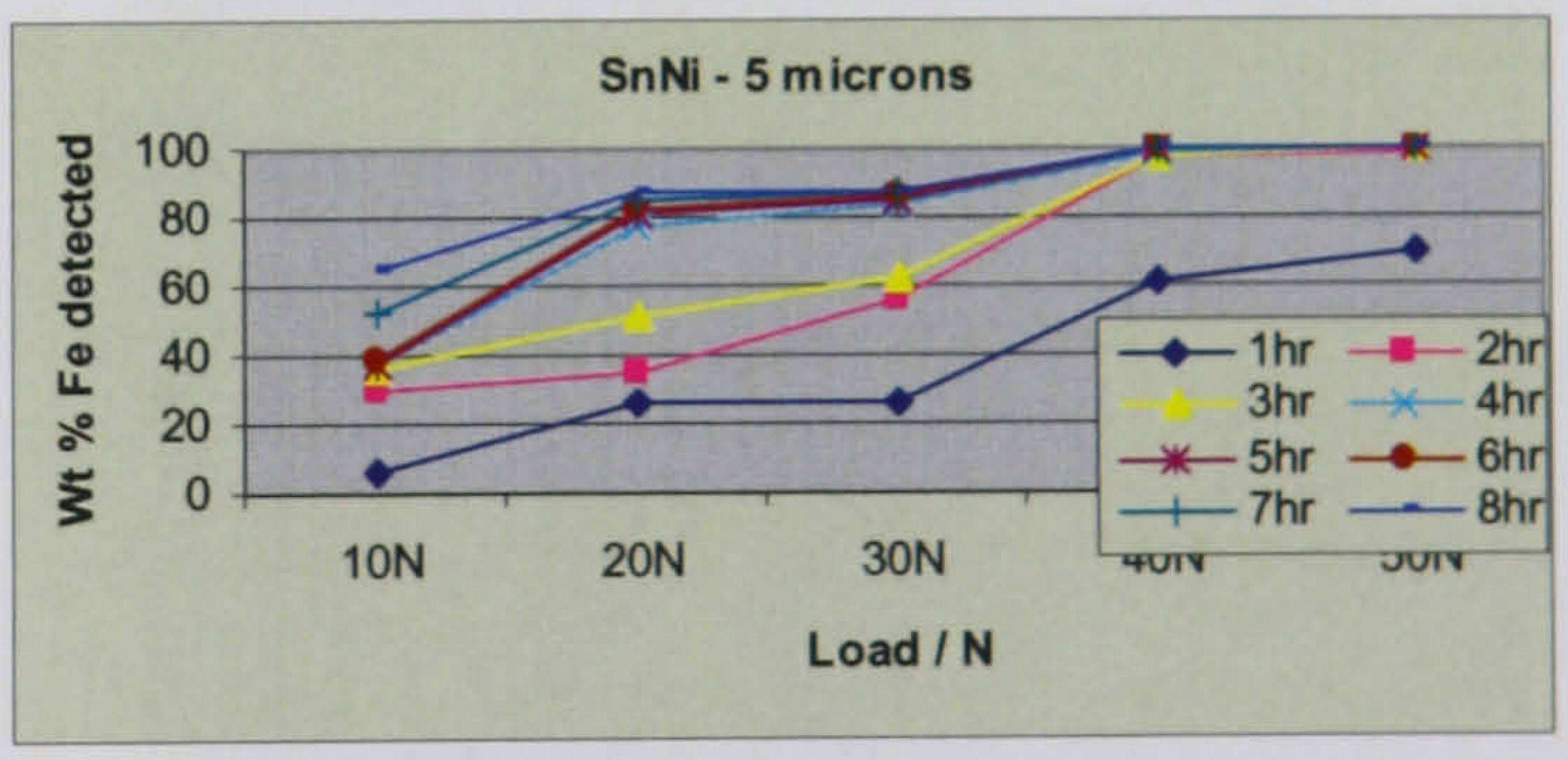

Figure 7.9b – 5 micron thickness

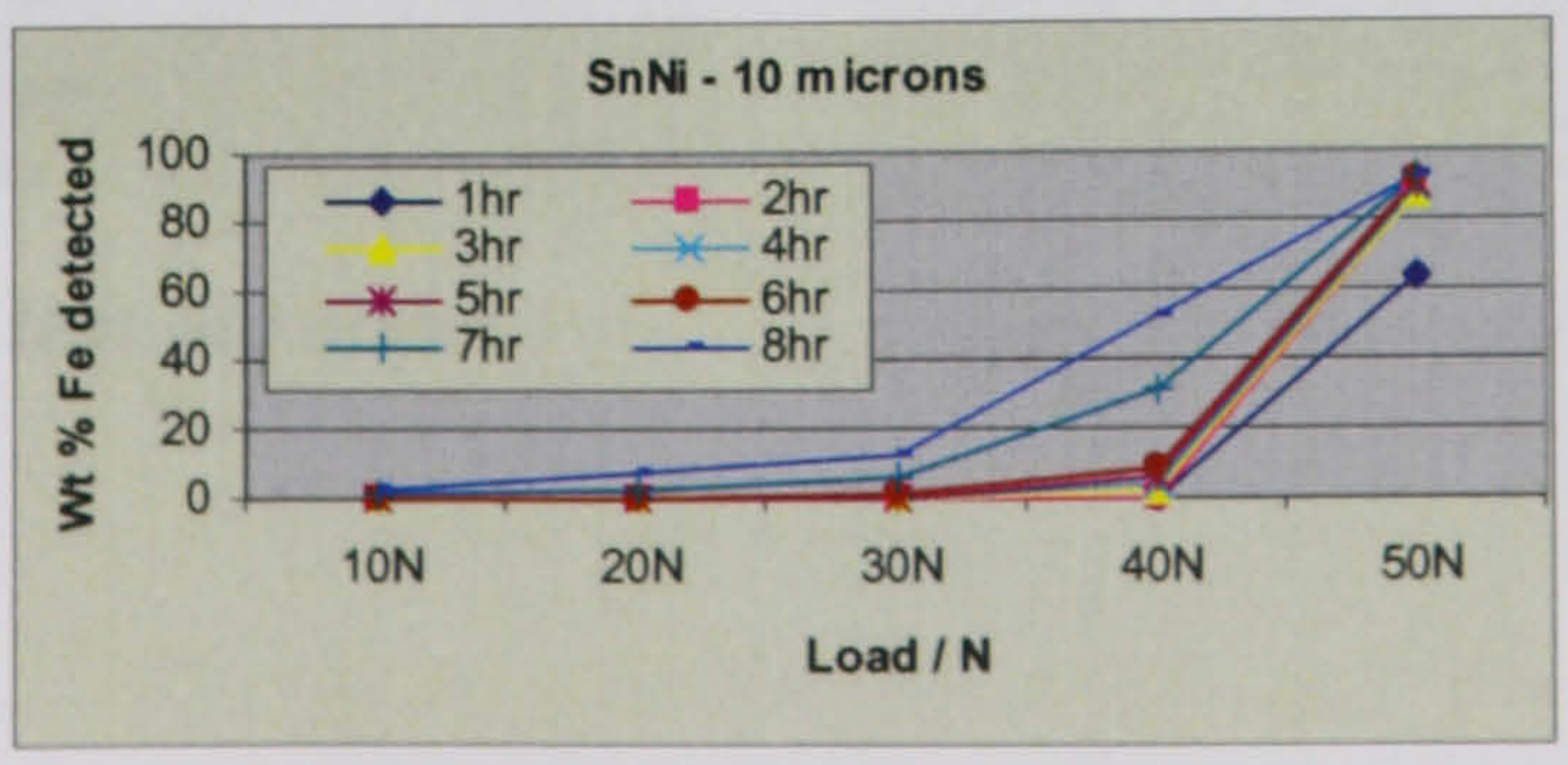

Figure 7.9c – 10 micron thickness

Effect of increasing coating thickness with respect to load

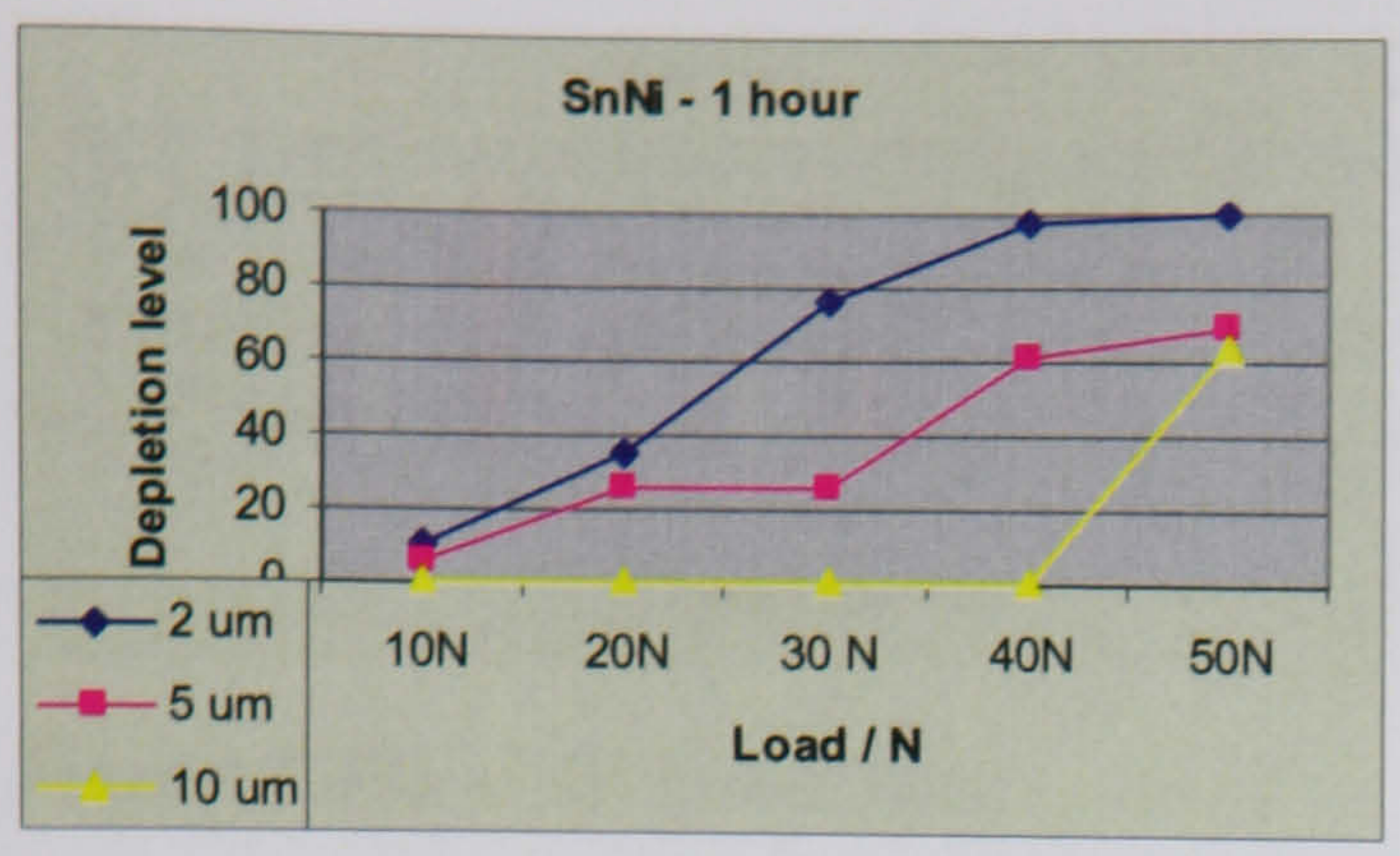

Figure 7.10a – 1 hour test duration

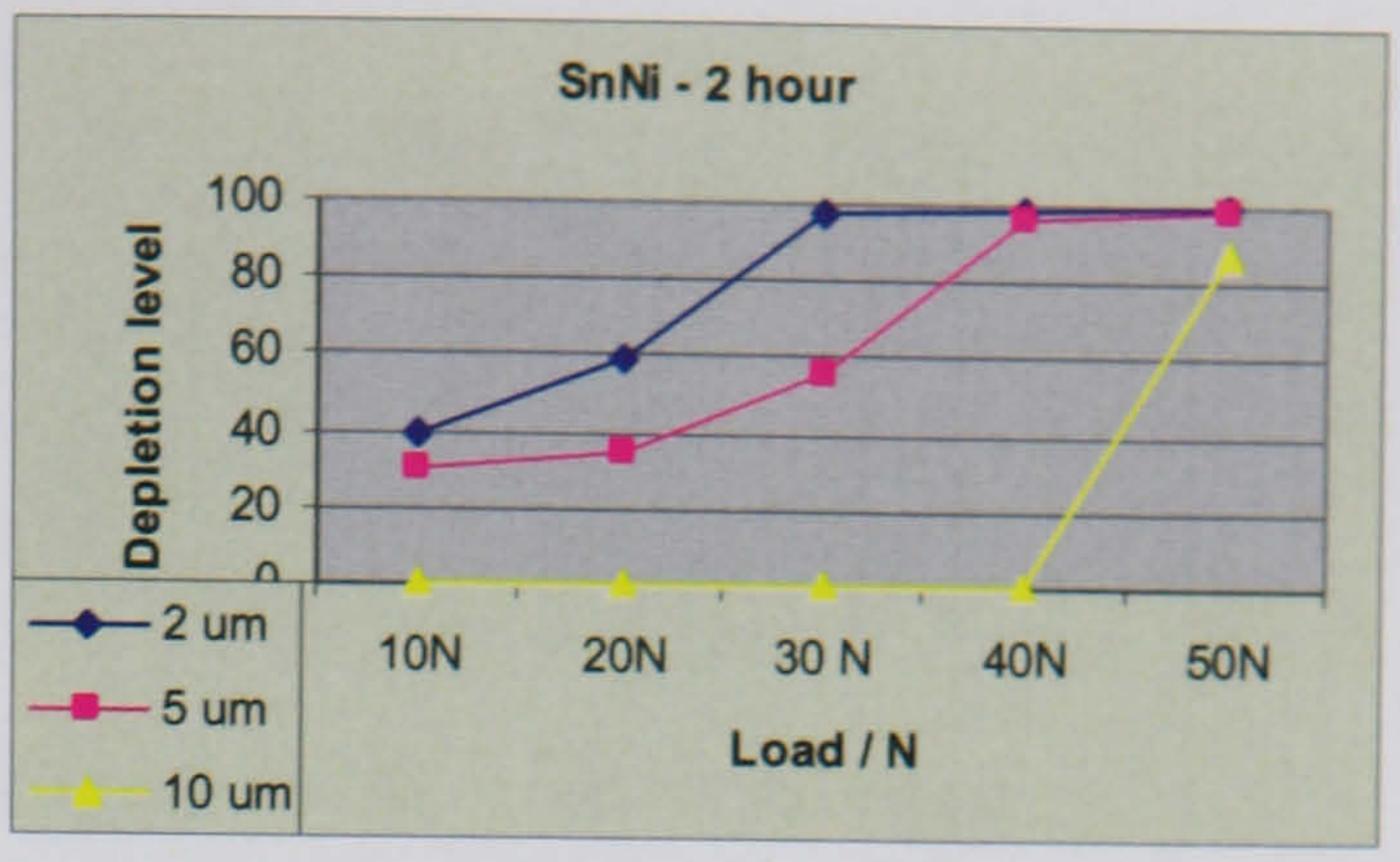

Figure 7.10b – 2 hour test duration

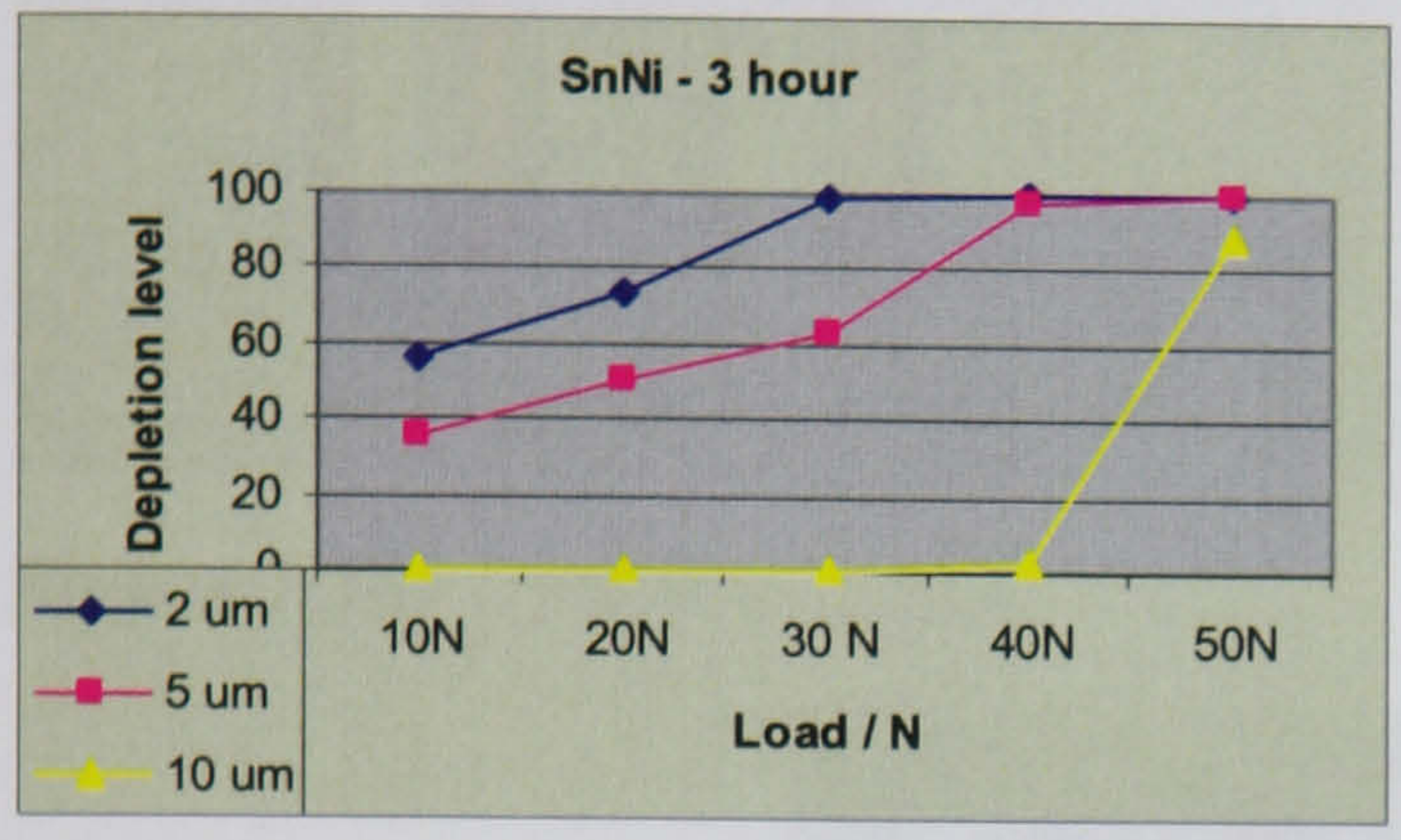

Figure 7.10c – 3 hour test duration

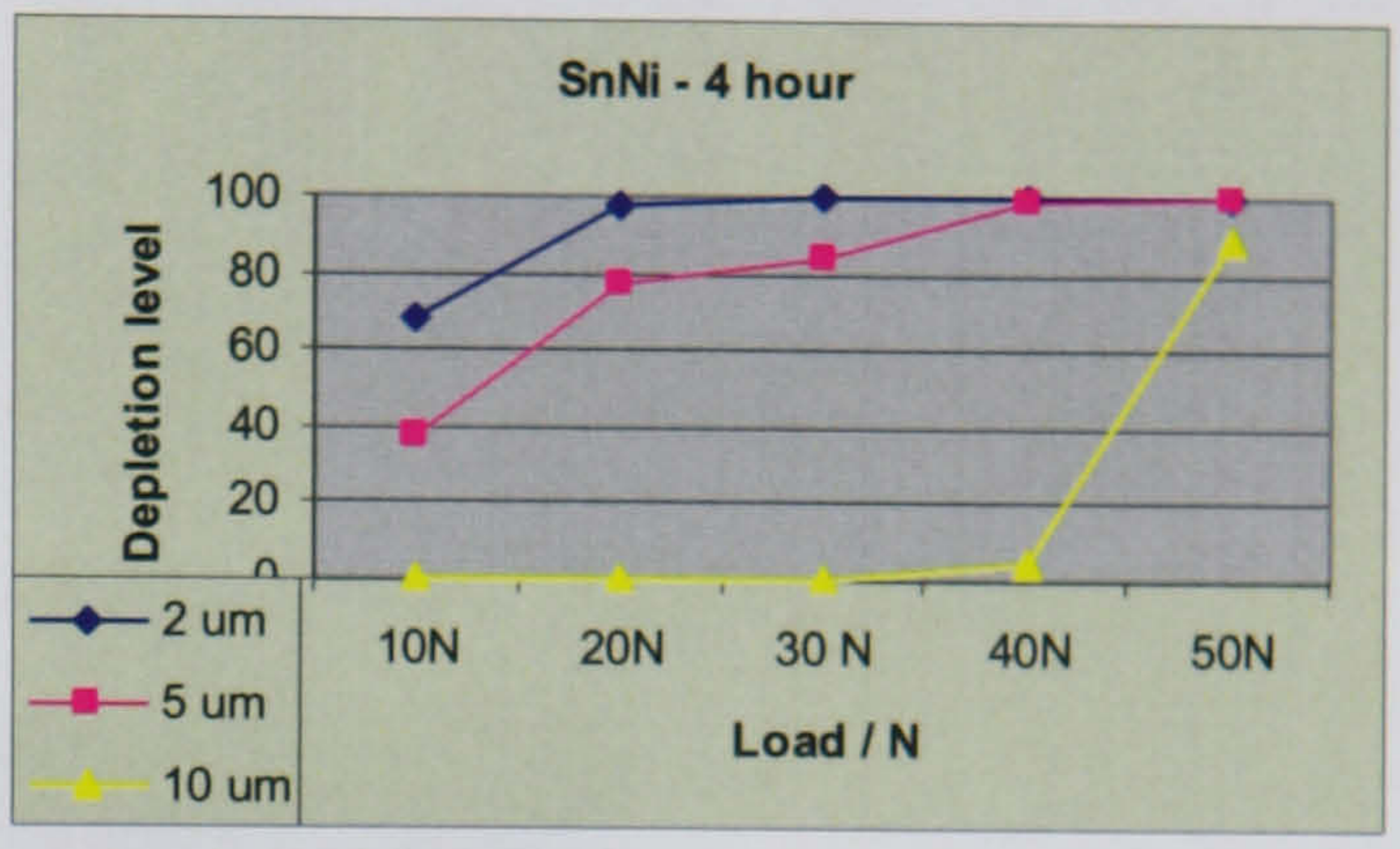

Figure 7.10d – 4 hour test duration

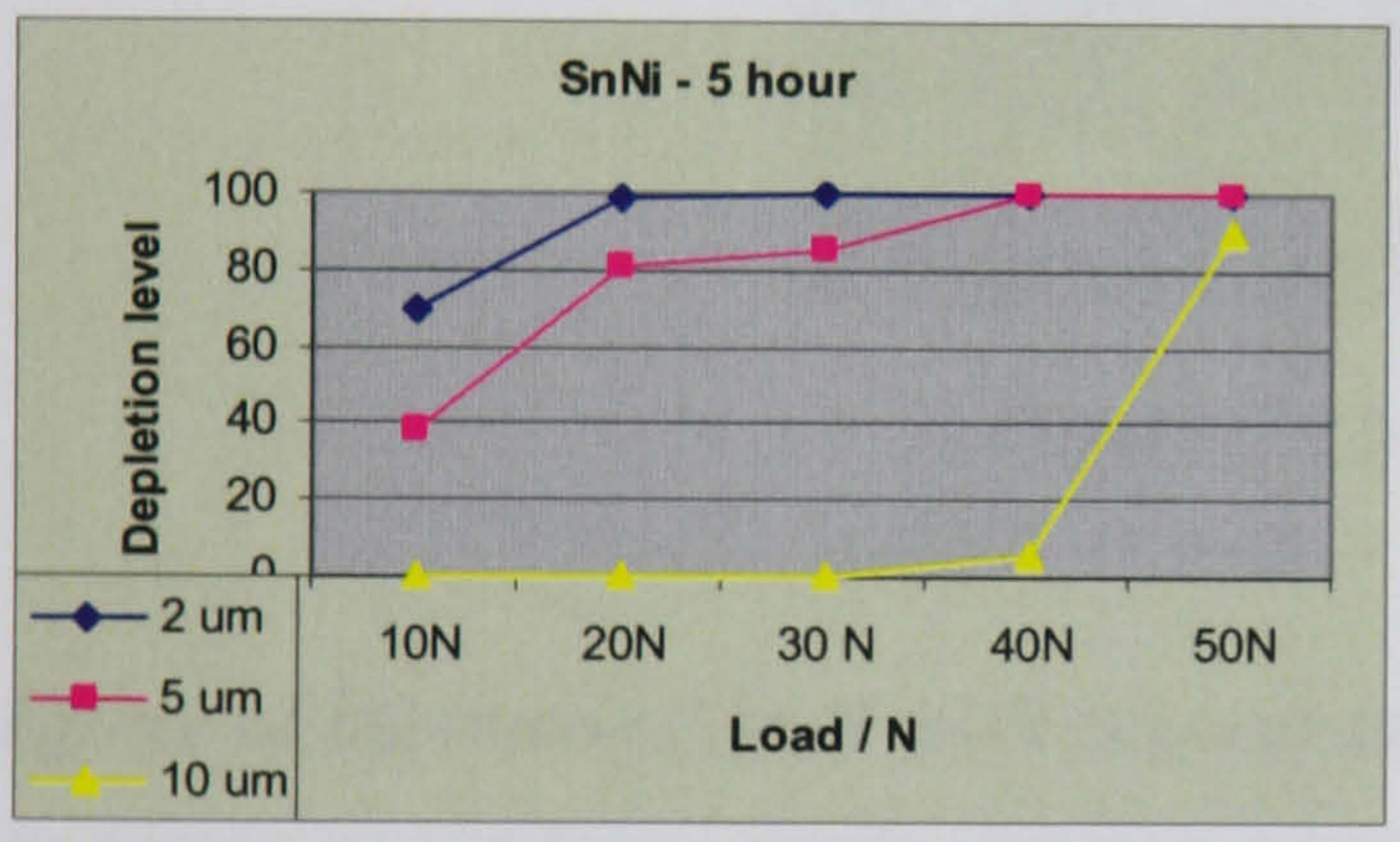

Figure 7.10e – 5 hour test duration

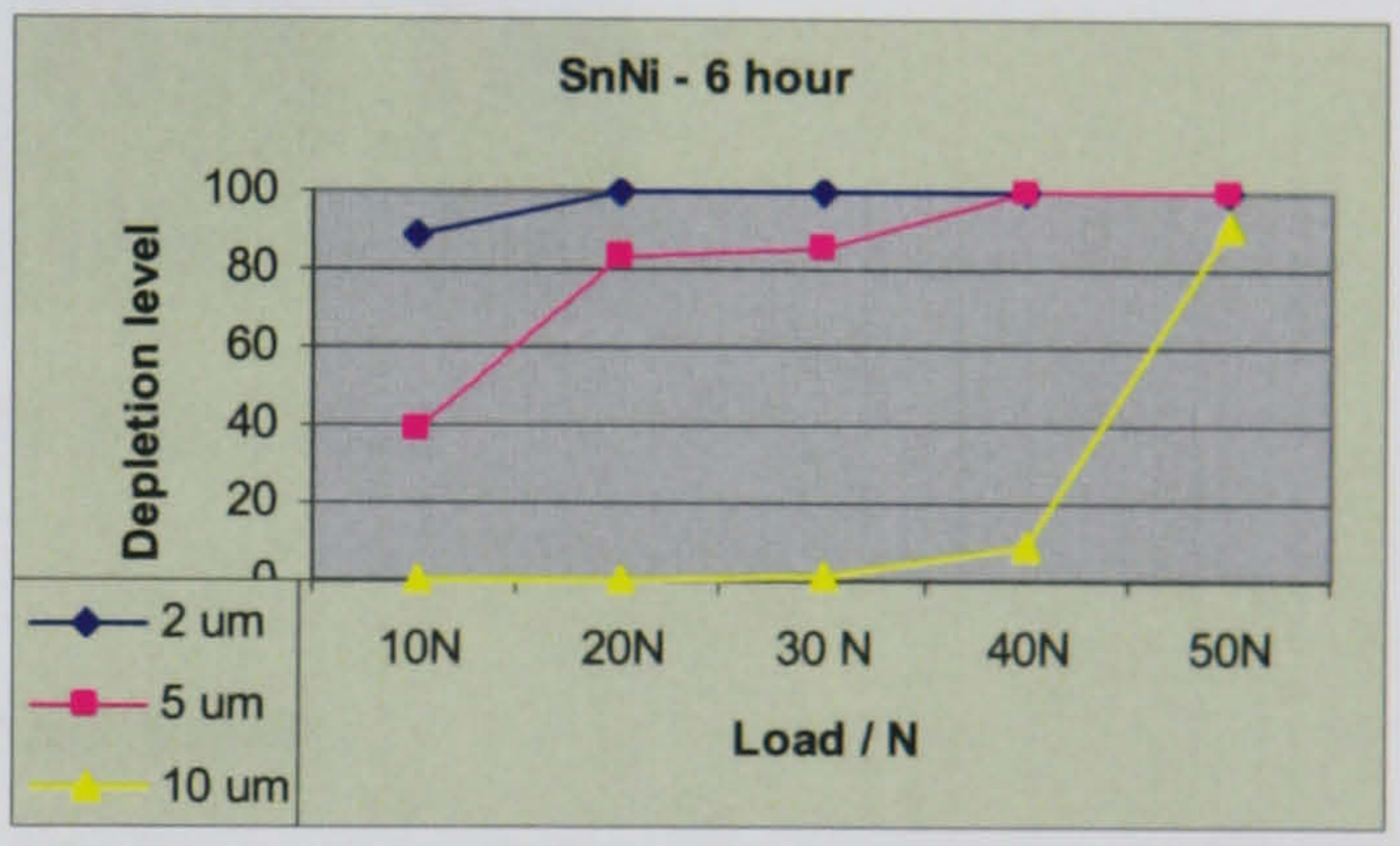

Figure 7.10f – 6 hour test duration

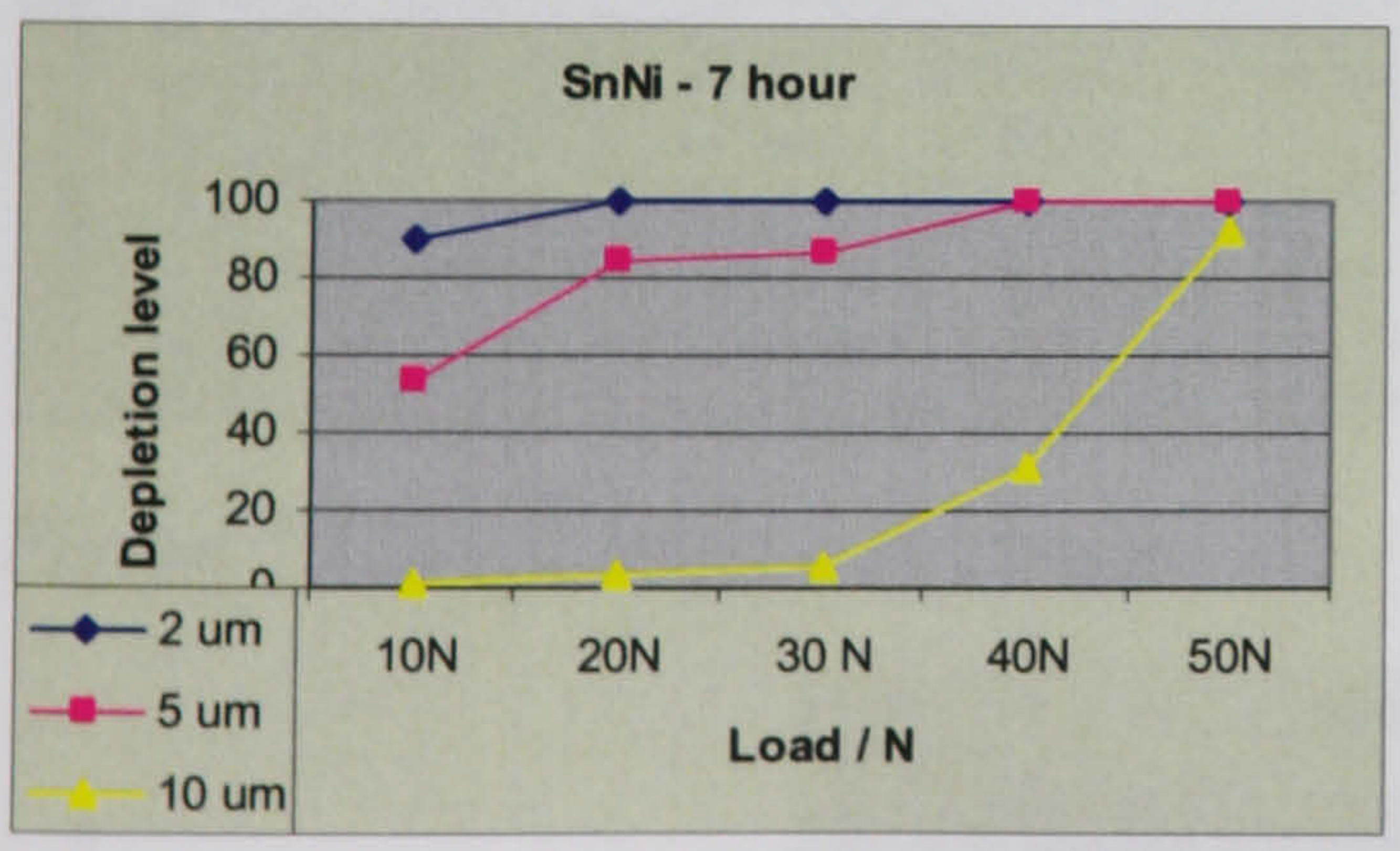

Figure 7.10g – 7 hour test duration

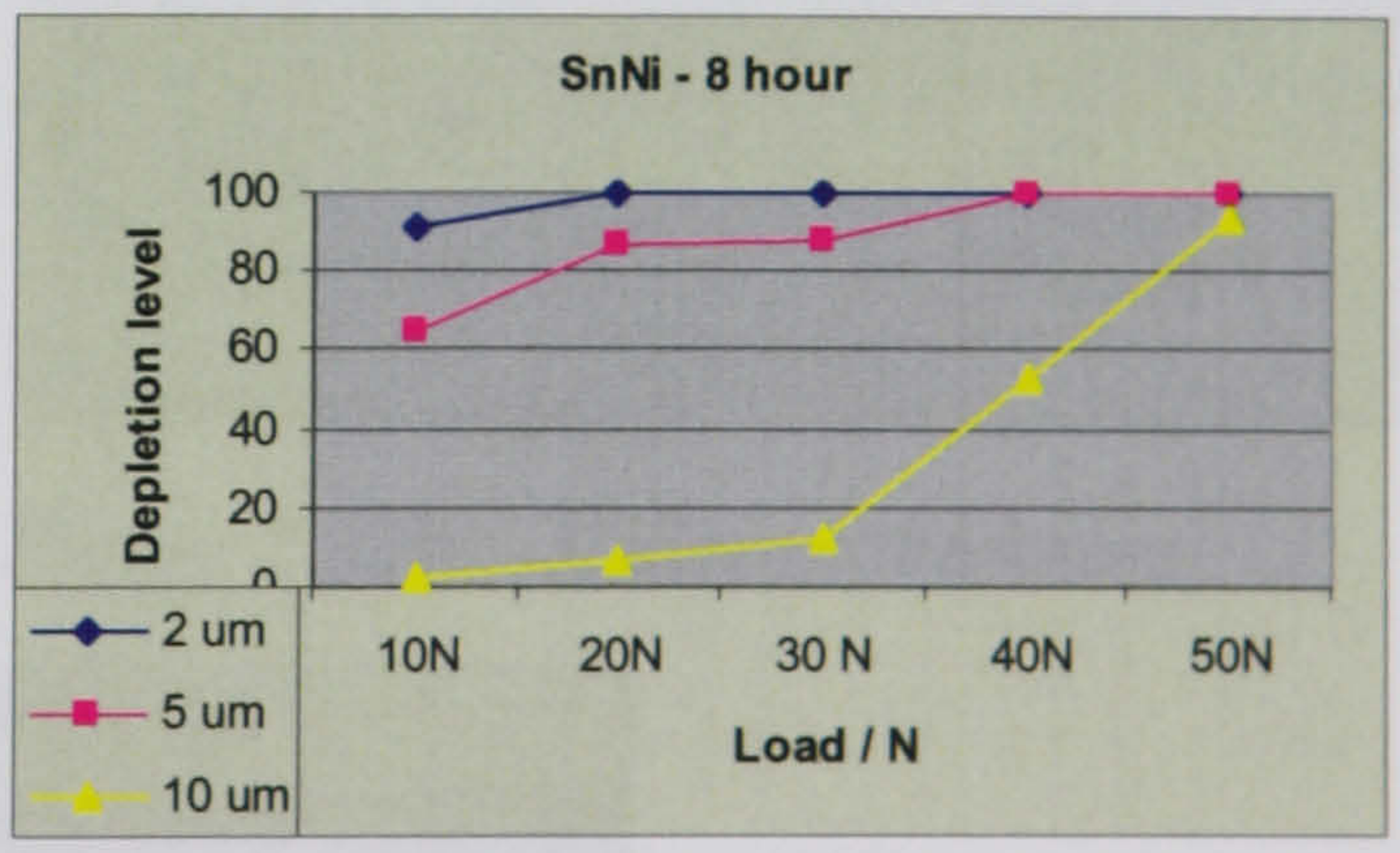

Figure 7.10h – 8 hour test duration

Effect of increasing test duration with respect to coating thickness

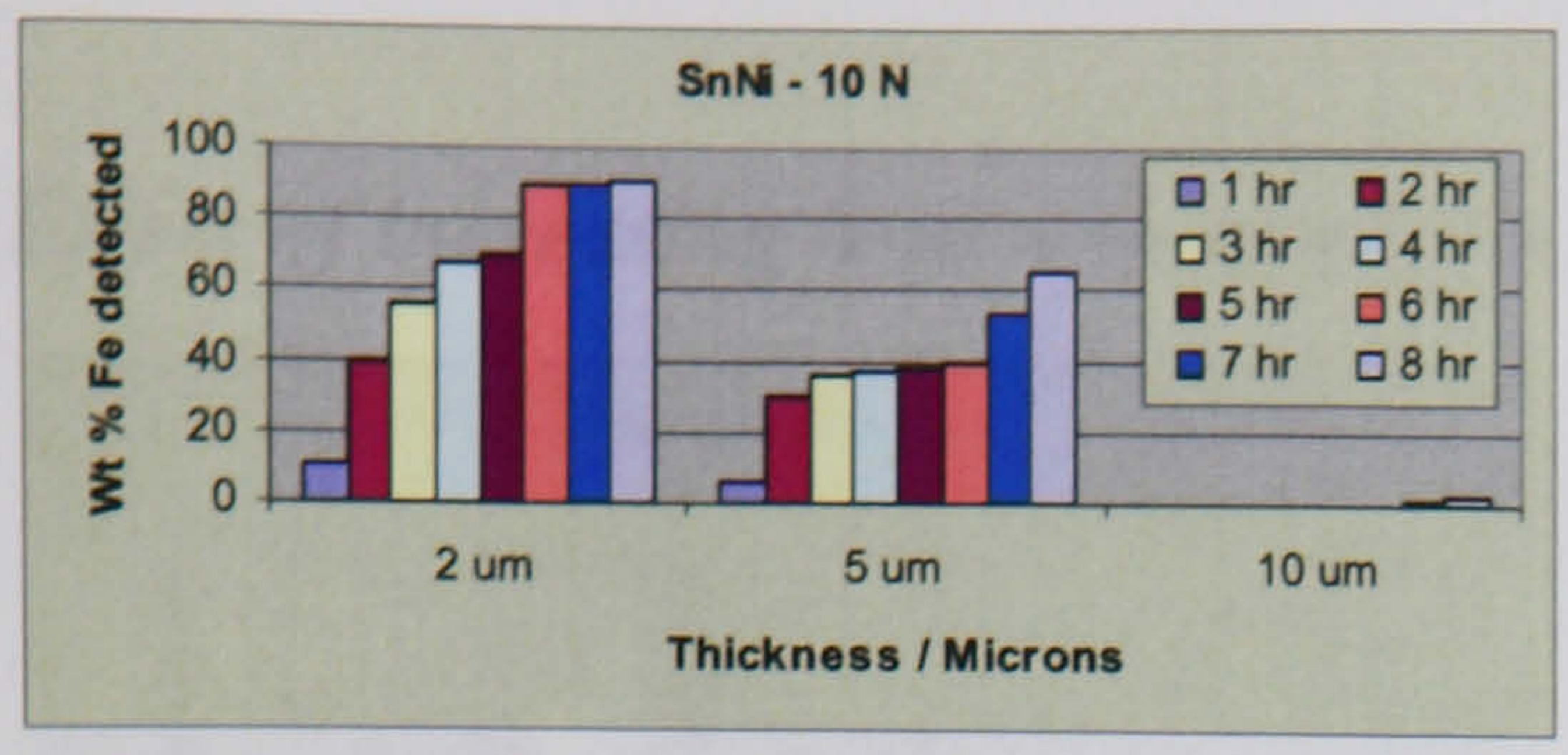

Figure 7.11a – 10 N test load

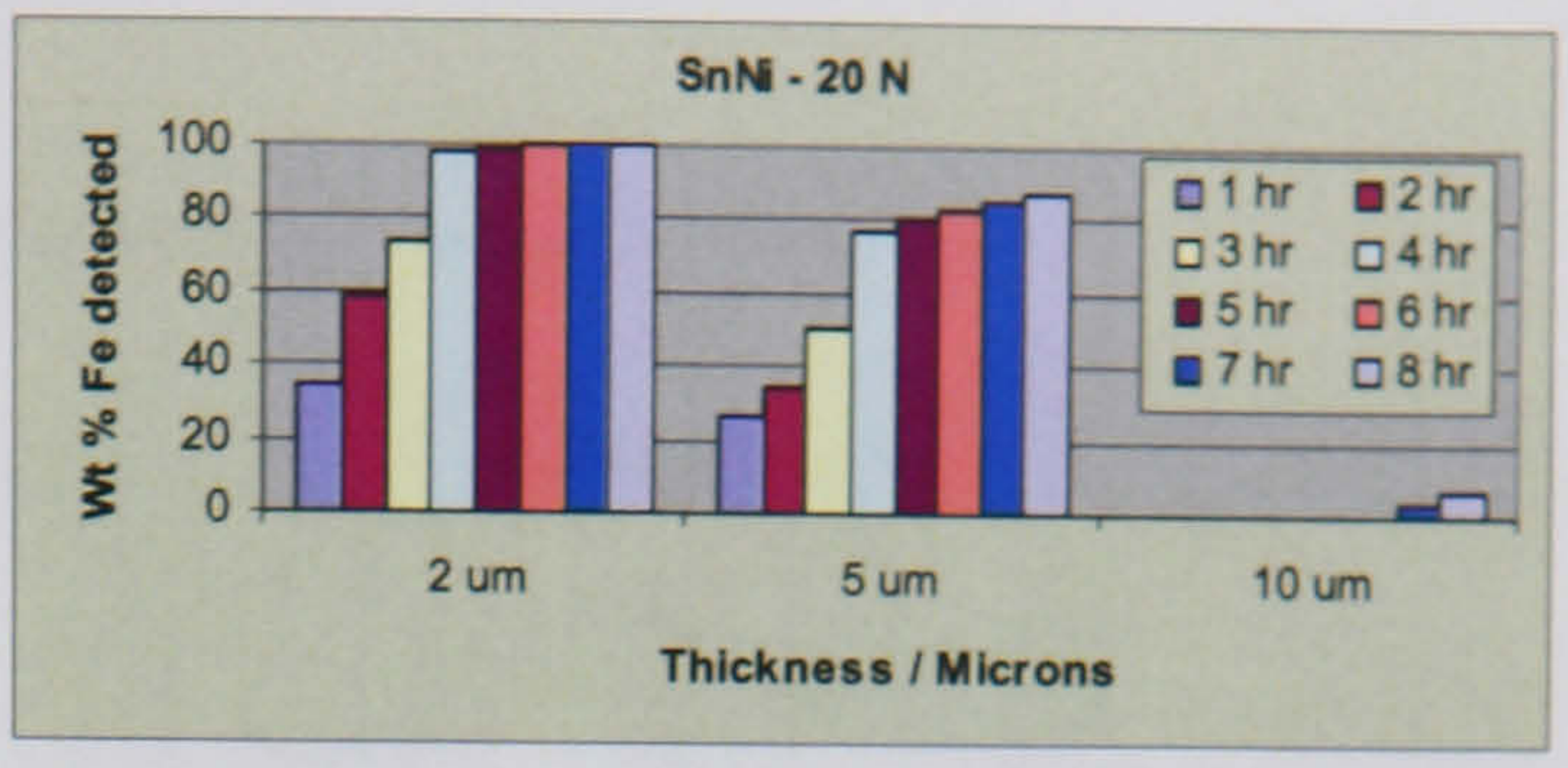

Figure 7.11b – 20 N test load

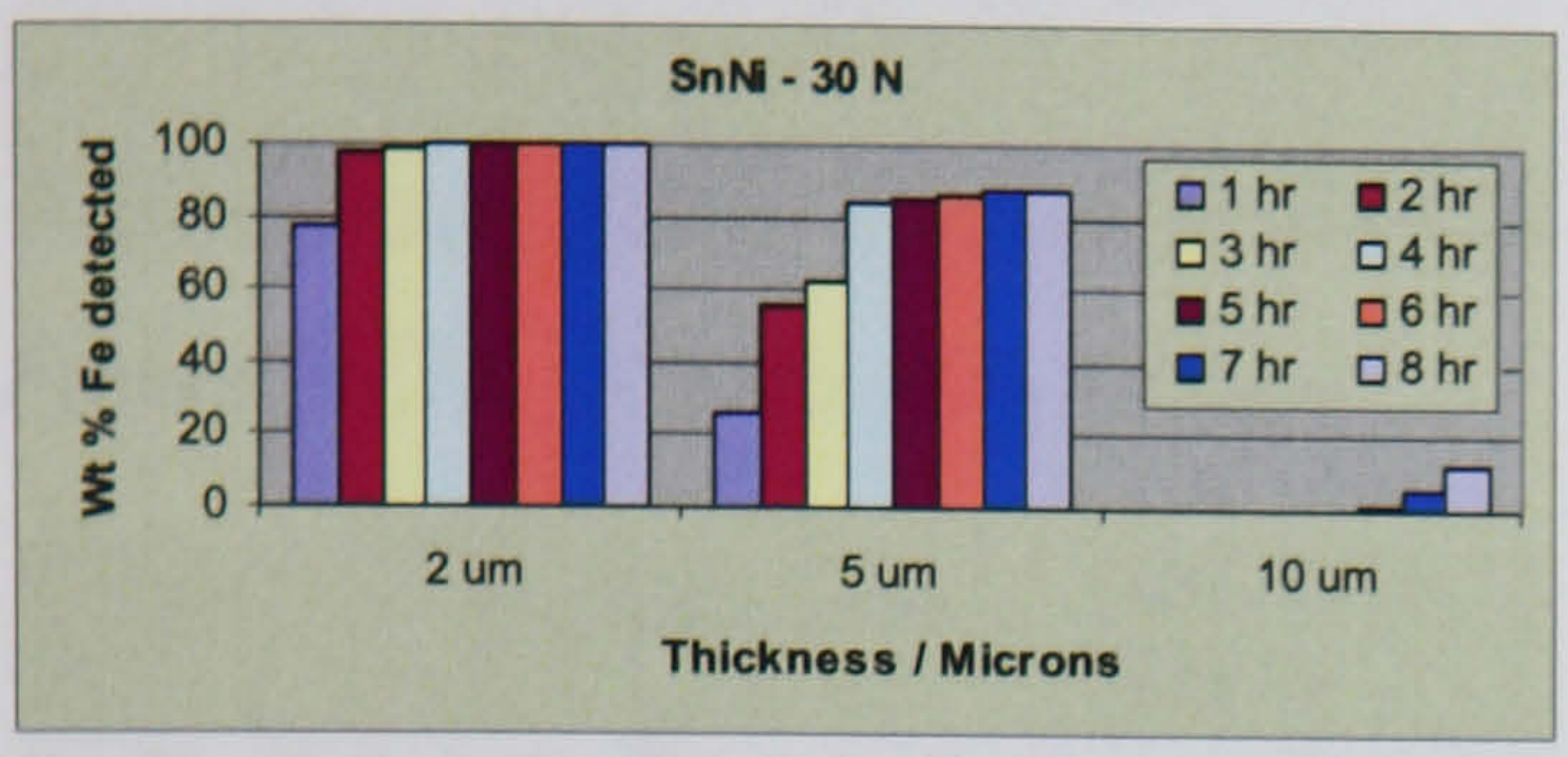

Figure 7.11c – 30 N test load

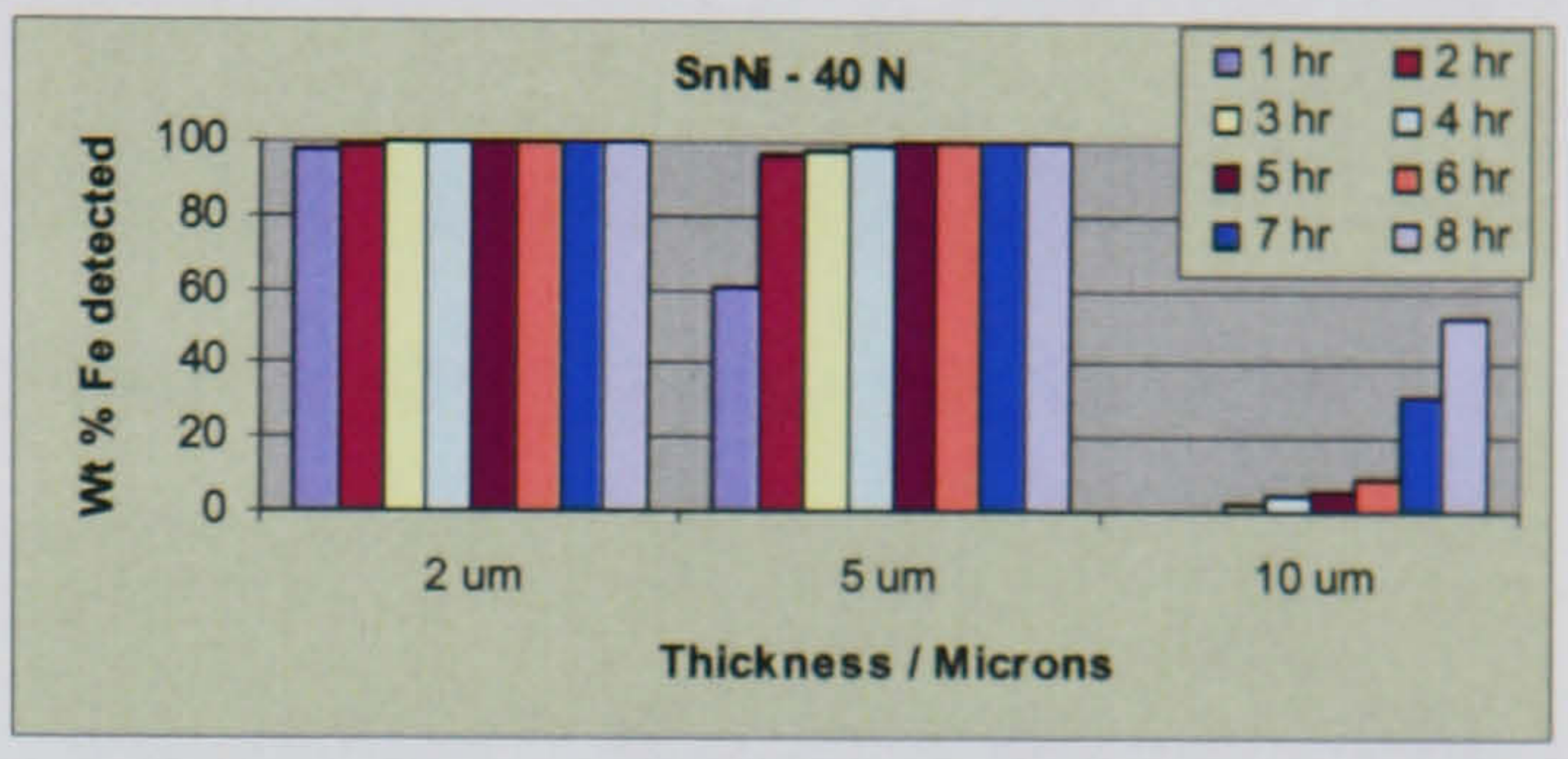

Figure 7.11d – 40 N test load

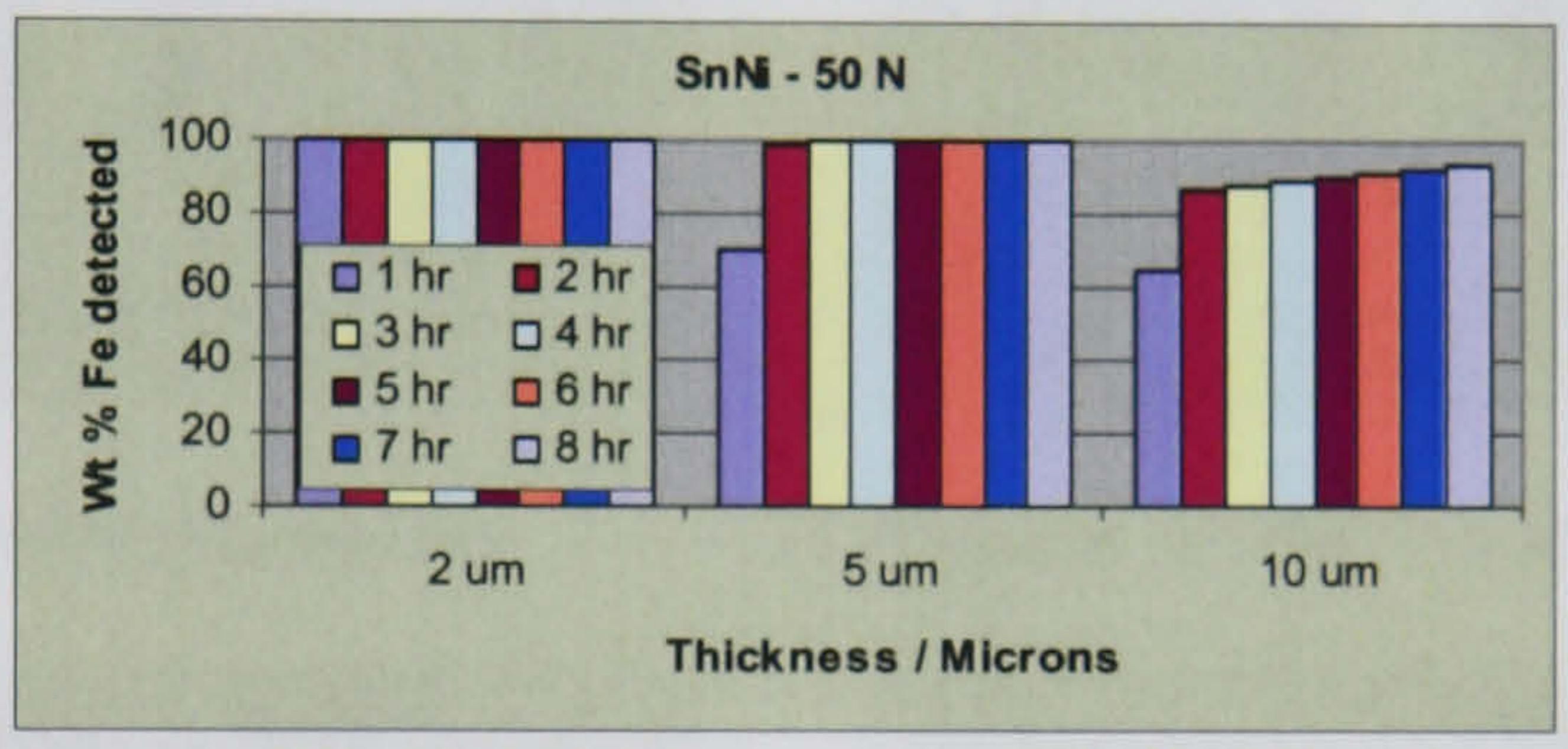

Figure 7.11e – 50 N test load

Effect of increasing load with respect to test duration

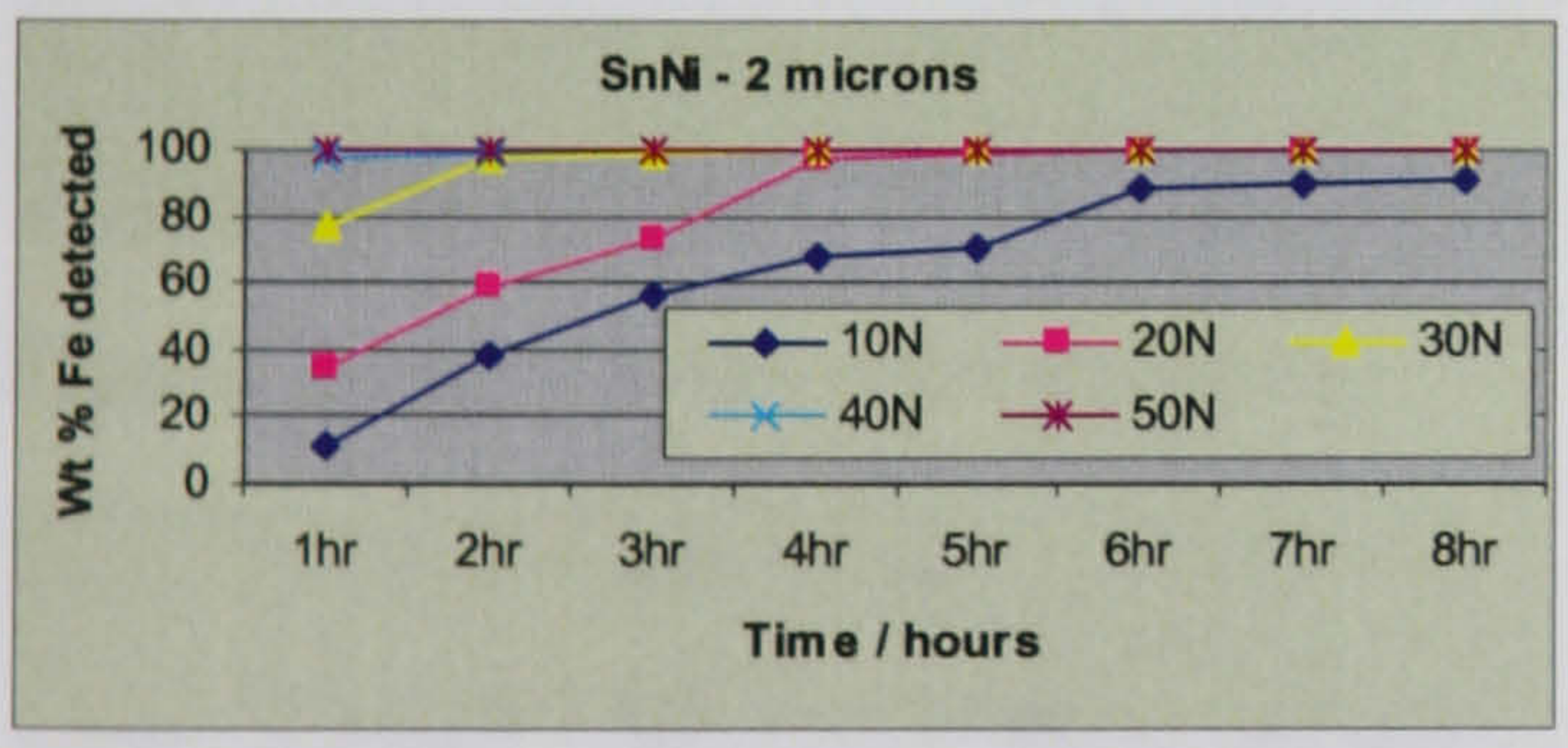

Figure 7.12a – 2 micron thickness

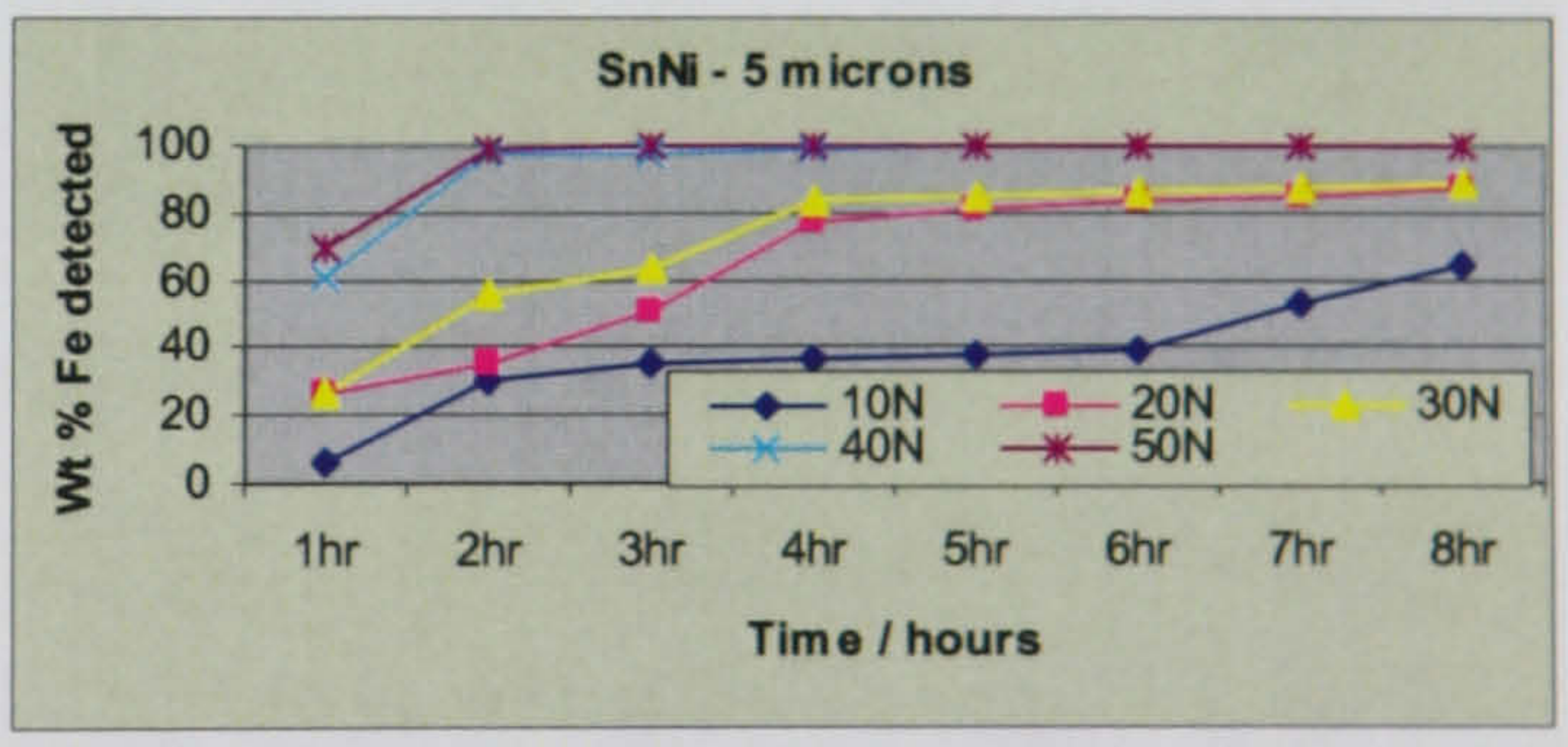

Figure 7.12b – 5 micron thickness

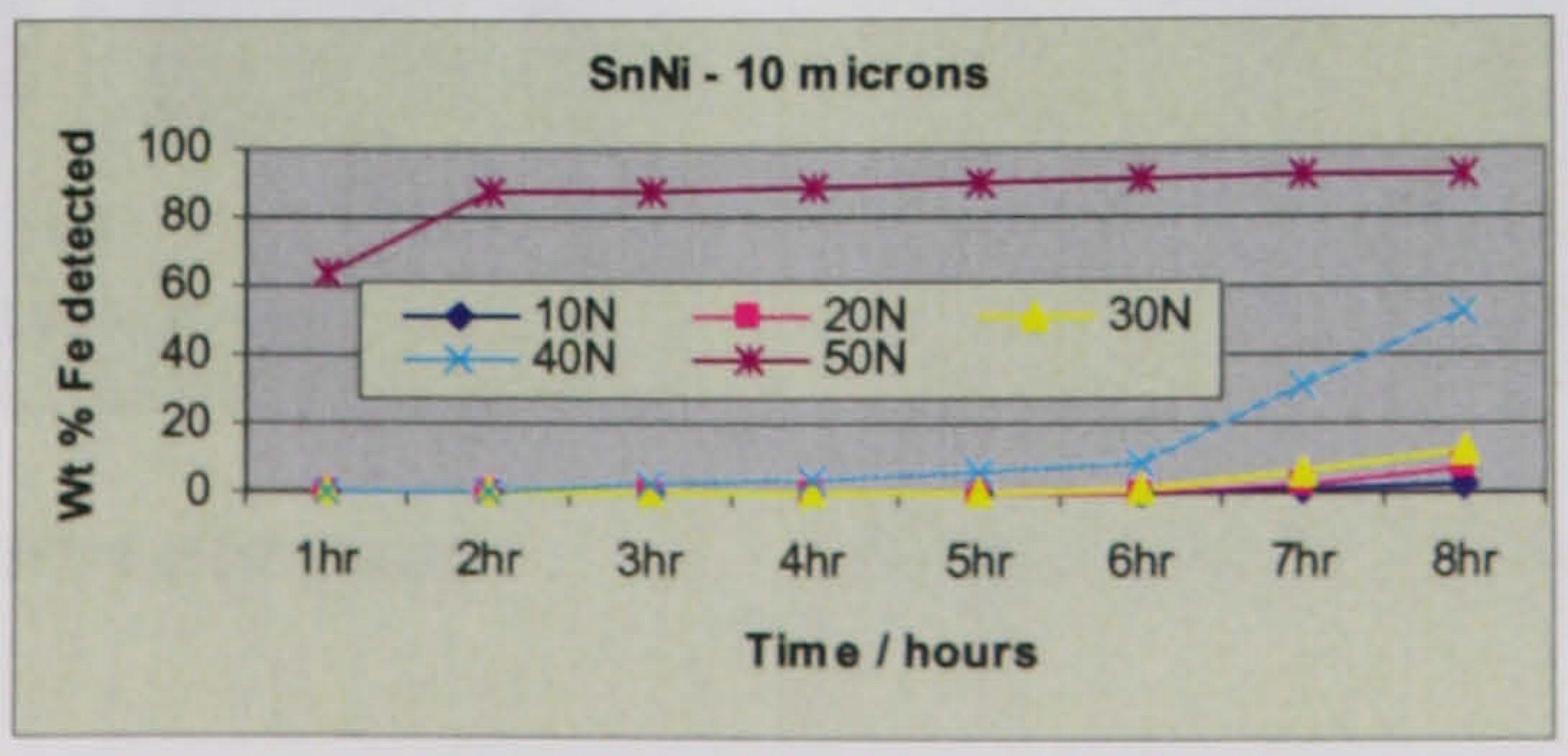

Figure 7.12c – 10 micron thickness

7.2.3 Tin-Copper Coating

Effect of increasing load with respect to increasing coating thickness

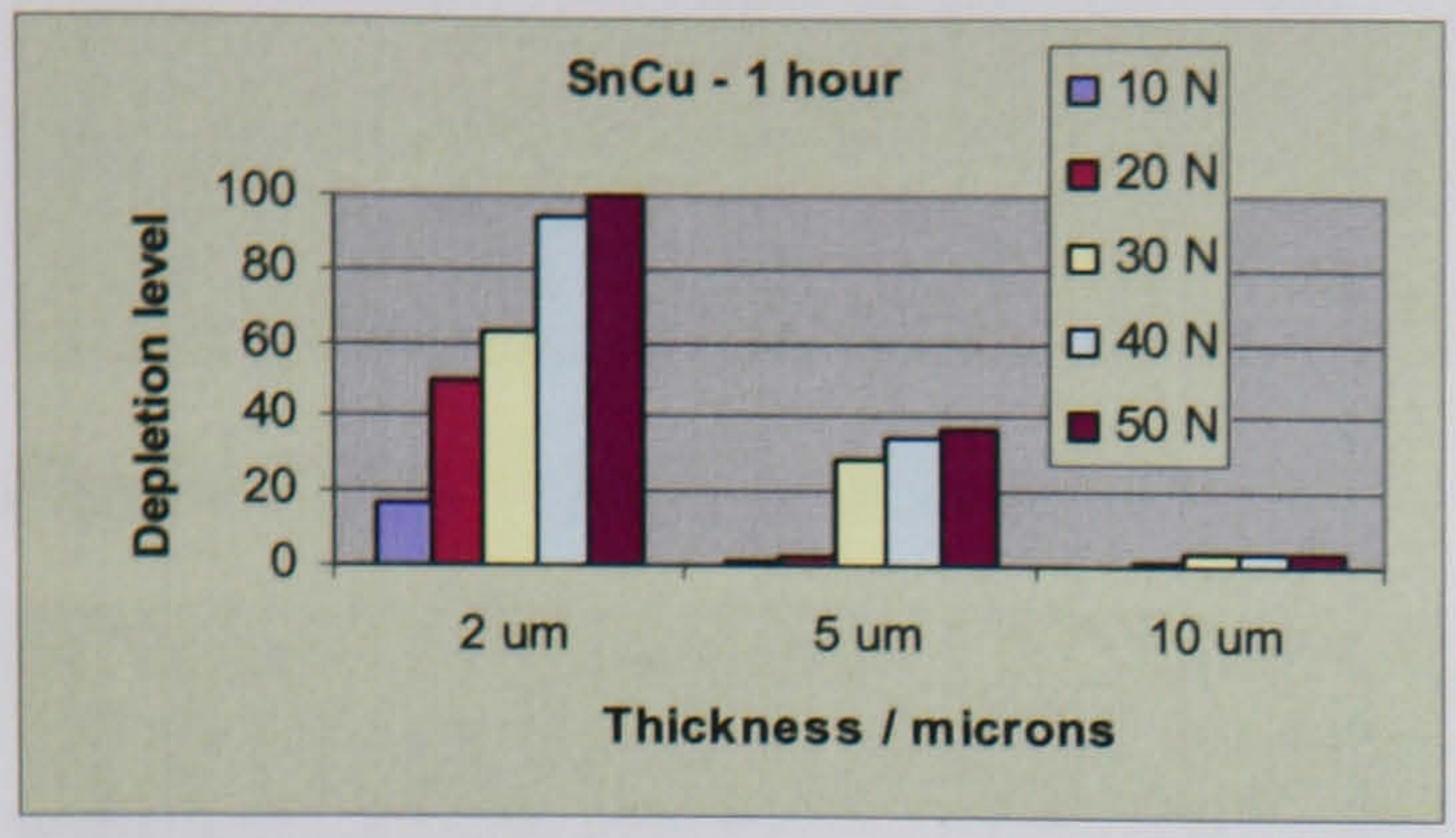

Figure 7.13a – 1 hour test duration

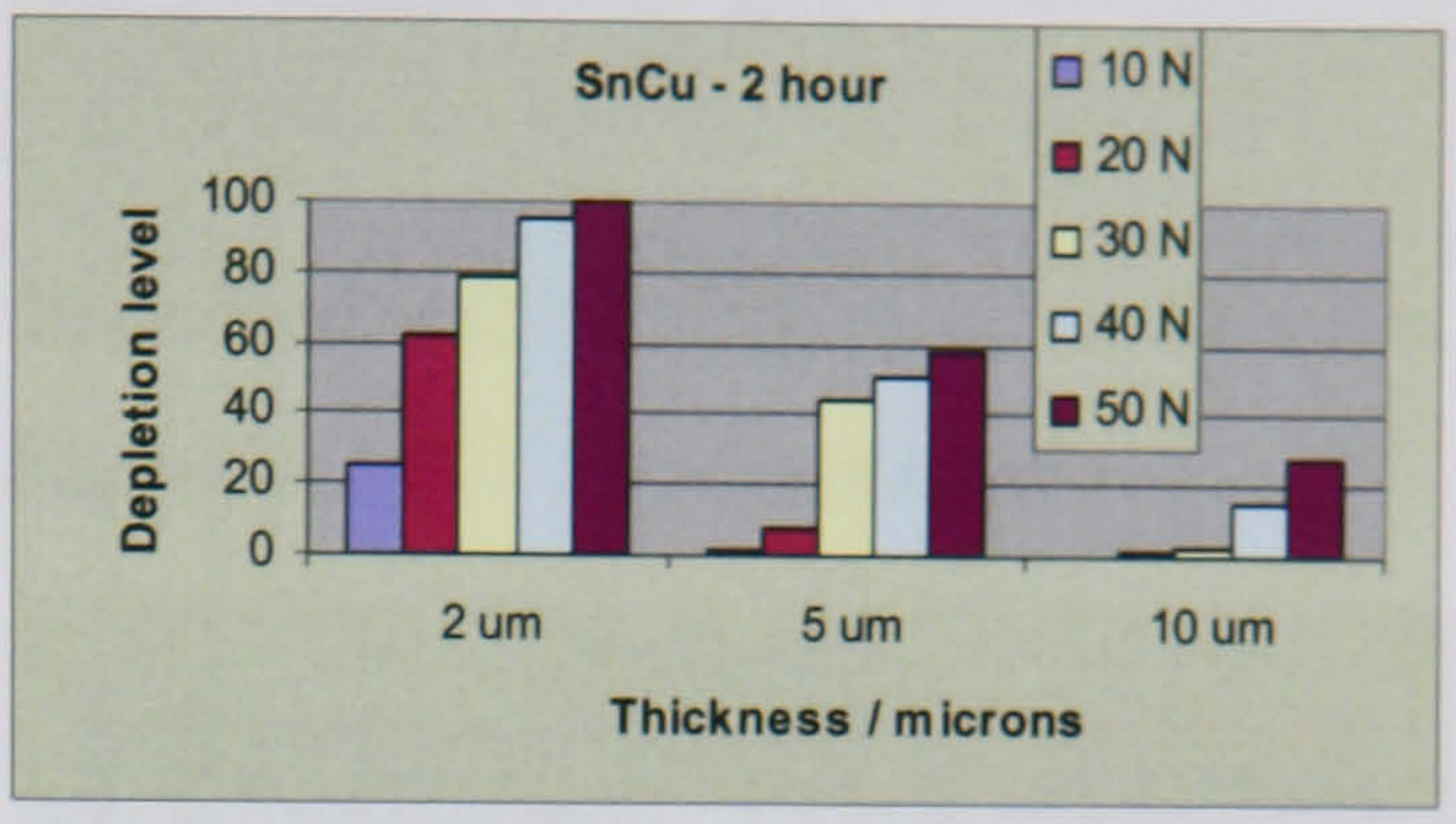

Figure 7.13b – 2 hour test duration

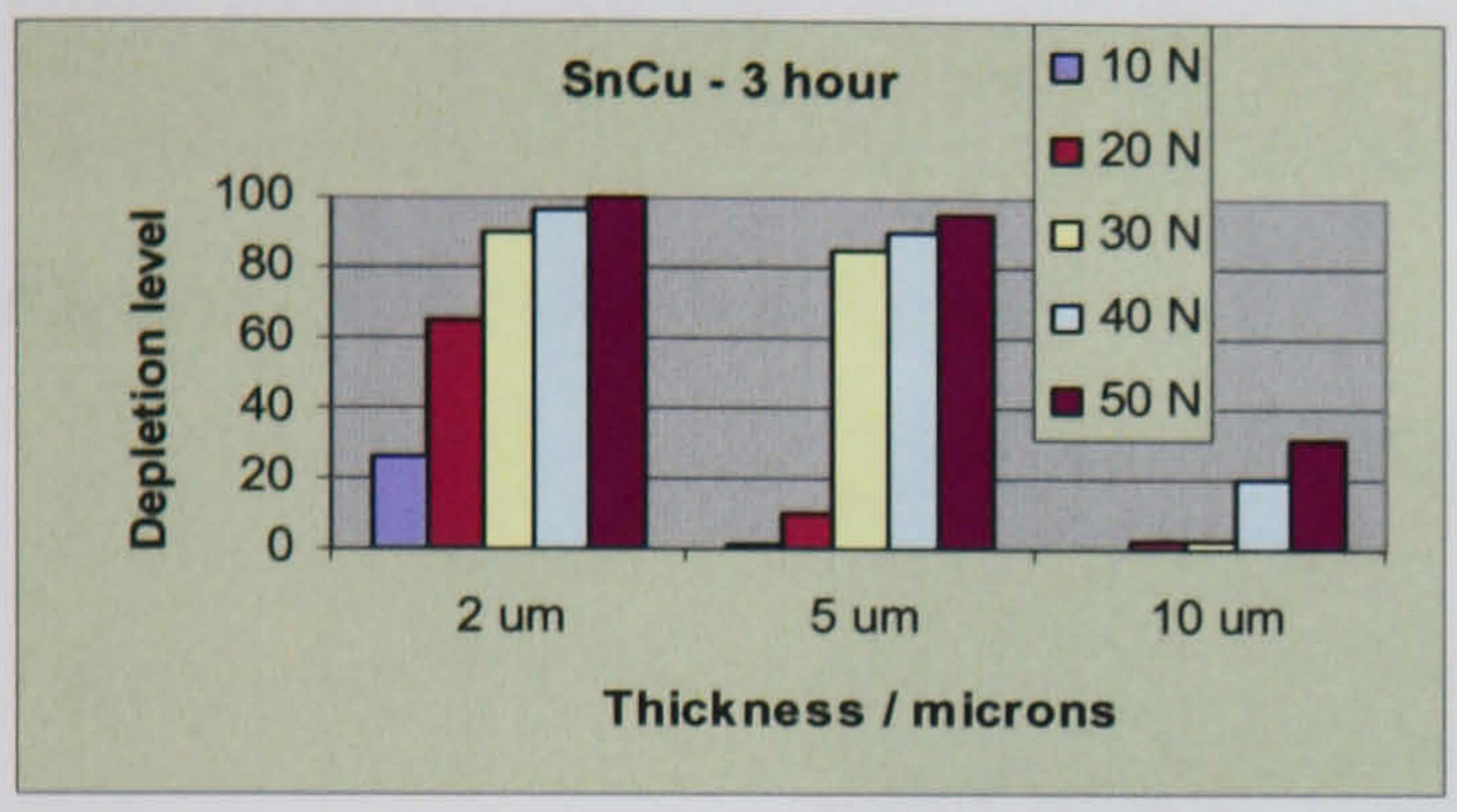

Figure 7.13c – 3 hour test duration

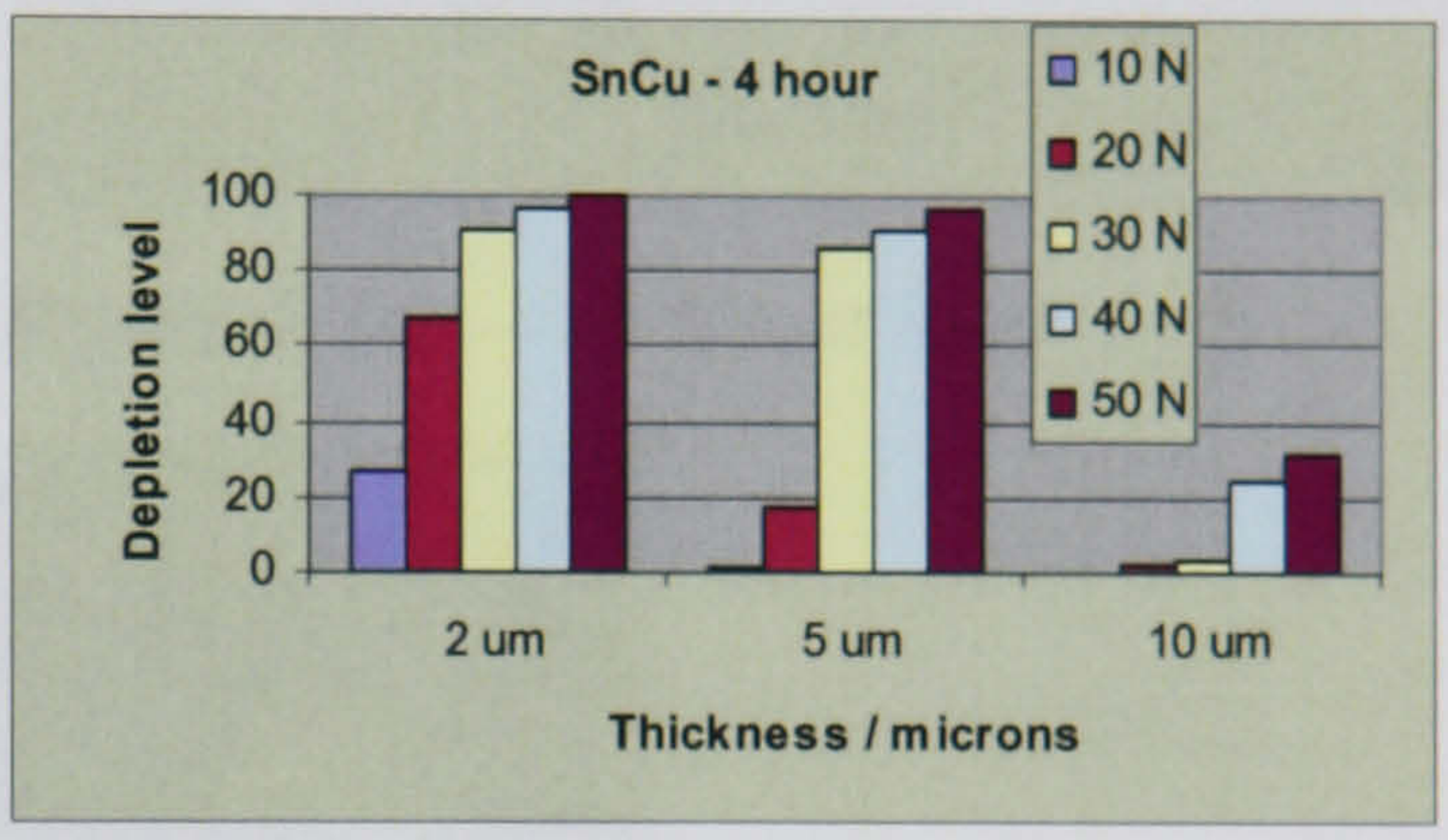

Figure 7.13d – 4 hour test duration

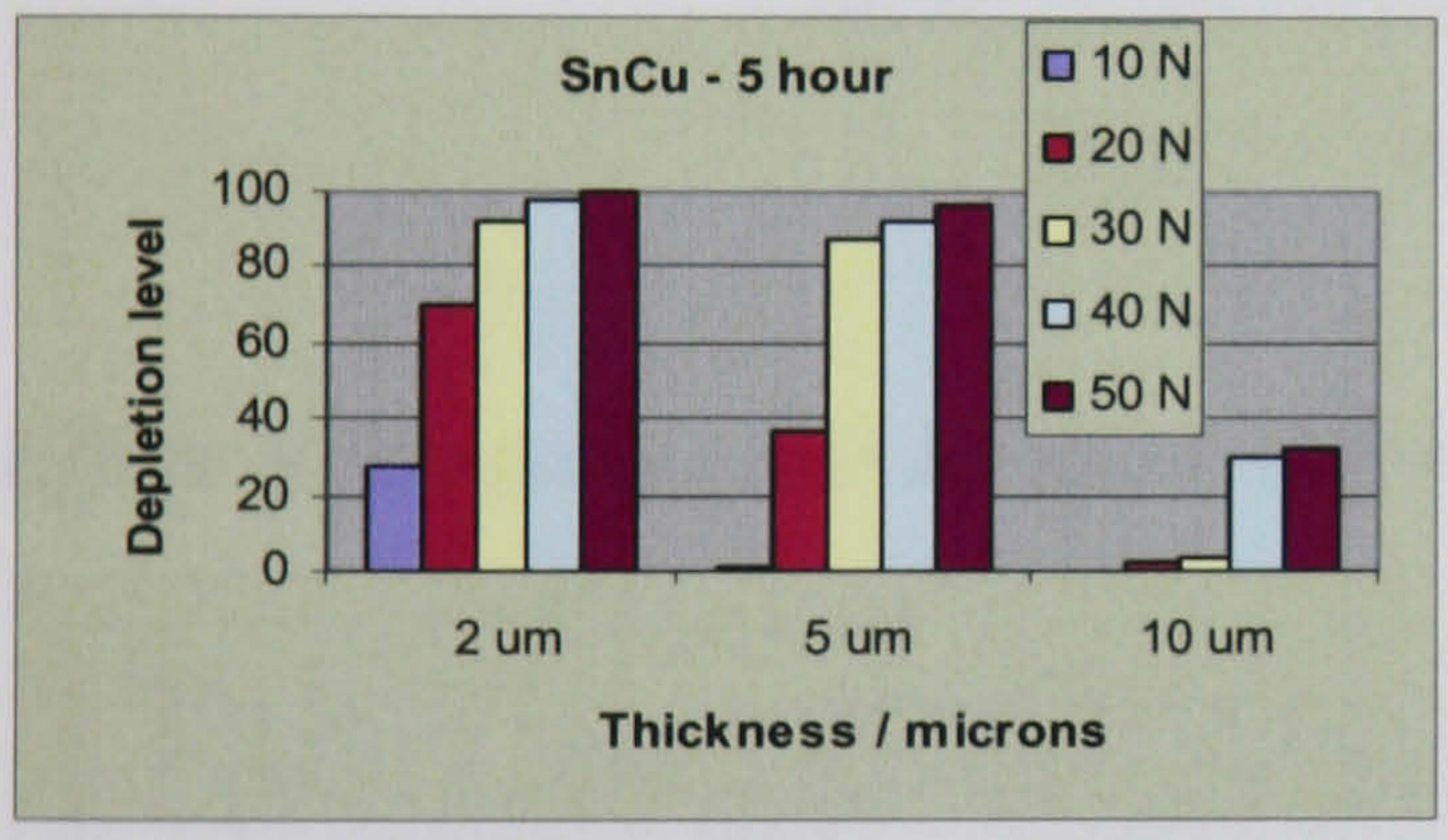

Figure 7.13e – 5 hour test duration

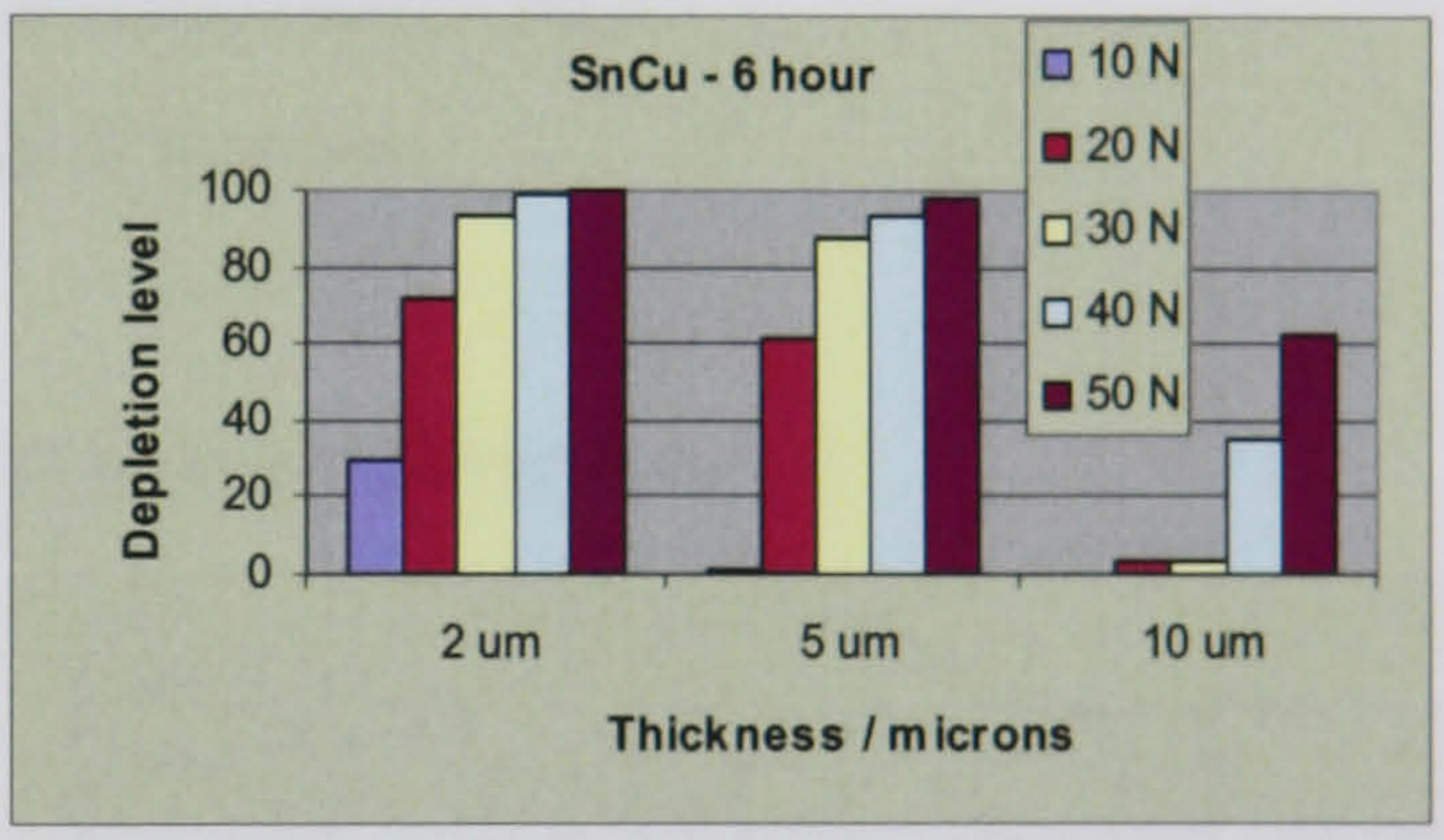

Figure 7.13f – 6 hour test duration

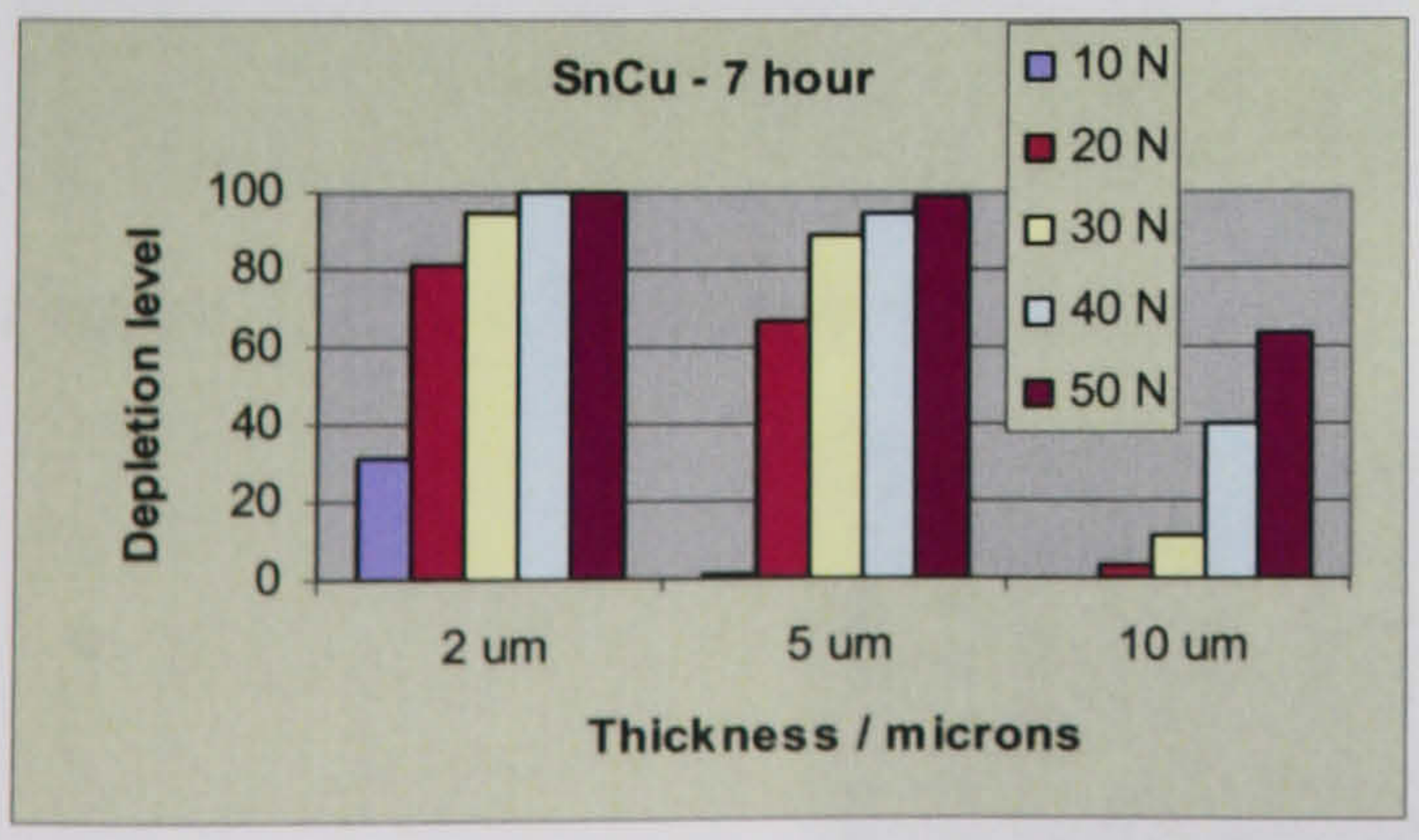

Figure 7.13g – 7 hour test duration

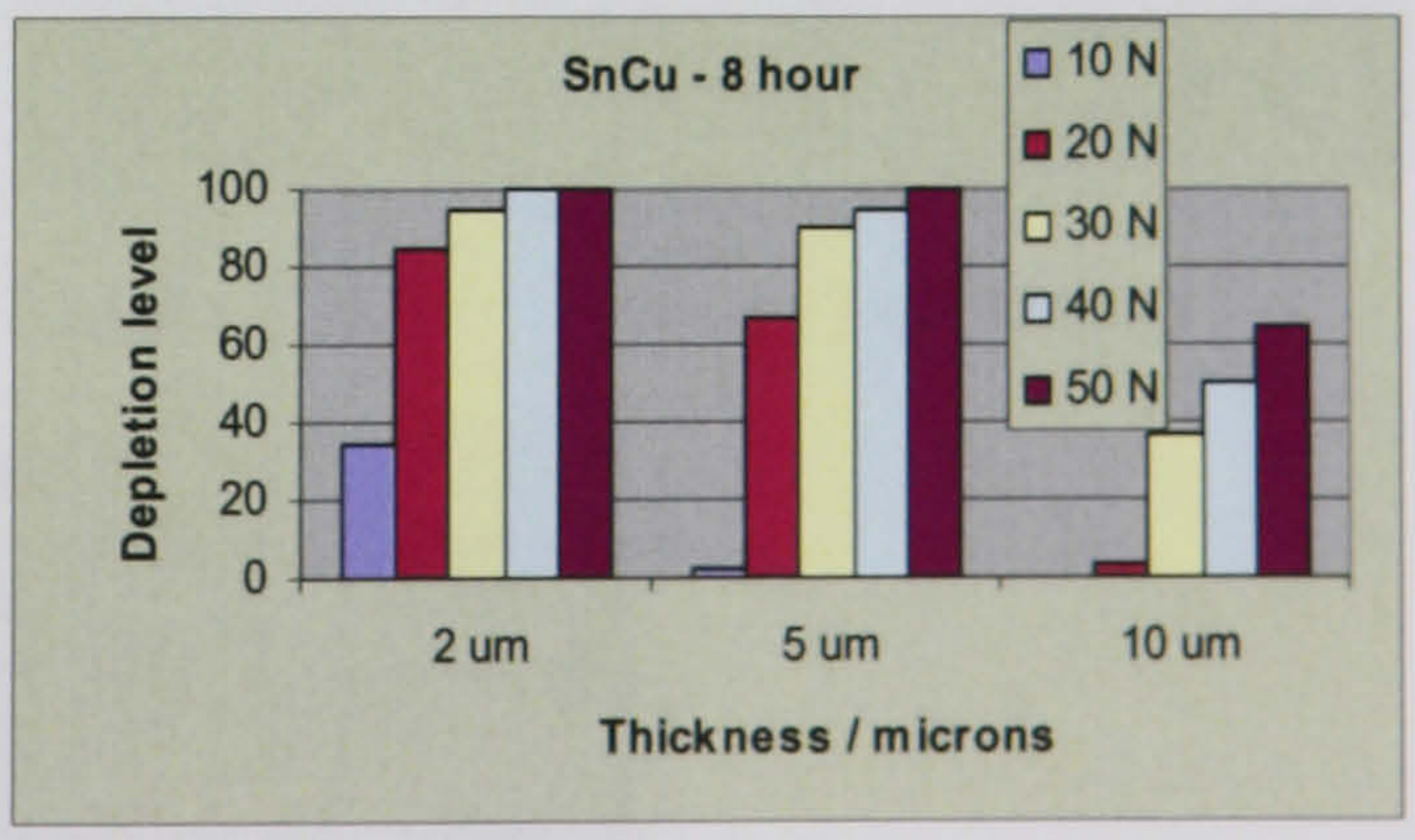

Figure 7.13h – 8 hour test duration

Effect of increasing coating thickness with respect to increasing test duration

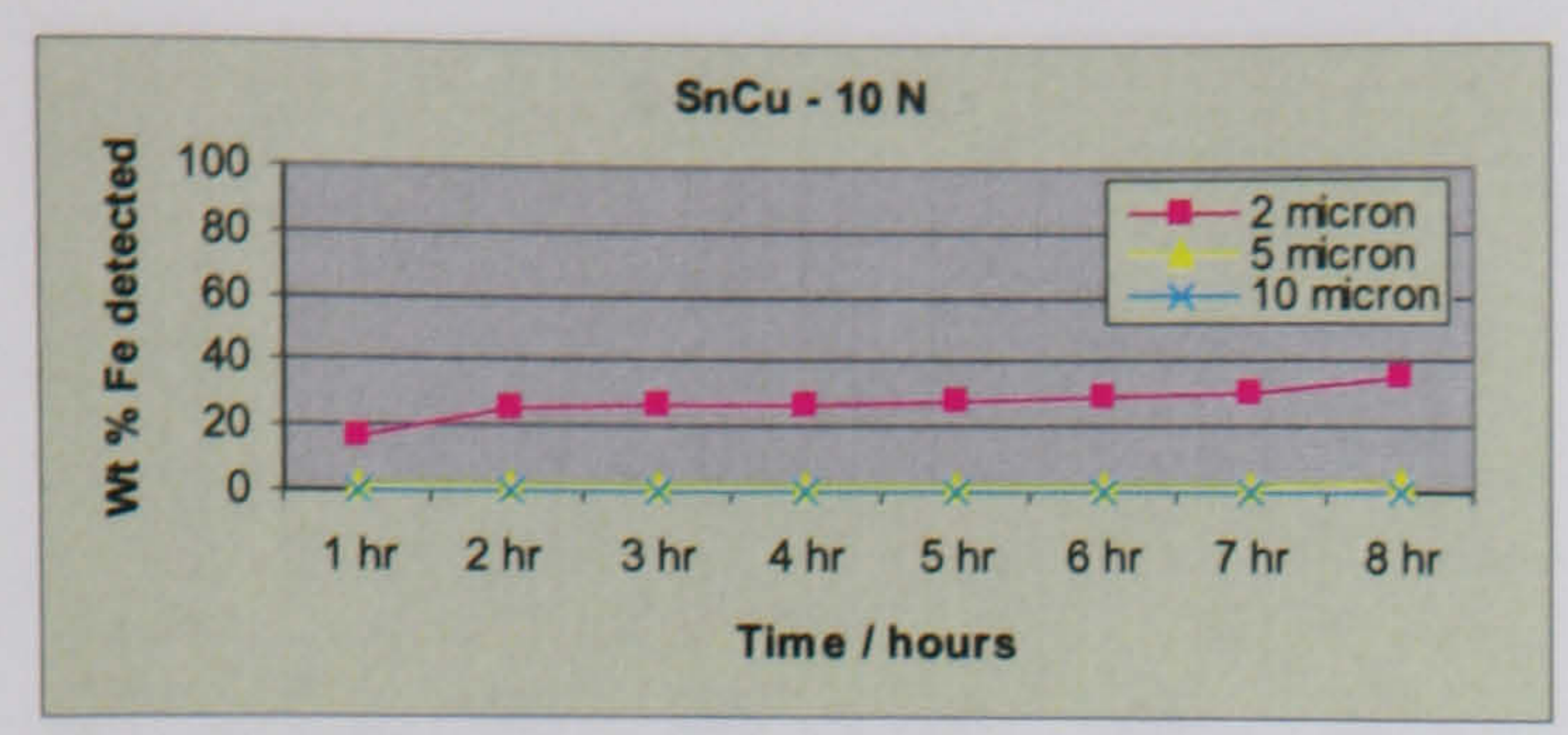

Figure 7.14a – 10 N test load

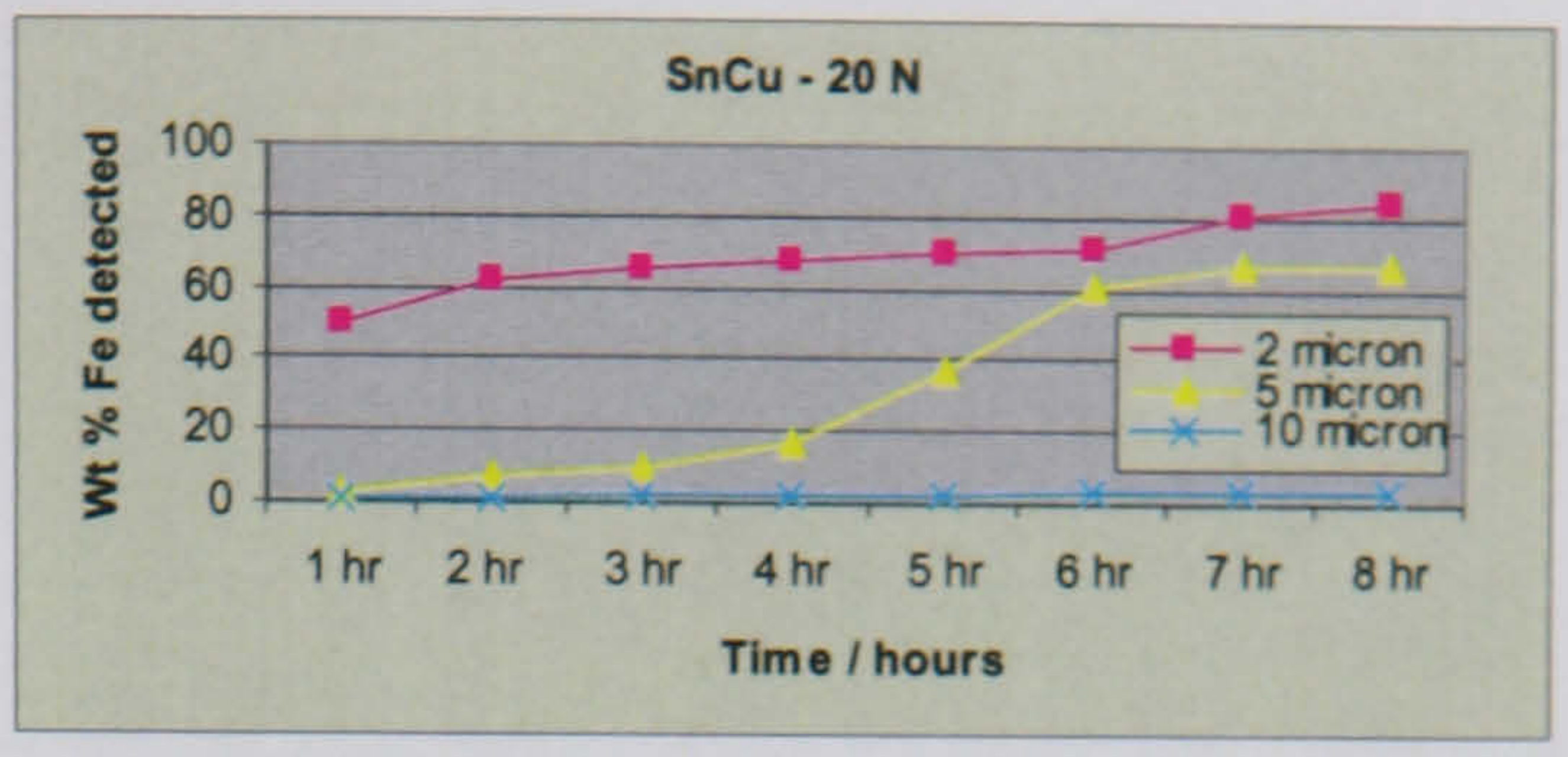

Figure 7.14b – 20 N test load

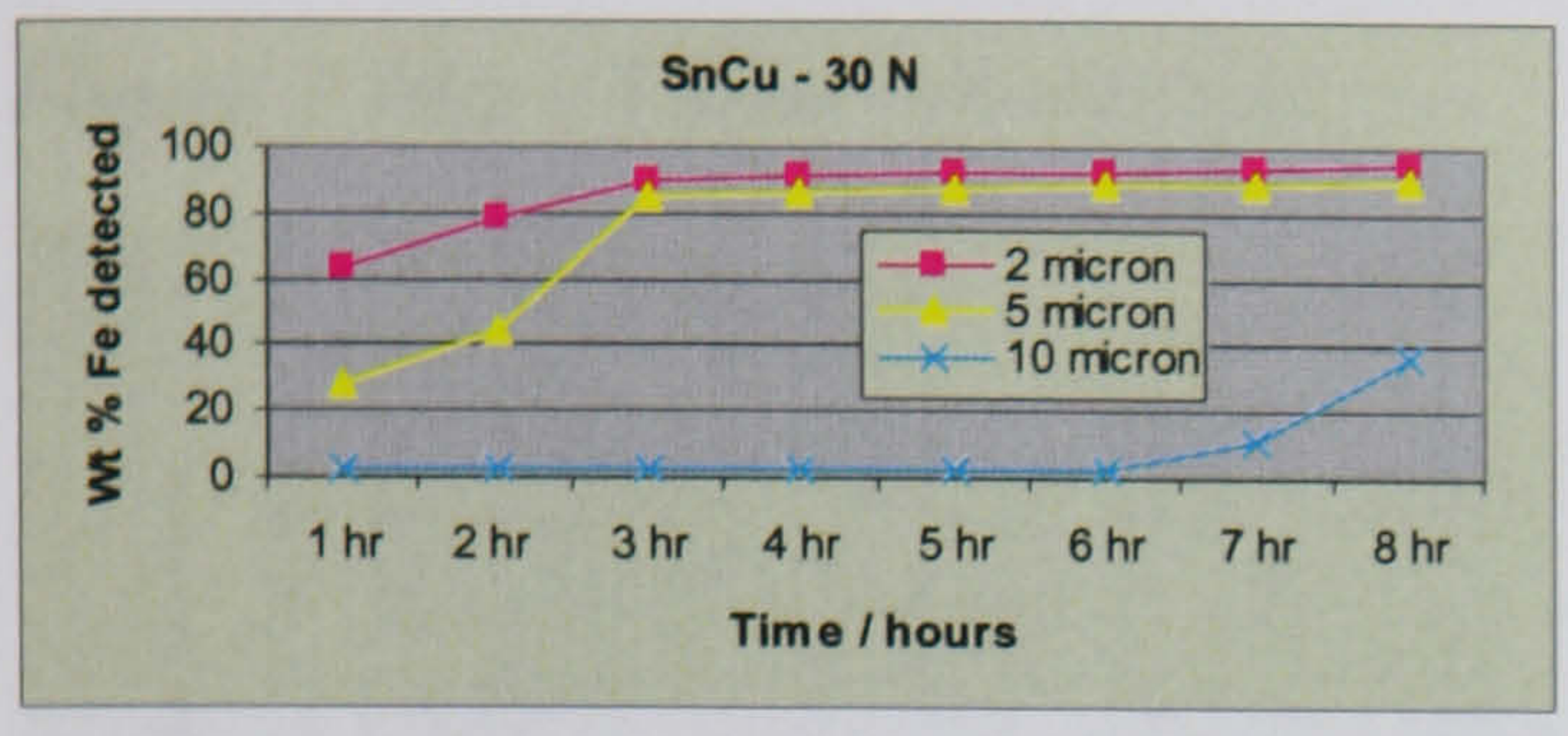

Figure 7.14c – 30 N test load

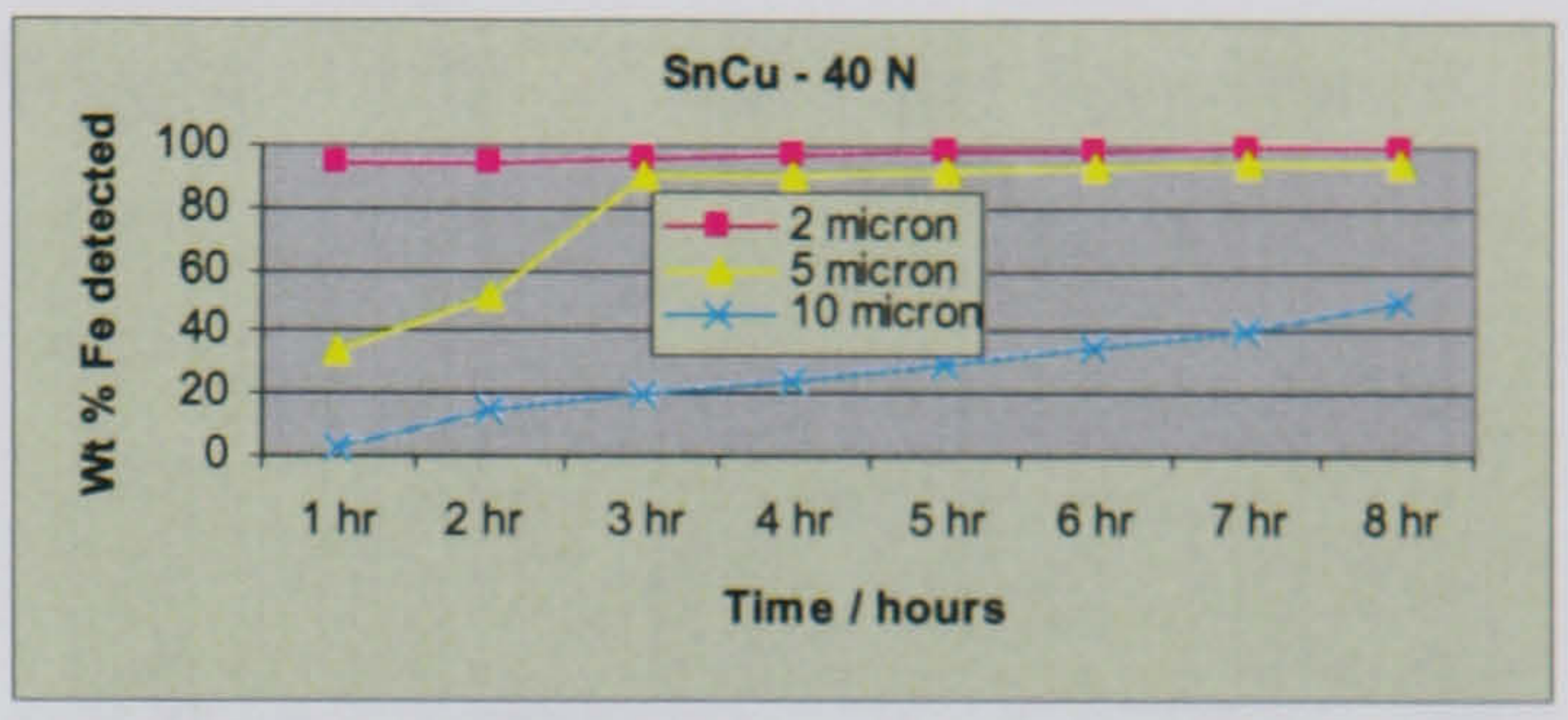

Figure 7.14d – 40 N test load

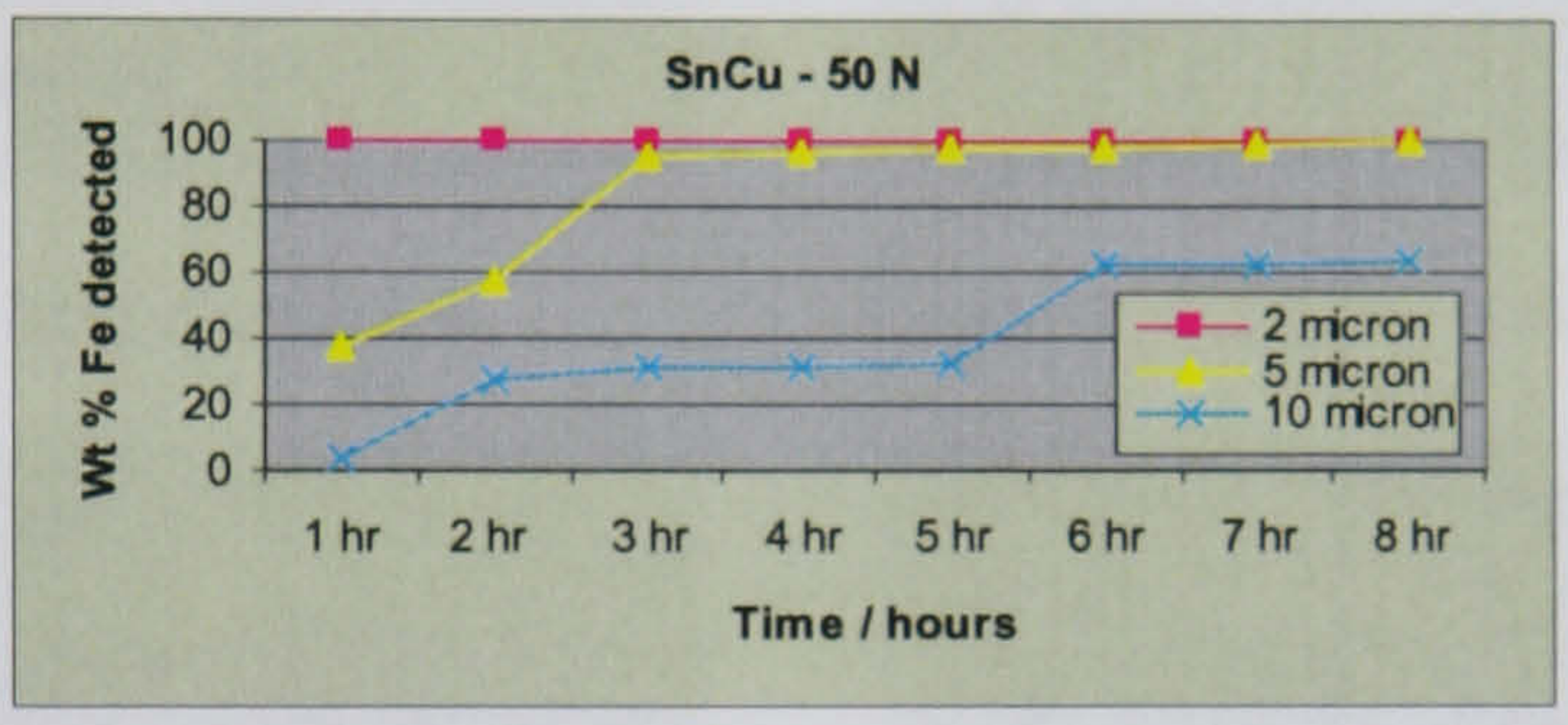

Figure 7.14e – 50 N test load

Effect of increasing test duration with respect to increasing load

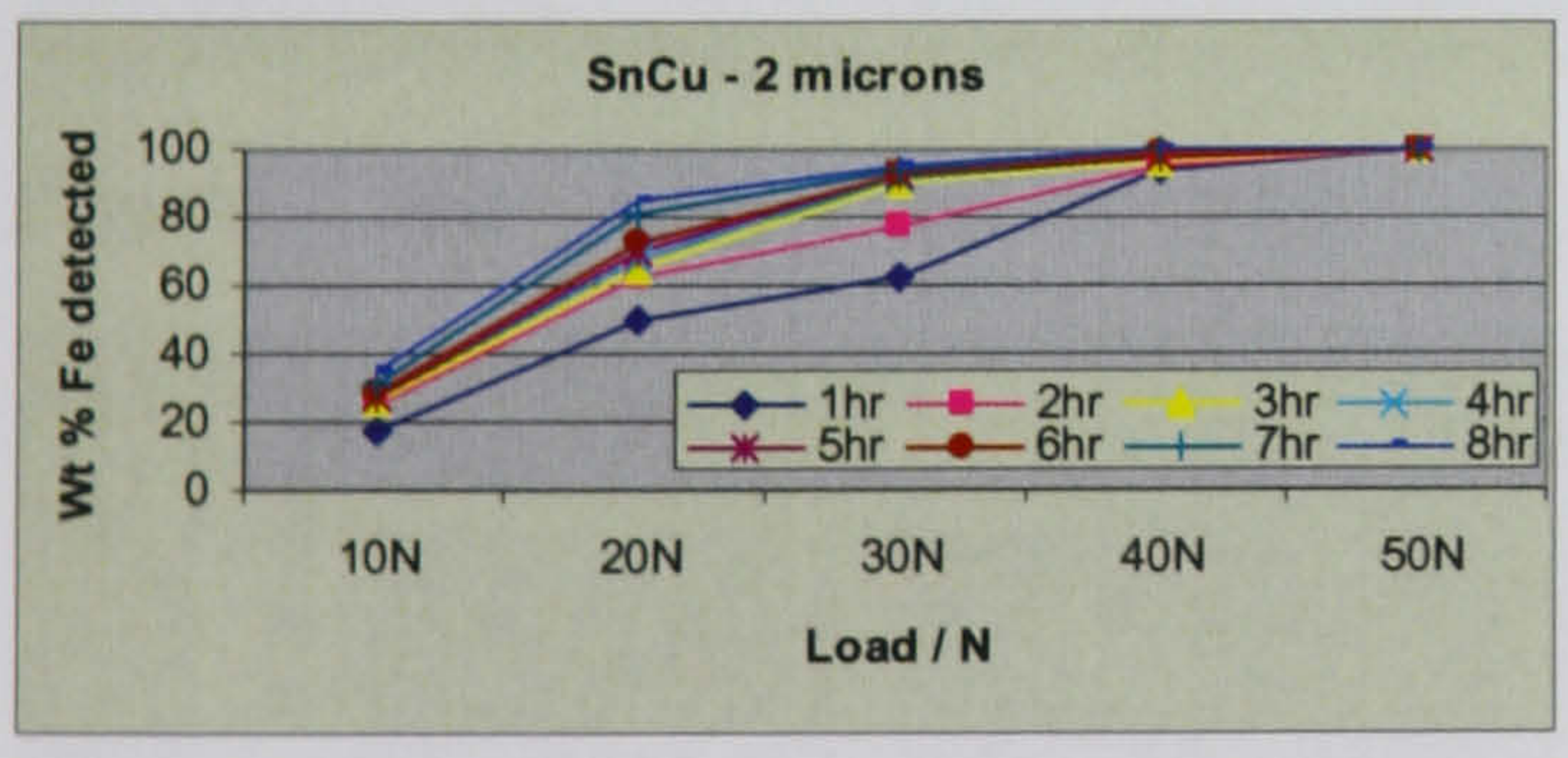

Figure 7.15a – 2 micron thickness

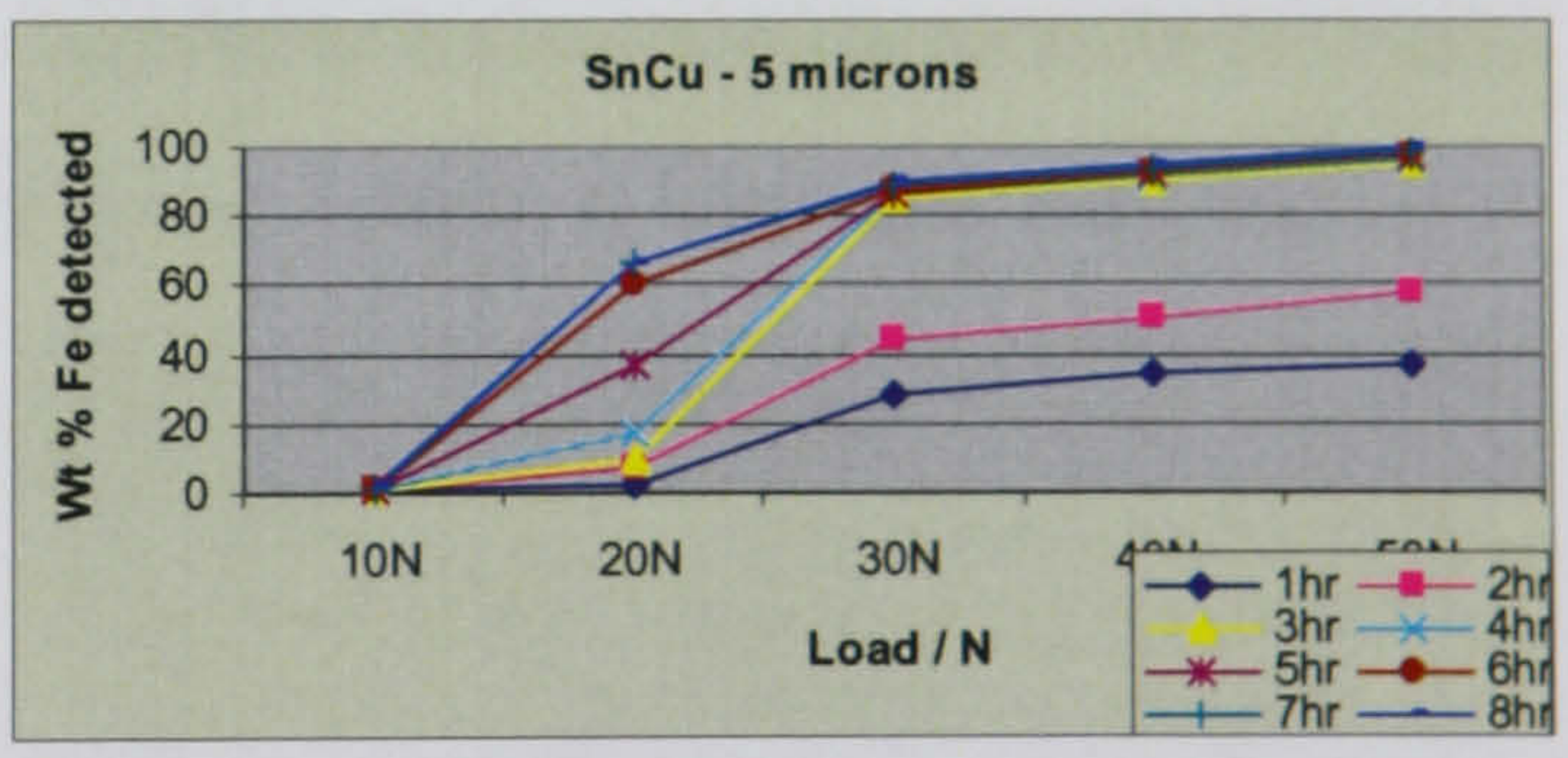

Figure 7.15b – 5 micron thickness

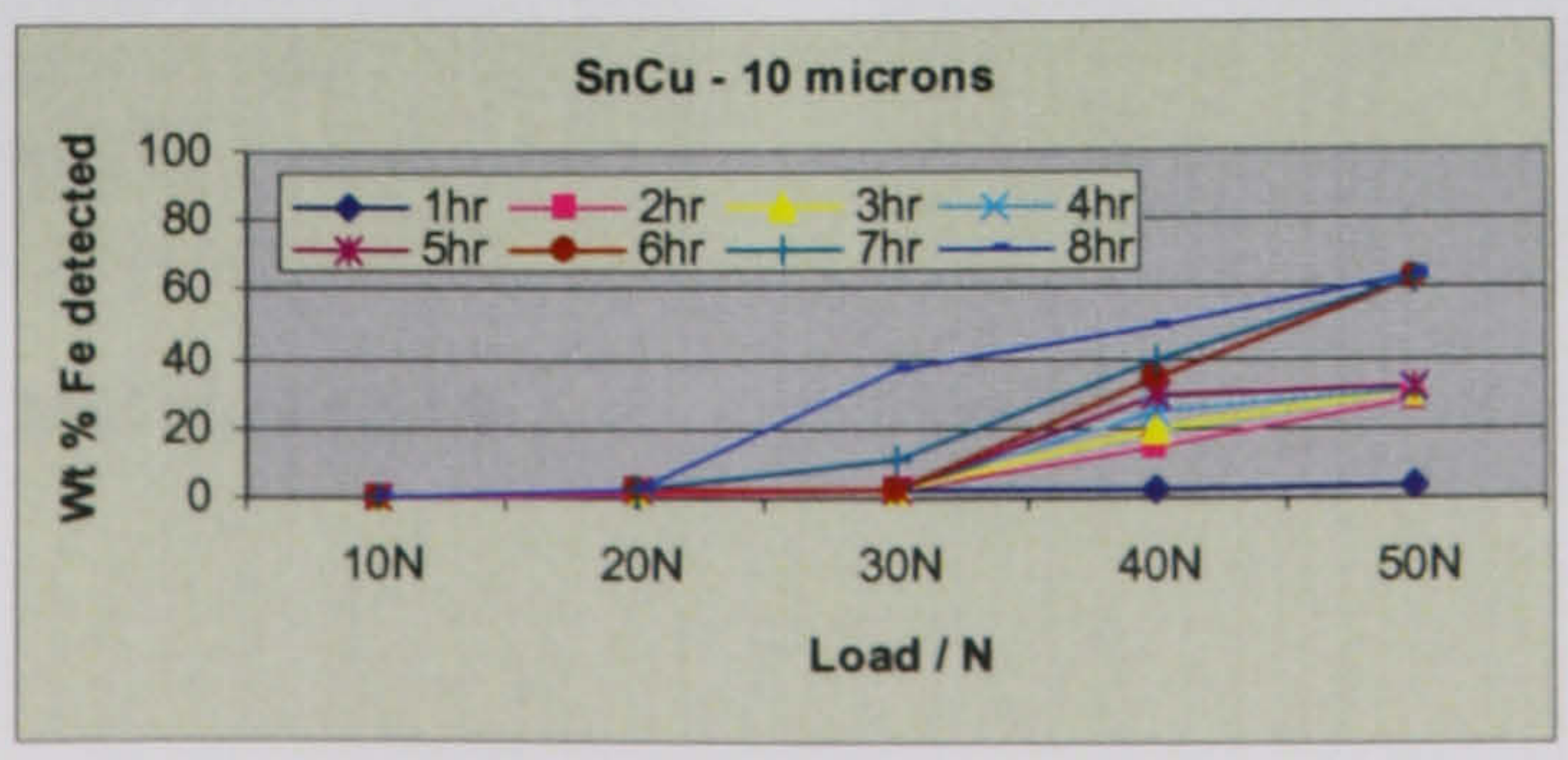

Figure 7.15c – 10 micron thickness

Effect of increasing coating thickness with respect to load

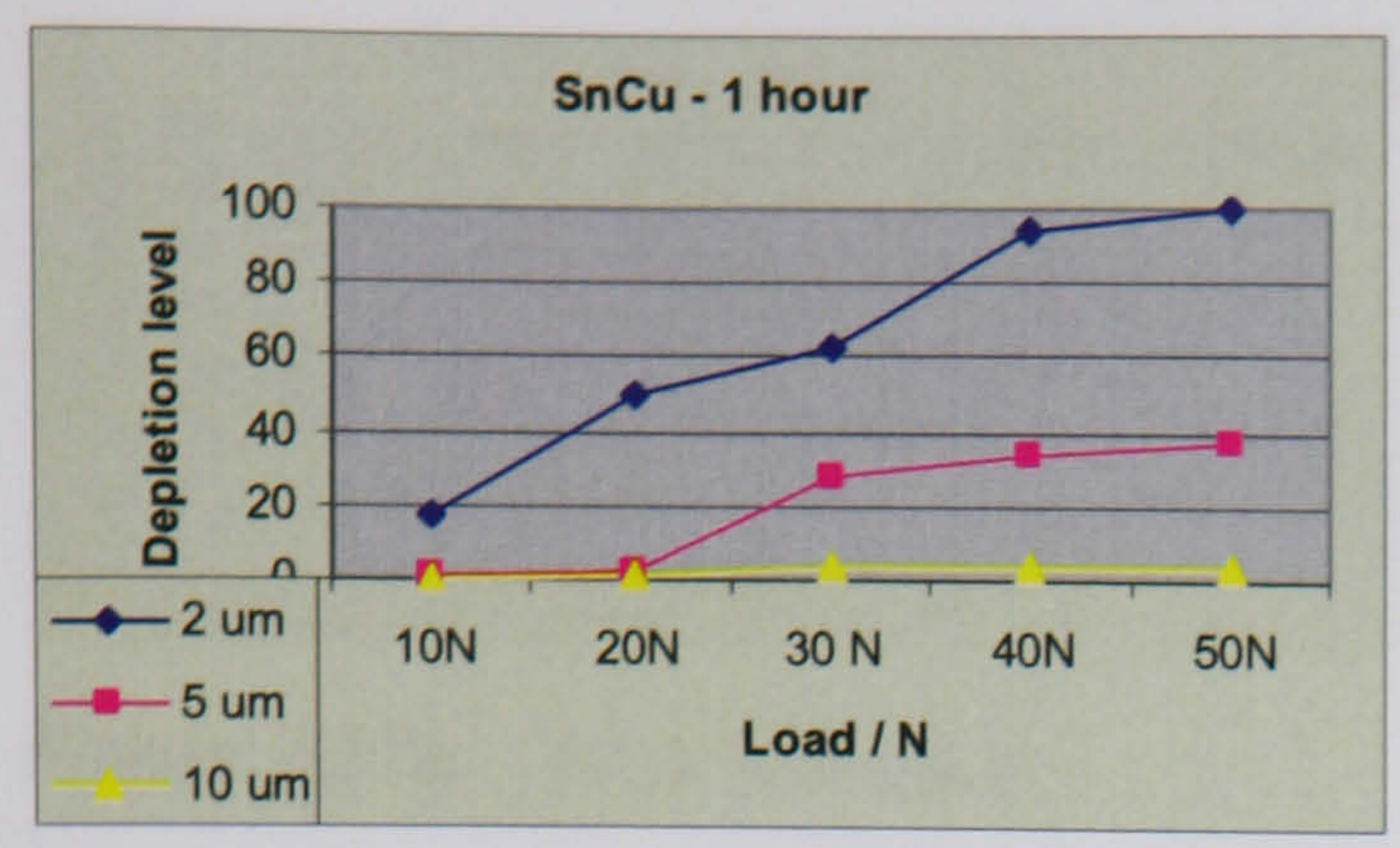

Figure 7.16a – 1 hour test duration

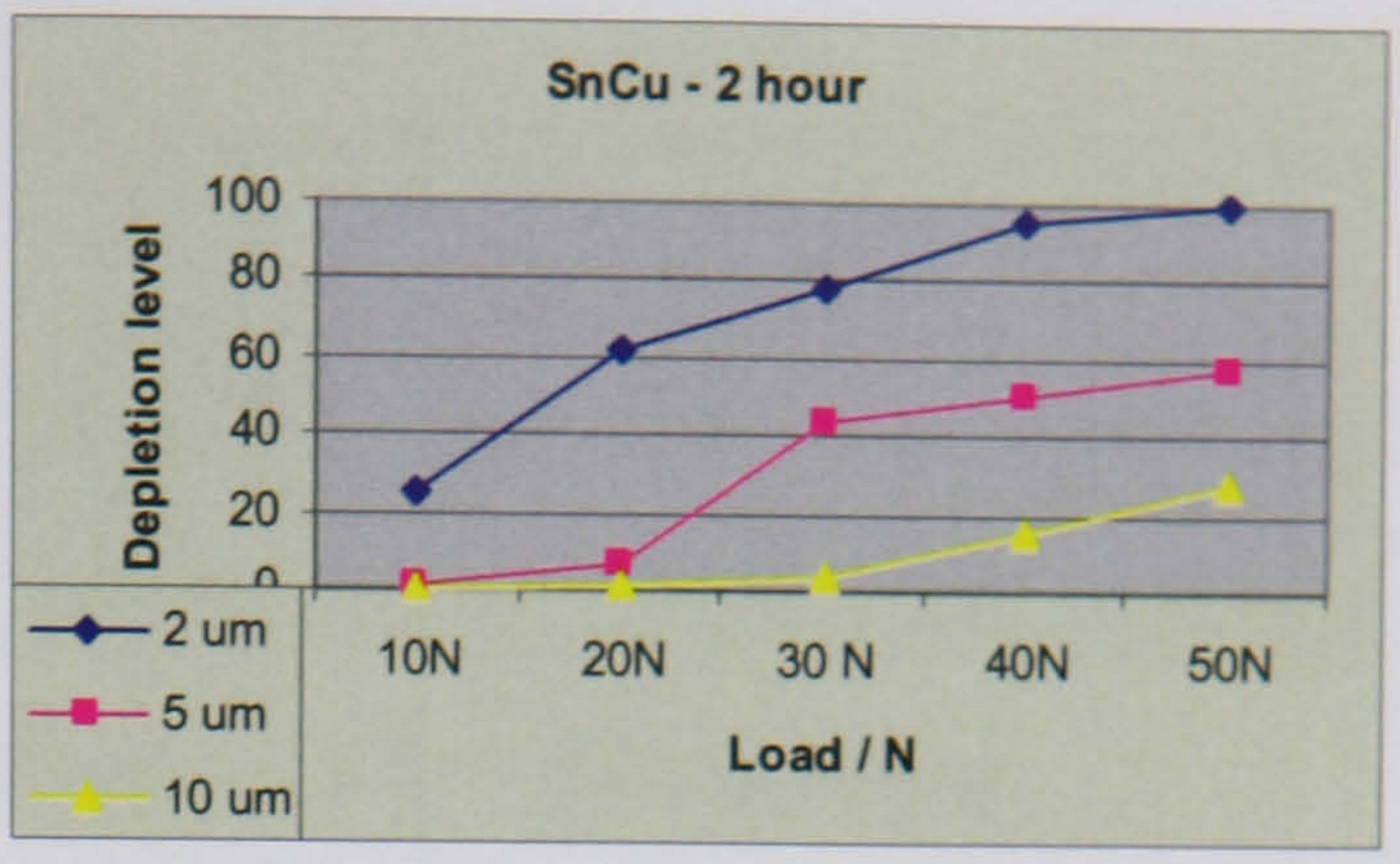

Figure 7.16b – 2 hour test duration

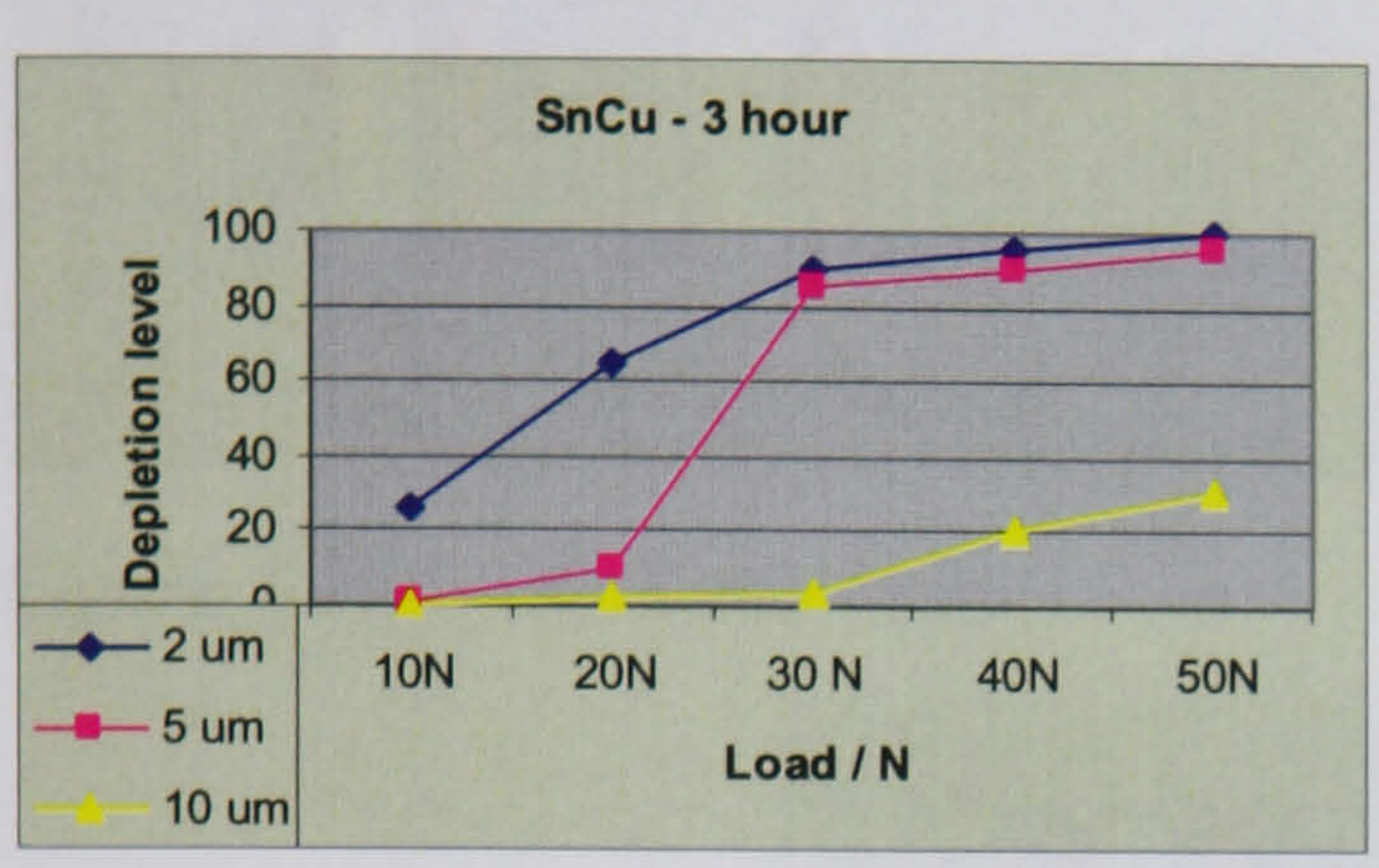

Figure 7.16c – 3 hour test duration

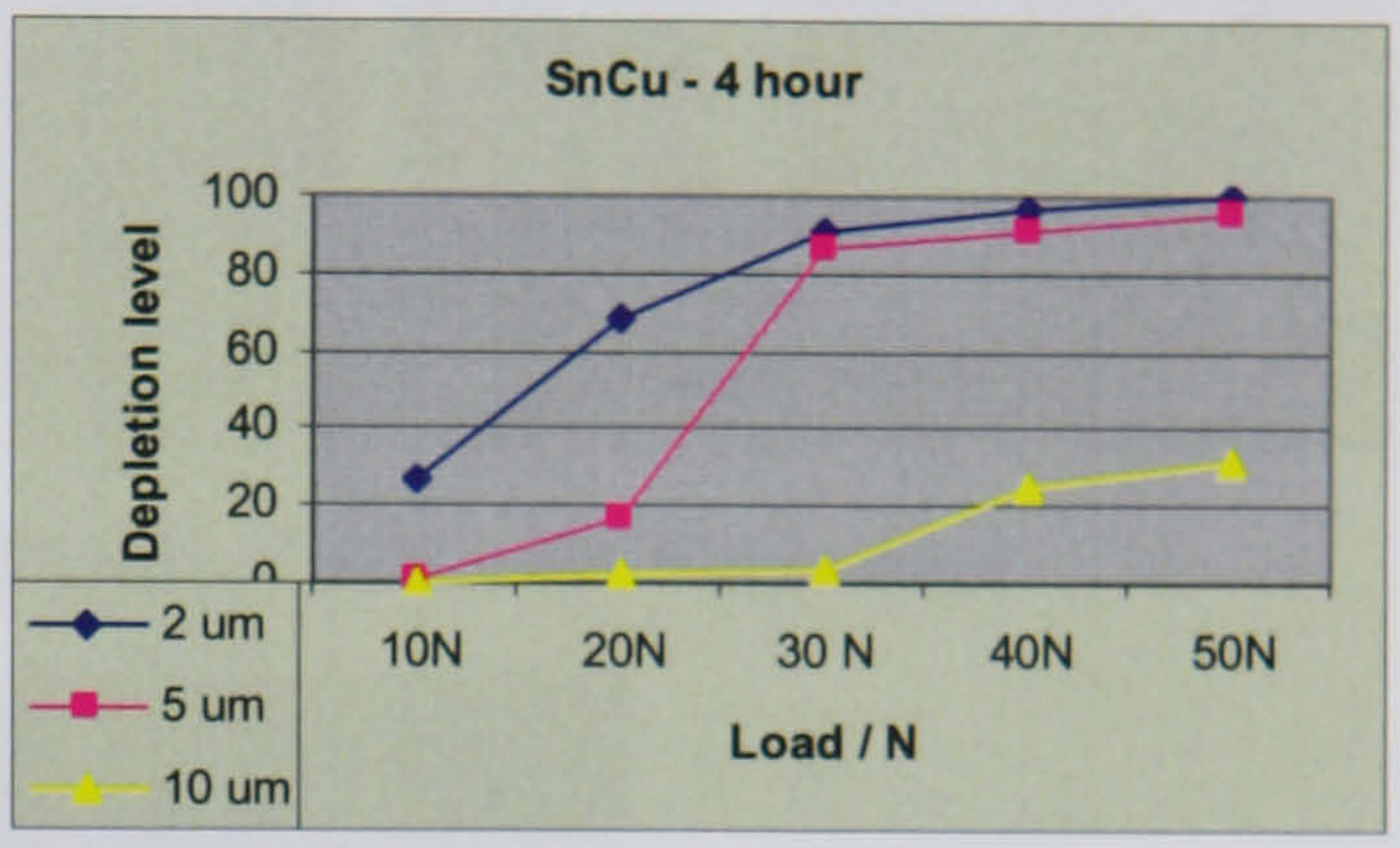

Figure 7.16d – 4 hour test duration

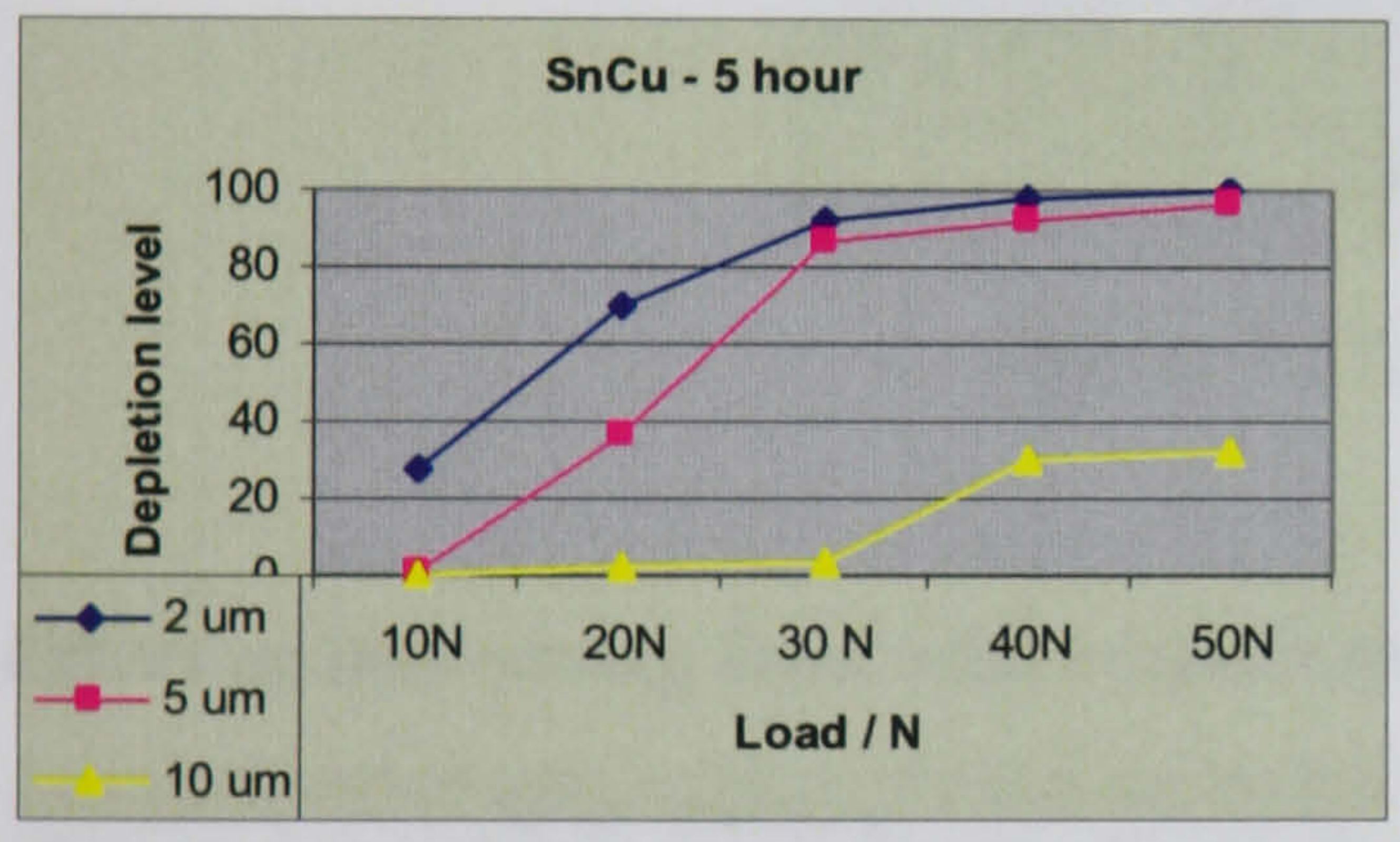

Figure 7.16e – 5 hour test duration

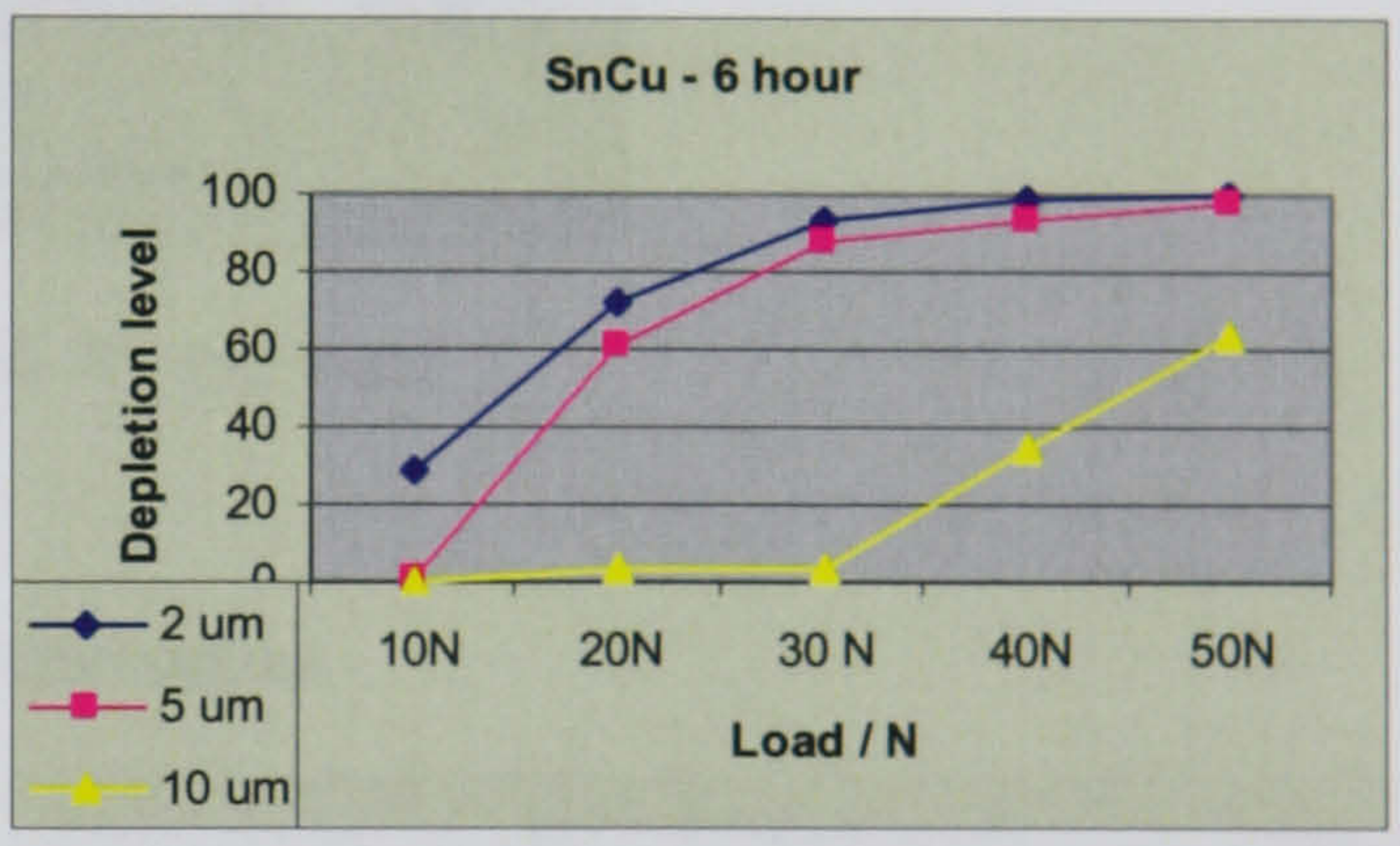

Figure 7.16f – 6 hour test duration

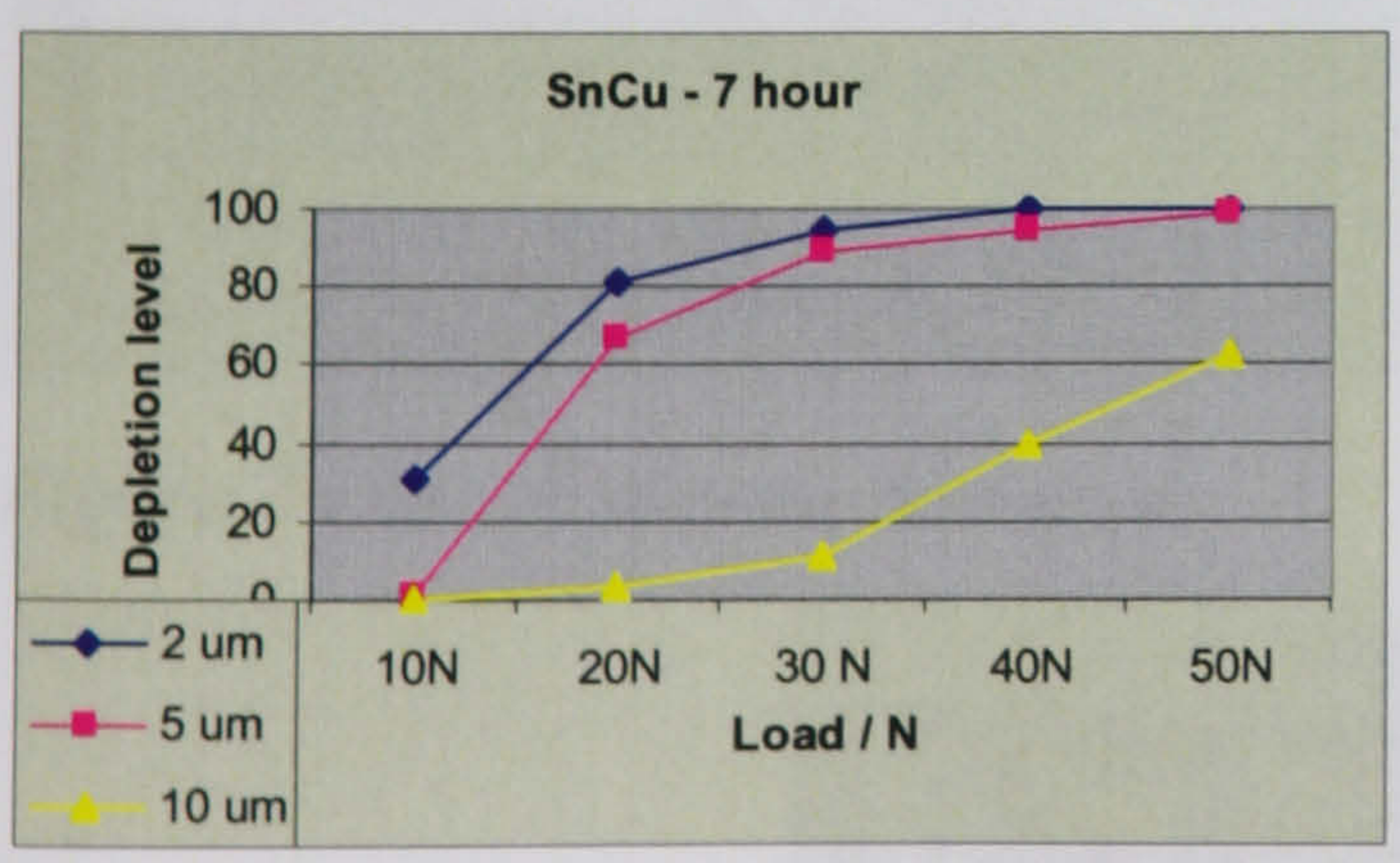

Figure 7.16g – 7 hour test duration

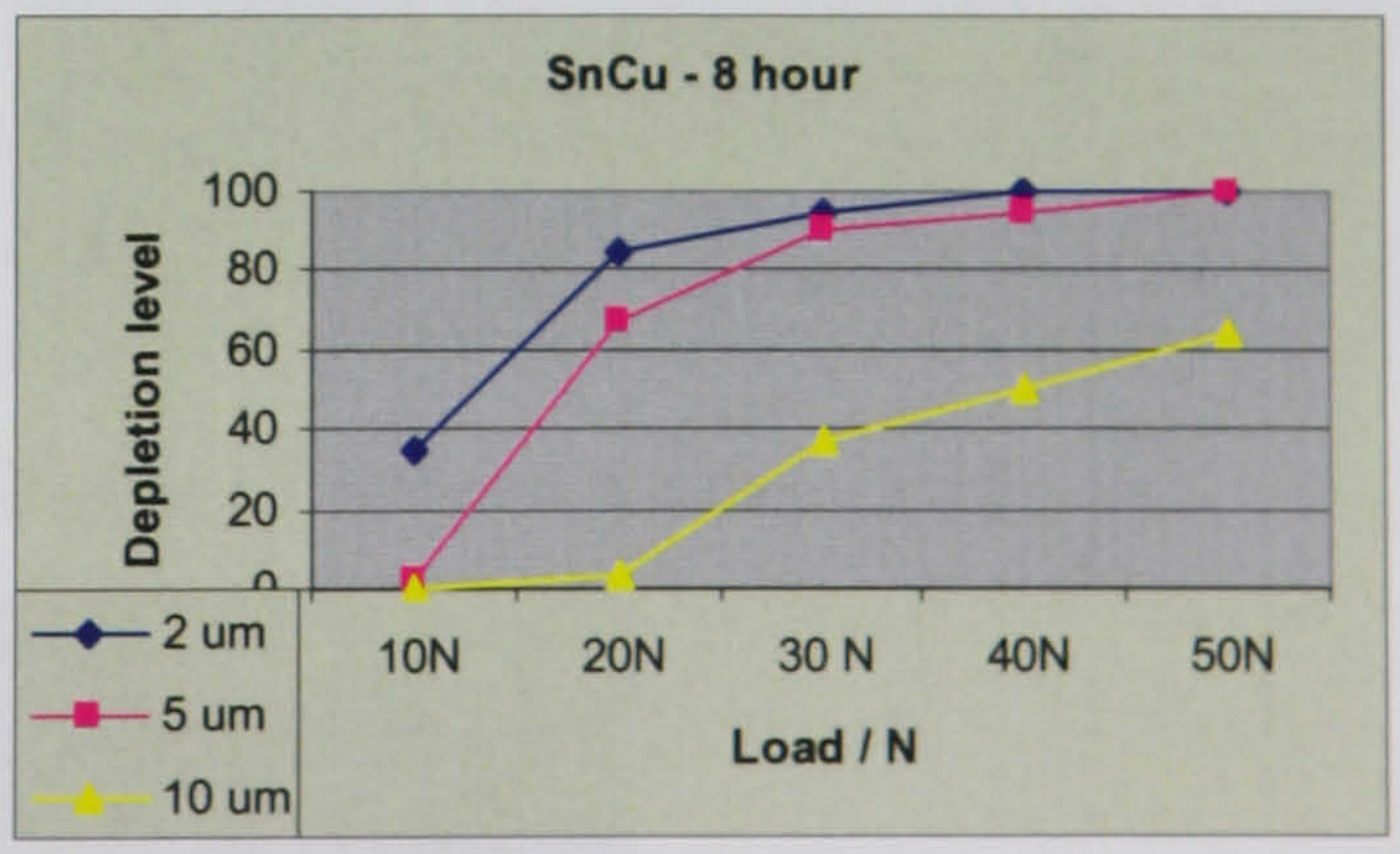

Figure 7.16h – 8 hour test duration

Effect of increasing test duration with respect to coating thickness

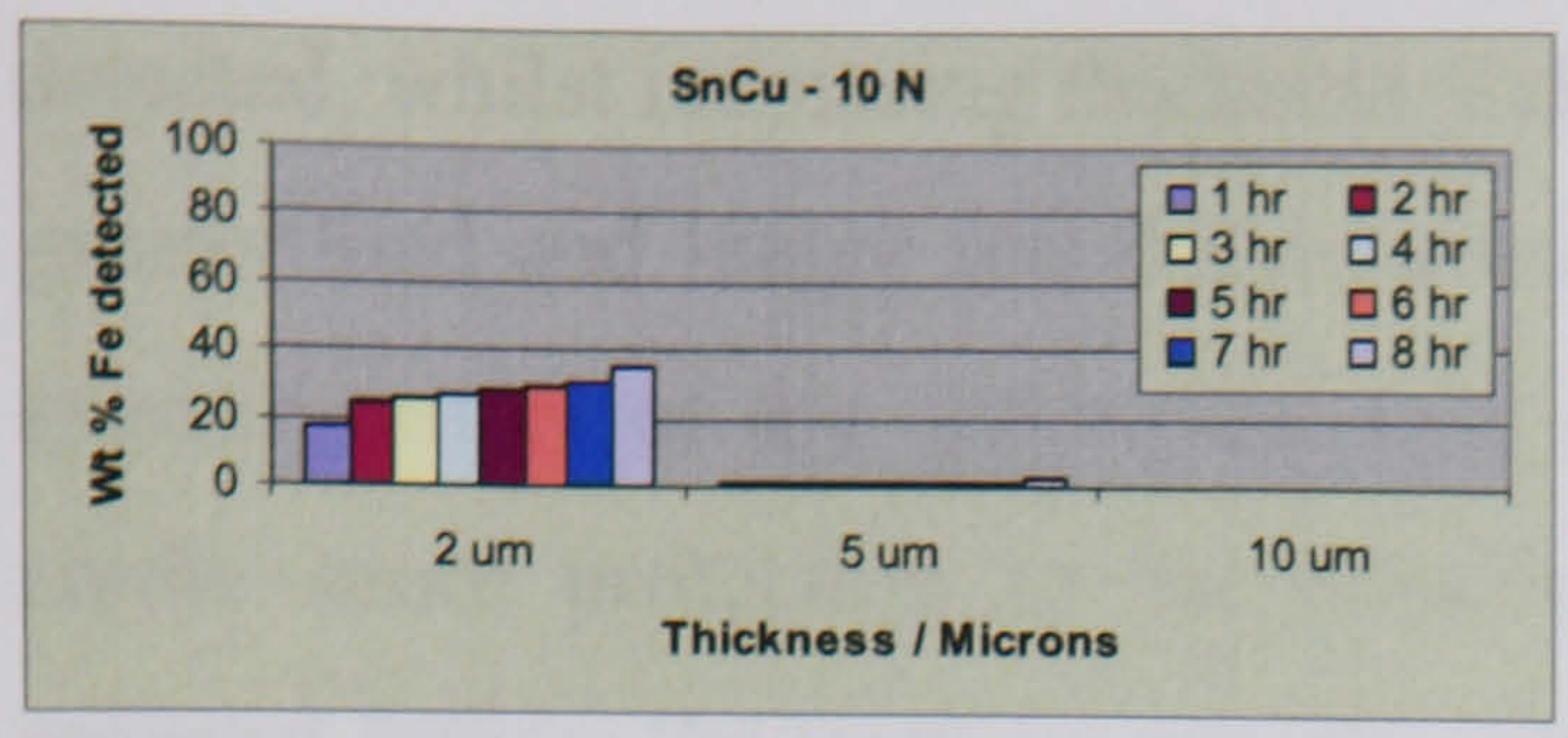

Figure 7.17a – 10 N test load

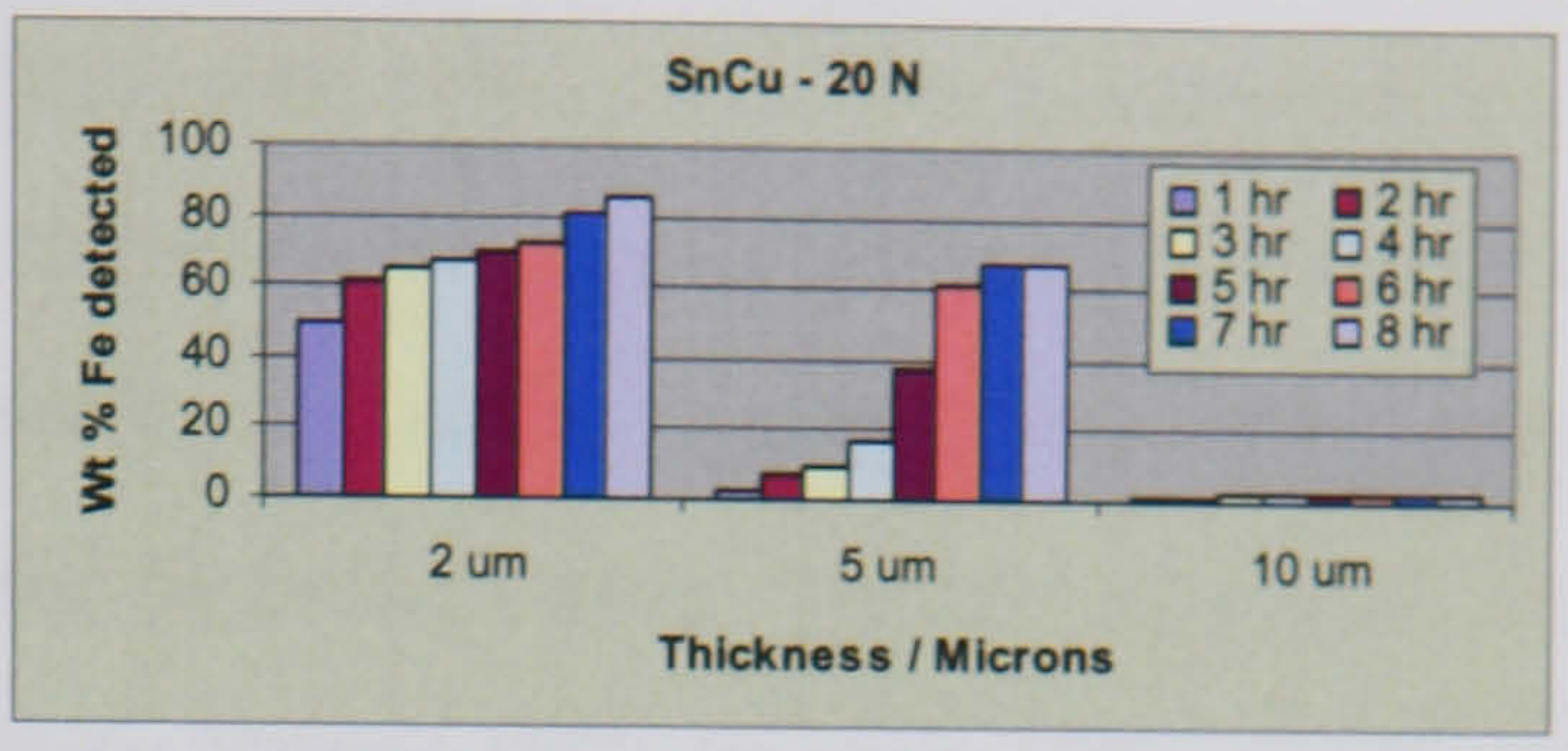

Figure 7.17b – 20 N test load

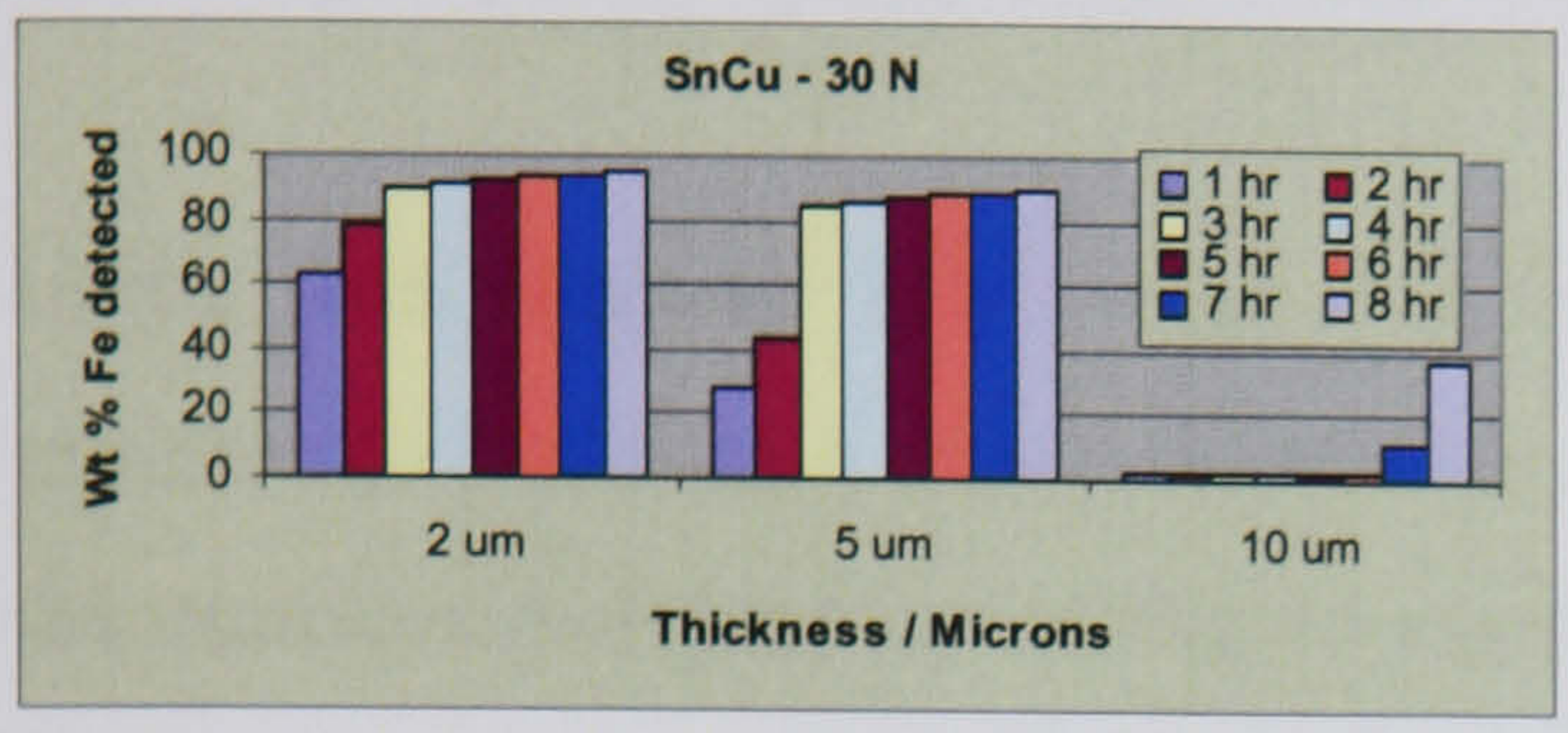

Figure 7.17c – 30 N test load

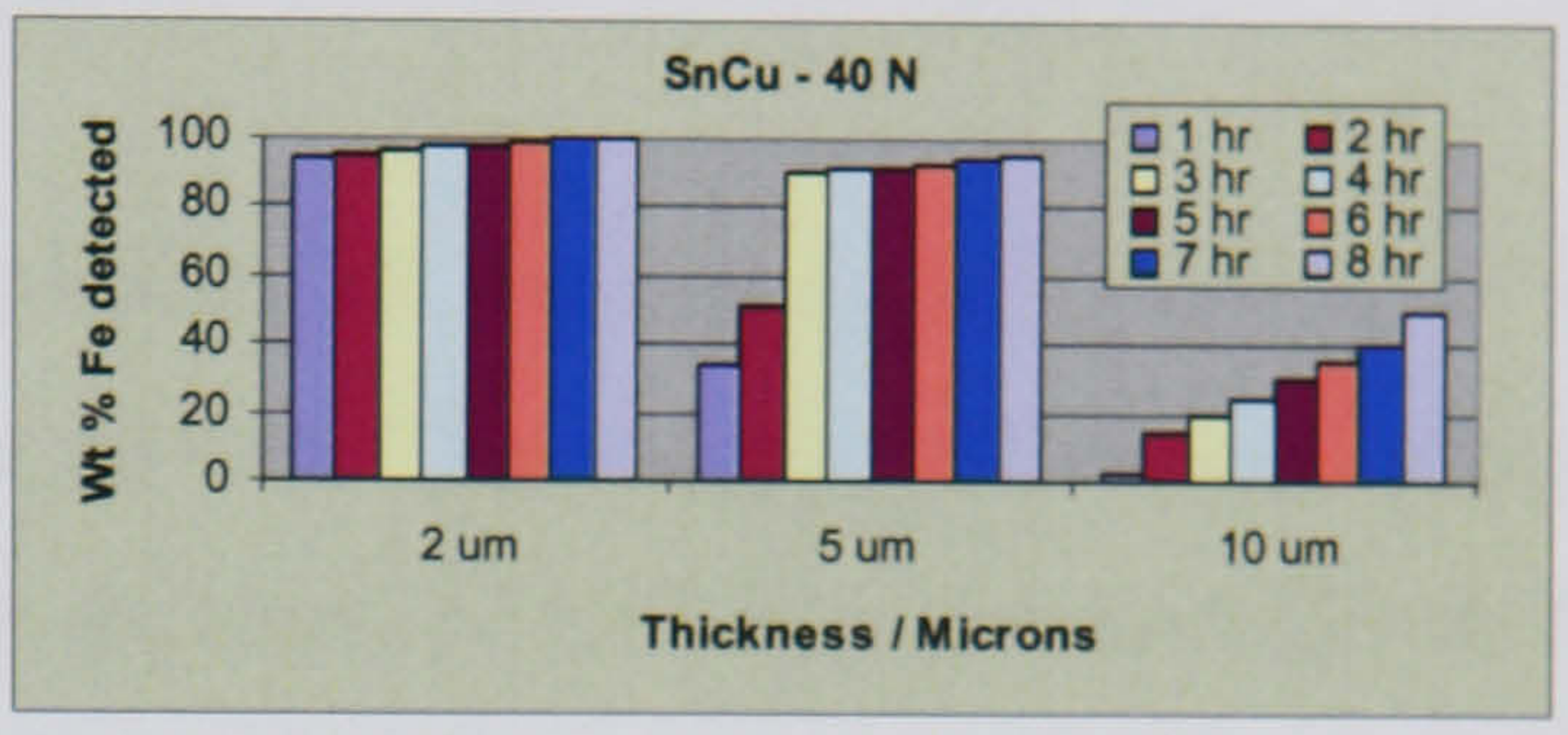

Figure 7.17d – 40 N test load

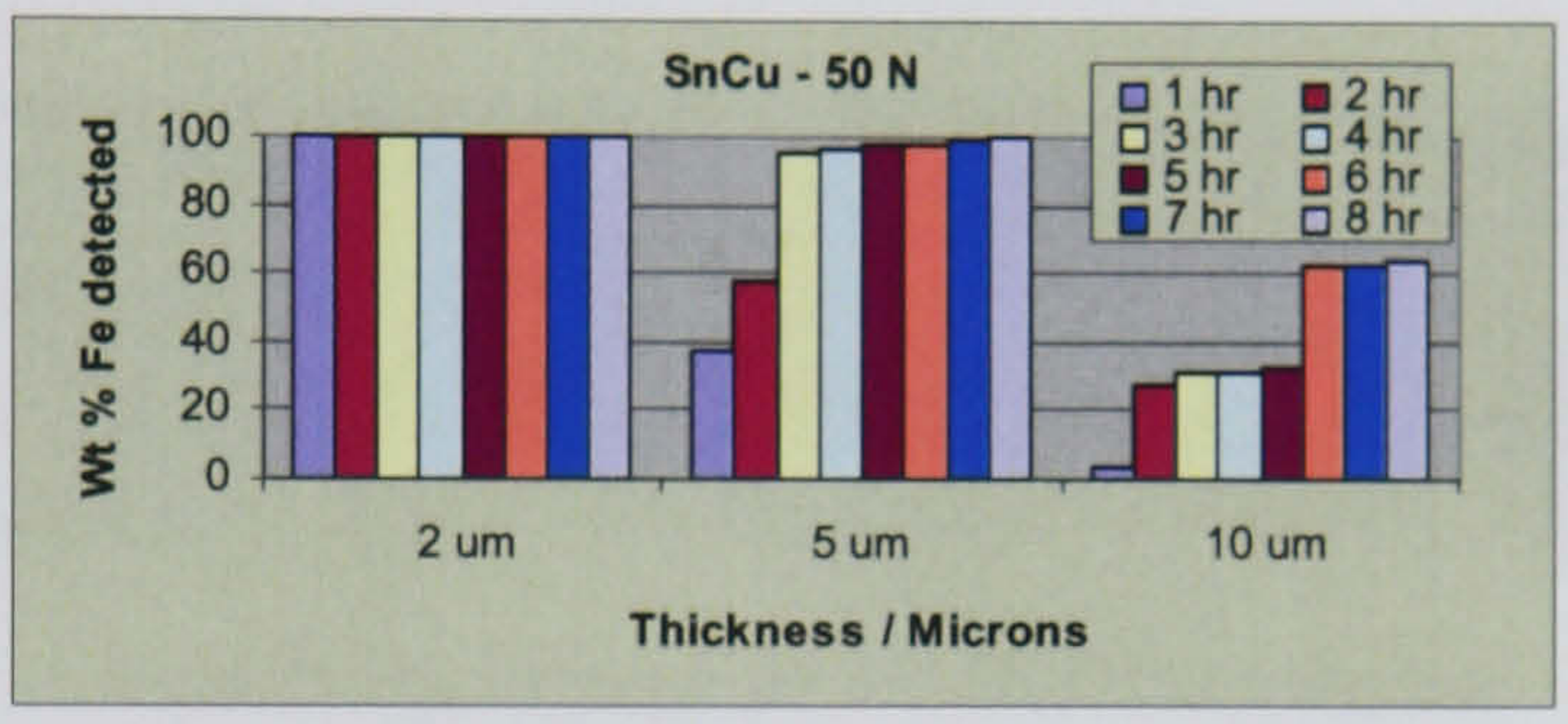

Figure 7.17e – 50 N test load

Effect of increasing load with respect to test duration

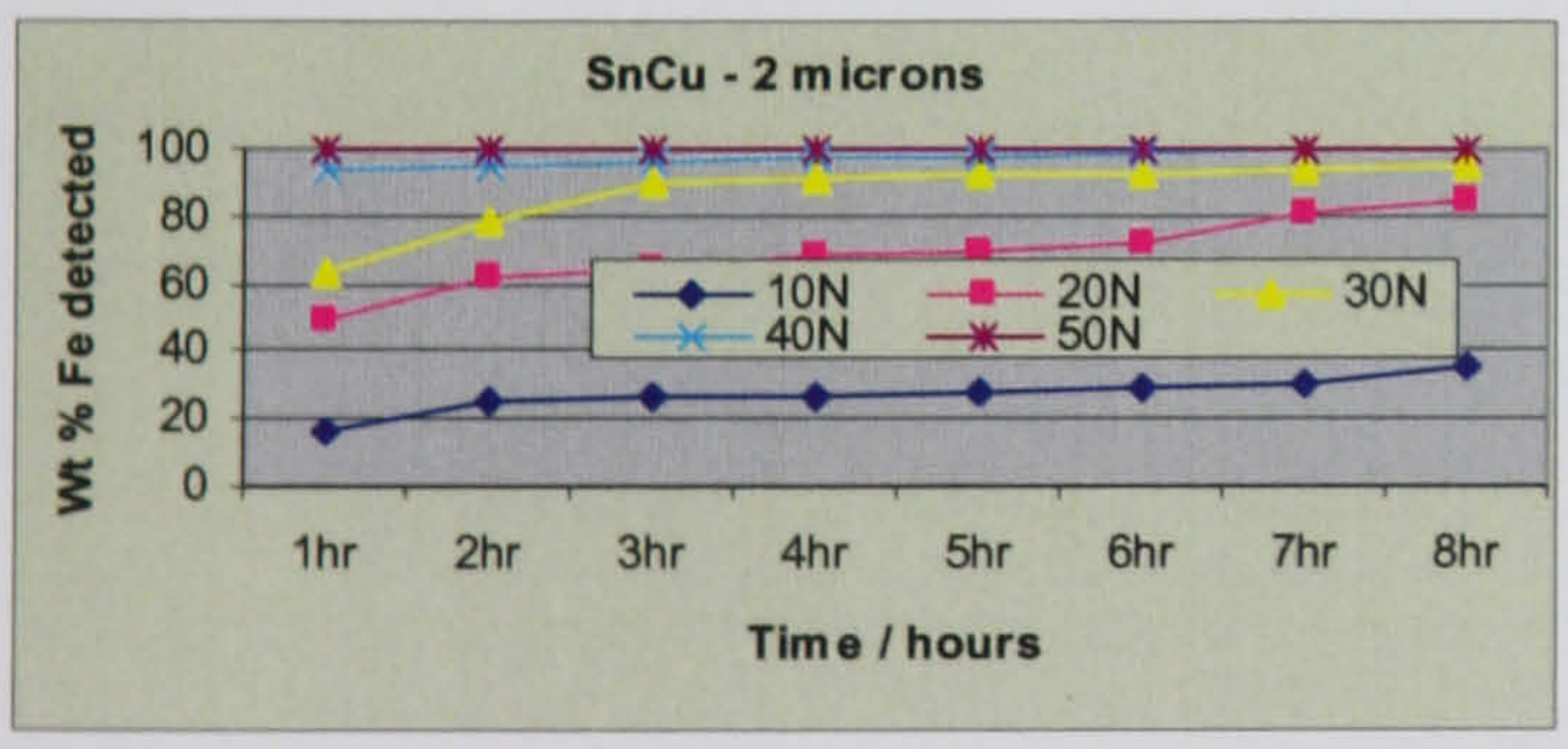

Figure 7.18a – 2 micron thickness

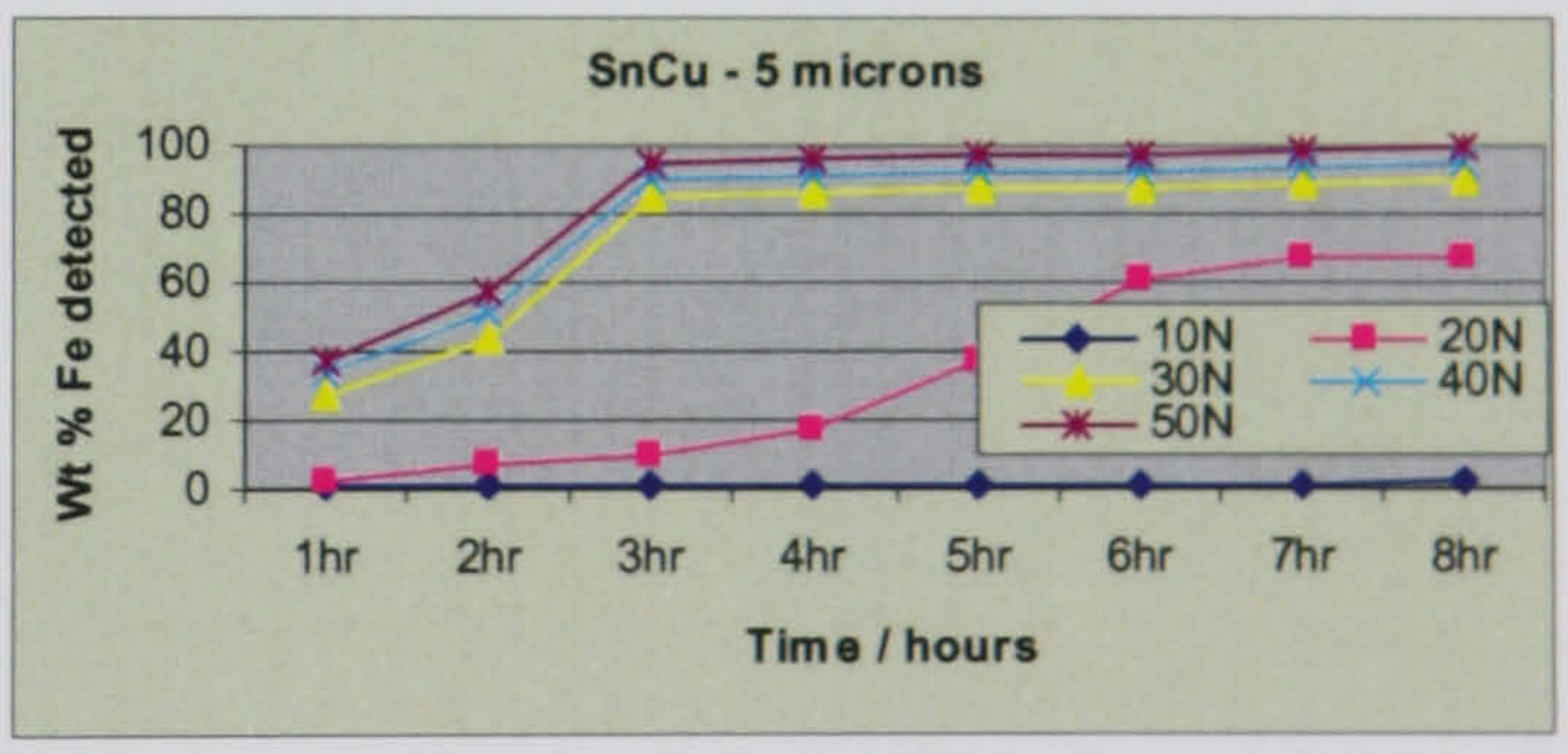

Figure 7.18b – 5 micron thickness

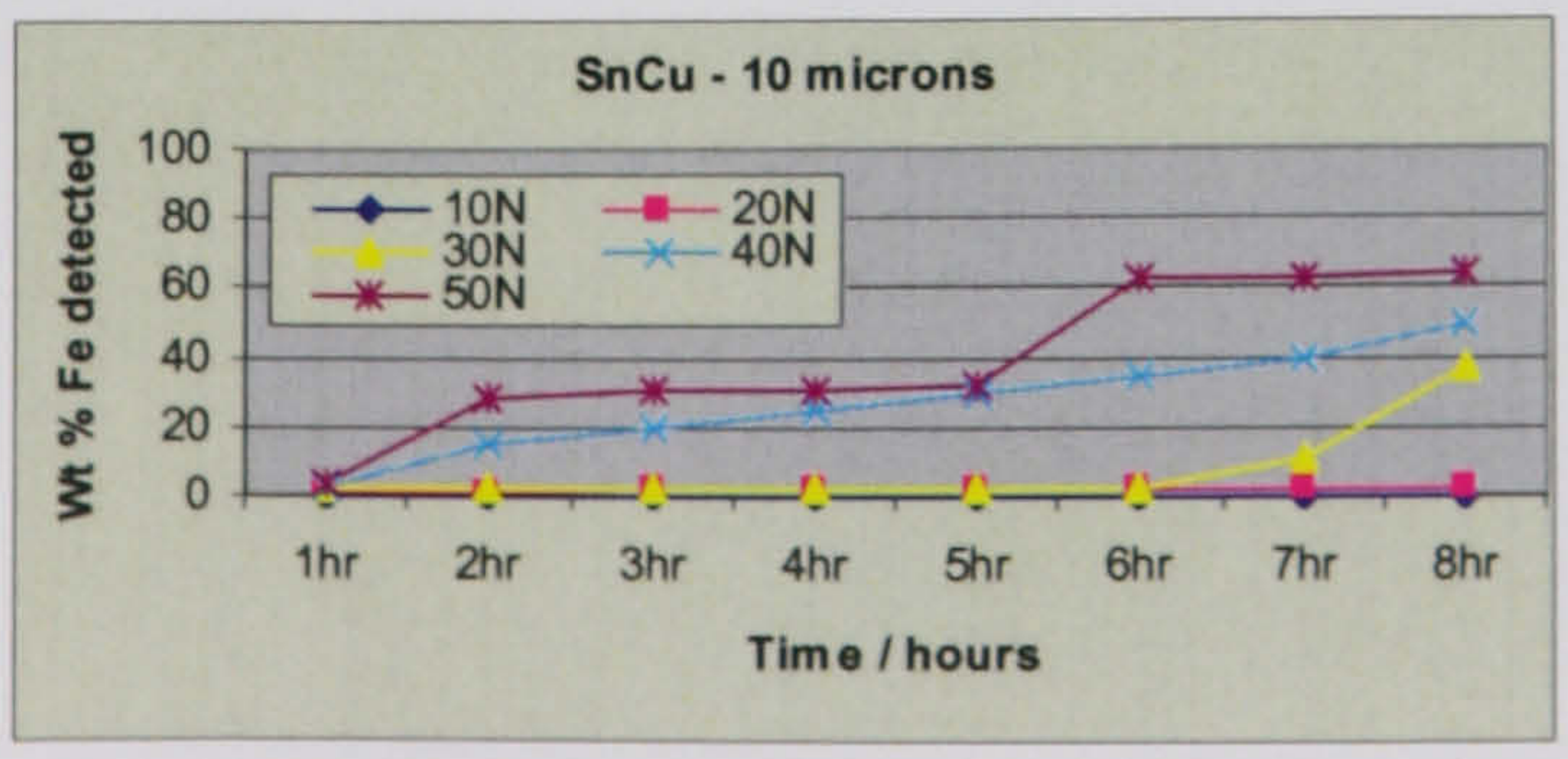

Figure 7.18c – 10 micron thickness

In all cases, increasing load and test duration resulted in a higher value of iron detected, whilst increasing thickness yielded less detectable iron. This is expected as a greater load and longer test duration would mean more coating material is removed, exposing more of the underlying steel substrate. A greater coating thickness would confer more protection to the substrate and provides more coating material for removal before the steel is exposed. The above trends indicate that using EDX for detecting exposed iron is a viable method for progressively monitoring wear.

Using data acquired from wear scar examinations of the individual coatings, it is possible to build up a results matrix for each deposit. The shading of the cells within the matrices is dependant on the exposed iron detected by the EDX, and each 20 wt % iron increment is assigned a category, as presented in Table 7.1.

Negligible	Moderate	Significant	Critical	Failure
0 – 20	20 – 40	40 – 60	60 – 80	80 – 100

Table 7.1 – Legend defining shading used in Results Matrices for each condition/range of wt % Fe detected

Using this system, a results matrix was compiled for tin, tin-nickel and tin-copper, and this is presented in Table 7.2.

Testing Force / N	Testing duration / hrs	Tin 2 µm	Tin 5 µm	Tin 10 µm	Tin-Nickel 2 µm	Tin-Nickel 5 µm	Tin-Nickel 10 µm	Tin-Copper 2 µm	Tin-Copper 5 µm	Tin-Copper 10 µm
10	1	▒	░	░						
	2	▓	▒	░	░	░		░		
	3	▓	▓	░	▒	░		░		
	4	█	▓	░	▓	░		░		
	5	█	█	▒	▓	░		░		
	6	█	█	▒	█	░		░		
	7	█	█	▓	█	▒		░		
	8	█	█	▓	█	▓		░		
20	1	█	█	▒	░	░		▒		
	2	█	█	▓	▒	░		▓		
	3	█	█	█	▓	▒		▓		
	4	█	█	█	█	▓		▓		
	5	█	█	█	█	█		▓	░	
	6	█	█	█	█	█		▓	▓	
	7	█	█	█	█	█		█	▓	
	8	█	█	█	█	█		█	▓	
30	1	█	█	█	▓	░		▓	░	
	2	█	█	█	█	▒		▓	▒	
	3	█	█	█	█	▓		█	█	
	4	█	█	█	█	█		█	█	
	5	█	█	█	█	█		█	█	
	6	█	█	█	█	█		█	█	
	7	█	█	█	█	█		█	█	
	8	█	█	█	█	█		█	█	░
40	1				█	▓		█	░	
	2				█	█		█	▒	
	3				█	█		█	▒	░
	4				█	█		█	█	░
	5				█	█		█	█	░
	6				█	█		█	█	░
	7				█	█	░	█	█	▒
	8				█	█	▒	█	█	▒
50	1				█	▓	▓	█	░	
	2				█	█	█	█	▒	░
	3				█	█	█	█	▒	░
	4				█	█	█	█	█	░
	5				█	█	█	█	█	░
	6				█	█	█	█	█	▓
	7				█	█	█	█	█	▓
	8				█	█	█	█	█	▓

Table 7.2 – Results Matrix for Testing Conducted on Tin, Tin-Nickel and Tin-Copper coatings

7.3 RESULTS: COMPARISONS BETWEEN COATINGS

7.3.1 Coating Depletion over Time

In order to assess the coatings alongside one another, the types of deposit, at the three different thicknesses, were plotted on the same set of axis against time, for each of the five loads applied. These are presented in Figure 7.19.

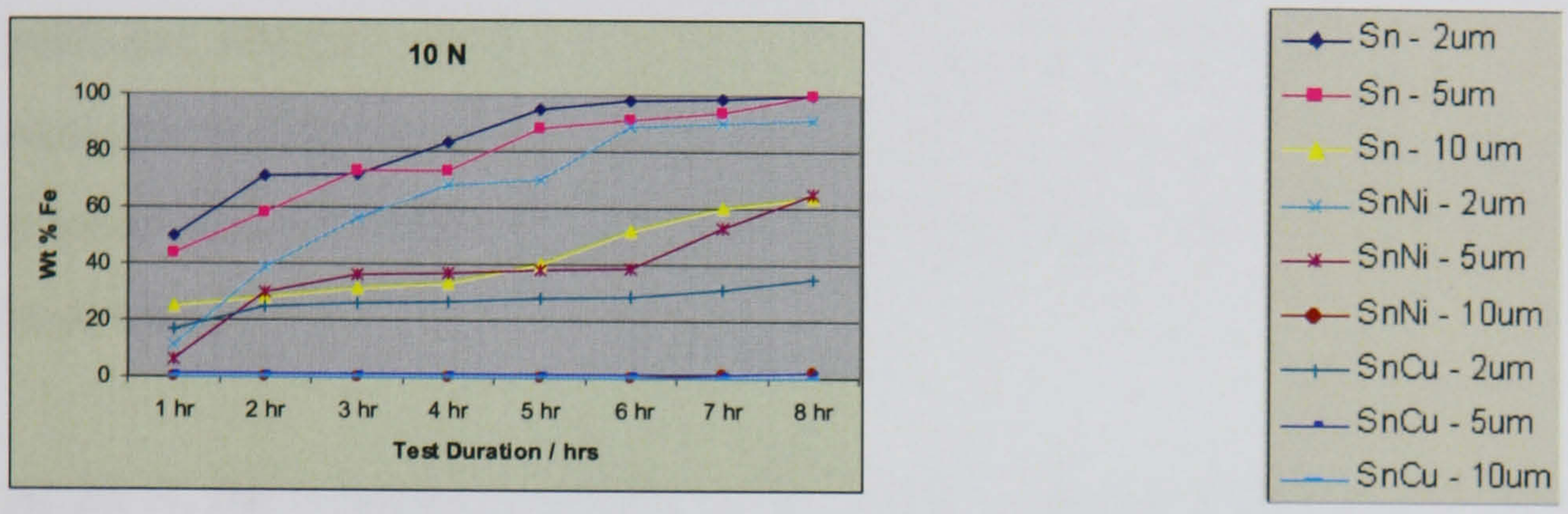

Figure 7.19a – 10 N test load

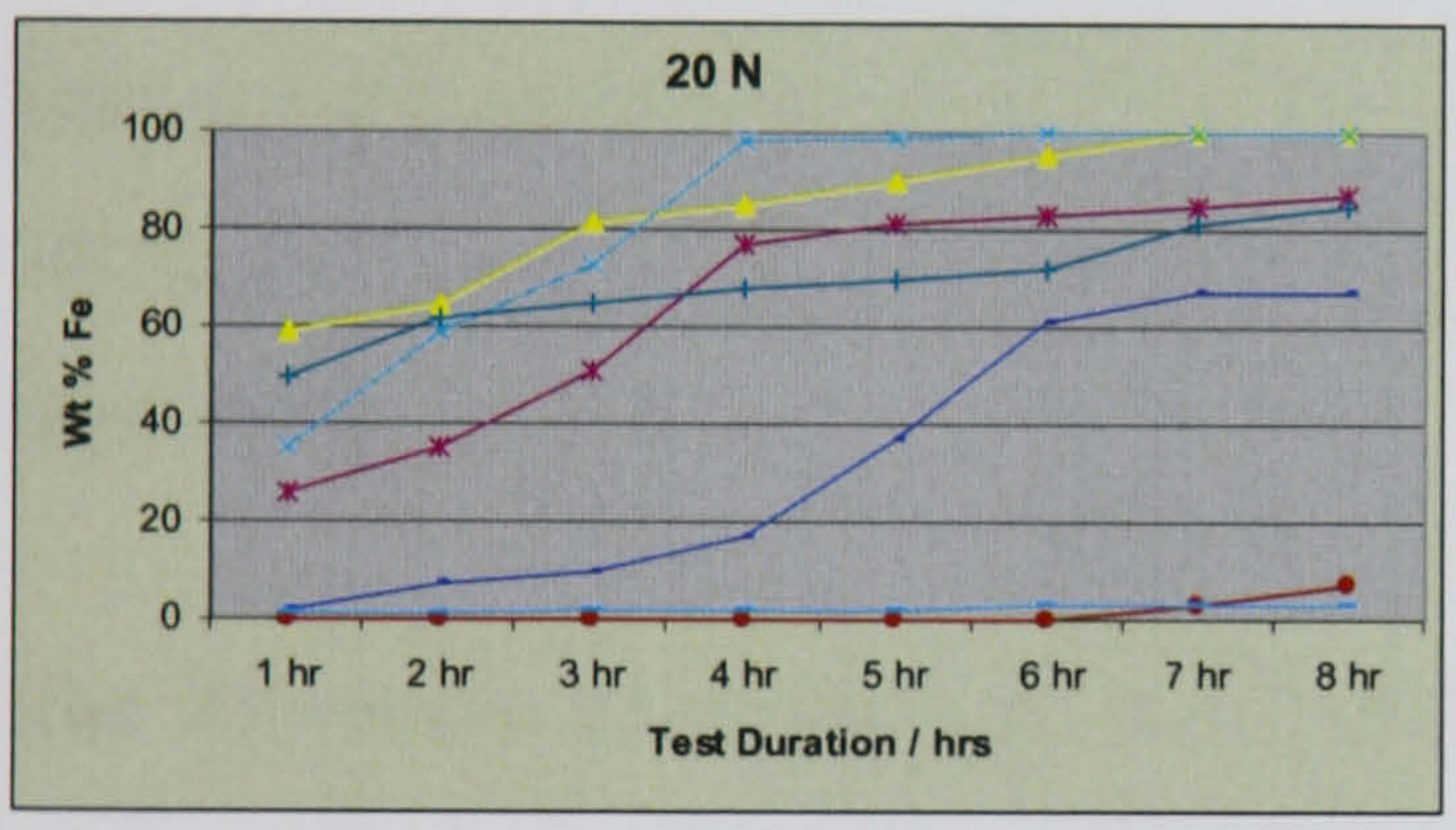

Figure 7.19b – 20 N test load

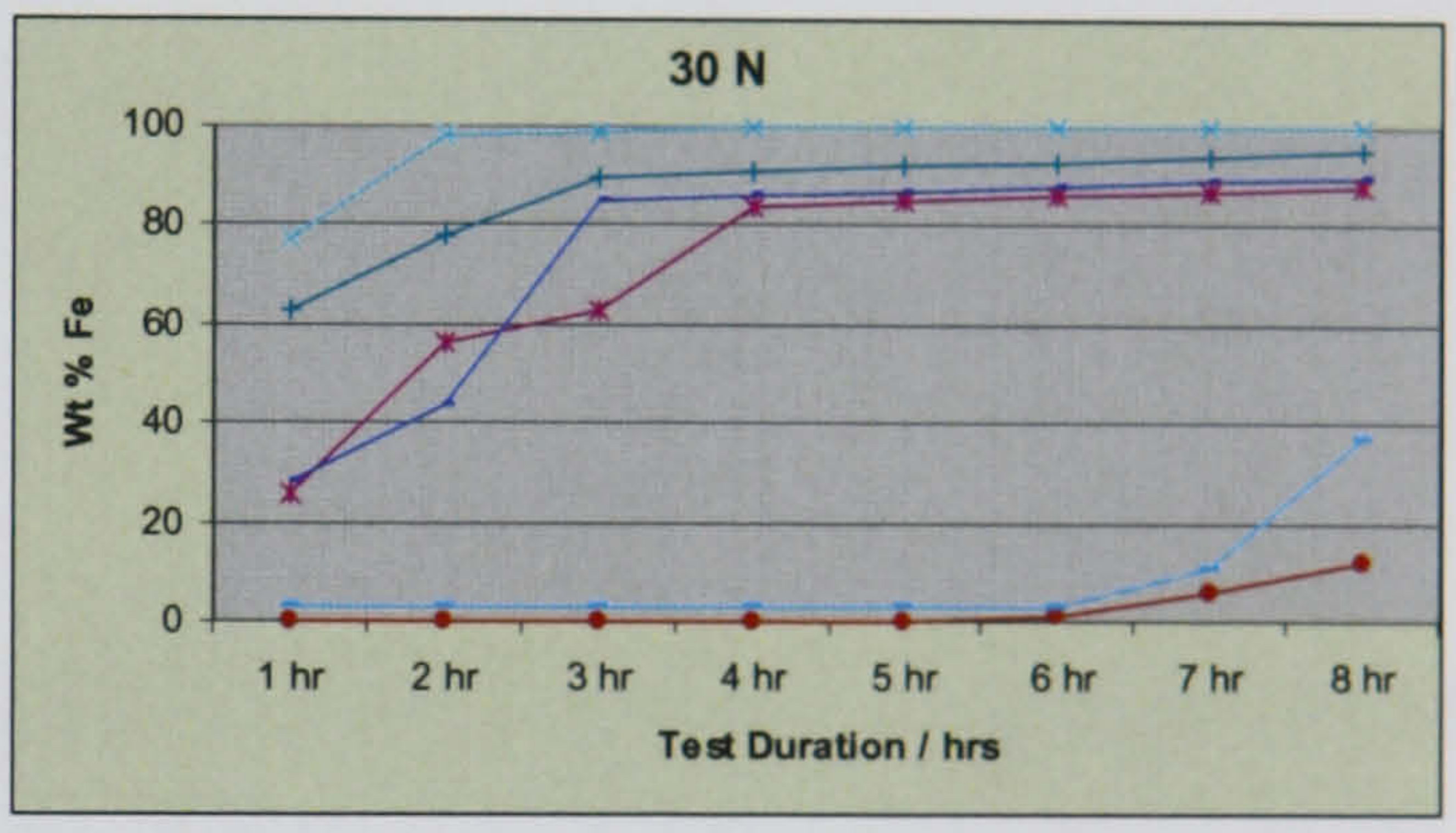

Figure 7.19c – 30 N test load

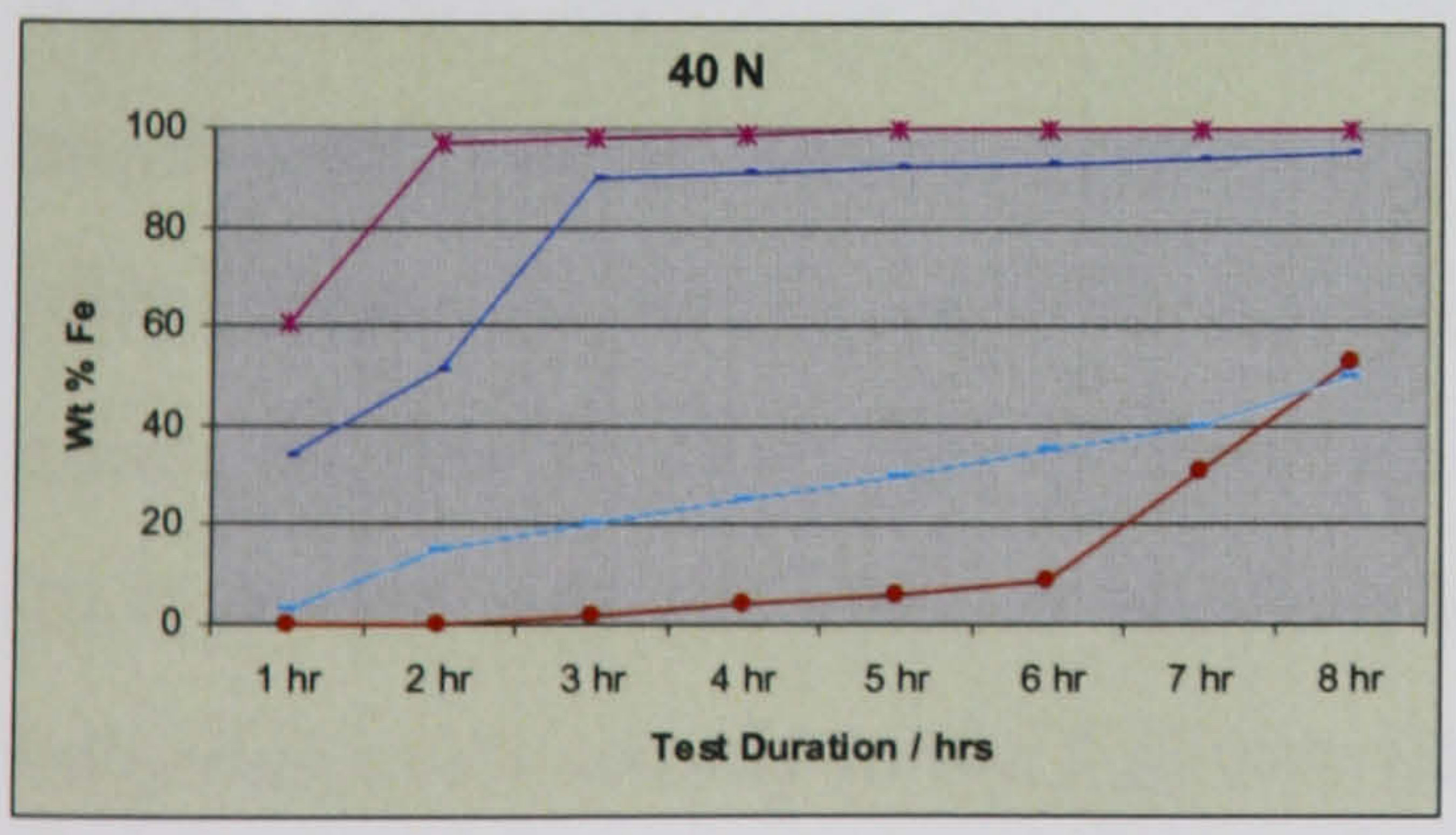

Figure 7.19d – 40 N test load

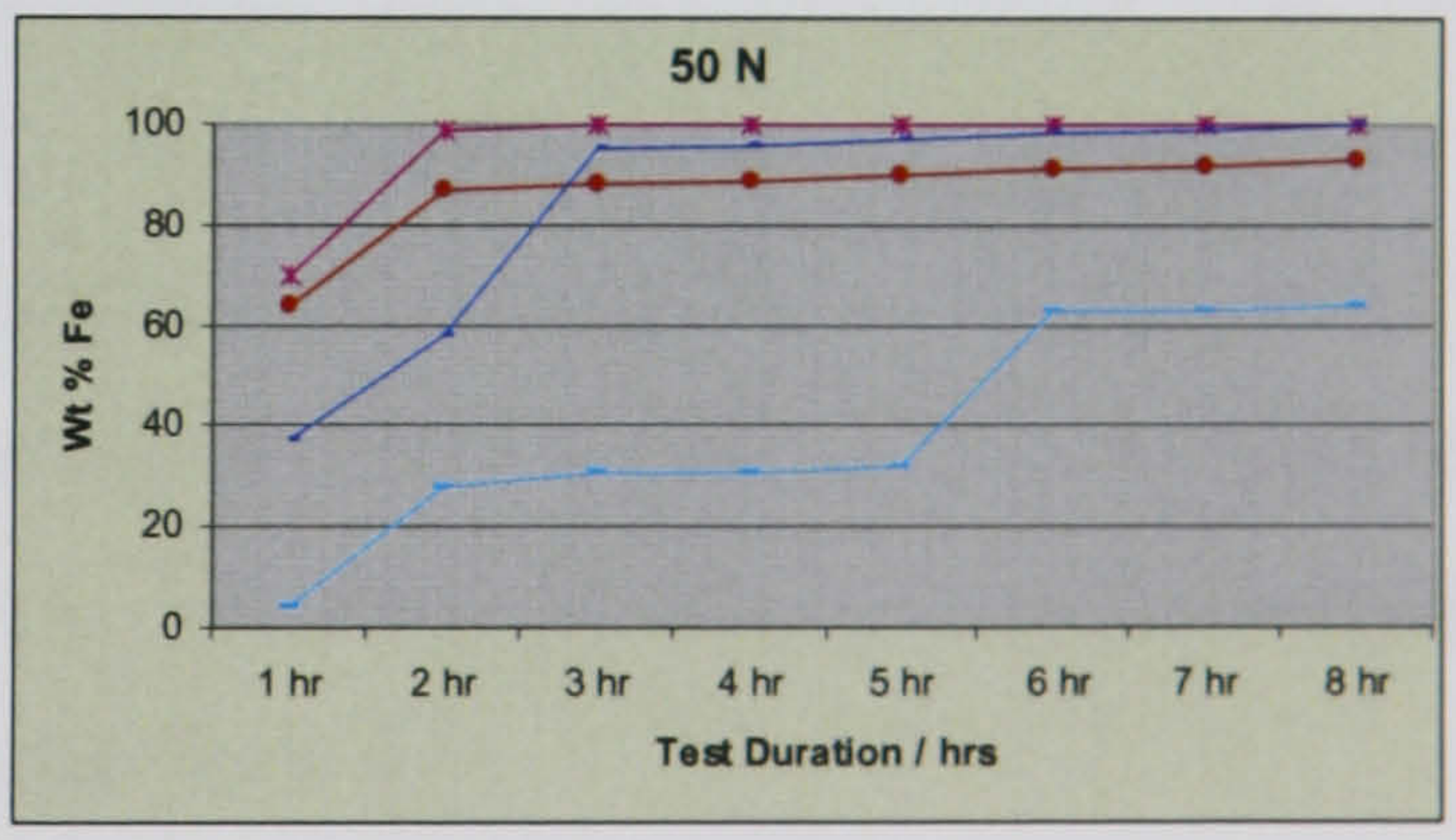

Figure 7.19e – 50 N test load

Both the 2 and 5 micron tin deposits are already significantly removed even with a 10 N load after just an hour of testing, from around 4-5 hours test duration, the coatings are practically depleted. The results for these two tin coatings are not included in the

20 N graph and onwards. as they were found to deplete from the onset with testing at the higher loads.

The 2 micron coating of tin-nickel appears to be resilient after the first hour. but then deteriorates significantly with the 10 N load. Failure of the coating occurs at around 4 hours with 20 N, and at the onset with 30 N. The 10 micron coating of tin performs similarly to the 2 micron tin-nickel deposit, with failure occurring at 3 hours with 20 N. and at the onset with 30 N. At testing with 10 N. the 10 micron tin coating performs similarly to the 5 micron tin-nickel, with the 2 micron tin-copper coating performing slightly better. The other two thicker coatings of tin-copper and the 10 micron tin-nickel deposit show little evidence of any affect at 10 N. even after an 8 hour test.

At 20 N, the 5 micron tin-nickel and 2 micron tin-copper coatings perform similarly. with failure occurring at around 5-7 hours. The 5 micron tin-copper commences with little significant damage after 1 hour, but depletes rapidly over the 4-6 hour region. At 30 N, the 2 and 5 micron coatings of both tin-nickel and tin-copper all fail by the 4 hour mark.

The 10 micron tin-nickel and tin-copper coatings are both resilient to damage after 8 hours of testing with 20 N. With 30 N, the tin-nickel appears to outperform the tin-copper. which begins to show evidence of substrate exposure after 8 hours. The tin-nickel continues to resist at 40 N, and the first signs of significant coating removal is after 7 hours, by which time the tin-copper appears to have reached a plateau. After 8 hours. the two coatings behave similarly. Testing the two 10 micron alloy coatings at 50 N reveals a larger contrast between the two, with the 10 micron tin-nickel coating behaving more closely to the 5 micron tin-copper deposit.

7.3.2 Time to Complete Coating Removal

As well as monitoring the depletion of the coating as testing time elapses, it is also important to assess the retention of the coating as testing force increases. To this end, a plot is created of the times taken to yield 80 wt % iron at the measured wear scar area against testing load (Figure 7.20).

Where a coating had yet to fail at the maximum eight hour test duration, the failure time was deduced by extrapolation of its data acquired for testing at 1 – 8 hours. Of particular note was that the 10 micron deposits of tin-nickel and tin-copper had yet to reach the point of failure at eight hours, even with the highest load. With extrapolation of their test results from 1 – 8 hours of testing, it was possible to estimate these values.

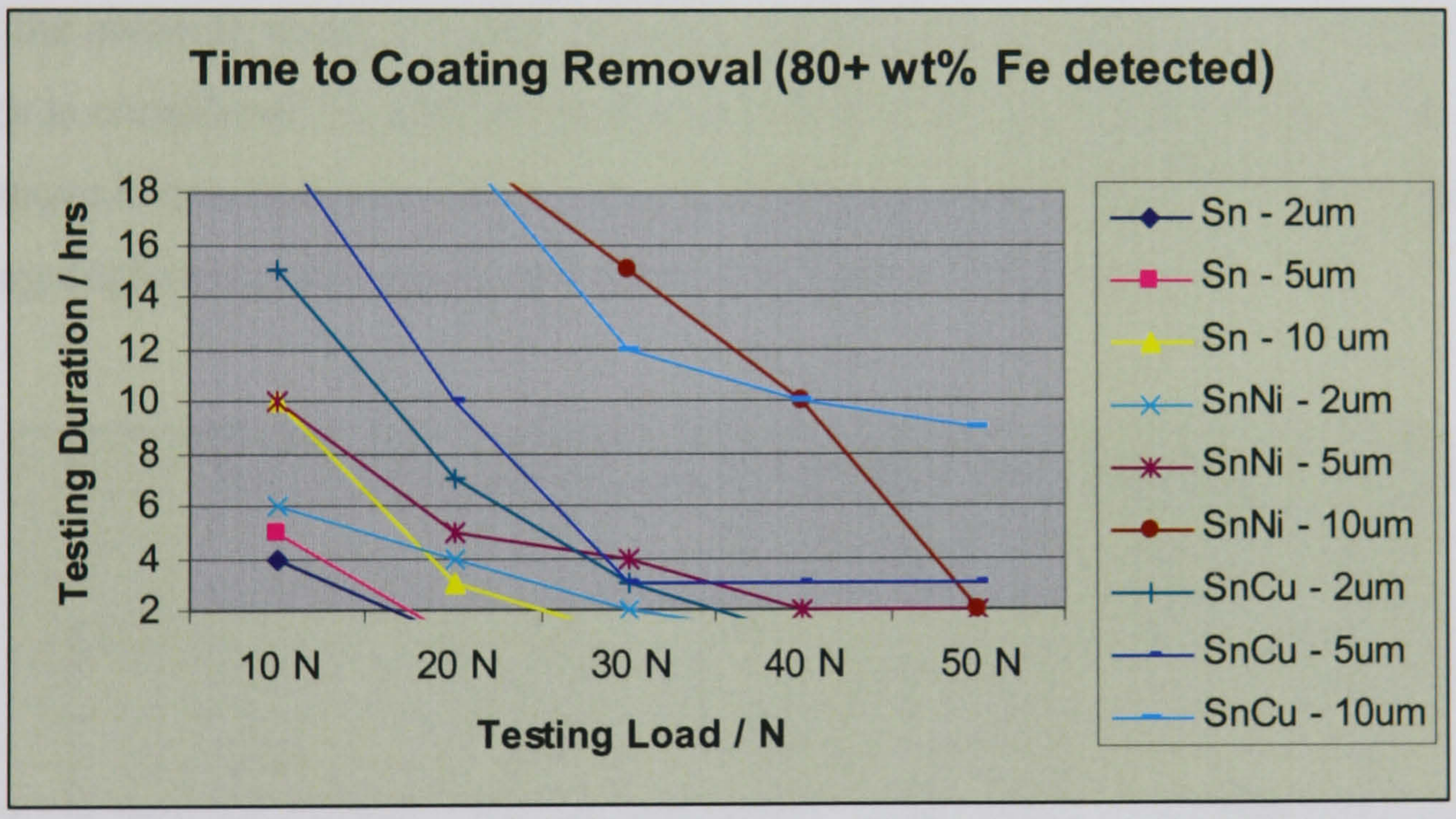

Figure 7.20 – Time taken to reach Critical Level of Coating Removal

Figure 7.20 enables the evaluation of the most resilient coating material assessed to near total removal for each load used. As expected, the tin coating depletes at the onset.

The 10 micron tin-nickel coating appears to exhibit similar levels of resistance to coating removal to the 10 micron tin-copper coating.

When the thickness is decreased to two and five microns, however, the tin-copper does appear to out-perform the tin-nickel.

7.3.3 Time to Breach of Coating

The assumption that detection of 80 wt % iron and above constitutes failure is an arbitrary field that has been assigned to the most severe category of coating removal in this research.

In reality, breach of a deposit could potentially condemn a component and inhibit the coating's ability perform its intended role. In some industries, it is seldom that a coating is completely depleted from a component before it is replaced, since the first sign of failure could be when the underlying substrate is initially exposed.

With the above in mind, it is also important that the time to detection of initial coating breach is considered for each of the deposits assessed. The point at which 20 wt % Fe and above is detected is chosen, as this is the boundary between the first two stages of coating depletion in this study, and graph is presented in Figure 7.21.

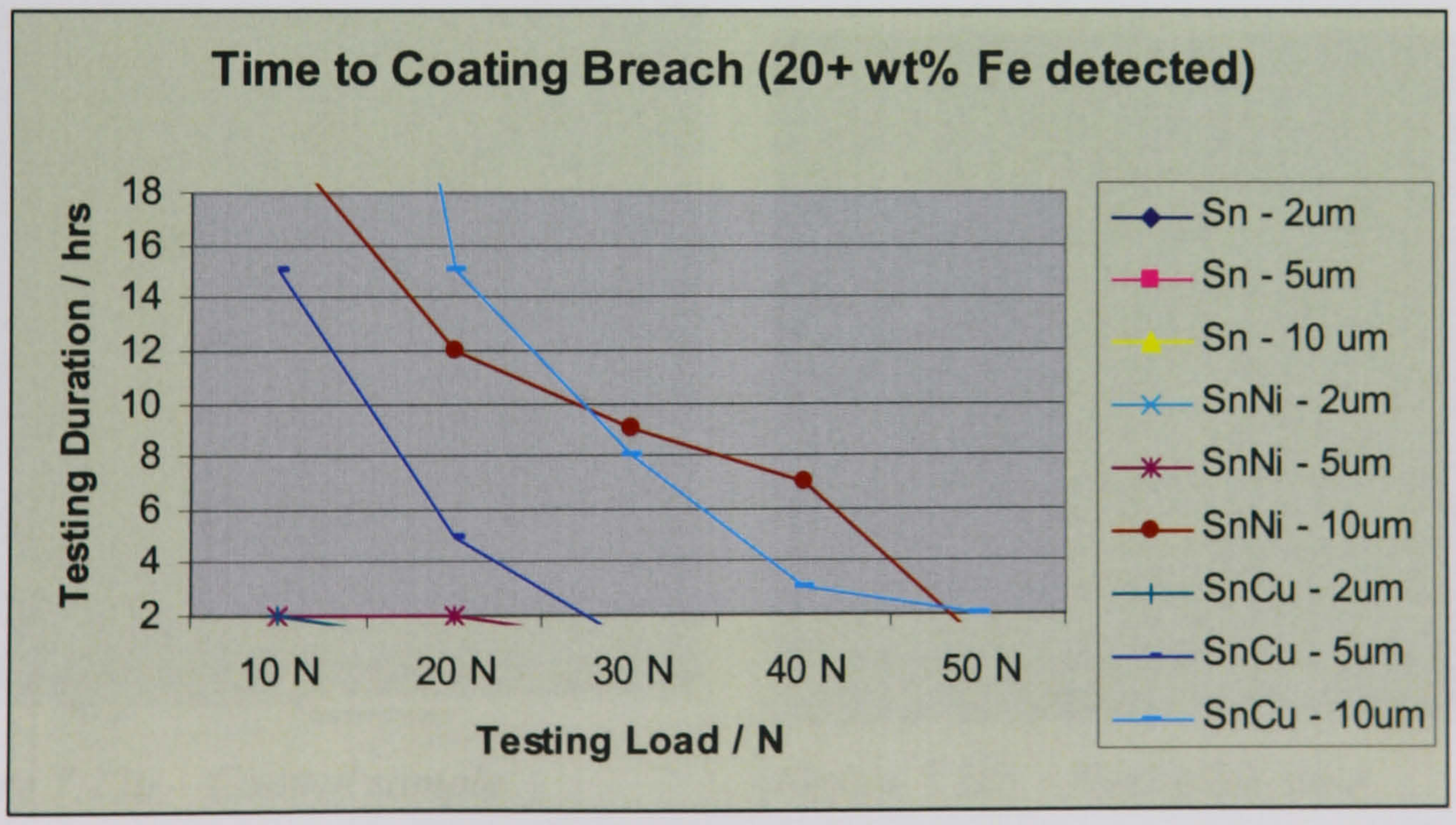

Figure 7.21 – Time taken to reach Moderate Level of Coating Removal

Although there are less data represented in Figure 7.21 than in Figure 7.20, the trend discussed before remains; the 10 micron deposits of tin-nickel and tin-copper appear to behave similarly, whilst the 2 and 5 micron tin-copper coatings seems to significantly out-perform their respective tin-nickel counterparts.

7.4 SEM EXAMINATION OF WEAR SCAR

The wear scars are also examined with Scanning Electron Microscopy in order to understand the nature of the mechanism behind the coating removal and depletion. This is achieved by high magnification assessment of the coating area affected by the interaction with the ceramic ball, particularly at the boundaries of the scar.

7.4.1 Surface Inspection

First impressions of the wear scar appearance are apparent during the EDX acquisition stage, where the scar exhibits a progressively more damaged appearance as the degree of coating retention develops from a Negligible status to a Critical one. This is presented by the series of images in Figure 7.22, showing deterioration of the tin-nickel coating, which is also representative of the tin and tin-copper coatings.

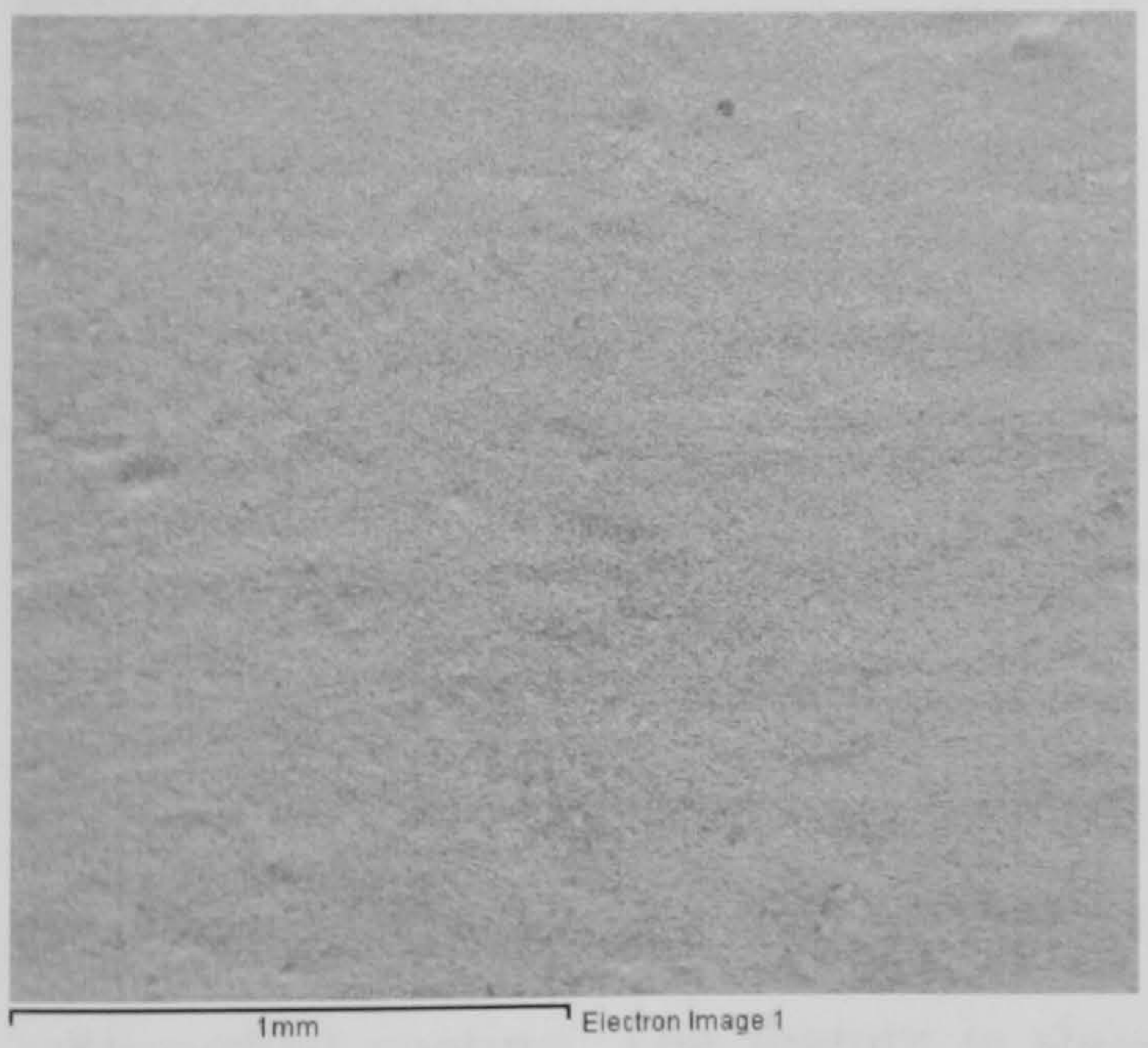

Figure 7.22a – Control sample

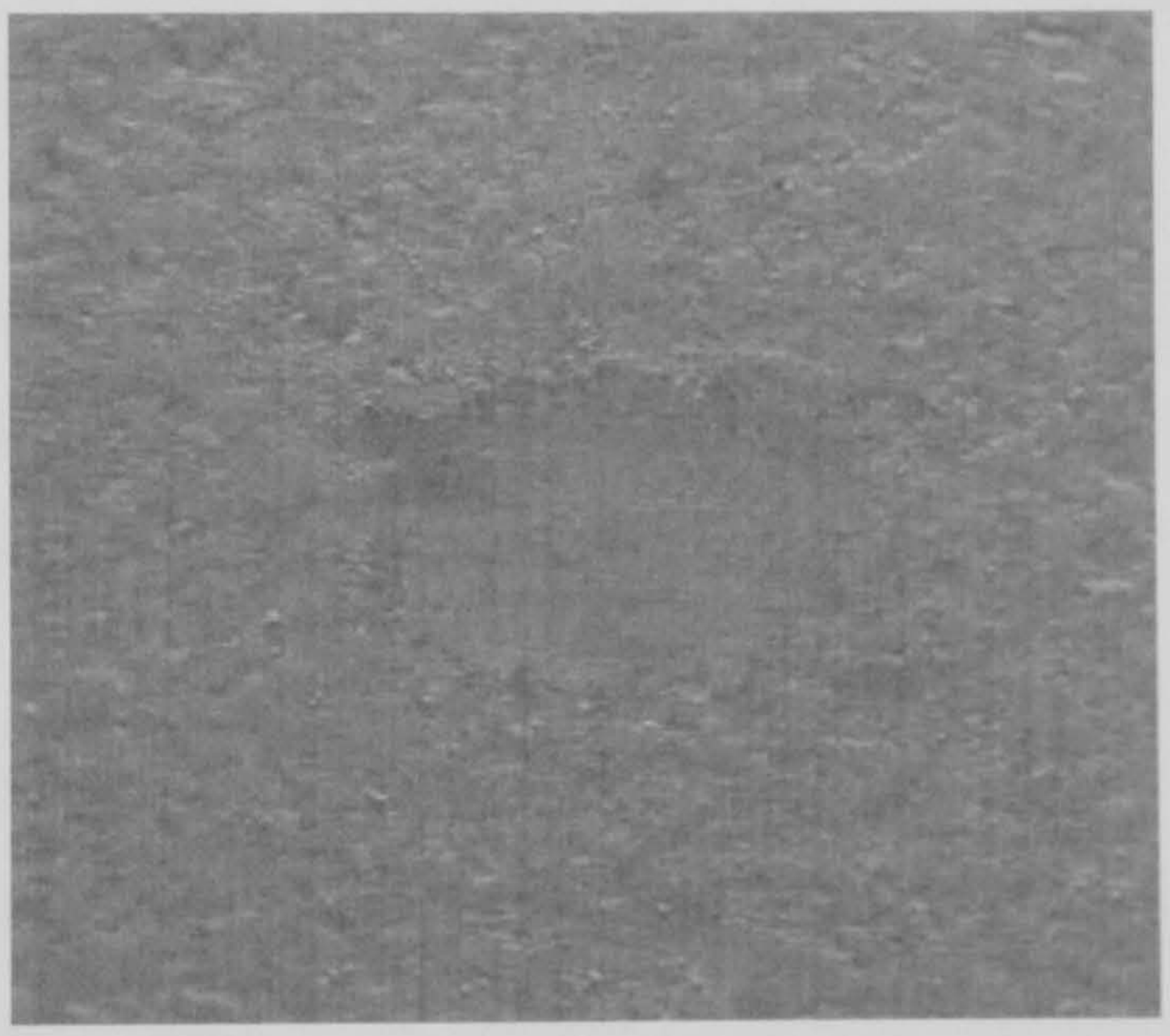

Figure 7.22b – Negligible state

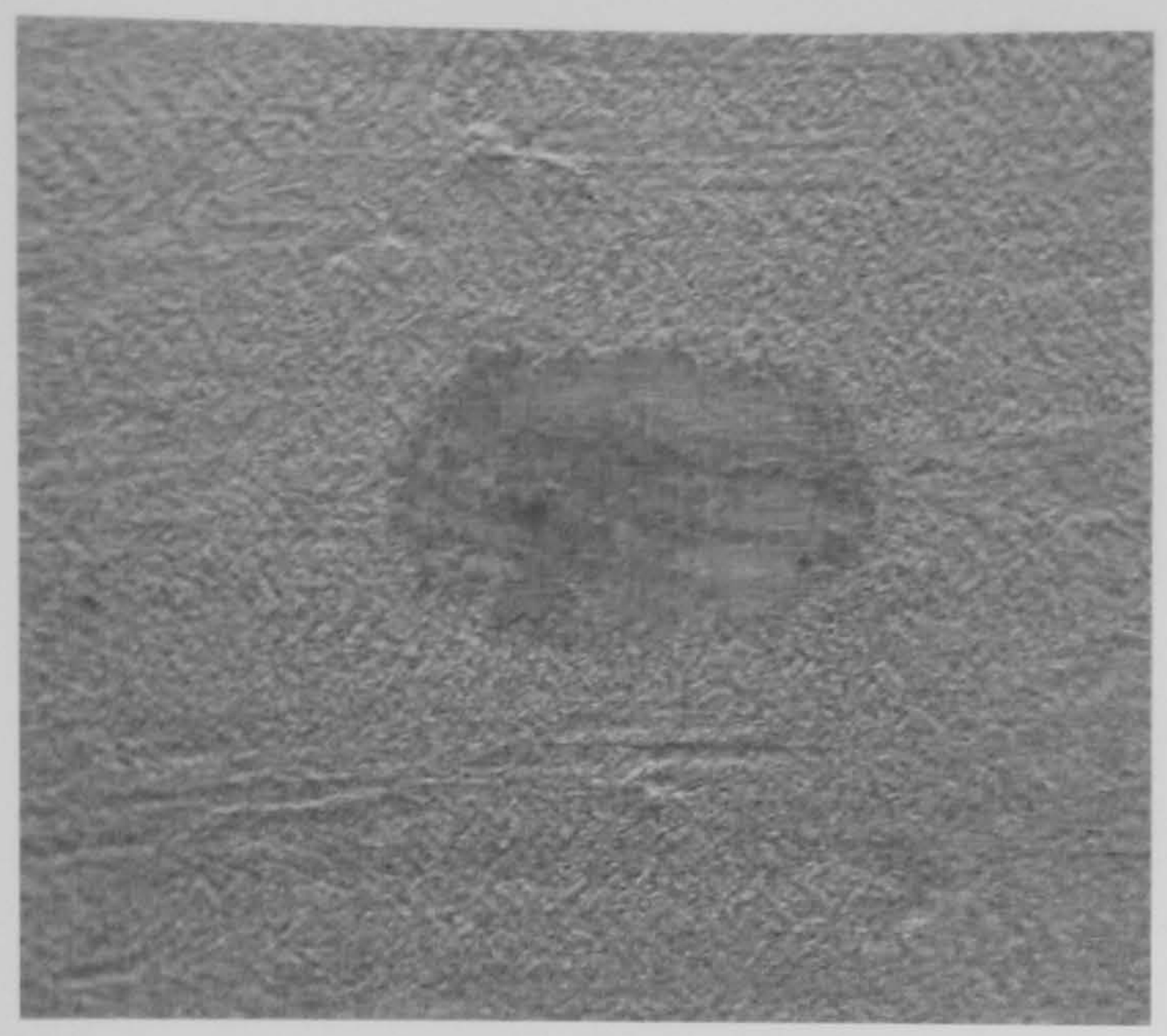

Figure 7.23c – Moderate state

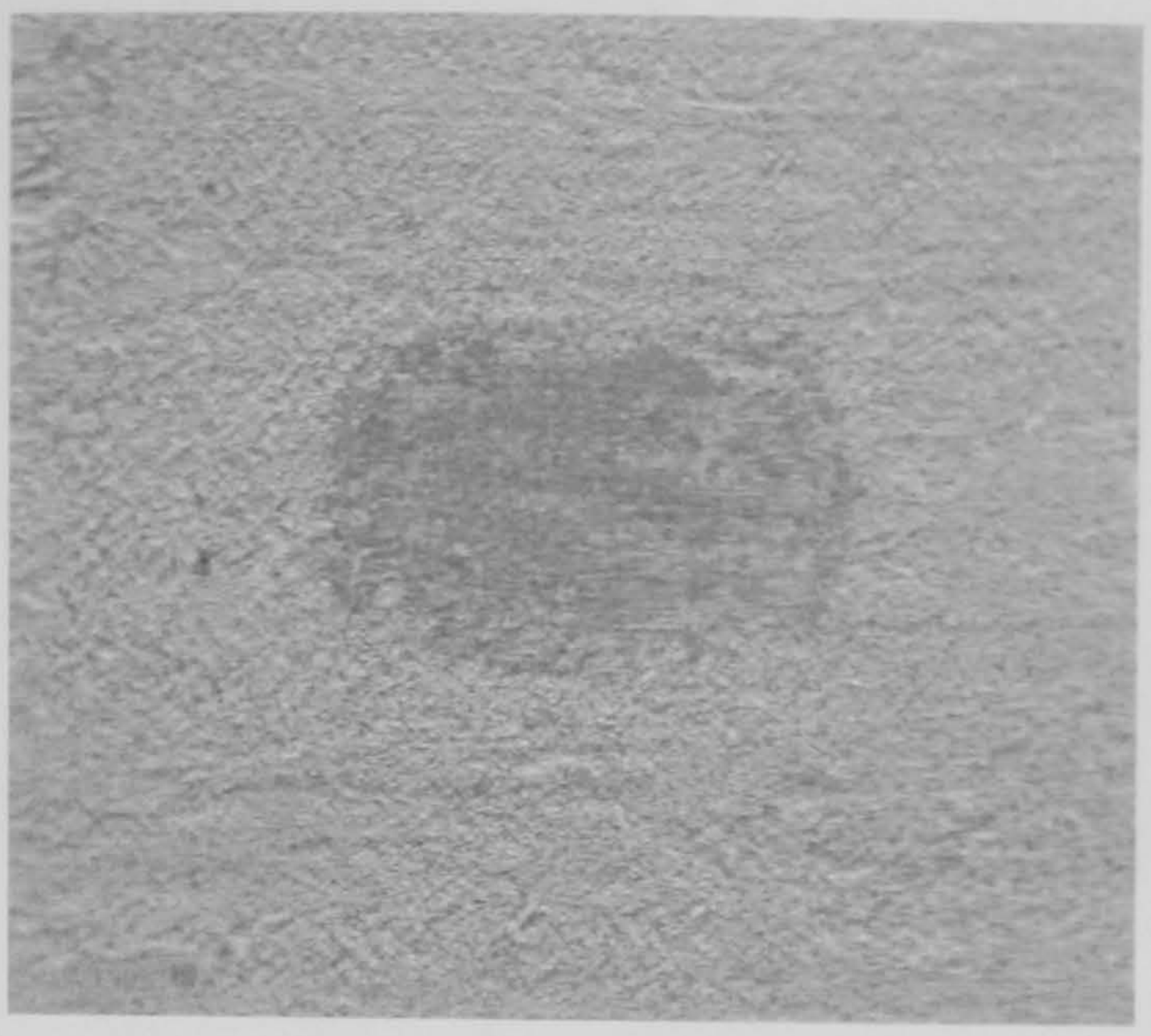

Figure 7.23d – Significant state

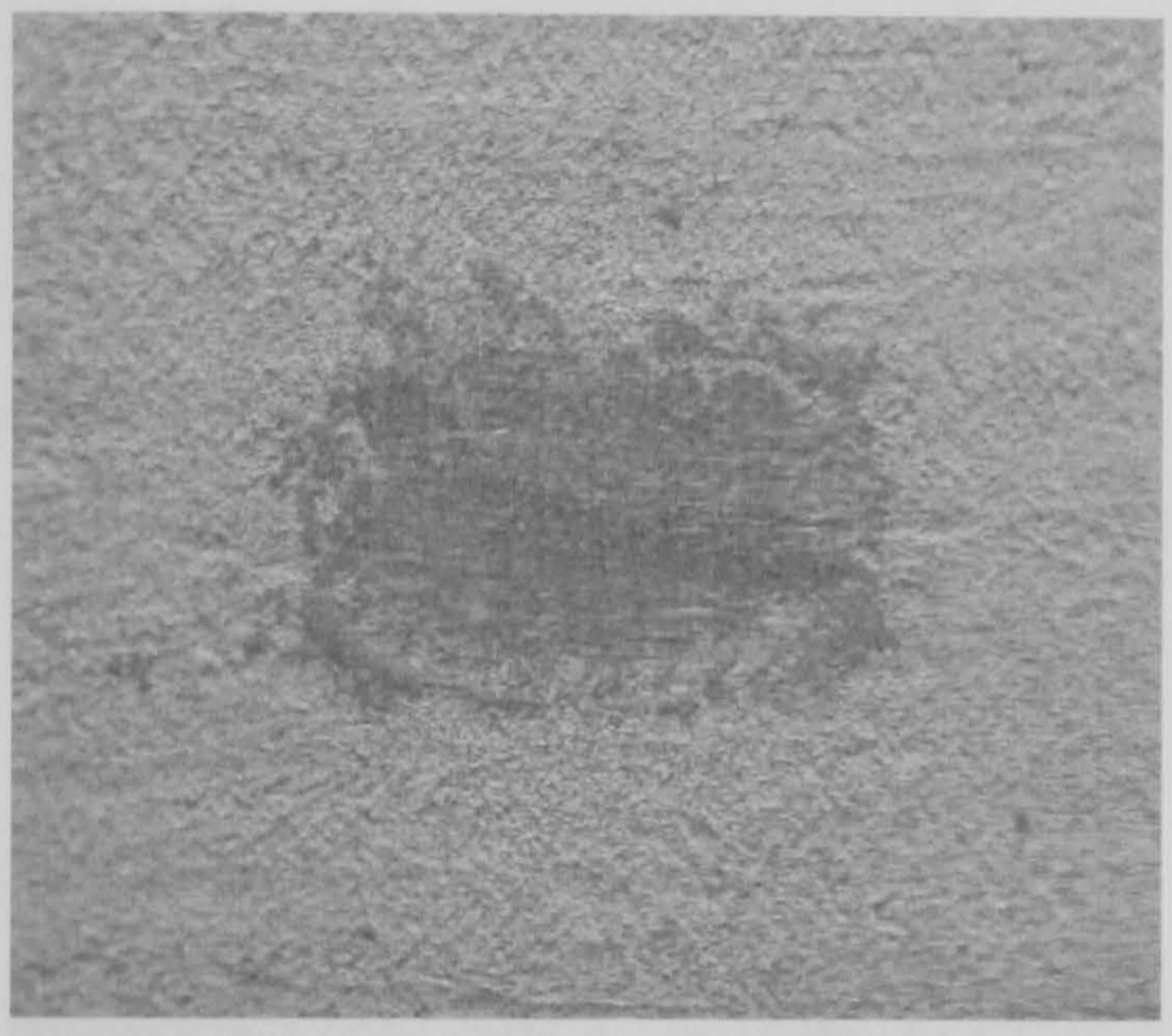

Figure 7.23e – Critical state

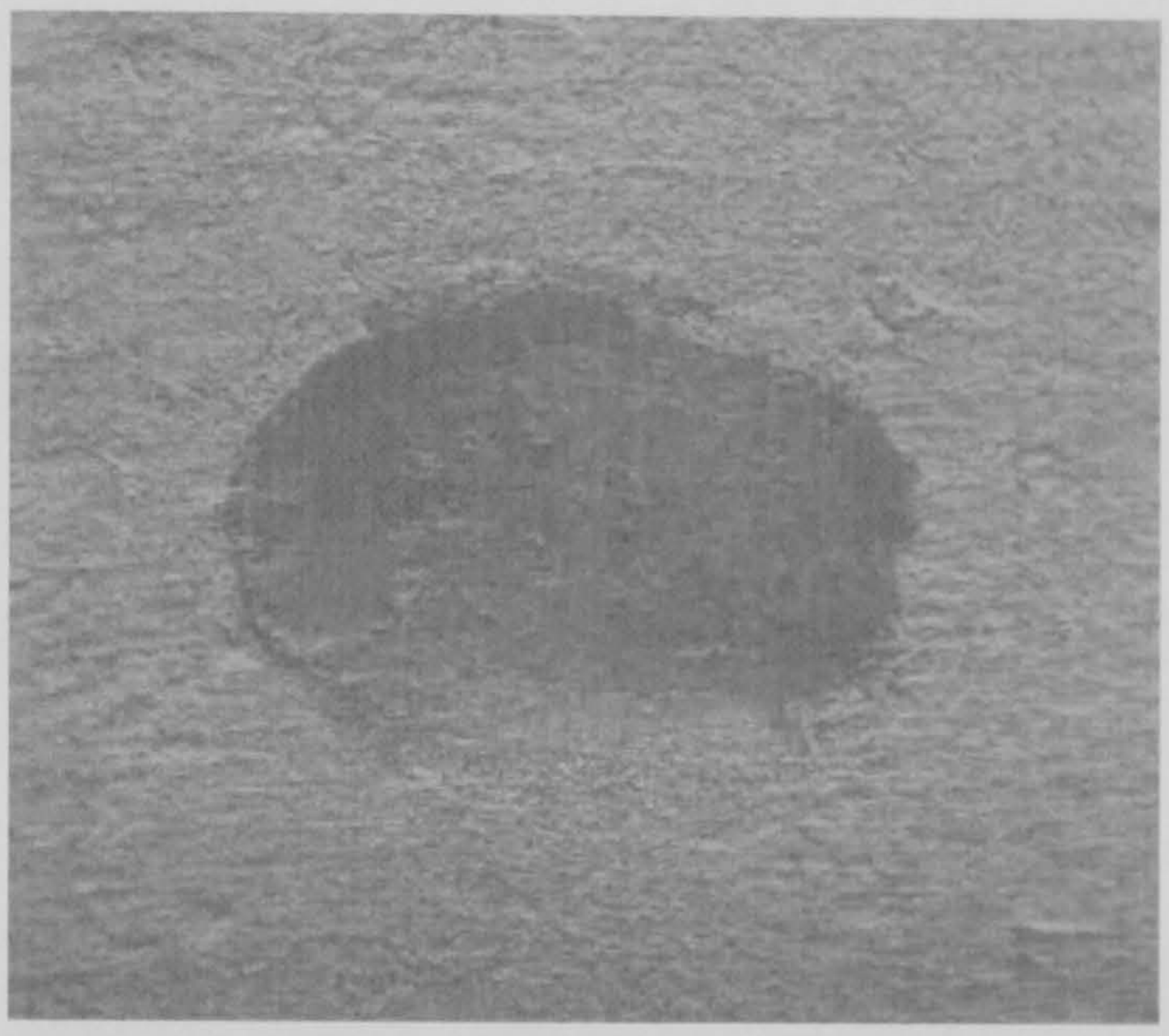

Figure 7.23f – Failed state

The above progression of the wear scar, with the gradual depletion of the coating clearly visible, is expected. To understand the way by which the coating is removed, however, requires examination at a higher magnification.

Inspection of the wear scar edges at high magnifications reveal what appears to be an elevation in topography that seemingly rises above the height of the rest of the undisturbed coating. The feature is shown in Figure 7.24, which is of tin, although also representative of the tin-nickel and tin-copper coatings.

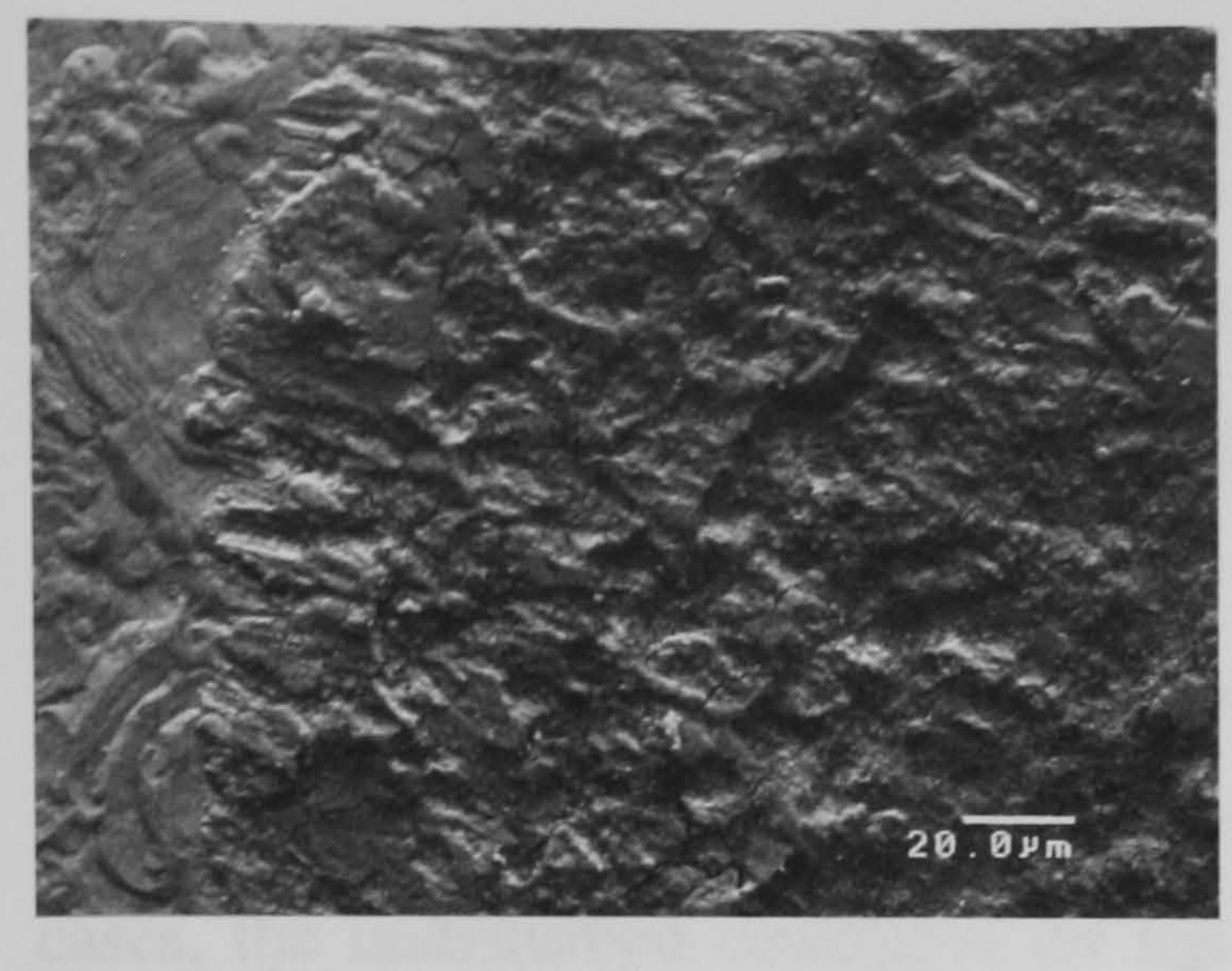

Figure 7.24a – Moderate state

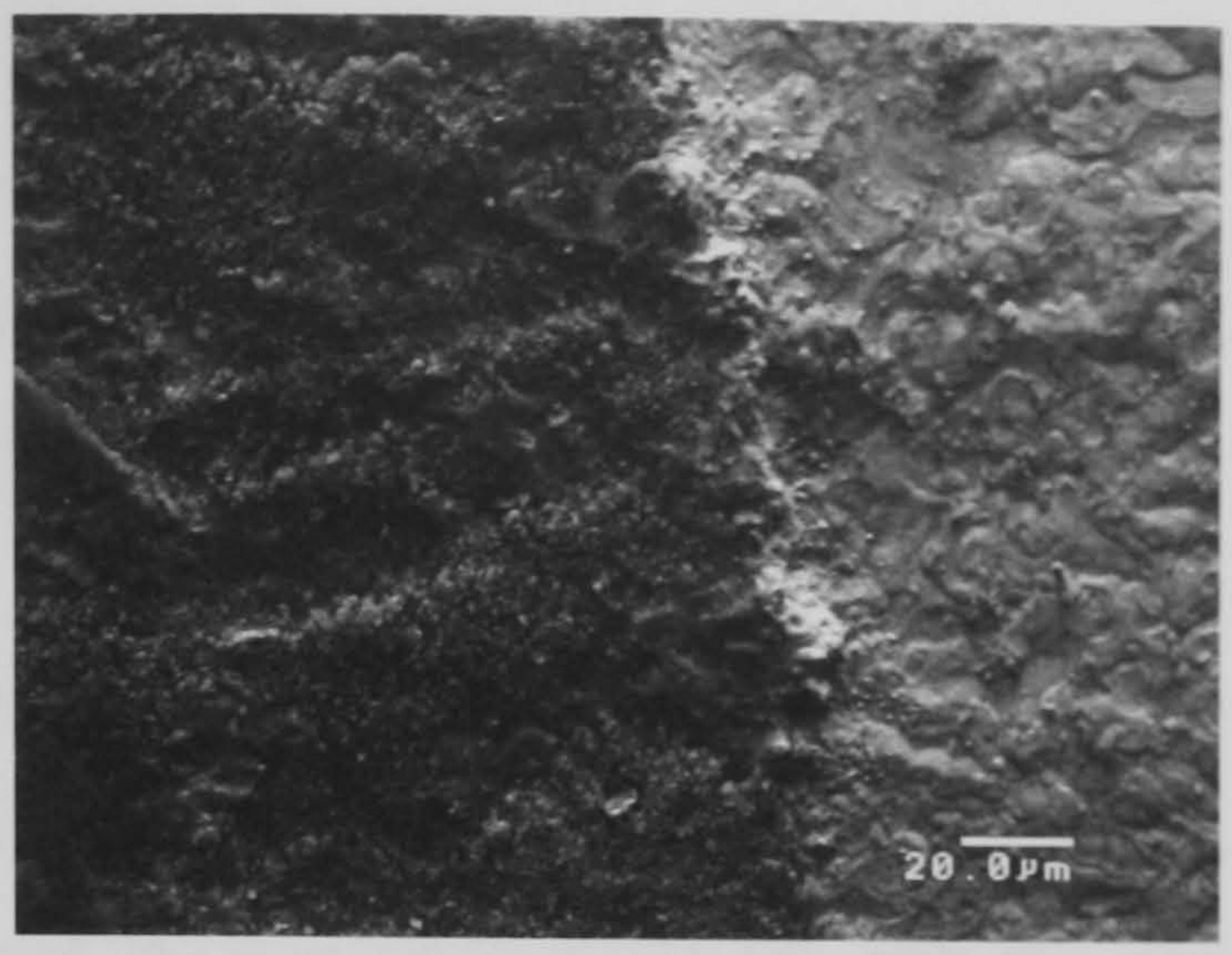

Figure 7.24b – Critical state

This is unexpected, since the wear scar is expected to be an area of missing coating material, suggesting that there should be a dip in topography as one traverses the boundary from the undisturbed coating to the scar area.

Examination of the area in the centre of the wear scars revealed areas where the coating appeared to be retained in various zones. As the severity of the coating removal increased, the number of these zones reduced. Examples of these zones are shown in Figure 7.25.

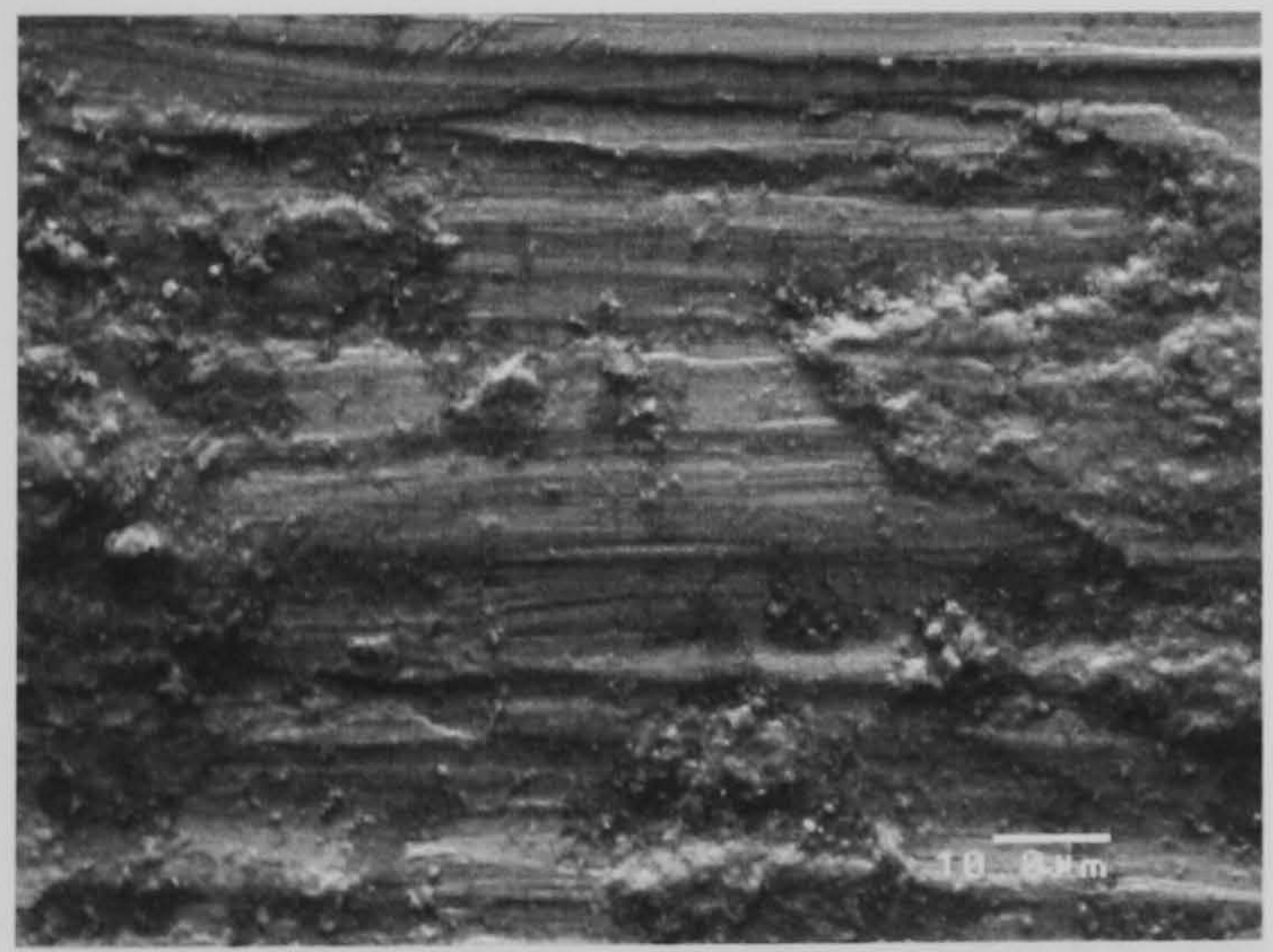

Figure 7.25a – Moderate state

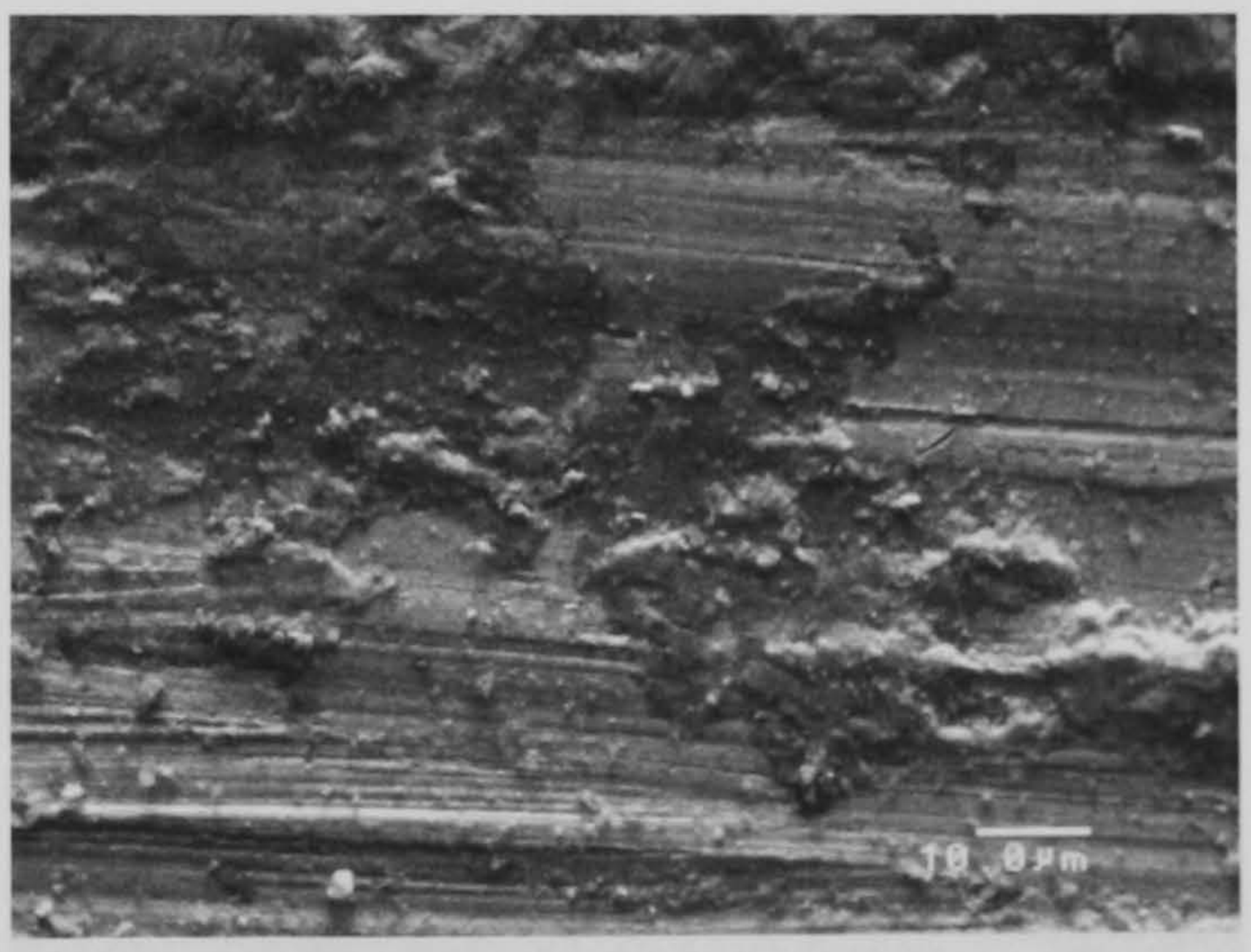

Figure 7.25b – Critical state

7.4.2 Cross-sectional Analysis

With the observations from Section 7.4.1 in mind, the wear scars are microsectioned and metallographically prepared with techniques described earlier in the thesis.

The first areas examined are the elevated features associated with the edges of the wear scar and Figure 7.26 show examples of these in the cross-sectioned state. In both cases, the undisturbed coating is on right and the wear scar is on the left; the two zones are separated by a mound-like feature that encircles the wear scar area.

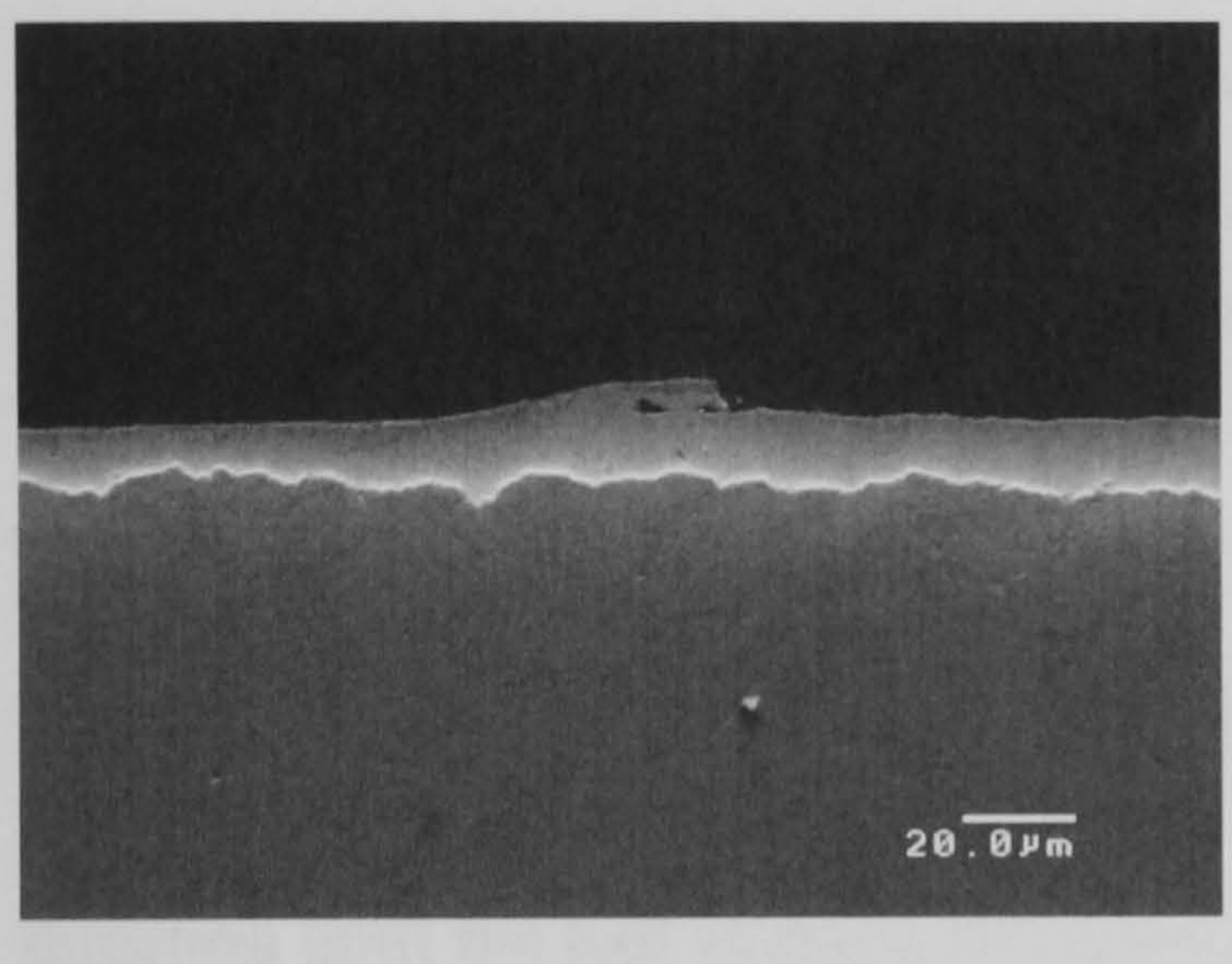

Figure 7.26a – Moderate state

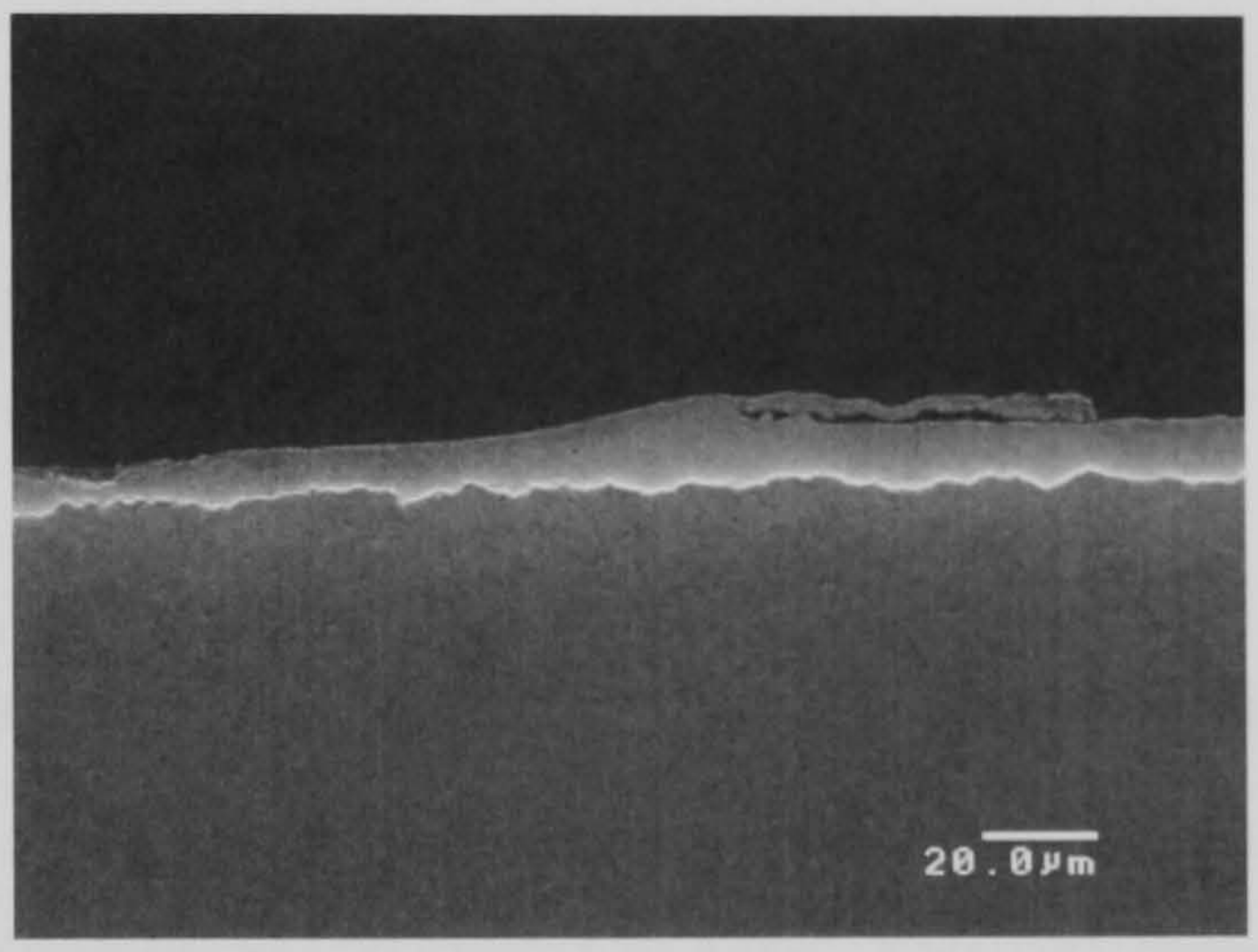

Figure 7.26b – Critical state

As can be seen from the micrographs above, the elevation appears to be composed of an accumulation of coating material. Figures 7.27 show these areas at a higher magnification.

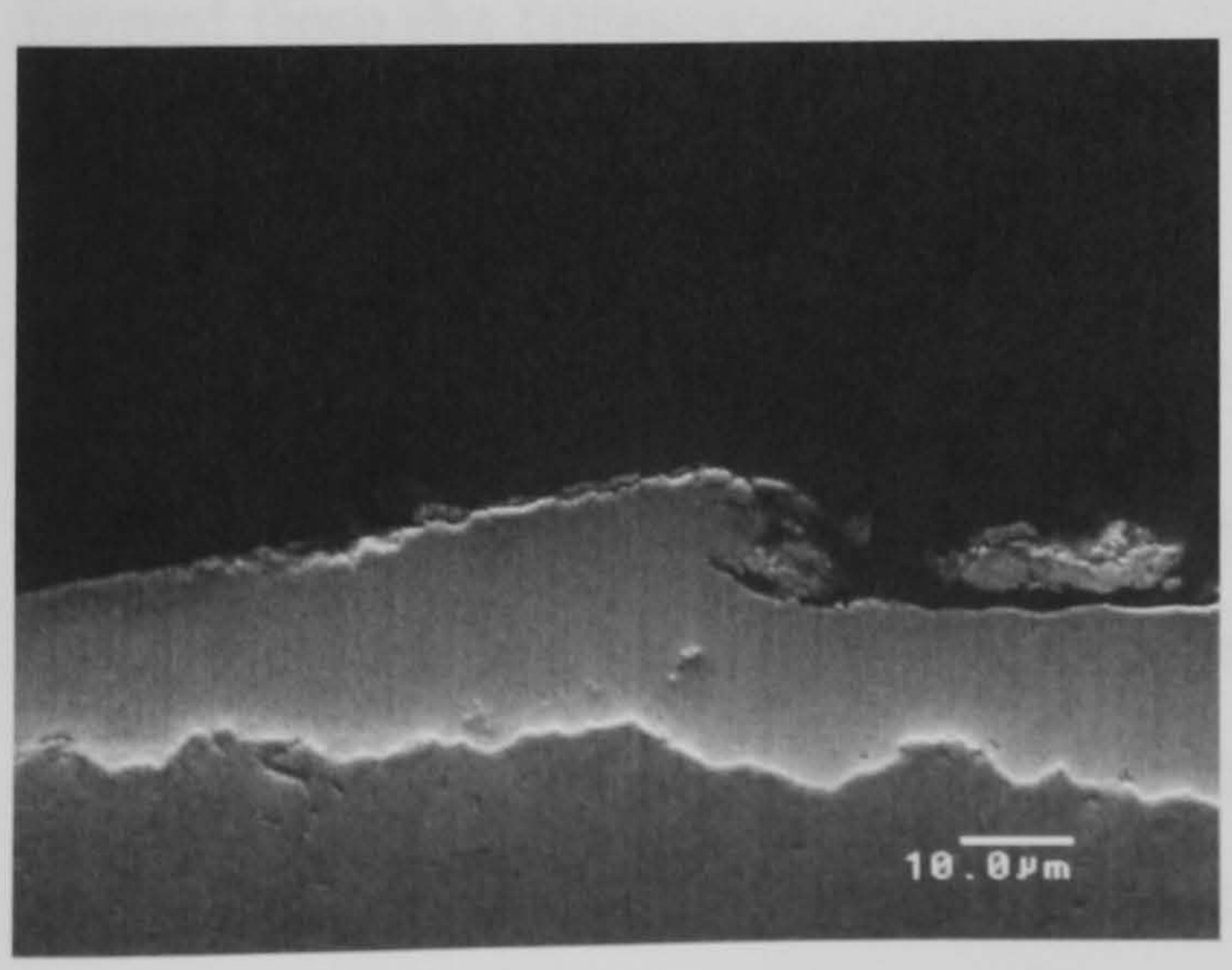

Figure 7.27a – Moderate state

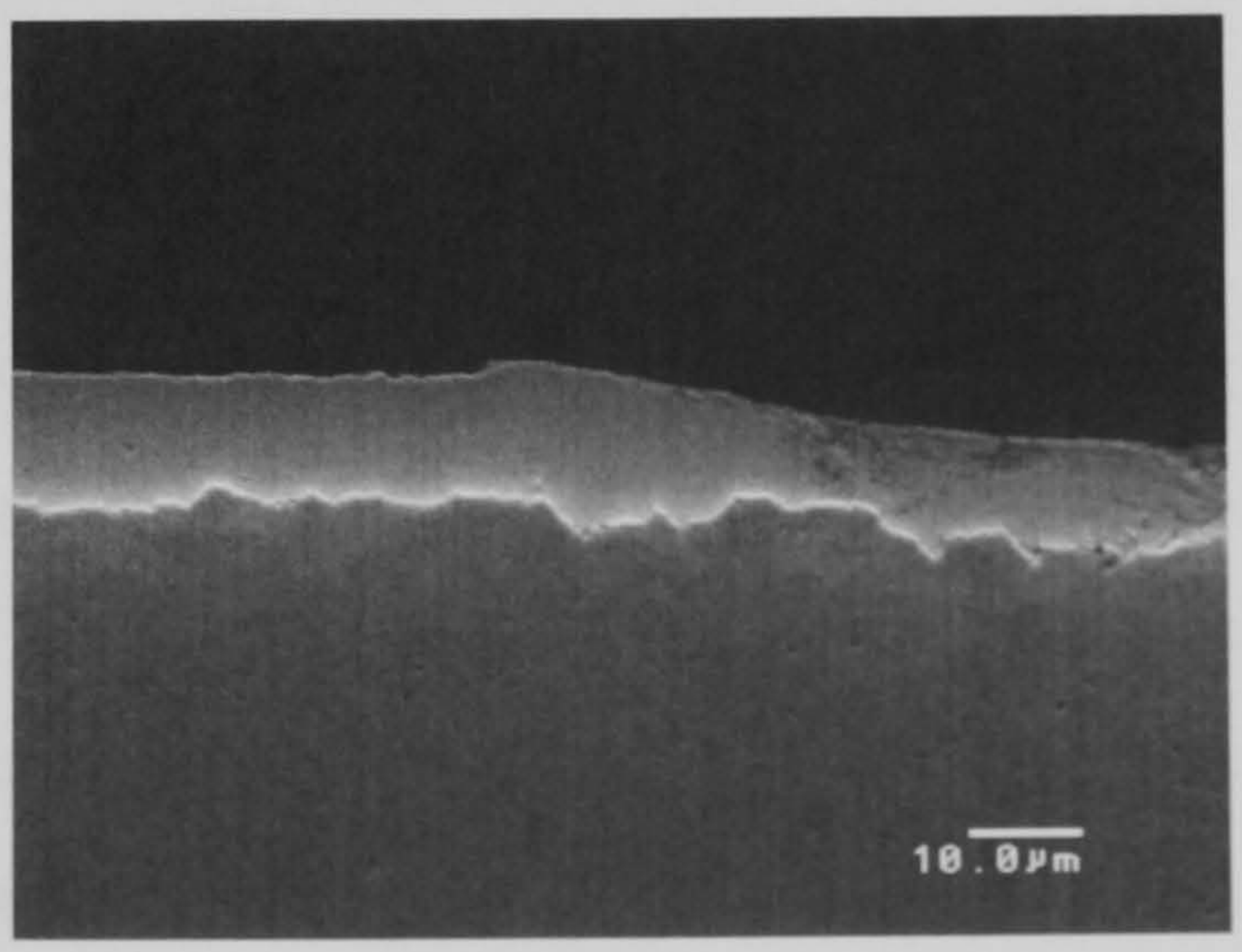

Figure 7.27b – Critical state

The action of coating material collection at the edges of the wear scars suggest some form of transit mechanism that is resulting from the repetitive forward backward movement of the ceramic ball over the coating. It is believed that this phenomenon is due to the ductile nature of tin and the two tin alloys investigated, which is reflected by the lack of any cracks or brittle fracture in any of the samples seen. The absence of interfacial cracking and adhesive failure is an indication of the importance of an appropriate substrate pre-treatment step prior to the electrodeposition.

It is understood that successful modelling of wear, although not well established, requires information regarding where cracks are initiating from, in order to ascertain further information on the nature of the debris formed [35]. The lack of crack propagation within the coating material, or at the interface with the substrate, suggests that conventional fracture mechanics cannot be used to explain and predict the failure mechanisms observed.

One theory is that the ductile coating material is disturbed by the alternating forward/backward movement of the ceramic ball. Material is pushed by the ball in one direction until the ball changes direction and leaves the material behind. The ball then proceeds to push material in the other direction until it completes its stroke and changes direction again.

In this way, progressively more material is collected at the extreme ends of the ball's trajectory until the test duration has elapsed, by which time, a wear scar has been formed from the continuous pushing of material away from the centre of the wear test area.

The area in the middle of the wear scar is also examined in the cross-sectioned state (Figure 7.28). From the micrographs, the removal is seemingly determined by the topography of the substrate. For example, the coating deposited on a particularly elevated portion of steel would be initially susceptible to deformation. Since the electrodeposition follows the contours of the substrate, the coating applied to the troughs of the substrate appear to be afforded some protection and are seemingly the last of the coating to be removed.

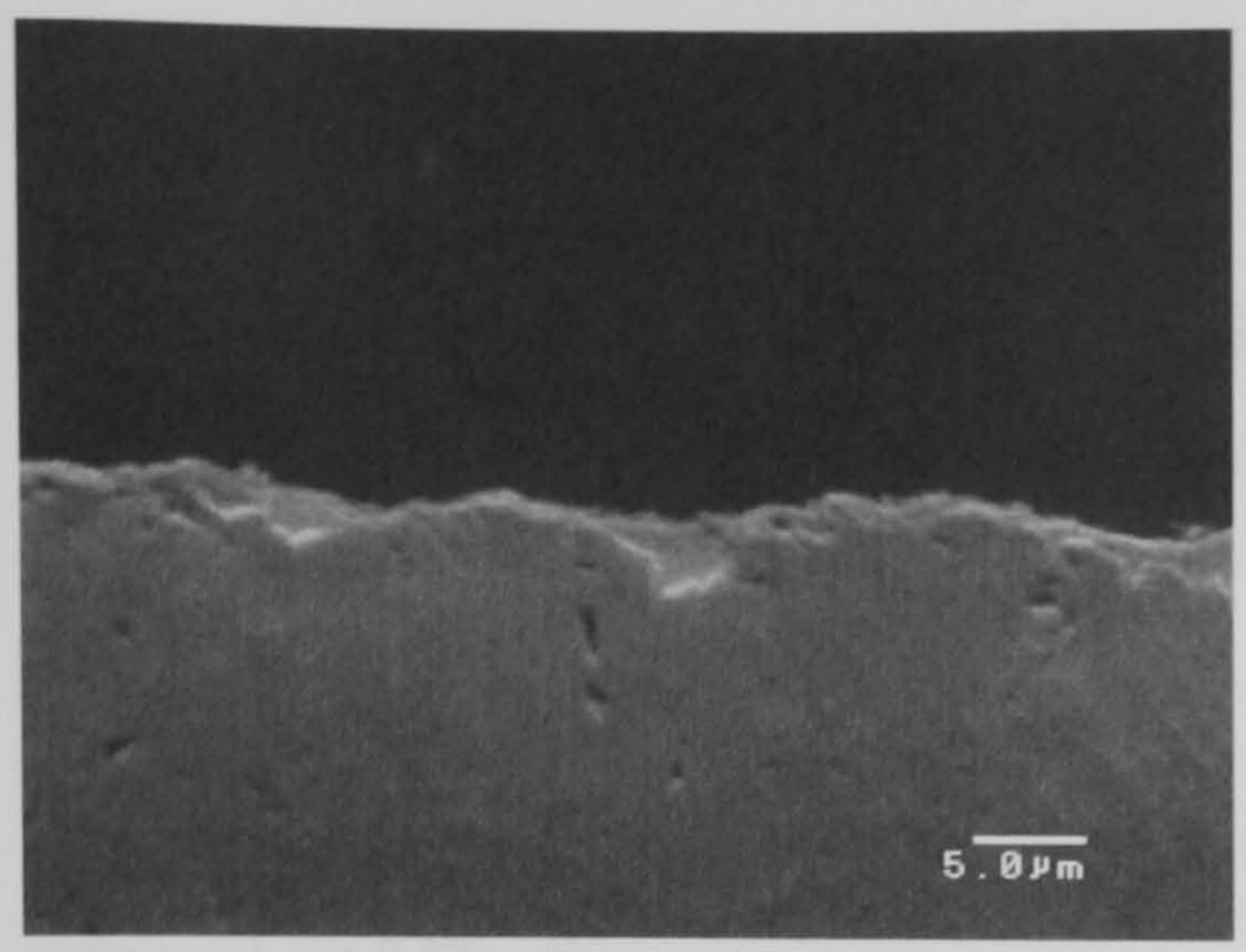

Figure 7.28a – Moderate state

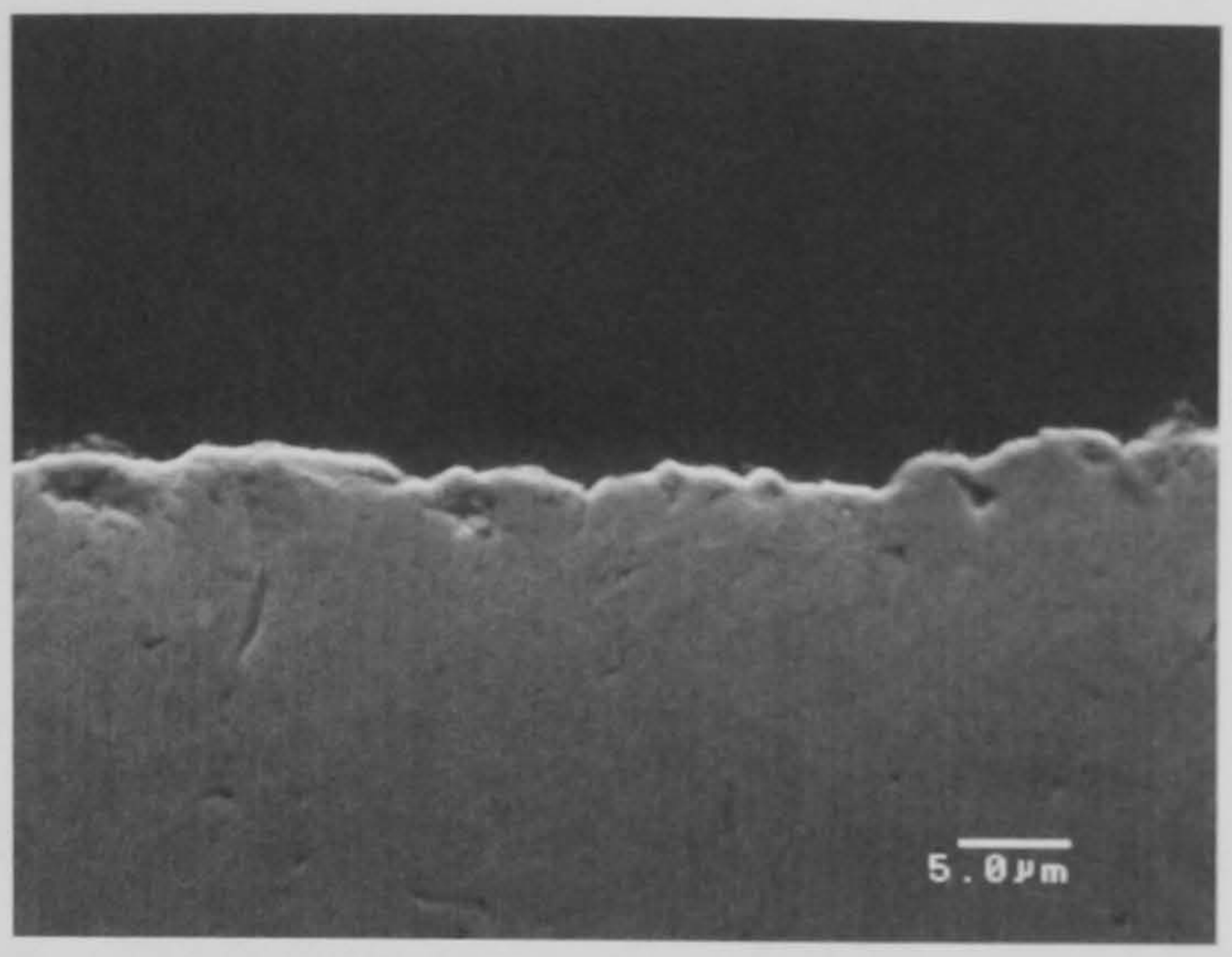

Figure 7.28b – Critical state

It therefore makes sense that the pre-treatment stage has a strong influence on the coating retention, although there are conflicting consequences of having a substrate with a high surface area. A coating applied to such a substrate would be particularly prone to removal at the onset, with the coating at the crests being the most vulnerable. As the wear continued, the high surface area of the substrate could offer more topographical protection to the coating, making the last few pockets of coating particularly difficult to remove. Although, it can be argued that by such a stage the coating has already failed to fulfil its duty and it is the substrate that is mainly being abraded.

As a side observation, it was noticeable from the cross-sectioned micrographs that the areas of exposed steel were significantly smoother than the topography of the steel that was covered with the coating. Bearing in mind the pre-treatment measures described in Chapter Three used to increase the surface area of the steel substrate, this observation would suggest that the ceramic ball, having displaced the coating, is already starting to abrade the steel. It is understood that the steel undergoes an adhesive wear mechanism caused by iron transfer to the ceramic ball [63] and an abrasive wear mechanism resulting from oxidised steel debris [56].

7.5 CHAPTER SUMMARY

As expected, the degree of damage introduced to a surface coating, from an abrasive ball on plate configuration, is proportional to test duration, coating thickness and applied load.

Again, as expected, the pure tin coatings were found to be the least resistant to coating removal and the first deposits to be breached. Testing at 30 N was already found to remove the thickest deposit at the shortest test duration increment, and therefore no testing was attempted at 40 and 50 N.

The tin-nickel and tin-copper alloys were found to be significantly more resilient, which is also expected given that tin has historically been alloyed with other metals to improve its mechanical properties. As an example, a two micron deposit of tin-nickel was found to behave similarly to a ten micron coating of tin. A more durable deposit is obviously more desirable since the service lifetime of the coating is longer, and labour and material costs will be reduced.

Tin-copper was found to be slightly more resistant to coating removal than tin-nickel in general. As a comparison, the results of a two micron deposit of tin-copper and a five micron of tin-nickel were similar. At the greatest thickness assessed, ten micron, the tin-copper and the tin-nickel deposits performed similarly, with the tin-nickel even being found to be slightly superior under certain conditions. Given that it is accepted that tin-copper exhibits adequately favourable wear resistance to be used as a coating on bearing materials in industry, it appears that, under certain circumstances, tin-nickel could also be adopted to offer a similar level of resistance. The advantages of using a tin-nickel deposit over a tin-copper one are mainly in the production aspect:

- Cyanide-based plating baths are still widely regarded as the most effective for electroplating tin-copper. Tin-nickel plating baths are cyanide-free.
- Regular control and monitoring of a tin-copper electroplating process is required to deposit the alloy in the desired proportions, with the tin:copper ratio being influenced by factors such as temperature, bath composition and

current density. Tin-nickel is consistently deposited in the Sn65Ni30 ratio despite wide fluctuations in its plating conditions.

The coating removal mechanism appears to be the result of the ductile tin or tin alloy material seemingly pushed out towards the edges of the wear scar by the ball as it traverses across the coating surface. The coating material is progressively transported to these locations, with the most vulnerable areas being those where the coating is adhered to the elevated portions of the substrate topography. Although a more even substrate finish could promote a more predictable and uniform removal pattern, the greater surface area conferred by the rougher substrate promotes greater adhesion with the coating.

The mechanism behind the coating removal observed in the SEM examination is discussed in greater detail in Chapter Eight. Also included is the influence of thermal effects from the dry sliding condition, and its correlation with the findings in this Chapter in order to generate further discussion regarding the differences in performances between the tin-nickel and tin-copper coatings.

CHAPTER EIGHT
DISCUSSION

8.1 INTRODUCTION

The purpose of the Discussion Chapter is to consider the results from the wear testing and to try to provide explanations and theories to account for the findings. It is understood that two of the more common ways which protective coatings can fail are by build-up of wear debris and breakdown of lubricant [35, 63]. Owing to the relatively soft nature of the coatings, and the absence of lubrication in the sliding wear, neither of these failure mechanisms are applicable.

The Chapter aims to confer better understanding and appreciation of the conclusions derived from this research, whilst alternative parameters or test conditions can be considered for any future extension on work of this nature.

8.2 DISPLACEMENT OF COATING MATERIAL

The examination of the wear scar with Scanning Electron Microscopy in Chapter Seven revealed evidence of coating material being transferred across the length of the wear displacement to the edges by the ceramic ball. The movement of the tin and tin alloy suggests that plastic deformation is induced by the action of the sliding motion of the ball, coupled with the downward force from the applied load.

It is possible that some elasticity initially occurs within the coating material as it is pushed towards the full displacement of the ceramic ball, however, this is likely to be restricted to the onset of ball movement, since, at the strains observed, Hooke's law is no longer applied.

8.2.1 Analogies with Metal Forming Processes

Basic metal-forming can be separated into two categories; formation by displacing the material from one location to another, or by removing it to yield the desired shape [64]. Whilst the coating material in this study has certainly been removed from the steel substrate by sliding contact with the ceramic ball, this has seemingly been achieved through a two-stage process. The coating has firstly been displaced by a plastic deformation process, and then removed from the destination location, at the edges of the wear scar, due to the volume of the accumulated material being overly susceptible to falling away from the rest of the sample.

If the movement of the coating material is considered, an analogy can be made with rolling, where a sheet of metal is passed between a pair of rollers that are separated by a distance that is less than the thickness of the original sheet. The metal is moved through the gap between the rollers by their rotating action, yielding a sheet of metal of the same thickness as the distance between the two rollers (Figure 8.1).

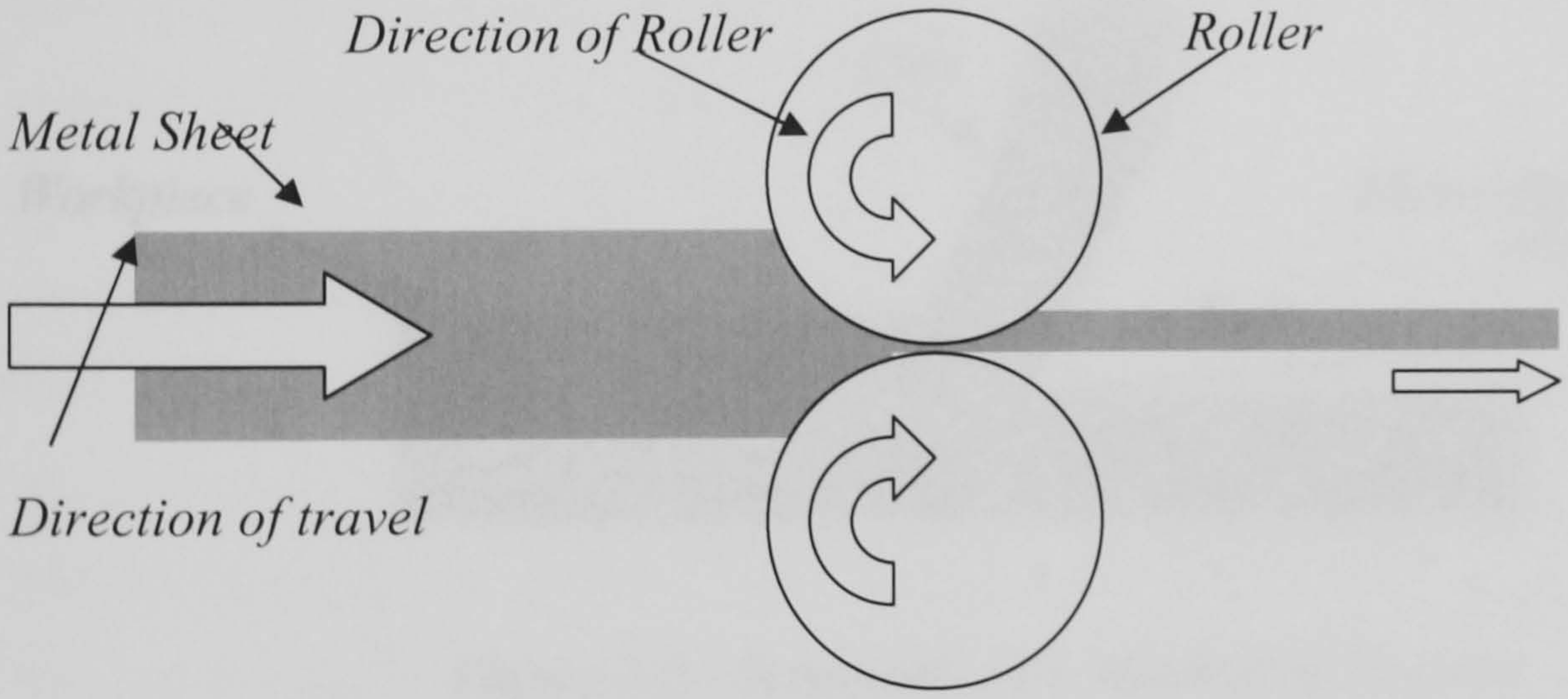

Figure 8.1 – Schematic of a Rolling Process

Whilst rolling involves two rotating tool pieces, the displacement of the coating material in this research is carried out by the compressive action between the substrate, to which the coating is adhered to, and a ceramic ball which is fixed in position by the ball holder. The main difference between the rolling process and the manner of coating displacement resulting from the wear testing is that, in the latter case, the distance between the ceramic ball and substrate is not predetermined. The normal force applied to the ball promotes the distance to be as nominal as possible, with a distance of zero (i.e., direct contact with the steel) ultimately intended. The initial distance would be the thickness of the coating, however, this will gradually decrease as more coating material is displaced.

Another analogy can therefore be made with a machining process, where a tool is used to remove material from the surface of a workpiece by linear movement (Figure 8.2). In some ways, this analogy is better because the movement of a tool on the workpiece is not dissimilar to a single stroke of the ceramic ball moving on the surface of the coating material. The chip formation from displaced workpiece material is also akin to the accumulation of the coating material. On the other hand, machining takes place with a pre-determined depth, whilst the normal force applied to the ceramic ball is always seeking to reduce the clearance between the ball and substrate. The shape of the tool, which is typically a wedge-like face, is also different. The ceramic ball does not have the same degree of cutting efficiency due to the round nature of the ball face that comes in contact with the coating material.

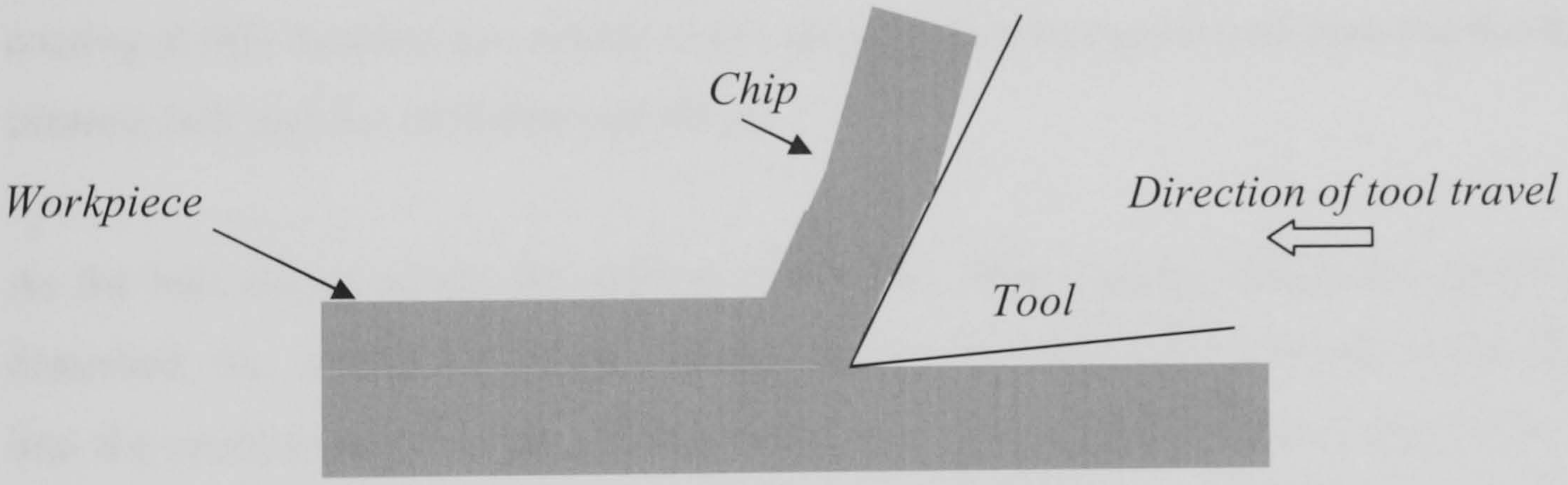

Figure 8.2 – Schematic of a Machining Process

Although there are clear similarities between the way by which the sliding ball displaces the coating material and some of the processing techniques used in industry to form metals, the differences are also apparent.

8.2.2 Understanding the Wear Scar Formation

To re-consider the wear scar formation in this research, the normal force applied on the ceramic ball onto the tin or tin alloy forces the tip of the ball into the coating (Figure 8.3).

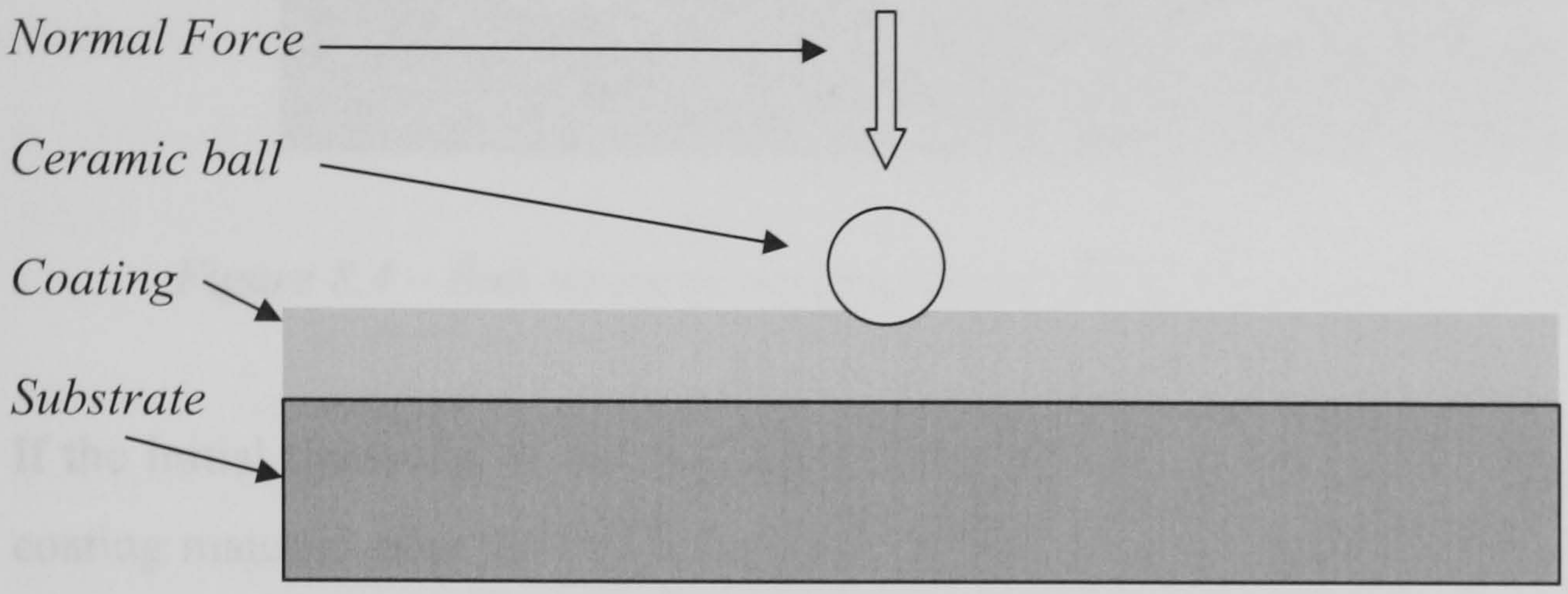

Figure 8.3 – Ball is forced into the coating by normal force

The degree of depression made in the coating by the ball is dependent on the load applied onto the ball and the hardness of the coating. This subjects the relatively soft coating at this location to a compressive stress as it is being pressed between the hard ceramic ball and the hard steel substrate.

As the ball moves across the surface of the test piece, coating material is inevitably disturbed, the volume of which is dependant on the depth that the ball is imbedded into the coating and also the sliding distance. Coating material that is moved by the ball is subjected to a pushing force, and a tensile force separates these locations from the coating bulk. The action of a hard material penetrating a softer material and displacing it can be referred to as "ploughing" [64]. Figure 8.4 shows the displacement of coating material to form the wear scar.

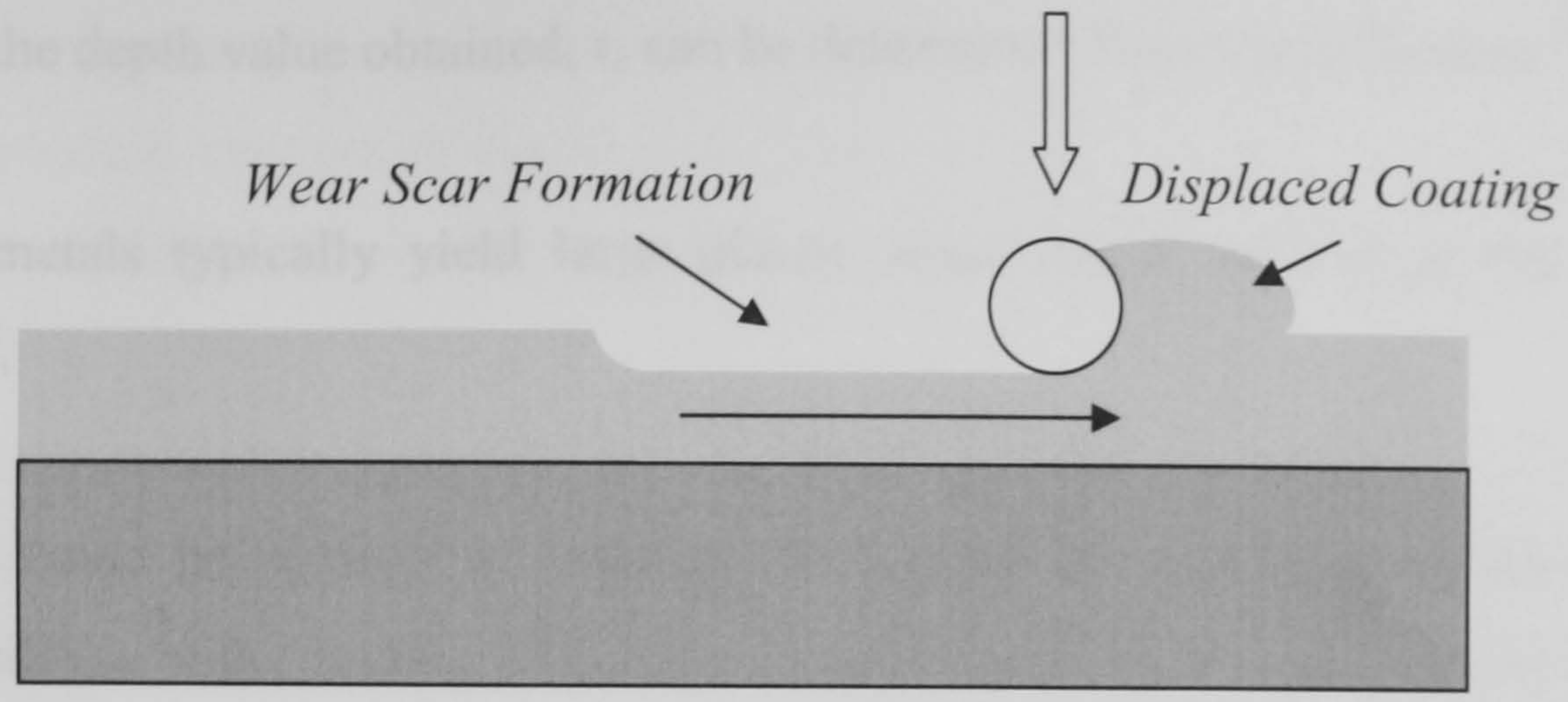

Figure 8.4 – Ball moves across coating and displaces coating material

If the initial thickness of the coating material is given as t_0 and the thickness of the coating material after the ball has performed one stroke across the surface of the test piece is t_1, the true strain in the axial plane (ε) from one stroke of the ball across the face of the test piece can be expressed as:

$$\varepsilon = \int_{t0}^{t1} \frac{dt}{t} = \ln\frac{t1}{t0} = -\ln\frac{t0}{t1}$$

At the same time, the conventional strain (e) would be:

$$e = \frac{t1 - t0}{t0} = \frac{t1}{t0} - 1$$

In both cases, the strains are compressive, and the true and compressive values are accompanied by the suffix, c, to indicate this. In addition, the equations are also reversed to express the strains as positive, which is consistent with common metalworking practice. Hence:

$$\varepsilon_c = \ln\frac{t0}{t1} \quad \text{and} \quad e_c = \frac{t0 - t1}{t0} = 1 - \frac{t1}{t0}$$

t_1 can be calculated by using the ceramic ball in a hardness test, using the appropriate force. The depth of the indent made by the ball can be evaluated by measuring its diameter and correlating the value with the diameter of the ball. With t_0 already known and the depth value obtained, t_1 can be determined from the difference [64].

Sliding of metals typically yield large plastic shear strains of >10 at the sliding interface [35].

In theory, it could be possible to calculate the volume of wear by using the normal load (P), hardness of the coating (H), cross-sectional area of the wear scar (A) and the length of the wear scar (L), by the equation, wear volume = PAL / H

The limitation to this method is that the calculation assumes that the wear scar is of a standard geometrical shape and that any change in topography and dimensions involves material removal [56]. In practice, however, materials can undergo severe plastic deformation.

8.3 INFLUENCE OF HEAT

Although the wear testing is conducted at ambient temperature, the large plastic strain and high strain rate inevitably generates heat [35]. This is especially important when coupled with heat produced from the dry sliding setup, as the rate of wear could be greatly accelerated [65-71]. For many coatings, the fatigue strength drops significantly with an increase in temperature [29], e.g., a PbSnCu coating will wear 3-5 times faster as temperature is increased from 140 to 165°C [2]. In some applications, a limit is set for maximum operating temperature, e.g., thrust bearings in some turbines have a warning limit of 70°C [29]. These discoveries and measures are attributed to the operating temperatures approaching the melting point of the tin phase in the alloys [30].

A further consideration is the influence of flash temperature, which is understood to be a key factor dictating the onset of the failures [65-71]. This usually occurs at a localised point of contact between asperities and the resulting temperatures can reach very high values within a short time window [56]. Flash temperatures are especially important because, whilst bulk heating of the system is inevitable, flash temperatures can approach the melting point of one the materials in contact. A number of studies have been conducted to accurately gauge flash temperature and its effects, however, although the temperature has been found to be sufficient to cause lubricant breakdown and microstructural changes in contact surfaces [56], evaluating the exact temperature is complex due to the difficulty in simulating contact between surface asperities [63].

The consequence of heat generated is considered in this part of the discussion by looking at two particular properties of the materials in question. The first is thermal diffusivity, which measures the ability of a material to dissipate heat away from a localised heat source. The other property considered is the degree of expansion caused by the heating, which is measured by the coefficient of thermal expansion. If the materials involved all respond to the heat by expanding at different magnitudes, a thermal fatigue mechanism could be introduced, which could exacerbate damage introduced by the wear.

8.3.1 Thermal Diffusivity

One of the problems associated with coating materials is that inevitable heat generated during wear can rapidly lead to faster wear rates [70, 71]. This problem is especially pertinent to harder materials because a larger amount of energy is required to remove the surface irregularities, and this energy is dissipated in the form of heat. An example of this is the greater heat generated from machining hard metals over softer ones.

Tin is an extremely soft material, however, as the research documented in the earlier Chapters have shown, both tin-nickel and tin-copper are significantly harder. In order to compensate for the greater heat inevitably generated, both these alloy coatings need to be able to dissipate heat away from the wear location at a greater rate than tin achieves this.

The ability to dissipate heat is measured by thermal diffusivity, and a higher value is more desirable in this application. Thermal diffusivity is calculated by:

Thermal Conductivity / Thermal Capacity per unit volume

Volumetric thermal capacity is, in turn, calculated by:

Specific Heat Capacity / Density

The thermal diffusivity is dependant on good adhesion between the coating and substrate, since the presence of separation between the two will allow in debris or lubricant which can retard the flow of heat away from the wear area. This is not such a problem for the materials considered in this research, since the characterisation of the deposited coatings already revealed evidence of good adhesion.

By using the data for Thermal Conductivity, Specific Heat Capacity and Density of tin, nickel and copper, the Volumetric Thermal Capacity and, ultimately, the Thermal Diffusivity values for the three metals are evaluated. From these, the Thermal Diffusivities for the tin-nickel and tin-copper alloys assessed in this research are calculated (Table 8.1).

	Thermal Conductivity ($Wm^{-1}K^{-1}$ or ($Js^{-1}m^{-1}K^{-1}$)	**Specific Heat Capacity ($JK^{-1}kg^{-1}$)**	**Density (kgm^{-3})**	**Volumetric Thermal Capacity ($Jm^{-3}K^{-1}$)**	**Thermal Diffusivity (m^2s^{-1})**
Sn	66.8	213	7280	1550640	**4.31 x 10^{-5}**
Ni	90.9	444	8900	3951600	2.30 x 10^{-5}
Cu	401	385	8960	3449600	11.6 x 10^{-5}
Sn65Ni35					**3.71 x 10^{-5}**
Sn20Cu80					**10.1 x 10^{-5}**

Table 8.1 – Calculation of Thermal Diffusivity values for tin, tin-nickel and tin-copper

The thermal diffusivity of tin-copper is nearly three times that of tin-nickel, which is in turn slightly higher than that of tin. This suggests that the heat generated from testing of the tin-copper coating is conducted away from the wear area at a much greater rate than for the tin-nickel coating. The thermal diffusivity for tin-nickel is only slightly higher than that of tin, however, the significantly greater hardness of the alloy also means that it has more heat requiring dissipation.

If the heat is inadequately dissipated and allowed to rise to an appreciable level, the energy required to deform the coating falls and the already ductile material can be easier to flow without cracking. This change in material behaviour at elevated temperatures is consistent with the principles behind hot-working, which is typically carried out at around 60% of, or at 50°C below, the materials' melting point [64]. From examination of the SEM micrographs of the cross-sectioned wear scars, the absence of cracking and evidence of flow, exhibited by the accumulated material at the wear scar edges, it is possible that temperatures of these scales have been approached.

Using the calculated value for thermal diffusivity (k), along with speed of the ball (v) and depth of the coating material removed (d), it is possible to determine the thermal number (R^*) for each of the coatings by using the following formula [71]:

$$R^* = \frac{vd}{k}$$

The thermal number, however, is designed to calculate heat generated from a cutting operation, and its adoption would only enable the evaluation of heat generated from a single stroke of the ball on plate sliding test. Given the number of strokes used in the tests conducted in this research, it would be impractical to pursue this avenue of analysis.

8.3.2 Coefficient of Thermal Expansion

Another consideration is the Coefficient of Thermal Expansion (CTE) of the materials involved, since the any mismatches could cause localised heating of the wear zone to initiate thermal fatigue. These are presented in Table 8.2.

	Coefficient of Thermal Expansion (K^{-1})
Sn	23.5×10^{-6}
Ni	13.3×10^{-6}
Cu	17.0×10^{-6}
Fe	12.1×10^{-6}
Sn65Ni35	20.4×10^{-6}
Sn20Cu80	18.3×10^{-6}

Table 8.2 – CTE values for materials involved in the wear testing

The difference in coefficients of thermal expansions between iron and tin-nickel is greater than that of iron and tin-copper. Therefore, in the event of localised heating, although the affected area of tin-copper would expand at a different rate to the steel substrate, the degree of expansion for tin-nickel with respect to steel would be slightly greater. With the mismatches in CTE between tin-nickel coating and the steel substrate being the greater, any stresses generated from the heating could be encouraged to relieve themselves in the form of interfacial cracking at the coating-substrate interface. This adhesive failure would in turn compromise the tin-nickel alloy's ability to dissipate heat and further aggravate the effects of the wear testing.

8.4 CHAPTER SUMMARY

A mechanism for the displacement of coating material resulting from the ball on plate sliding wear in this research is suggested to account for the findings observed from examining the wear scar. It is believed that the normal force applied to the ceramic ball forces the ball into the coating, whilst its sliding action generates a "ploughing" effect, where coating material is pushed by the ball until the ball changes direction. This causes the wear scar to form as the material is deposited at the edges around the wear area, where it accumulates and eventually breaks off.

It is unknown how much heat, if any, is generated from the wear testing, since much of this will be due to the surface topography of the coating, assuming that the heat is mainly derived from the plastic deformation of asperities and protrusions at the point of contact. Another consideration is that the heat generated is likely to be localised at random locations, making its detection and monitoring difficult.

With the above in mind, and the previous literature and experience indicating that wear of harder materials tend to generate more heat, both thermal diffusivity values and coefficients of thermal expansion for the two alloys indicate the tin-copper alloy is less susceptible than the tin-nickel alloy to localised heating.

For some other coatings, heat generated in service is a particular concern because of the issue of oxidation [70]. If the oxidation occurs at the grain boundaries, then intergranular cracking could be encouraged, leading to a decrease in material strength, whilst some metals like titanium are significantly embrittled. Another concern for wear applications is that some oxide crystals are particularly hard and could act as abrasive particles, accelerating the wear process. Oxidation does not appear to be a problem for tin-nickel and tin-copper, with both alloys exhibiting a high level of corrosion resistance in past studies.

CHAPTER NINE
CONCLUSIONS AND FURTHER WORK

9.1 CONCLUSIONS

The research documented in this thesis evaluates the feasibility of tin-nickel coatings for applications where tin-copper is already established.

A semi-quantitative method for assessing wear performance is derived and implemented to compare the deposits of tin, tin-copper and tin-nickel.

Using existing electrochemical techniques for applying tin and tin-alloys, uniform deposits are coated onto steel wear test coupons of specified dimensions. The pre-treatment stage of the process is initially optimised by establishing the most effective method of preparing the steel substrate surface prior to the electroplating (chemical etching resulted in a surface area increase of ~60%, whilst abrading with SiC yielded an increase of up to 44%). The deposits are then characterised to ensure that complete uniform coating coverage, as well as correct compositional and thickness values are obtained.

The appropriately coated wear test coupons are assessed in a dry sliding environment via a ball-on-plate configuration type micro-friction machine using a range of test durations and applied loads. The resulting wear scars are analysed with EDX, and the weight percentage of iron detectable is reported. The iron value generated is used as a measure of the amount of underlying steel substrate exposed by the wear action on the coatings.

Based on the results, it was confirmed that the amount of exposed substrate increased with an increasing testing load and duration, and a thicker deposit hindered the rate of wear, as expected. The tin-nickel and tin-copper deposits were both found to be significantly superior to the tin coating in terms of coating retention.

It was found that the coating removal mechanism for all three materials tested seemingly involved the progressive displacement of coating material, by the ceramic ball, to the edges of the wear scar, where it is accumulated.

The performance of the tin-nickel and tin-copper coatings compared closely with similar levels of exposed steel detected under the same testing regime. In general, the tin-copper was slightly more resilient, particularly at two and five microns, however, at ten microns, the tin-nickel appeared to be more resistant under certain conditions.

The generation of heat, although not monitored, is understood to have an influencing factor in the coating retention performances between tin-nickel and tin-copper. Tin-copper has both a greater ability to dissipate heat and a less contrasting coefficient of thermal expansion with the steel substrate than tin-nickel. As a result, any heat generated from the dry sliding, which could contribute to a greater degree of wear, would be more difficult to disperse from the location of contact and have a greater impact for tin-nickel than for tin-copper.

Given that tin-nickel can be electrodeposited with cyanide-free plating baths, and that its Sn65Ni35 composition is much easier to consistently replicate, tin-nickel coatings can be an environmentally friendly and cost-effective alternative to tin-copper in some applications.

9.2 FURTHER WORK

9.2.1 Further Comparisons between Tin-Nickel and Tin-Copper

Increase Testing Parameter Range

Although tin-copper deposits were found to generally out-perform tin-nickel, there are certain conditions under which the latter coating was superior. Further work could be conducted into classifying the exact range of test conditions (i.e., duration and load) and tin-nickel thicknesses where this applies in order to identify opportunities where the alloy could be a viable alternative to tin-copper. This avenue of research could involve the extension to the range of test conditions documented in this thesis, e.g., increasing the testing load and duration, or using smaller increments to improve data interpolation.

An alternative to carrying out the actual testing to address the wider parameter range would be to adopt a finite element modelling approach to the research.

Oxidation Effects

Wear testing is also sometimes conducted in a vacuum environment, and past comparative studies between these studies and a reactive environment have shown that the latter conditions has led to a greater degree of oxidation in the contact materials and the debris generated, which impacts on the wear behaviour [30, 35].

By replicating the testing in this research under vacuum conditions, it would be possible to ascertain the impact played by the oxidising atmosphere. Since oxidation is a particular issue, the EDX acquisition stage could be modified to detect for oxygen as well as iron.

Hardness

Although hardness and wear of a material is often misconceived to be heavily related, the influences that hardness has on wear is varied and complex [35]. A study has already been carried out to study the abrasion of materials of different hardness and the effect of this property in generating a range of surface area changes [43]. Taking hardness measurements of the deposits in this research, possibly using nano-hardness testing, owing to the coating thicknesses, would enable the correlating of the coating removal with hardness.

9.2.2 Compare Ball-on-Plate Results with other Configurations

The principle of analysing the wear scar with EDX for exposed substrate material can be potentially applied to any form of damage, provided it can be accurately controlled. In this research, a ball on plate set-up was used to provide an elliptical wear scar, however, the analysis could have been similarly conducted on a wear scar introduced by another configuration, e.g., rotating disc.

9.2.3 Investigate Other Tin Alloys

It is already accepted that the action of alloying can improve the mechanical properties of tin, and although some of these alloys may have environmental concerns, e.g., tin-bismuth, tin-lead and tin-cadmium, other tin alloys could also be investigated. One suggestion is tin-zinc, which has already been shown to be an effective corrosion resistant coating.

In the same way that different tin alloys could be adopted, the method could also be used to assess other coating materials. A silicon nitride ceramic ball was used for this research, however, a ball composed of another material could be used to assess the effects of the abrading material. Certainly, for harder coatings, a different ball could be more appropriate.

9.2.4 Compare with other traditional methods of assessing wear

It has already been stated that traditional methods for wear assessment is not suitable for evaluating tin coatings, however the degree of inappropriateness could be quantified and demonstrated by actually using a method, such as weight loss. Generating such data would provide further justification behind the need to design and implement the alternative method documented in this research.

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