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The Formation of Metal/Metal-Matrix Nano-Composites by the Ultrasonic Dispersion of Immiscible Liquid Metals

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THE FORMATION OF METAL/METAL-MATRIX NANOCOMPOSITES BY THE ULTRASONIC DISPERSION OF IMMISCIBLE LIQUID METALS

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ABSTRACT

Ultrasonic energy has been used to disperse one liquid metallic component in a second immiscible liquid metal, thereby producing a metallic emulsion. Upon lowering the temperature of this emulsion below the melting point of the lowest-melting constituent, a metal/metal-matrix composite is formed. This composite consists of sub-micron-to-micron-sized particles of the minor metallic phase that are embedded in a matrix consisting of the major metallic phase. The zinc-bismuth case was used as a model system, and ultrasonic dispersion of a minor bismuth liquid phase was used to synthesize metal/metal-matrix composites. These materials were subsequently characterized using scanning electron microscopy and energy-dispersive x-ray analysis.

INTRODUCTION

The special properties that can be obtained by forming metal-matrix composites have previously been extensively documented. While much of the prior attention given to these materials has been focused on metal matrices reinforced with ceramic particles or fibers [1], the results reported for metal/metal-matrix composites show that the latter are no less interesting. For example, a new class of metal/metal matrix materials has been developed that exhibits extraordinary mechanical properties [2, 3, 4]. These materials are composed of a mixture of Cu plus 10-30% of a metal X that is immiscible with Cu. The mixture is severely deformed to produce a nanometer-scale microstructure of immiscible X filaments (or lamellae) within the Cu-matrix. Such processed composites have a strength that is substantially higher than those reported for any traditional Cu alloy.

In efforts to improve the mechanical properties – in particular the hardness – of materials, Singh *et al.* have dispersed approximately 20 wt.% Bi in Zn, using a melt-spinning technique [5]. This technique produced a metal/metal-matrix composite of nanosized Bi spheres entrained in a Zn matrix where the size of the Bi particles was controlled by adjusting the wheel speed used in the melt-spinning process. Hardness measurements performed on these materials showed that a decrease in the size of the Bi nanodispersoids leads to an increase in hardness.

In the present work, a new approach to the formation of bulk metal/metal-matrix composites is presented. High-intensity ultrasound has been used to disperse one metallic liquid in a second immiscible liquid metal thereby forming a metallic emulsion. When this emulsion is cooled, a metal/metal-matrix composite is formed consisting of minor-phase particles dispersed in the solidified major phase.

The basic idea of using ultrasound for mixing immiscible *liquids* is, of course, not new. In 1926, Wood and Loomis [6] reported that if two immiscible liquids such as oil and water are simultaneously subjected to ultrasonic radiation, an emulsion or colloidal suspension is formed as

a result of the forces acting at the interface between the liquids. A further extensive study of the mechanism of emulsification and coagulation by ultrasonic waves in water-oil and mercury-water/organic liquid systems was carried out by Bondy and Söllner [7,8].

A previous study of the influence of ultrasound on the production of unusual metallic mixtures was described by Schmidt and Ehret [9] and Schmidt and Roll [10]. Part of their work focused on the dispersion of 35 wt.% Pb in Al. By applying ultrasound with a frequency of 10 kHz to the melt, the Pb phase could be dispersed, forming spherical inclusions with a diameter of approximately 30 μm embedded in the Al matrix. However, the mixing of the components was incomplete, and a significant residue of Pb was found at the bottom of the crucible. More recently, a group in China has reported the use of ultrasound for the preparation of fine ceramic-particulate-reinforced metal-matrix composites [11] in which high-intensity ultrasound was used to disperse micrometer-size ceramic particles homogeneously in an aluminum matrix.

EXPERIMENTAL PROCEDURE

In order to investigate the application of ultrasound to the formation of metal/metal-matrix composites, the Zn-Bi case was selected as a model system, since both metals are relatively easy to handle based on their chemical reactivity and low melting points. Additionally, the wide miscibility gap in the Zn-Bi phase diagram (See Figure 1) made this system a particularly attractive candidate for the ultrasonic formation of metallic emulsions in varying concentrations.

FIGURE 1: Equilibrium phase diagram of the Zn-Bi system showing the wide miscibility gap characteristic of this system [12].

The ultrasonic source used in the present experiments was a Misonix Sonicator Model W-385 that consists of a generator which feeds 20 kHz electrical energy to a transducer where it is transformed to mechanical vibrations. The ultrasonic energy is generated by a transducer that consists of a lead zirconate titanate piezoelectric driver. When subjected to an alternating applied voltage, this piezoelectric material expands and contracts at the 20 kHz driving frequency. The transducer is mechanically coupled to an acoustically resonant Ti-alloy horn assembly that vibrates in a longitudinal direction and transmits the high-frequency motion to the horn tip. A highly tapered Ti horn (termed a microtip) was used to achieve high-amplitude ultrasonic vibrations. A schematic representation of the ultrasonic processing system is shown in Figure 2.

The Zn-Bi composition selected for the present experiments consisted of 10 wt.% Bi. Once the two metals were weighed to achieve the appropriate proportions, they were then melted in a SiO₂ tube using a propane torch and were heated to approximately 650°C. To minimize oxide-formation, argon gas containing 4% H₂ was continuously sprayed over the surface. When the desired melt temperature was reached, the torch was turned off and the sonication process was initiated by immersing the vibrating microtip in the liquid. While the Ti-alloy used for the horn and tip represents the best horn material from the mechanical and acoustic point of view – combining outstanding acoustic properties with lightness, strength, abrasion resistance and chemical inertness – it tends to form an alloy with the Zn-phase. This interaction results in degradation of the microtip when it is immersed in the melt. Accordingly, in order to minimize the reaction of the Ti-tip with the sample, the sonication process had to be limited to short durations – typically 10-30 seconds. In the present experiments, the melt is first sonicated for 10-15 seconds while it begins cooling down at a typical cooling rate of 10°C per second. The solidification process is subsequently accelerated by spraying water on the outside of the SiO₂ tube, while maintaining the sonication conditions, until the solidification is complete. This results

FIGURE 2: Schematic representation of the ultrasonic system.

in a total sonication time of 20-30 seconds. The resulting composite samples were then polished to obtain a flat surface suitable for examination in the scanning electron microscope.

EXPERIMENTAL RESULTS AND DISCUSSION

FIGURE 3 (a) and (b): SEM image of a Zn-Bi composite obtained by sonication of the two molten immiscible liquid metals.

Figure 3(a) shows an SEM image of a composite metal/metal-matrix sample obtained after the sonication of a Zn plus 10 wt % Bi melt. Energy Dispersive X-ray analysis (EDX) confirms that the light colored dispersed particles are Bi, while the gray background consists of Zn. As evident in the micrograph, the Bi phase forms essentially spherical particles that are embedded in the Zn-matrix. This dispersion is, however, far from homogeneous: Figure 3(a) clearly shows Bi-particles with diameters ranging from more than 50 μm to less than 5 μm . Additionally, significantly smaller particles with diameters below 0.5 μm can be detected, as revealed in Figure 3(b). The presence of these sub-micron particles of Bi indicates that the application of high-intensity ultrasound can be a powerful tool for the formation of nanocomposite materials through

the creation of metallic emulsions. However, it is clear from the observed microstructures that the major problem to be overcome in order to obtain uniform materials is achieving a marked improvement in the monodispersed size-distribution of the minor-phase particles.

In order to gain insight as to how metal/metal-matrix composites with a more-monodispersed minor phase can, in fact, be achieved by ultrasonic dispersion methods, a better understanding of the operative mechanisms responsible for the dispersion and the various parameters that control these mechanisms is needed. While previous investigations [6,7,8] have clearly shown that sonication of a liquid or melt significantly influences its behavior, there is, at present, no general consensus regarding the exact nature of the operative ultrasonic mechanism. According to Bondy and Söllner [7,8], the emulsification of immiscible liquids is due to the collapse of acoustic cavitation bubbles. Here "cavitation" refers to the formation, growth, and collapse of bubbles in liquids [13] that are initiated at nucleation sites where the tensile strength of the liquid is dramatically lowered -e.g., at small trapped gas bubbles. When sound passes through the liquid, these bubbles oscillate as a result of the rapid expansion and compression waves created by the sound field. As the bubble oscillates, it grows through several mechanisms and finally collapses catastrophically. When cavitation takes place near an interface, major changes in the nature of the bubble collapse occur. A markedly asymmetric collapse happens that generates a jet of liquid directed at the interface. This liquid jet may thus represent a mechanism for the injection of one liquid phase in the other. An other concept for the emulsification of immiscible liquids that does not involve cavitation has been presented by Suslick [14]. According to this model, ultrasonic compression and expansion effectively "stress" the liquid surfaces -eventually overcoming the cohesive forces that hold large droplets together. The larger droplets eventually burst into smaller droplets, and the liquids are thus emulsified.

Given the current lack of an accepted and appropriate model for the ultrasonic emulsification of liquids, an empirical investigation involving systematic variations of the ultrasonic parameters employed in the processing of a specific model system such as Zn-Bi is indicated. For a Zn-Bi sample with a fixed Bi concentration, three main parameters control the sonication process. These are: (1) the intensity of the applied ultrasound, (2) the sonication-time, and (3) the temperature of the melt as subjected to the ultrasound. Experiments are presently underway to explore the effects of variations of these important parameters in the case of the emulsification of Zn-Bi mixtures. In the case of experiments designed to explore increased time for ultrasonic processing, as noted earlier, the Ti-alloy used here for the ultrasonic horn tip reacts with Zn. Therefore, it has been necessary to keep the sonication time short and the temperature of the melt relatively low in order to minimize melt/tip interactions. In an attempt to avoid this limitation, some preliminary experiments have been carried out with a stainless steel tip. The first results show no indications of a reaction between the tip and the melt, and this system will be utilized in future experiments carried out for the purpose of exploring the effects of variations in the parameters noted above on the emulsification of immiscible liquid metals.

CONCLUSION

The present investigations have shown that high-intensity ultrasound can be effectively used to disperse one liquid metallic component into another thereby forming metal/metal-matrix composites. In the case of the Zn-Bi system, the composite material consists of essentially spherical particles of Bi embedded in a Zn matrix. Dispersed nanophase Bi particles with diameters below 0.5 μm can be formed, however, the overall distribution of the size of the dispersed Bi phase is rather broad. Future investigations will, therefore, focus on new methods

for more effectively controlling the size distribution of the minor metallic phase particles formed by ultrasonic dispersion techniques. Additionally, the resulting metal/metal-matrix Zn-Bi composite specimens will be characterized in terms of their physical, electronic, and mechanical properties and techniques for extending this general ultrasonic dispersal approach to higher melting point immiscible metals will be investigated.

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REFERENCES

1. For a review, see I. A. Ibrahim, F. A. Mohamed, and E. J. Laverna, *J. Mater. Sci.*
2. J. Bevk, J. P. Harbison, and J. L. Bell, *Appl. Phys.* **49**, 6031 (1978).
3. D. Verhoeven, F. A. Schmidt, E. D. Gibson and W. A. Spitzig, *J. Metals* **38**, 20 (1986).
4. D. Verhoeven, F. A. Schmidt, L. L. Jones, H. L. Downing, C. L. Trybus, E. D. Gibson, L. S. Chumbley, L. G. Fritzmeier, and G. D. Schnittgrund, *J. Mater. Eng.* **12**, 127 (1990).
5. B. Singh, R. Goswami, and K. Chattopadhyay, *Scripta Metall. Mater.* **28**, 1507 (1993).
6. W. Wood and A. L. Loomis, *Phil. Mag. S.7.* **4**, 417 (1927).
7. C. Bondy and K. Söllner, *Trans. Faraday Soc.* **32**, 556 (1936).
8. K. Söllner and C. Bondy, *Trans. Faraday Soc.* **32**, 616 (1936).
9. G. Schmidt and L. Ehret, *Zeitschr. Elektrochem.* **43**, 869 (1937).
10. G. Schmidt and A. Roll, *Zeitschr. Elektrochem.* **45**, 769 (1939); **46**, 653 (1939).
11. L. Ma, F. Chen, I. Shu, *J. Mater. Sci. Lett.* **14**, 649 (1995).
12. Hansen, Constitution of Binary Alloys, 2nd ed. (McGraw-Hill Book Company, New York, 1958).
13. H. G. Flynn in Physical Acoustics, edited by W. P. Mason (Academic Press, New York, 1964), **1B**, p. 57.
14. K. S. Suslick, *Scientific American* **260**, 80 (1989).