Improved Mechanical Properties in New, Pb-Free Solder Alloys

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The mechanical properties of solders benefit from uniform dispersion of fine precipitates and small effective grain sizes. Metallurgical methods of attaining such a beneficial microstructure have been investigated in two new, near-eutectic, Pb-free solder alloys systems—Sn-Zn-In (m.p. ~188°C) and Sn-Ag-Zn (m.p.~217°C). It has been found that small alloying additions of Ag dramatically improve the mechanical properties of the ternary Sn-8Zn-5In alloy. The improvement is attributed to the elimination of the coarse and nonuniform distribution of plate-like dendrites and refining the effective grain size in the solidified microstructure. Also, small amounts of Cu dramatically improve the ductility in the ternary Sn-3.5Ag-1Zn alloy. The quaternary Sn-3.5Ag-1Zn-0.5Cu has better mechanical properties than the binary Sn-3.5Ag alloy because it has a uniform fine dispersion of precipitates and a small effective grain size. The combination of high mechanical strength and high ductility is likely to yield improved fatigue resistance properties in the interconnection of electronic components.

Key words: Lead-free solders, mechanical properties, microstructure

INTRODUCTION

Lead-tin (Pb-Sn) alloys are the most prominent solders for the interconnection and packaging of modern electronic components and devices. However, there are environmental and health issues concerning the toxicity of Pb present in these solders. These concerns have inspired a great deal of research to determine if the use of Pb-free replacement alloys is feasible.[1] Current manufacturing technologies are based upon the 183°C melting point of the eutectic 63Sn-37Pb or near-eutectic 60Sn-40Pb, and the search for an appropriate Pb-free solder alloy with an equivalent melting point has posed a considerable challenge.

An underlying microstructural feature that leads to better mechanical properties in eutectic and near-eutectic Pb-Sn alloys are fine, uniform dispersions of the α-Pb and β-Sn phases within small eutectic colonies (small effective grain size). Such property enhancements have been observed in high cooling rate (quenching) experiments.[2] However, the inherent instability of the Pb-Sn alloy phases, with respect to coarsening, will unavoidably cause degradation of this beneficial microstructure and, hence, mechanical properties over time. A desirable new solder should be more stable with respect to microstructural coarsening and deform uniformly throughout the joint microstructure.

Simple examination of the binary phase diagrams for the Sn-9Zn[3] and Sn-3.5Ag[4] eutectic systems indicate that there is little solid solubility of either minority constituent in the β-Sn phase near room temperature. Therefore, the solder alloys based on these two systems show promise in being more resistant to microstructural coarsening than the eutectic and near-eutectic Pb-Sn alloys. Since quenching in a mi-

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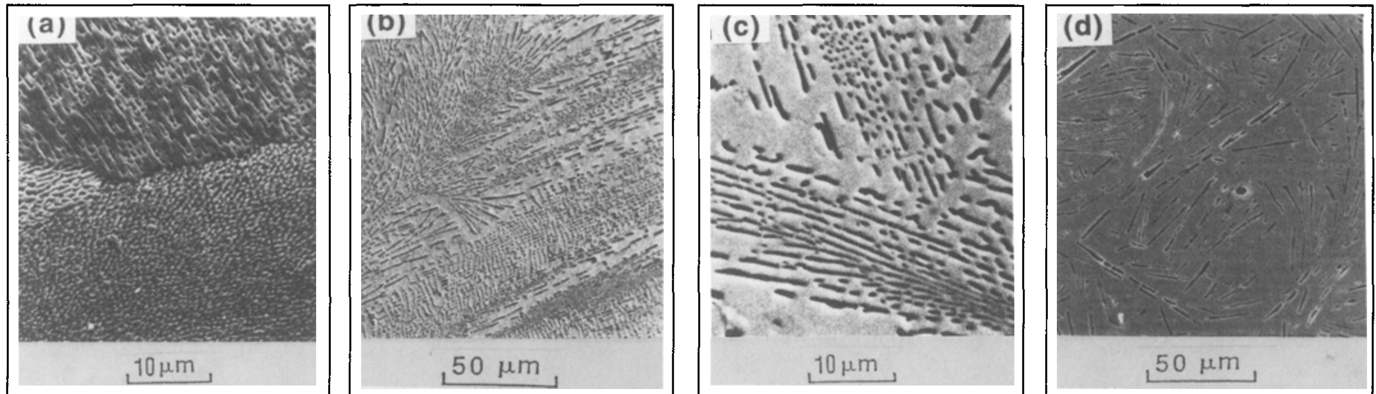

Fig. 1. Scanning electron micrographs for solder alloys of (a) Sn-9Zn, (b) Sn-8Zn-5In, (c) Sn-8Zn-5In (higher magnification), and (d) Sn-8Zn-5In-0.1Ag. The Ag addition suppresses the undesirable plate-like dendrite formation caused by the In additions and results in a smaller effective grain size.

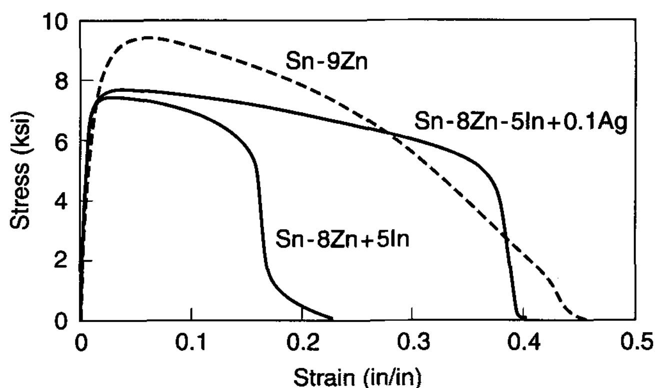

Fig. 2. Room temperature tensile stress-strain curves for the Pb-free solders of Sn-8Zn-5In and Sn-8Zn-5In-0.1Ag compositions. The curve for the binary eutectic Sn-9Zn solder alloy is shown for comparison.

crostructure with a fine, uniform phase distribution and small effective grain size is not always practical in manufacturing, alternative metallurgical methods of attaining such a beneficial microstructure have been investigated in two new, near-eutectic, Pb-free solder alloy systems: Sn-Zn-In[5–7] (m.p. ~188°C) and Sn-Ag-Zn[5,7,8] (m.p. ~217°C).

EXPERIMENTAL PROCEDURE

Alloy specimens were prepared from the pure (>99.99%) metals. The alloys were melted into 100 gm ingots within quartz tubes (14 mm inside diameter) under argon atmosphere, by homogenizing and repeatedly shaking at 800°C over 8 h. The air-cooled ingots were swaged to 3.7 mm, melted within 4 mm diameter quartz tubes with an argon atmosphere over-pressure, and then forced-air cooled within the quartz jacket. Eutectic and near-eutectic Pb-Sn specimens manufactured in this manner possess an as-cast grain size of about 40 microns.

The solder rods were then machined into round tensile specimens with a 12.7 mm gauge length and a 3 mm gauge diameter. Room temperature tensile testing was performed at strain rates of 1.0×10^{-3} s^{-1}. Differential scanning calorimetry (DSC) at successive 10 and 5°C per minute heating and cooling rates was used to investigate the melting characteristics of the alloys.

THE NEAR-EUTECTIC Sn-Zn-In SYSTEM

The Sn-9Zn eutectic melts at 198°C and consists of two phases—a body-centered tetragonal β-Sn matrix phase and a secondary phase of hexagonal Zn containing less than a per cent of Sn in solid solution.[3] The scanning electron microscope (SEM) image of the Sn-9Zn alloy in Fig. 1a exhibits large grains with a fine, uniform two-phase eutectic colony solidification structure. The matrix phase with the light contrast is β-Sn and the darker needle-like phase is the Zn-rich phase. The addition of 5% In to Sn-9Zn results in a depressed melting temperature of ~188°C and a markedly altered solidification microstructure.[5–7] The ternary composition was altered to Sn-8Zn-5In for a more eutectic-like melting character. The SEM micrograph of the Sn-8Zn-5In alloy shown in Fig. 1b shows that the In addition causes the formation of a rather undesirable microstructure; i.e., a much coarser and less uniform microstructure containing a plate-like dendritic structure which also consists of two phases. The plate-like dendrites appear to have branched out during solidification. These coarse plates are rather nonuniformly distributed and are composed of a fine dispersion of small Zn-rich needles, or platelets, oriented in the growth direction and are imbedded in the β-Sn phase. The areas between dendrite branches are filled with a similar morphology, although with a much lower concentration and sparser distribution, as shown in Fig. 1c. The dendritic plates with the fine dispersion of Zn precipitates should be stronger than the inter-dendritic regions. Energy dispersive x-ray analysis (EDXA) indicates that the dendrite growth plates contain slightly less In than the inter-dendritic regions. This type of solidification microstructure induced by the In addition can profoundly degrade the mechanical properties of the alloy due to the nonuniform distribution of the mechanically harder dendritic plates leads to preferred crack growth at the softer inter-dendritic regions.

The undesirable dendritic solidification structure present in the Sn-Zn-In alloy can be modified by small additions (as low as 0.1 wt%) of Ag.[9] Shown in Fig. 1d is an SEM micrograph of the Sn-8Zn-5In-0.1Ag alloy microstructure. It is apparent from the micrograph

that the addition of only 0.1% Ag effectively inhibits the uncontrolled growth of the large plate-like dendritic structure that was shown in the micrograph of Fig. 1b for the ternary Sn-8Zn5In alloy. The cause for the microstructural changes induced by the Ag addition is not clearly understood at this time. The Ag appears to promote a higher nucleation density of solid phases during solidification. The high density and apparent random relative positioning of these solid phase nuclei causes them to immediately impinge upon one another and keep the large plate-like structure from forming. The resultant microstructure (Fig. 1d) has a finer effective grain size, or eutectic colony structure, than the binary eutectic Sn-9Zn alloy (Fig. 1 a) although the size of the Zn-rich phase precipitates is larger. It is believed that the small additions of Ag go primarily into solution within the β-Sn phase, since no evidence of Ag-containing precipitates has yet been found. When a larger addition of Ag is added (0.5 wt. %), isolated Ag-Zn precipitates form near needles of the Zn-rich phase within some colonies. The Ag-Zn precipitates do not appear to have much influence impeding dendrite growth or nucleating the eutectic colonies.

The effect of Ag additions on mechanical properties can be seen from the tensile test data shown in Fig. 2. Significantly improved ductility in the Ag-doped alloy compared to the ternary Sn-8Zn-5In is evident. The large decrease in ductility caused by In additions to the binary Sn-9Zn alloy is due to inter-dendritic plate separation under stress, as can be seen by the flat plate-like facets on the fracture surface of the Sn-8Zn-5In specimen shown in Fig. 3. The Ag-doping eliminates the adverse dendritic structure, thus restoring ductility commensurate with the binary eutectic Sn-9Zn alloy. In the tensile curves in Fig. 2, both the binary Sn-9Zn and the quaternary Ag-containing alloys fail at about the same level of ductility. After the peak tensile stresses are reached at ~0.05 strain, the binary Sn-9Zn has a much steeper slope. This steeper slope indicates the formation of a localized neck. The much shallower slope of the Ag-containing alloys indicates that the deformation up to failure is distributed much more uniformly throughout these alloys. More uniform deformation is a desirable characteristic for fatigue resistance and is a result of the fine, random distribution of the eutectic colonies.

The additions of both 0.1 and 0.5% Ag to Sn-8Zn-5In result in similar tensile behavior, while a small amount of ductility appears to be lost when as much as 1% Ag is added. The greater amounts of Ag do not change the scale of the eutectic colony structure, but the number of Ag-Zn precipitates increases dramatically over 0.5% Ag. It should be noted that the loss in ductility associated with the increase in Ag-Zn precipitates at larger Ag alloying contents is not accompanied by an increase in strength, the reasons for which are not completely understood at this time.

Besides Ag, small additions of Cu were found to be beneficial. The effect of Cu additions to the solidification microstructure and subsequent ductility of the Sn-8Zn-5In alloy was found to be essentially the same as that of the Ag additions, except that the 1% Cu addition appeared to be less ductile than the 1% Ag alloy. The only appreciable difference between the Ag and Cu additions to the ternary Sn-8Zn-5In alloy is their effects on the melting character of the alloys. At 0.1% additions, both Ag and Cu appear to retain the near-eutectic melting character of the alloy, with Ag reducing the melting point very slightly from 188 to 187°C. The increase to 0.5% Ag again shows a clean eutectic melting character at 187°C, but the 0.5% Cu addition results in the appearance of a small amount of higher melting material (presumably the Cu-Zn phase) which does not completely melt until ~200°C. At 1% additions of both Ag and Cu, there is a large amount of higher melting point material, with both the Ag-Zn and Cu-Zn precipitates melting at approxi-

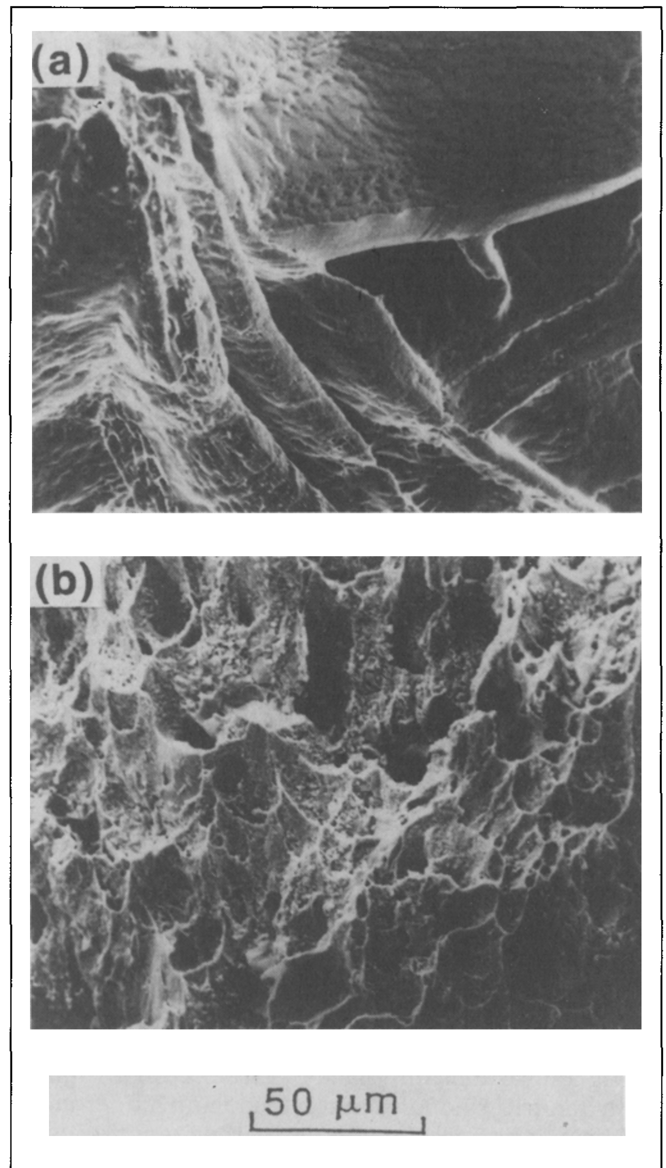

Fig. 3. Fracture surfaces of the (a) Sn-8Zn-5In and (b) Sn-8Zn-5In-0.1Ag solder alloys. The Ag-free alloy displays undesirable plate-like fracture features and the Ag-containing alloy displays the more desirable ductile dimples on the fracture surface.

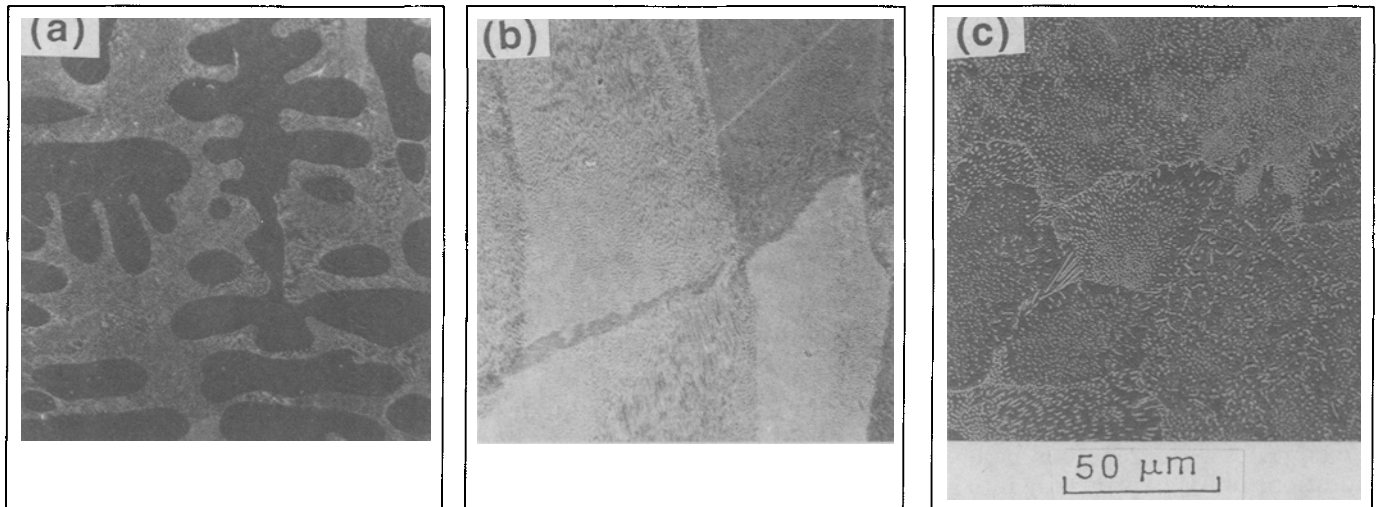

Fig. 4. Scanning electron micrographs of (a) Sn-3.5Ag, (b) Sn-3.5Ag-1Zn, and (c) Sn-3.5Ag-1Zn-0.5Cu showing the 1% Zn addition suppressing the formation of β-Sn dendrites and the additional 0.5%Cu addition reducing the effective grain size.

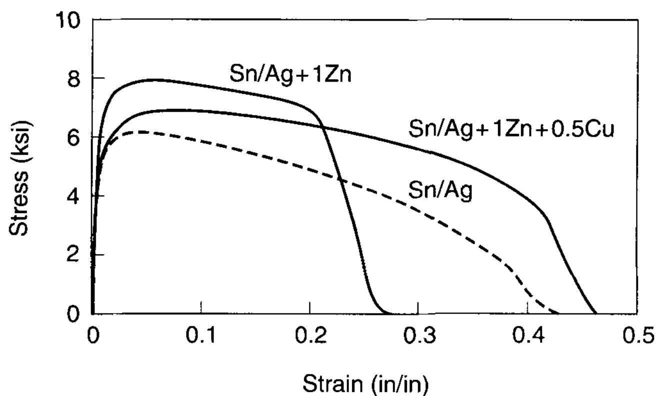

Fig. 5. Room temperature tensile stress-strain curves for the Pb-free solders of Sn-3.5Ag-1Zn and Sn-3.5Ag-1Zn-0.5Cu compositions. The curve for the binary eutectic Sn-3.5Ag solder alloy is also shown for comparison.

mately 200–205°C. The differences in melting behavior between the Ag and Cu additions indicate that small Ag additions may be preferable to Cu additions in maintaining a near-eutectic melting behavior.

THE NEAR-EUTECTIC Sn-Ag-Zn SYSTEM

It is difficult to significantly reduce the melting temperature of the Sn-3.5Ag binary eutectic by large solute additions to the β-Sn matrix phase and still maintain good mechanical properties.[10] The solidification microstructure of the binary eutectic Sn-3.5%Ag alloy is shown in the SEM image of Fig. 4a. The dark contrast dendritic globules are the β-Sn phase and the lighter contrast inter-dendritic regions contain the eutectic dispersion of Ag_3Sn precipitates within a β-Sn matrix. This soldification microstructure of Sn-3.5Ag alloy can be improved by eliminating the large β-Sn dendritic globules and introducing a finer more uniform two-phase distribution throughout the alloy. Previous work[5,7,8] has shown that this can be accomplished by a 1% addition of Zn. The 1% Zn addition suppresses the formation of β-Sn dendrites and results in a uniform dispersion of Ag_3Sn precipitates throughout the microstructure, as can be seen in the micrograph of Fig. 4b. The fine, uniform dispersion of precipitates throughout the alloy is responsible for the significant strength increase exhibited by the Sn-3.5%Ag-1%Zn alloy over that of the binary Sn-3.5% Ag alloy.

Besides the more uniform distribution of the Ag_3Sn precipitates throughout the alloy microstructure, the 1% Zn alloy also results in an increased effective grain size. As seen in Fig. 4b, there are large grains, or eutectic colonies, separated by sharp, almost linear, boundaries. It is well known that large grain sizes in metals and alloys often lead to a decrease in ductility or fracture toughness. The ductility in the Sn-3.5%-1%Zn ternary alloy is reduced compared to that in the Sn-3.5Ag binary alloy, which becomes more evident if the deformation occurs at slower deformation rates. The Sn-3.5Ag-1%Zn alloy[5,7,8] decreases the eutectic melting point to 217°C and has been shown to be extremely resistant to creep at 125°C. Increased ductility should result from a smaller effective grain size. Such grain refinement is accomplished by adding a small amount of Cu (0.5-1.0%) in addition to the ~1%Zn.[11]

The microstructure of the quaternary Sn-3.5%-1%Zn-0.5%Cu alloy, shown in the SEM micrograph of Fig. 4c, resembles that of the ternary Sn-3.5%Ag-1%Zn alloy in that there is a fine dispersion of precipitates throughout the microstructure and the formation of precipitate-free β-Sn dendritic globules has been completely suppressed. However, in contrast to the ternary alloy, the quaternary alloy possesses smaller and more irregularly shaped eutectic colonies. In some colonies, the dispersion of precipitates is not as fine and the precipitates tend to be slightly larger. Energy dispersive x-ray analysis results indicate the precipitates in the regions with the coarser precipitate distribution tend to have a greater amount of Zn and Cu incorporated into the Ag-Sn precipitates.

The microstructural changes that occur as a result of the quaternary 0.5%Cu addition to the ternary Sn-

3.5%-1%Zn alloy have a pronounced effect on the mechanical properties, as shown in the comparative tensile curves in Fig. 5. At the lower deformation rates used in this work (1.0×10^{-3} s^{-1} compared to 3.33×10^{-1} s^{-1} in Ref. 8), the ternary Sn-3.5%Ag-1%Zn alloy has over 30% more ultimate tensile strength than the binary Sn-3.5%Ag alloy, but the ductility (as measured by the total elongation to failure) decreases from 40% to 25%. The quaternary addition of 0.5%Cu, through microstructural modifications, recovers the lost ductility caused by the 1%Zn addition to the Sn-3.5%Ag binary alloy. Thus, the quaternary alloy exhibits improvements in both the strength and ductility as compared to those of the binary Sn-3.5%Ag eutectic.

Figure 5 also shows that after the peak tensile stresses at ~0.05 strain, the binary Sn-3.5%Ag has a much steeper slope than the quaternary Sn-3.5%Ag-1%Zn-0.5%Cu alloy. Again, this steeper slope indicates the formation of a localized neck. The shallower slope of the Cu-containing alloys indicates that the deformation up to failure is distributed much more uniformly throughout the material. The observation that both strength and ductility increased together with more uniform deformation is significant because it indicates that more work is required to fracture this alloy by extensive deformation. The greater resistance to fracture and more uniform deformation of these alloys is likely to enhance fatigue resistance. Pb-Sn alloys with finer eutectic colonies have previously been found to exhibit improved fatigue resistance.[2]

Adding excess Cu and/or Zn beyond 1% levels causes the precipitation of different intermetallic phases and noticeable changes in the microstructure. The comparative micrographs in Fig. 6 show the different morphologies that develop as the amounts of Cu and/or Zn are increased. These different intermetallic phase particles tend to be very coarse (20 μm in size) and deplete the surrounding region of small Ag_3Sn precipitates which form the basis of precipitation hardening in the Sn-Ag based eutectic alloy. The microstructure then begins to resemble that of the original Sn-3.5%Ag binary alloy, only now with the globular β-Sn dendrites containing a few large Cu or Zn rich precipitates, rather than many small precipitates. These regions then become precipitate-free zones. The presence of these coarse precipitates and the accompanying nonuniformity in the microstructure is most likely the cause of the observed decrease in the ductility of the alloys with excess Cu or Zn as compared to the Sn-3.5%Ag-1%Zn-0.5Cu alloy.

SUMMARY

The mechanical properties of solders benefit from uniform dispersions of fine precipitates and small effective grain sizes. Such a desirable microstructure must also be stable in order for the benefits to be realized over long periods of time and at elevated temperatures. Lead-free alloys based on Sn-9Zn and Sn-3.5Ag, because they are more resistant to coarsening and are promising from a mechanical properties standpoint. It has been found that small alloying additions of Ag dramatically improve the mechanical properties of the ternary Sn-8Zn-5In alloy. The improvement is attributed to the elimination of the coarse and nonuniform distribution of plate-like dendrites and refining the effective grain size in the solidification microstructure. The Sn-8Zn-SIn alloys with 0.1 to 0.5% Ag additions exhibit a near-eutectic melting point comparable to that of near-eutectic Pb-Sn alloys, and is very promising as a Pb-free drop-in replacement. The quaternary Sn-3.5Ag-1Zn-0.5Cu, while only reducing the melting point to ~217°C, has better mechanical properties than the binary Sn-3.5Ag alloy because of its uniform fine dispersion of precipitates and a small effective grain size. The combination of high mechanical strength, good ductility, and homogeneous deformation of the alloy is likely to yield improved fatigue resistance properties in the interconnection of electronic components.

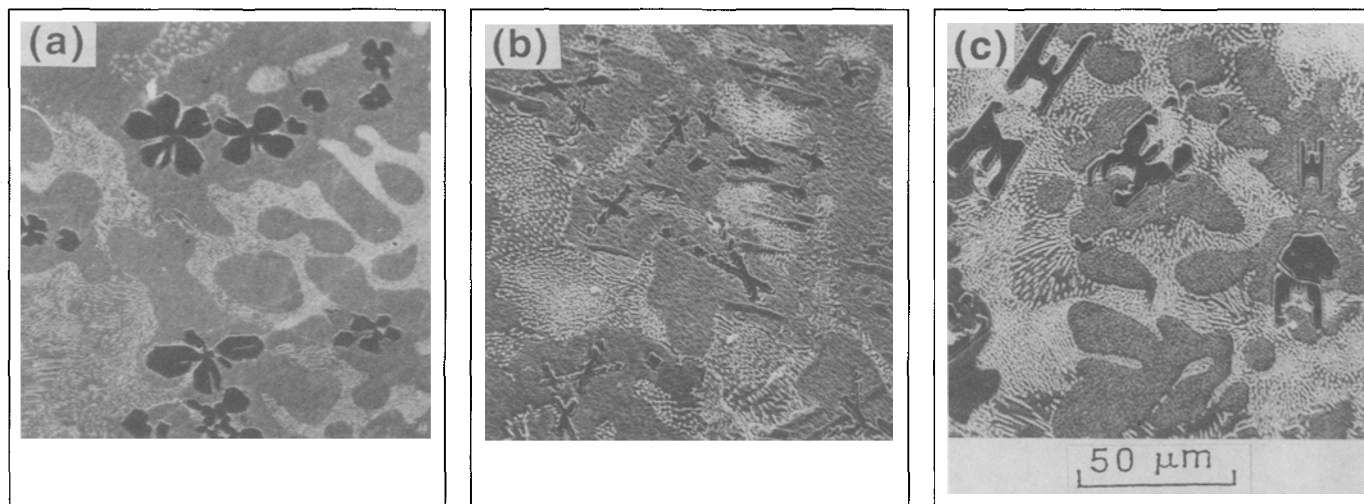

Fig. 6. Scanning electron micrographs for Sn-3.5%Ag-Zn-Cu with (a) 2%Zn-2%Cu, (b) 2%Zn-1%Cu, and (c) 1%Zn-2%Cu contents showing the different intermetallics that form and the associated precipitate-free zones.

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