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Composition-dependence of core-shell microstructure formation in monotectic alloys under reduced gravity conditions

N. Wang*, L. Zhang, Y.L. Peng, W.J. Yao

The Key Laboratory of Space Applied Physics and Chemistry, Ministry of Education, School of Science, Northwestern Polytechnical University, Xi'an 710072, China

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Solidification microstructures have been examined in Cu—Pb and Fe—Sn alloys over a wide range of hypermonotectic compositions in which the core—shell structure was produced under reduced gravity condition in a 3 m drop tube. The contributions of alloy composition to the formation potential of core—shell microstructure were determined. It was found that the core—shell structure was obtained in the alloys with compositions near and on the left side not far away from critical point and it could be double- and triple-layer. The low melting point phase, Pb-rich phase in Cu—Pb alloys and Sn-rich phase in Fe—Sn alloys, always forms the shell in two-layer structure and it also forms the core in the three-layer structure. The Marangoni velocity was calculated to show the migration characteristics. The alloys with the critical composition experiences the longest migration period partly due to the less time consuming of the spinodal decomposition than the nucleation and partly due to the deepest miscibility gap, so that the core—shell microstructure is produced easily. With the composition departs from the critical point to the two sides in the miscibility gap, the formation ability of the core—shell structure decreases. The small migration velocity caused by the different thermophysical parameters of the two liquid phases for the alloy with the composition larger than the critical value leads to the difficulty for forming the core—shell structure.

1. Introduction

One characteristic of the phase diagrams of monotectic alloys or some peritectic alloys (Cu—Fe and Cu—Co etc.) is that there exists a stable or metastable liquid miscibility gap over a wide range of compositions, Fig. 1. The highest point on the binodal line is generally called critical point. When an alloy is cooled into the gap, liquid—liquid phase separation occurs and it leads to a coexistence of two liquid phases, A-rich L_1 phase and B-rich L_2 phase. This separation process may proceed via either nucleation-growth (NG) or spinodal decomposition (SD). One phase with minor volume fraction is usually called the minority phase (MP), which exists as droplets (MPDs) (For SD type, after initial stage transition). If the liquid mixture is exposed to some external factors such as temperature gradient, solute gradient, and/or density difference, MPDs will be driven to move and various patterns formations will occur. One typical case is the macroscopic layer-structure in connection with gravitation factor, in which a denser phase is in the lower part of the specimen while another lighter phase is in the upper part [1,2]. The other case found recently is that, if MPDs migrate to the center part in a spherical or cylindrical sample, a typical structure, core—shell structure, can be produced [3–8].

The research interest in the formation mechanisms of the core—shell microstructure is enhanced by the recent finding that the materials with this structure are the promising candidates for modern electronic packaging technology [9]. Previous investigations have revealed that the migration of one liquid phase driven by Marangoni convection is a key factor [3–8]. Due to the variation in the interfacial energies between the separated MPDs and the matrix, MPDs will be driven to migrate from the cold side to the warm side and congregate into an aggregation, the core. The temperature inside a spherical specimen prepared by the atomization or drop tube technique, increasing from the edge to the center, provides such a thermal gradient and can produce a spherical core in the specimen center. Such an explanation is plausible because the core—shell structure usually is obtained preferably under the microgravity or reduced gravity conditions,

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* Corresponding author.
E-mail address: nan.wang@nwpu.edu.cn (N. Wang).

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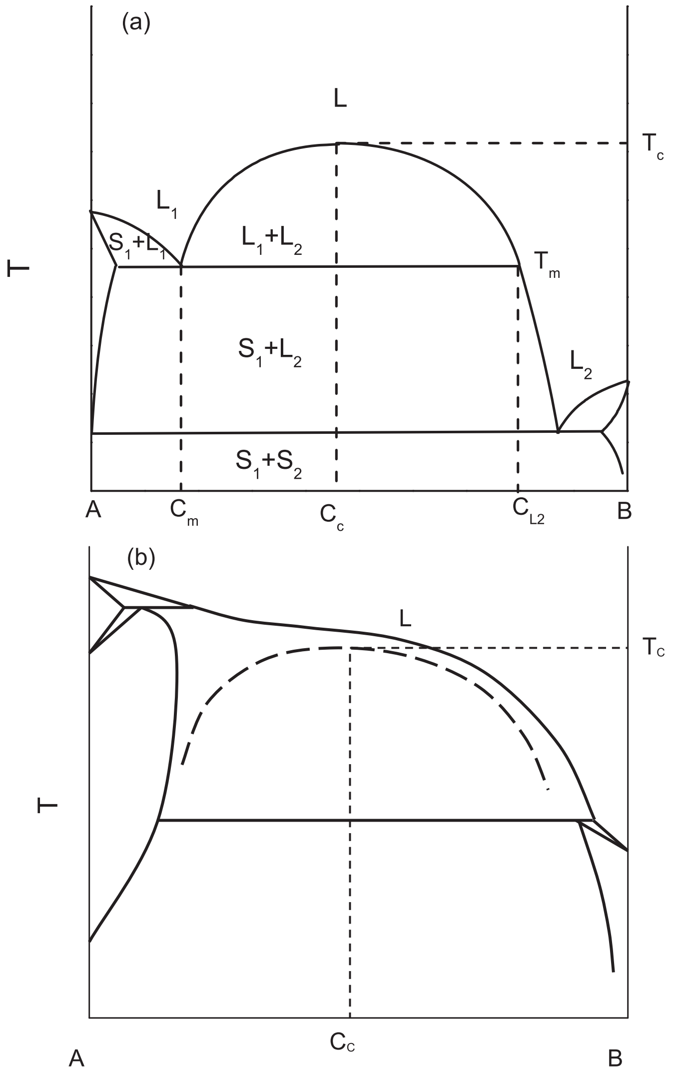

Fig. 1. Schematic illustrations of phase diagrams of (a) monotectic alloy with stable miscibility gap and (b) peritectic alloy with metastable miscibility gap (dashed curve). C_c and T_c are critical composition and temperature, respectively.

where Marangoni migration has stronger effect than the Stokes motion.

Although the Marangoni convection provides an explanation to the core–shell structure formation, the most works have been carried out for the alloys with specific compositions. One question is still not clear: over which composition range in the miscibility gap can the core–shell structure form?

The formation ability of the core–shell structure mainly depends on the Marangoni velocity of the minority phase and can be expressed as follows [10,11]:

$$V_m \approx \frac{-2r_d}{3\mu_d + 2\mu_m} \frac{\lambda_m}{\lambda_d + 2\lambda_m} \frac{\partial \sigma^{L_1/L_2}}{\partial r} \tag{1}$$

where r_d is the radius of the migrating droplet, μ_d and μ_m the viscosities of the droplet and matrix, λ_d and λ_m the thermal conductivities of the droplet and matrix, and $\partial\sigma^{L_1/L_2}/\partial r$ is the interfacial energy gradient. For checking the composition range for the core–shell structure, the effect of the composition on the above parameters should be considered.

Several effects of the composition should be considered. 1) It changes MP and its volume fraction. Different MPs have different viscosities and thermal conductivities. This will lead to the variation in the Marangoni velocity. 2) The variation in composition alters the interfacial energy, which also contributes to the Marangoni velocity. 3) The variation in composition changes the unmixing manner of the new liquid phase via NG or SD, which have different effects on the growth rate of MPDs. At the same time, the MPD's radius with SD type is much larger than with NG [12]. Therefore, through changing the phase separation type to change the MPD's radius can influence the Marangoni velocity too. The interaction of these three effects could affect the formation of the core–shell structure.

The aim of the present paper is to check this point. For this purpose, Cu–Pb and Fe–Sn monotectic alloys are selected for investigation and their phase diagrams [13] are shown in Fig. 2. Both alloys have the miscibility gaps with wide range of compositions. The drop tube technique is employed in this work. One advantage of this technique is that it can provide a microgravity (or reduced gravity) environment, so that the Stokes motion can be suppressed to a certain degree and the Marangoni migration effect will be revealed efficiently. The other advantage is that different size specimens will be produced and the size effect on the migration period can be determined.

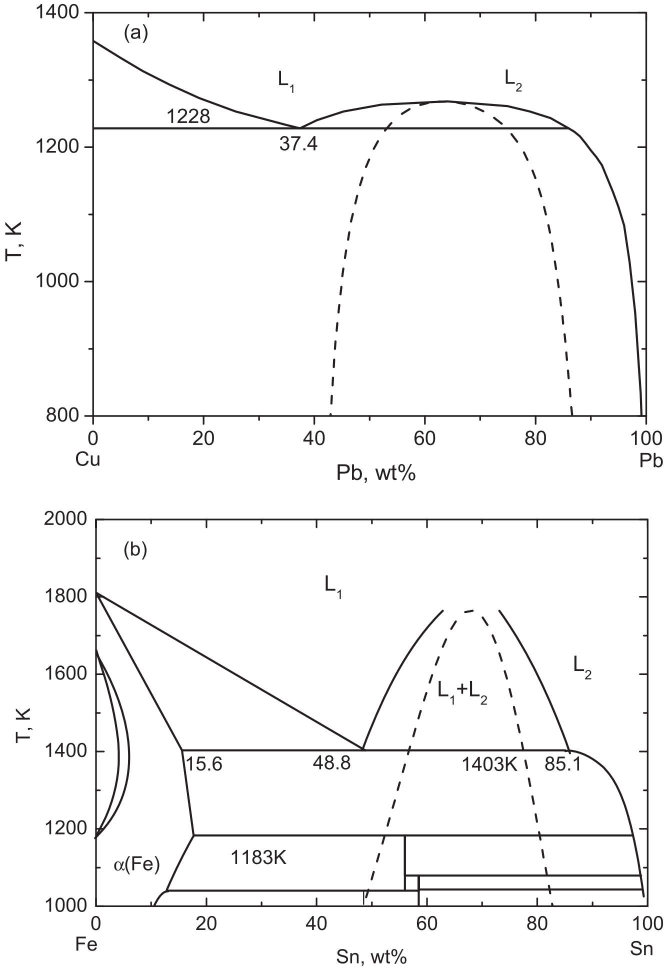

Fig. 2. Phase diagrams of (a) Cu–Pb and (b) Fe–Sn monotectic alloys. Dashed curves are calculated spinodal lines.