# PROCESSING OF IMMISCIBLE ALLOYS BY A TWIN-SCREW RHEOMIXING PROCESS

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## Summary

Immiscible alloys with a microstructure in which a soft phase dispersed homogeneously in a hard matrix have great potential applications in advanced bearing systems, especially for automotive industry. Though the melt of an immiscible alloy is miscible at the temperature above the miscibility gap, it decomposes into two liquids when it passes through the liquid miscibility gap. Despite great efforts made worldwide, including extensive space experiments, no casting techniques so far can produce the desirable microstructure. Based on the extensive experience in mixing the immiscible organic liquids offered by the polymer processing community, a rheomixing process for immiscible alloys has been successfully developed at Brunel University using a twin-crew extruder. This paper presents the twin-screw rheomixing process and the experimental results on rheomixing of the immiscible Zn-Pb alloys.

Key words: processing, immiscible, rheomixing, microstructure.

## 1 Introduction

The immiscible systems have great potential applications in advanced bearing systems, electrical contacts and superconducting devices. Unfortunately, it has not been possible to produce those alloys by casting techniques due to liquid phase separation at the early stages of solidification [1]. There are two most important factors that contribute to the separation of immiscible liquids. One is Stokes' motion that is caused by the density difference between two liquids, and the other is the Marangoni motion that results from the temperature gradient, i.e., the liquid droplet moves to a higher temperature area in order to reduce the interfacial energy.  The phase diagram (**Figure 1**) of the immiscible Zn-Pb system shows that though the melt of an immiscible alloy is miscible at the temperature above the miscibility gap, it will decompose into two liquids when it passes through the liquid miscibility gap, with the lighter liquid being on top of the heavier liquid.

In order to overcome the effect of Stokes' motion and Marangoni motion on segregation of immiscible alloys, several methods have been used aiming at producing a uniform distribution of a softer phase in a harder matrix. The simplest way is to stir vigorously the melt to break up droplets [2] and keep droplets away from collision. Acoustic streaming generated in aluminium melt by ultrasonic waves has also been used to suspend and homogenize the lead droplets in the melts [3]. This technique can only get uniform dispersion of lead in aluminium matrix with less than 10wt.%Pb. Although preparing the alloy under microgravity field can eliminate the effect of Stokes' motion, it cannot avoid

Marangoni motion during the cooling process. A strip casting process was developed using the Marangoni motion generated by an artificial temperature gradient to counterbalance the Stokes' motion [4]. In addition, Uffelmann *et al* [5] used the Lorentz force technique to reduce the sedimentation due to density differences. However, the microstructures produced by this method were extremely inhomogeneous. Recently, the rheomixing process for processing immiscible alloys has been developed at Brunel University using a twin-crew extruder [6]. Fan *et al* [7] have successfully mixed the Zn-Pb and Ga-Pb immiscible alloys using this technology. In this paper we present the twin-screw rheomixing process and the experimental results on rheomixing of immiscible Zn-Pb alloys.

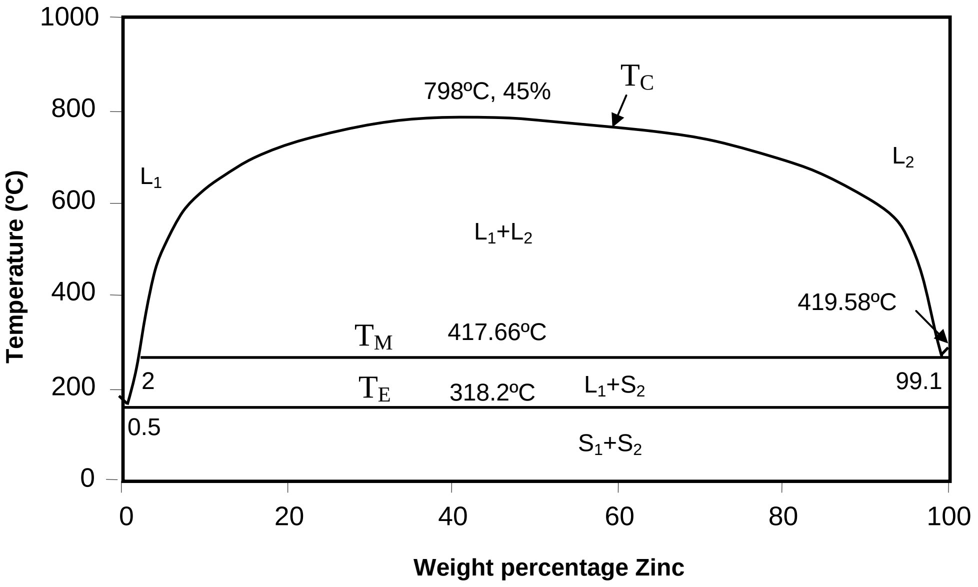


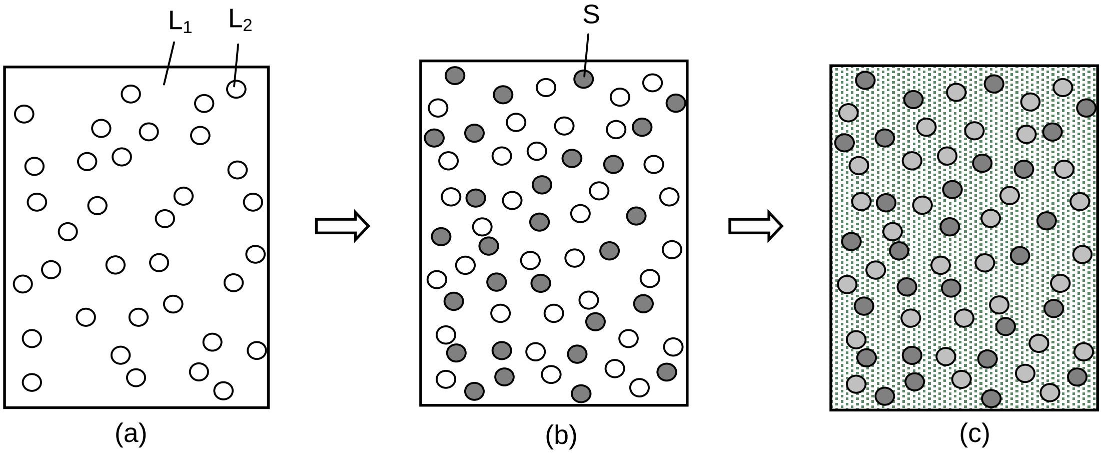
***Figure 1:** Phase diagram of binary immiscible Zn-Pb system.*

## 2 Twin-screw rhoemixing process

The twin-screw rheomixing process is designed to create a solid microstructure in which a softer phase distributed finely and uniformly in a harder matrix. This is achieved by a two-step mixing strategy, as schematically illustrated in **Figure 2**. In the first step, a fine liquid suspension is created within the miscibility gap by the intensive shear mixing action offered by a twin-screw extruder. This shear mixing action is so intensive that it can override the demixing actions resulted from both Stokes' and Marangoni motions. Consequently, a fine and homogeneous liquid dispersion is created at a temperature just above $T_M$ (**Figure 2a**). Although the fine liquid dispersion created by high shear mixing action will slow down substantially the demixing process by both Stokes' and Marangoni motions, it is still unstable and will separate once the deformation filed is removed. This is called the initial stabilisation process. In the second step, the fine liquid suspension is further stabilised by introducing a primary solid phase at a temperature below $T_M$ creating a semisolid slurry (**Figure 2b**). Introduction of the solid particles increases the viscosity of the fine liquid suspension. The viscosity should be high enough that the viscous force can counterbalance the gravity force, and consequently both Stokes' and Marangoni motions can no long produce coarse separation. Further stabilisation of the fine liquid dispersion can also be achieved by introduction of fine and insoluble solid particles at a temperature above

$T_{M.}$ Finally, the stabilised semisolid slurry can be cast without causing any coarse phase separation (**Figure 2c**).

A twin-screw rheomixing machine with closely intermeshing, self-wiping and co-rotating twin screws has been used in this work, as illustrated schematically in **Figure 3**. It consists of a premixer, a liquid meal feeder, a high shear twin-screw extruder, an outlet valve and a central control system. The screws have a specially designed screw profile to achieve high shear rate and high intensity of turbulence and to enhance the positive displacement pumping action. The outlet valve situated at the end of the twin-screw extruder is used to increase the residence time, which is defined as the time interval when alloys stays inside the twin-screw extruder during processing. If the valve is opened before liquid metal is poured in, the resident time is mainly decided by temperature, viscosity of the liquids and the rotation speed of the twin-screw. The maximum rotation speed of the current prototype rheomixer is 1000 rpm, which corresponds to a shear rate of 4082 $s^{-1}$ in the gap between the tip of the screw flight and the inner surface of the barrel.



(a) initial stabilisation: creation of a fine $L_2$ dispersion in $L_1$;
(b) further stabilisation: formation of a primary solid phase S in $L_1$ through a monotectic reaction;
(c) monotectic solidification of $L_1$ and eutectic solidification of $L_2$.

***Figure 2:** Schematic illustration of the two-step mixing strategy to achieve fine and homogeneous dispersion microstructure from immiscible alloys (Ref. [7])*

Rheomixing can be operated in the following modes depending on the characteristics of specific alloy systems:

- Feeding a homogeneous liquid at a temperature above the miscibility gap
- Feeding a premixed liquid mixture at a temperature between $T_C$ and $T_M$
- Feeding simultaneously two separate liquids at the right proportion for the alloy
- Feeding artificially stabilised semisolid slurry created by introduction of solid particles.

It should be pointed out that twin-screw extruders do not have efficient distributive mixing action, and therefore, a premixer is required to achieve coarse mixing of the separated liquids before feeding the coarse mixture into the extruder.

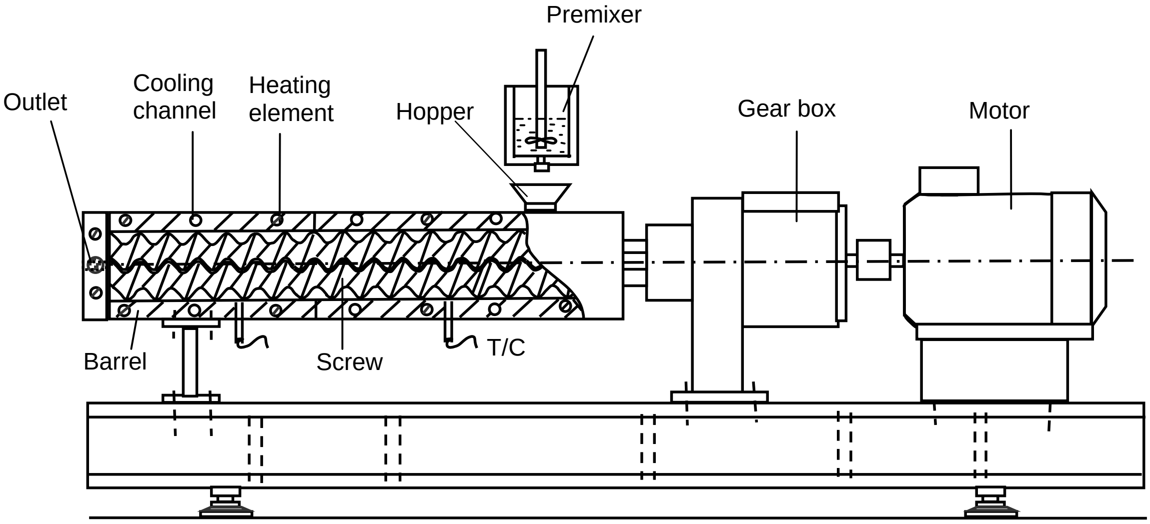


***Figure 3:*** *Schematic illustration of twin-screw machine*

## 3 Experimental and results

Elemental lead and zinc with a purity of 99.97% and 99.8%, respectively, were used in this work. The melting was conducted in a resistance furnace. In order to obtain chemical homogeneity, the temperature of liquid metal was held for at lest 30 minutes with occasional mechanical stirring.

The temperature of the feed hopper was set usually at a temperature 50°C above the barrel temperature to avoid premature solidification in the feed hopper. Depending on the mixing programme, the barrel temperature can be preset either above or below the monotectic temperature. During the development of the twin-screw rheomixing process, the following batches of mixing experiments have been carried out. In all these experiments the liquid feed was either a homogeneous liquid, or a premixed phase mixture.

- Set the extruder at a temperature just above the monotectic temperature, shear the liquid for 20 seconds, and discharge the fine phase mixture into cold water for sampling.
- Set the extruder at a temperature just above the monotectic temperature, shear the liquid for 20 seconds, cool the extruder to a temperature just bellow the monotectic temperature at a controlled cooling rate while shearing continues, shear for a further 10 seconds before sampling.
- Set the extruder directly at a temperature just below the monotectic temperature, shear for 20 seconds to create semisolid slurry before sampling.

For all those experiments, different combinations of feeding method, rotation speed, shearing time can be performed to evaluate the effect of a particular processing parameter on the quality of the immiscible alloys. Samples from the rheomixing experiments were examined and quantified for volume fraction, particle size and morphology, and particle distribution in the matrix.

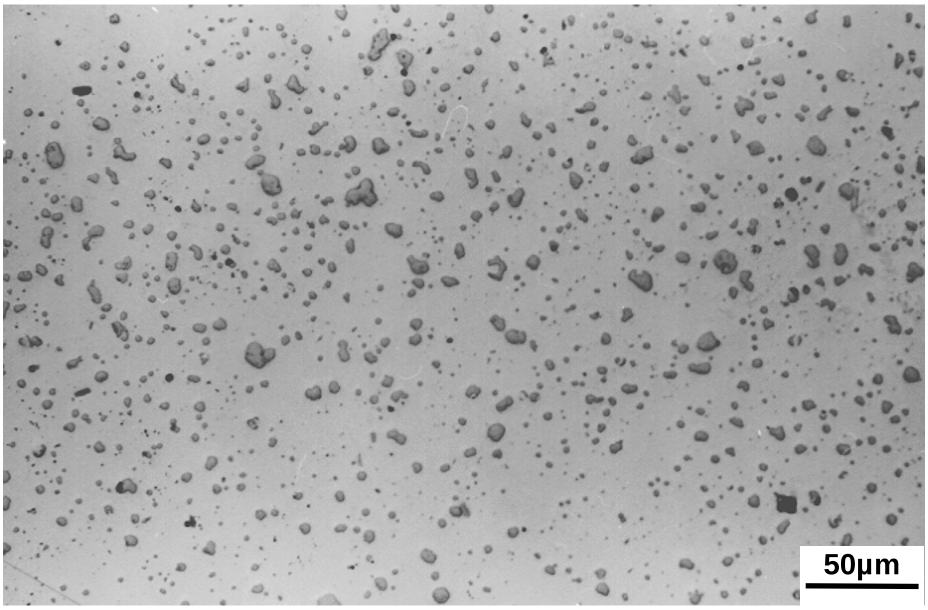


***Figure 4:*** *Microstructure of rheomixed immiscible Zn-15wt.%Pb alloy. Dark particle is Pb and bright matrix is Zn (unetched).*

Our experimental trials have revealed the following facts:

- Feeding methods do not contribute significantly to the final microstructure as long as premixing is carried out properly.
- Fine liquid suspension achieved by shear mixing at a temperature just above the monotectic temperature is highly unstable; it does not allow solidification without phase separation.
- Mixing at a temperature just below the monotectic temperature appears to be more efficient than other mixing schemes used.

A secondary electron image of the rheomixed Zn-15wt.%Pb alloy is shown in **Figure 4**. The dark phase and bright phase were identified as Pb phase and Zn phase, respectively, using EDX analysis. **Figure 4** shows that equiaxed Pb particles with an average diameter of 5μm are uniformly dispersed in a Zn matrix.

## 4 Discussion

The scientific basis for the two-step mixing strategy is briefly discussed here. It is now clear that liquid phase separation within the liquid miscibility gap is caused by both Stoke's motion in the gravity field and Marangoni motion in the nonuniform temperature field. Marangoni motion is proportional to the temperature gradient. In the twin-screw extruder the temperature gradient in the liquid phase is extremely small due to its intensive shear mixing power. Thus, Marangoni motion is not expected to contribute to the phase separation to any significant degree. Therefore, only Stoke's motion is considered here. The velocity of Stoke's motion ($U_S$) of a liquid droplet of viscosity $\eta'$ and size $r$ in a liquid matrix of viscosity $\eta$ can be expressed as

$$U_S = \frac{2g\Delta\rho(\eta+\eta')}{3\eta(2\eta+3\eta')} r^2 \qquad (1)$$

where $\Delta\rho$ is the density difference between two liquids. Eqn (1) indicates that for a given immiscible system the velocity of Stoke's motion is proportional to the square of droplet size and reversely proportional to the viscosity of the liquid matrix. Therefore, in order to slow down Stoke's motion, one needs to reduce the droplet size and the viscosity of the liquid matrix. The dispersive mixing action offered by the twin-screw extruder seems ideal for reduction of droplet size, while the viscosity of the liquid matrix can be effectively controlled by choosing the solid fraction of the semisolid slurry. This is the scientific basis for the twin-screw rheomixing process.

## 5 Concluding remarks

A twin-screw rheomixing process has been developed for processing the usually immiscible alloys. The rheomixing process is designed to create directly from immiscible liquids a microstructure in which a softer phase is dispersed finely and uniformly in a harder matrix aiming at advanced bearing applications. Application of the rheomixing process to the immiscible Zn-Pb system has demonstrated that the rheomixing process is capable of producing the desirable dispersed microstructure.

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