# The Measurement and Estimation of Density for Selected Liquid Alloys.

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## Abstract

The simulation modelling of metal processes requires realistic; accurate and self-consistent thermophysical properties as input data. In particular, solidification models have been shown to be sensitive to small changes in the density of the liquid alloy. This paper compiles experimental data for the density of some selected liquid aluminium; magnesium and nickel-base alloys. Comparison with ideal mixing calculations for aluminium and magnesium alloys shows agreement between the calculations and the experimental results within the measurement uncertainties. For nickel alloys there is discrepancy between the ideal model and experiment. These differences are interpreted in terms of the measured non-ideality of mixing of Ni-Al binary alloy and other reported binary interactions.

*Density; liquid; aluminium alloys; nickel alloys; magnesium alloys; measurement; estimation.*

## 1. Introduction

Advanced computer simulation technology is now a popularly adopted tool for modelling various industrial metallurgical processes [1]. One aspect of these models is the requirement for realistic, accurate and self-consistent thermophysical properties as input data [2]. Common examples of the properties required are specific heat, latent heat, thermal conductivity, viscosity and density of the solid and liquid metal alloys. Unfortunately, reliable data for many alloys of industrial interest are often not readily available.

In a simulation to study predictions for the directional solidification of a turbine blade from the nickel-base superalloy, CMSX-4, the results of a sensitivity analysis of systematic changes in several thermophysical properties values as input parameters [4] based upon the results of the THERMOLAB project [19] with the density data [5]. They show that the sensitivities to several output parameters were most strongly affected by changes in the input density data. Density is also an important variable in the calculation of thermal conductivity from thermal diffusivity, and in the measurement of surface tension and viscosity. Because of the importance of density, this paper deals the measurement and modelling of the density of the liquid phase of commercially important aluminium, magnesium and nickel base alloys.

Measurement of the density of liquid alloys is difficult because of the high temperatures and the reactivity of some alloys [3], leading to modellers frequently relying on data derived from the literature (often for similar alloys and not the specific alloy of interest) or using estimates ranging from empirical methods to thermodynamic modelling. Examples of methods for estimating properties of commercial alloys may be found in references [9, 10, 11, 12, and 24]. The models adopted in this study were a simple rule of mixtures [21] using volume data derived from a review by Mills and Li [17] with the incorporation of a non-ideal volume of mixing using the method outlined by Brillo [22].

## 2. Experimental

As space is limited, for details of the experimental methods the reader is referred to original references. There are a number of methods for measuring volumes and density in liquid metals - these are briefly reviewed in [3]. In principle they may be divided into two broad classifications:

1) Measuring the volume of a drop of known mass at temperature. The levitated drop method (LD) [5, 22]; the sessile drop method (SD) [5, 6]; large drop [24]; and pinned drop [26] are based upon this principle.

2) Measuring the volumetric change in a liquid with temperature either using a pycnometer [7] or a modified dilatometer method employing a piston cell, referred to as piston dilatometry (PD) [8].

## 3. Model for Liquid Density

The model for density of liquid metals adopted in this work is described in detail by Brillo [22]. It assumes that the molar volume of the alloy can be expressed as:

$$V = \Sigma x_i V_i + {}^{E}V \qquad [1]$$

where V is the molar volume

$V_i$ is the molar volume of the $i^{th}$ component

${}^{E}V$ is the excess volume term

$x_i$ is molar fraction of $i^{th}$ component

$${}^{E}V = \Sigma x_i . x_j . {}^{0}V_{ij} + \Sigma x_i . x_j . x_k . {}^{T}V_{i,j,k} \qquad [2]$$

where ${}^{0}V_{ij}$ is the binary excess volume coefficient between the $i^{th}$ and $j^{th}$ components, and

${}^{T}V_{i,j,k}$ is the tertiary interaction coefficient between the $i^{th}$; $j^{th}$ and $k^{th}$ components.

The first term on the right hand side of equation 1 represents the ideal mixing volume assuming there are no interactions between the individual components. It requires molar volumes of the individual elements and the change of molar volume with temperature. The compendium prepared by Mills and Li [17] was used to derive the necessary parameters, since it is comprehensive and uses a consistent methodology for reviewing the data.

The first term in equation 2 represents binary interactions between components. It is assumed that further terms for expansion for the binary effects are negligible and that the coefficient $^{0}V_{ij}$ is temperature independent, leading to equation 3:

$$^{E}V_{i,j} = x_i.x_j.\ ^{0}V_{i,j} \qquad [3]$$

By fitting experimental data for $^{E}V_{i,j}$ versus $x_i.x_j$, which approximates to a parabola, values of $^{0}V_{i,j}$ may be derived. Some data by Brillo [22] and other work (see in particular volumetric behaviour of aluminium binary alloys [23]) relevant to the compositions of commercial alloys are listed in Table 1. Where there have been multiple measurements of $^{0}V_{ij}$ for the same system, some discrepancies are observed. One of the most important is that for Ni-Al which takes values of -5.0 [22] or -7.2 cm$^{3}$. mole$^{-1}$ derived from [27]. This has a significant difference in the correction for nickel base superalloys and will be discussed in more detail below.

The third term represents ternary interactions. Few data for the coefficient $^{T}V_{i,j,k}$ are available, although the correction for the Al-Cu-Si interaction listed by Brillo will be discussed in conjunction with the density of liquid aluminium alloy A319.

The density of the system is given by:

$$\rho = \Sigma\ x_i.M_i\ / V \qquad [4]$$

where $M_i$ is the atomic weight of the i$^{th}$ component.

Table 1: Excess volume for binary Al alloys

| System | $^{0}V_{ij}$, cm$^{3}$/ mole | Reference |
|---|---|---|
| Al-Ag | -2.7, -2.6 | [34], [35] |
| Al-Co | -8.0 | [27] |
| Al-Cr | -4.0 | [36] |
| Al-Cu | -3.4 | [34] |
| Al-Mg | -1.6 | [37] |
| Al-Ni | -5.0, -7.2 | [40], [27] |
| Al-Si | 0 | [38] |
| Cr-Ni | +0.74 | [39] |

$^{T}V_{Al.Cu,Si}$ = +19.7 cm$^{3}$/ mole

# 4. Experimental Data

## 4.1 Aluminium alloys

Figure 1 [8, 20, 28, 29] shows liquid densities for various selected aluminium alloys at their liquidus temperatures extracted from the original experimental points. All the measurements were made by the piston dilatometer method and a detailed discussion of the uncertainty of measurement indicates +/-2% with a confidence limit of 95% [8].

The measured liquid density at the melting point for aluminium is close to the value extracted from the literature and the data for a number of Al-Si alloys ranging from 5wt. % to 12 wt. % complement and agree with previous work by Goicochea *et al.* [30] who used a maximum bubble pressure technique. Data for Al-Si-0.3Mg alloys with Si varying from 5 wt. % to 12 wt. % are shown. The results for the most measured alloy, variously designated LM25, A356 or AlSi7Mg, are very similar. For the alloy A201 the data for the variation of density with temperature from Overfelt *et al.* [28] and from this work differ, and we favour the larger value, which agrees better with the other values reported for aluminium alloys.

## 4.2 Magnesium alloys

Figure 2 [20, 31, 31] shows density at liquidus temperature for selected magnesium alloys. A complication associated with most of these data is that they are extracted from published compendia and detailed references to the original work are not readily available. Enquiries by the present authors indicate that the data from [31] were obtained by piston dilatometry, but so far the method used to ascertain the value of the single point for AS41 [32] has not been successfully identified. The measured variations of density with temperature are similar for all the alloys investigated. There are no duplicate measurements for the same commercial alloy, and we experienced problems in the PD measurement of Elektron 21, which in several separate attempts leaked past the piston.

## 4.3 Nickel alloys

Figure 3 [5, 9, 13, 14, 15, 16, 20, 33, 42] shows liquid density at the liquidus temperature data from readily available references for nickel-base superalloys. The chemical compositions of the alloys may be found in the relevant references since space precludes a detailed listing. It is noteworthy that many workers quote the specification composition, not the analysed one of their sample. Especially when the composition specification range is wide, the range of values of density at the extremes of the composition range may be comparable to the experimental uncertainties in measurement.

For these alloys a wide variety of methods has been used by different workers. One difficulty is that references to the source of the data are not readily available in Sung's work [9]. Methods are suggested from our knowledge but need to be confirmed, making it difficult to judge the uncertainty of measurement. Alloys that have data from several sources are: CMSX-4; CM186LC; CM247LC; Inconel 713; TMS75 and CMSX-10. For the sake of clarity in the figure we have plotted an average value for alloys where multiple results are available, removing any data which was more than 2.5 % away from the mean as an outlier

As an example, the CMSX-4 data [5, 13, 14, 20] show that at the liquidus temperature there is range of densities from about 7680 to 7910 kg m$^{-3}$, *i.e.* a spread of about ±1.5% with a large spread in the temperature dependence of density, from -2.2 kg m$^{-3}$ °C$^{-1}$ [13] using a modified pycnometer and modified sessile drop to -0.37 kg m$^{-3}$ °C$^{-1}$ for piston dilatometry [20]. This large difference in temperature dependence leads to a divergence of the density values at higher temperatures.

**Table 2:** Errors/Uncertainties in typical methods to measure the density of liquid superalloys.

| | Method | Errors/Uncertainties | Refs. |
|---|---|---|---|
| PD | Piston dilatometer | Uncertainty ±2% at 95% confidence level | [8], [16] |
| SD | Sessile drop | Uncertainty ±0.1% | [5] |
| MSD | Modified sessile drop | Max. relative error ±0.75% | [6] |
| MP | Modified pycnometer | Max. relative error ±0.30% | [7] |
| LD | Levitated drop | Not specified | [5] |
| LD | Levitated drop | Error in density < ±1%<br>Accuracy of temperature dependence 5-10% | [18] |

Some indication of errors for the uncertainties of various methods is given in Table 2. Since only references [8] and [16] attempt to use the Guide to Uncertainty of Measurement (GUM) [40] to determine uncertainty, comparison of the uncertainties in measurements between the different methods is difficult. If we accept that ±2% is the typical uncertainty at the 95% confidence with a coverage factor of 2, at the liquidus temperature all the density data for CMSX-4 are within the scatter. It can be envisaged that it is difficult to establish the temperature dependence of density from individual absolute values of density measured with this uncertainty. The methods using relative measurement may give more confidence.

None of the materials used are from the same source so that small differences in composition may be contributing to the scatter in the results. Also, when specimens are exposed for a long time at temperature, volatile elements such as chromium will evaporate, so changing the composition and density during measurement.

# 5. Model Comparison

## 5.1 Aluminium alloys

In figure 1 the calculation of density at the liquidus temperature using the ideal model agrees for most systems within better than 1% with the experimental values. With the exception of the data for A201 and A319 [28], the measured temperature dependences of density agree closely with the calculated values. For A319, a correction for the Al-Cu interaction together with the ternary interaction for Al-Si-Cu shows a small difference between the ideal and the modified calculation. For A201 the Al-Cu and Al-Ag correction again has a little effect on the ideal calculation.

For Al-Cu, Al-Ni and Al-Ag systems, to produce a 1% change in density respectively would require ~8 wt. % (~4.2 at. %) Cu; ~5 wt. % (~2.4 at. %) Ni and ~15 wt. % (~4.2 at. %) Ag. As few commercial alloys reach these levels we recommend that the ideal calculation of density of liquid aluminium alloys provides a satisfactory approximation in common cases.

## 5.2 Magnesium alloys

An ideal calculation for the compositions of the measured magnesium alloys shows good agreement with the calculated values (figure 2) and general agreement in the temperature dependence of the density. There are few relevant binary interaction coefficients for Mg and relevant elements for commercial alloy compositions. On the basis of these comparisons we recommend that the ideal calculation provides a good approximation for the density of liquid magnesium alloys.

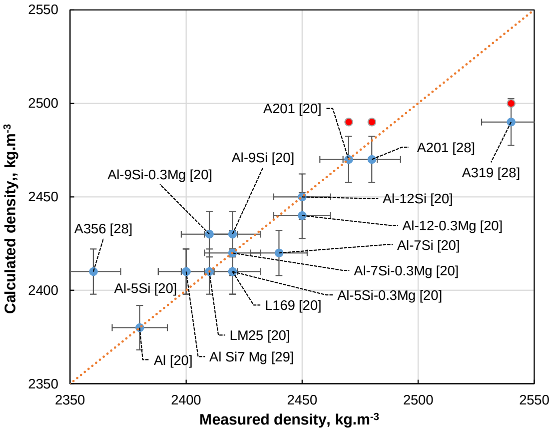

**Figure 1:** The comparison between measured and calculated density by ideal mixture at the liquidus temperature for aluminium systems. The error bars represent +/-0.5%. The three orange dots show the correction for binary and tertiary interactions using coefficients in table 1 for alloys A201 and A319.

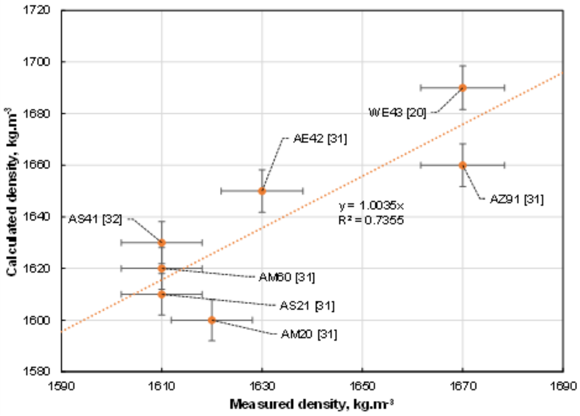

**Figure 2**: The comparison between measured and calculated density by ideal mixture model for magnesium alloys. The error bars represent =/-0.5 %.

## 5.3 Nickel base alloys

The ideal mixing model underestimates the liquid density of the nickel alloys containing significant Al. A correction for the binary interaction between Ni-Al using $^{0}V_{Ni\text{-}Al}$ of -5.0 cm$^{3}$/mole yields an improved fit (figure 3) between measured and calculated density at liquidus temperature. Using the alternative value of -7.2 cm$^{3}$/mole yields a consistently higher values than the measured values, and for this reason we have adopted the lower figure. For most compositions the combined interactions between Co-Al and Cr-Al yield only small upward corrections of the calculated densities compared to the Ni-Al interaction, whereas Ni-Cr yields a small downward correction. Thus care should be exercised for alloys with higher Cr levels such as Inco 939 (~22 wt. % Cr), and when the Al levels are low or zero (e.g. Haynes 282 and Inco 625) making it necessary to consider the additional binary terms.

It is noteworthy that the allowance for Ni-Al by the Brillo model [22] gives very similar results to the Mills et al. model [10] which is based on corrections for Ni-Al interactions using density data of the alloys.

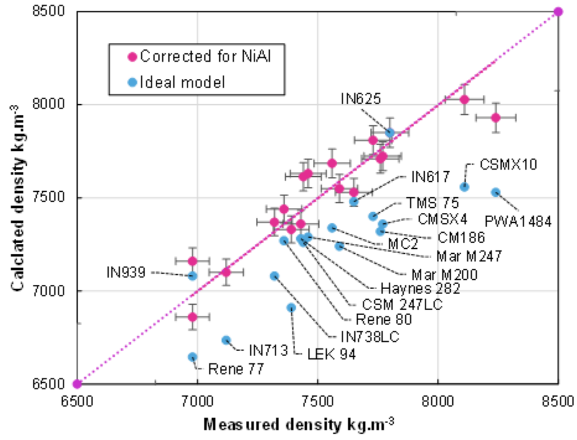

Figure 3: Measured density (average result where multiple results available) versus density calculated using ideal model and ideal model modified by binary interaction between Ni-Al with $^{0}V_{Ni\text{-}Al}$ = -5.0, cm$^3$/ mole. The error bars represent +/-1%.

## 6. Conclusions

This paper discusses some aspects of the experimental determination and modelling of density data of liquid aluminium, magnesium and nickel-base alloys.

1) For commercial aluminium alloys the ideal mixing model gives densities within +/-1% for most systems. For the non-ideal mixing associated with Al-Ni, Al-Ag and Al-Cu to be significant, composition limits are suggested for the respective elements.
2) For commercial magnesium alloys the ideal mixing model gives good agreement with the measured values, but there are few relevant binary data to account for non-ideal mixing.
3) The measured densities for liquid nickel base superalloys are significantly underestimated by an ideal model. The primary correction for non-ideality is the excess volume of Ni-Al, with Co-Al, Cr-Al and Ni-Cr contributing second order effects.

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