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**THE EFFECT OF Cu_6Sn_5 WHISKER PRECIPITATES
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ABSTRACT

Hollow, Cu_6Sn_5 intermetallic rods form within molten 60Sn-40Pb solder when it reacts with Cu. It is suggested that these rods form at the Cu surface by a screw dislocation mechanism and break off into the bulk solder. Hollow hexagonal intermetallics result when the core of the rod dissolves away and fills with molten solder. The mechanical properties of bulk 60Sn-40Pb solder with and without the Cu_6Sn_5 intermetallic rods were tested in tension, at -196°C , 20°C , and 125°C . The intermetallics had no effect on strength, but decreased elongation at the lower temperatures. The intermetallics had a large effect on the fracture characteristics. At -196°C failures initiate by interfacial separation between the intermetallic and solder matrix. At 20°C failures initiate at cleaved intermetallic rods. At 125°C the intermetallic rods appear to have little effect on the mechanical properties.

Key Words: Sn-Pb Solder, Cu_6Sn_5 Intermetallic, Intermetallic Whisker Formation, Intermetallic Precipitates, Mechanical Properties of Solder.

INTRODUCTION

The importance of Sn-Pb solder joints in the microelectronics industry makes it important that the microstructure and mechanical properties of the joints be fully understood. Sn-Pb solder is commonly used to join Cu surfaces. When the molten solder is in contact with Cu, intermetallic layers of Cu-Sn form¹⁻⁵. The brittleness of these interfacial intermetallics influences the mechanical integrity of the joint^{6,7}. In addition to these interfacial intermetallics, Cu₆Sn₅ intermetallics are found in the bulk solder region of the solder joint⁸. The interfacial intermetallic layers that form between Cu and Pb-Sn solder have been characterized¹⁻⁶. However, the means by which intermetallics form in the bulk solder and their effect on the mechanical properties of the solder are not well understood. This paper presents the results of an investigation of the morphology of the bulk intermetallics and their influence on the mechanical properties of Pb-Sn solder.

To characterize the intermetallics that form in a Pb-Sn solder/Cu joint a detailed microscopic examination was performed. To determine how bulk solder intermetallics influence mechanical properties bulk 60Sn-40Pb solder was tested in tension both with and without Cu₆Sn₅ intermetallics.

EXPERIMENTAL PROCEDURE

Samples of Cu/60Sn-40Pb solder were prepared to examine the Cu-Sn intermetallics that form on soldering. Two Cu plates were polished, etched and fluxed. These plates were bolted together with a 0.51 mm (0.02 in.) spacer to form a gap. The assembly was placed in a vacuum furnace that was backfilled with Argon. The solder and Cu were heated separately to 230°C, during which time residual flux evaporated off the Cu surfaces. The Cu plates were immersed into the solder bath. The assembly was then quickly cooled to room temperature. Samples were cut from the assembly and prepared for metallographic observation of the joint.

Fig. 1 diagrams the method by which ingots of 60Sn-40Pb were processed to include Cu-Sn intermetallics in the bulk solder. A coil of Cu foil was etched, fluxed, and placed in the vacuum furnace as described above. The coil was left in the molten solder for 15 minutes to allow some of the Cu to dissolve into the solder⁹. The Cu foil was then removed and the solder ingot quickly cooled. Tensile specimens were cut and machined from this ingot (and an ingot of pure 60Sn-40Pb, for comparison) in the dimensions of Fig. 2. The specimen was held by friction grips and strained to failure in a screw driven loadframe at a strain rate of 0.51 mm/min (0.02 in/min). Tests at -196°C were performed in a liquid nitrogen bath. Tests at 125°C were performed in a silicone oil bath with a temperature controller accurate to ±1°C. The fracture surfaces were then examined in the SEM.

RESULTS AND DISCUSSION

Microstructure

When molten 60Sn-40Pb solder comes in contact with Cu a two layer interfacial intermetallic microstructure develops (Fig. 3). The intermetallic structures are: ε-phase (Cu₃Sn) adjacent to the Cu, and η-phase (Cu₆Sn₅) adjacent to the solder. In addition to the

interfacial intermetallics, intermetallic rods are also found in the bulk solder of the joint (Fig. 4). The rods were determined to be η -phase Cu_6Sn_5 by Energy Dispersive x-ray Analysis in the SEM. The Cu_6Sn_5 phase was found by Hansen¹⁰ to be of the hexagonal B8_1 , NiAs type. The intermetallics have a rod-like hexagonal faceted morphology. It is interesting to note that the rods are often open ended tubes filled with solder. The unusual shapes of the intermetallics shown in Fig. 5 are found when the intermetallic rods are cut through different cross sections.

A possible explanation for the formation of the hollow intermetallic rods is the following. When the molten solder comes into contact with the Cu the Sn and Cu react to form Cu_6Sn_5 . The Cu_6Sn_5 can grow out into the molten solder as a hexagonal rod along a screw dislocation using the ledge mechanism, illustrated in Fig. 6. This proposed mechanism of intermetallic formation incorporates the theory where whiskers are produced in metals using a single screw dislocation along the long axis of the whiskers¹¹. The rod then breaks off, due to turbulence, into the molten solder where the Cu concentration is relatively low. The low Cu concentration causes the intermetallic rods to begin to dissolve. The screw dislocation core of the intermetallic rod, because of its higher energy, is the first portion of the rod to dissolve and is replaced by molten solder. Eventually the entire core of the rod is eliminated and a hollow tube of Cu_6Sn_5 intermetallic remains, filled with solder. Fig. 7 shows an intermetallic rod just after it has broken off. The core at one end is just beginning to dissolve. This figure also demonstrates the large size of the intermetallic rods.

Mechanical Properties

To study the effect that the intermetallic rods have on the mechanical properties of 60Sn-40Pb solder bulk solder, specimens were tested in tension. Samples of both 60Sn-40Pb solder and 60Sn-40Pb solder with intermetallics were tested at -196°C , 20°C , and 125°C . These temperatures were selected to clarify the temperature dependence of the effect. Fig. 8 shows typical stress vs. strain curves for 60Sn-40Pb solder tested at -196°C , 20°C , and 125°C . The ultimate strengths decreased with increasing temperature while elongation increases with increasing temperature.

Fig. 9a-c shows stress vs. strain plots that compare pure 60Sn-40Pb to 60Sn-40Pb with intermetallics at the three temperatures tested. Fig. 9a shows the samples at 125°C . There is little or no difference between the two samples; the ultimate strengths are both about 15 MPa. There is a small increase in total elongation for the pure 60Sn-40Pb sample. Fig. 9b shows the samples tested at 20°C . Again there is very little change in the ultimate strengths, which are about 45 MPa, but the total elongation is greater in the pure 60Sn-40Pb sample. Fig. 9c is the plot of the samples at -196°C . The ultimate strengths are still almost identical at 130 MPa. However, the elongation is substantially greater for the pure 60Sn-40Pb sample. The work hardening rate is increased significantly by the addition of the Cu_6Sn_5 intermetallic rods to the solder.

Fig. 10 shows macrographs taken of the solder samples tested in tension as a function of temperature and presence of intermetallics. The amount of plastic deformation also increases with an increase in testing temperature. The pure 60Sn-40Pb sample necked to a point at

125°C. The amount of secondary cracking was extensive in the 60Sn-40Pb with intermetallics tested at 20°C. The amount of visible plastic deformation was smaller in the samples containing the intermetallics. From the above observation the presence of intermetallics in the bulk solder influences the mechanical properties of the solder. To understand the effect of the intermetallics on the fracture mode the fracture surfaces were characterized in the SEM.

Fig. 11 is an SEM fractograph of pure 60Sn-40Pb failed at -196°C. The entire fracture surface is ductile. Fig. 12 is an SEM fractograph of 60Sn-40Pb with intermetallics failed at the same temperature. This figure clearly illustrates the hexagonal shape of the intermetallic rods and that the rods are tubes filled with ductile solder. The failure at -196°C is an interfacial separation between the intermetallic rods and the solder matrix. The temperature is so low that mass flow of the solder is very difficult. Apparently dislocations introduced during deformation pile up at the intermetallics rods eventually leading up to interfacial separation and failure. This hypothesis is further substantiated by the stress strain curve in Fig. 9c, which shows that the work hardening rate increases with the introduction of the intermetallic rods.

Fig. 13 is an SEM micrograph of the 60Sn-40Pb sample with intermetallics that failed at 20°C. This fractograph can be compared to that of the pure solder sample, at the same temperature, which is given in Fig. 14. At 20°C the fracture surface of the sample with intermetallics is composed of a large number of cleaved intermetallic rods. The larger intermetallic rods act as preferential nucleation sites for cracks and therefore the fracture surface is composed of large cleaved rods. The matrix around the intermetallics is also very ductile. At 20°C the 60Sn-40Pb solder is at .63 of its homologous temperature but the temperature is still low enough to make mass flow of the Pb-Sn matrix around the intermetallics difficult at the relatively high strain rate in the tensile test. This puts a stress upon the brittle intermetallic rods which cleave, initiating the failure. The cleavage of the rods during deformation leads to the extensive secondary cracking seen in this sample.

Fig. 15 is an SEM micrograph of the 60Sn-40Pb with intermetallics sample fractured at 125°C. The fracture is ductile with very few intermetallics present at the surface. This sample can not be compared with the pure 60Sn-40Pb sample as the pure specimen necked down to a point. At this elevated temperature the intermetallics had little influence on the fracture appearance of the 60Sn-40Pb with intermetallics sample. At 125°C the solder is at .86 of its homologous temperature so the Pb-Sn matrix can readily flow around the intermetallics during deformation. In contrast to the specimens fractured at lower temperatures, the intermetallics are not obvious initiation sites for failure at 125°C.

Other work¹² has investigated the room temperature tensile properties of 60Sn-40Pb soldered to Cu plates and found that the hollow intermetallic tubes formed in the joint had a beneficial influence on the fracture strength. This effect is currently under further investigation.

SUMMARY AND CONCLUSIONS

When molten 60Sn-40Pb solder comes in contact with Cu intermetallic hexagonal rods of Cu_6Sn_5 appear in the bulk solder. The rods apparently form at the Cu/molten solder interface through a screw dislocation ledge mechanism. When the rods break off into the low-Cu bulk redissolution begins at the core of the intermetallic rod which is replaced by molten solder. When the solder is solidified it contains residual hexagonal tubes of Cu_6Sn_5 intermetallic filled with solder.

The effect of the intermetallic rods on the mechanical properties of the solder was tested in tension as a function of temperature. The intermetallic rods had no effect on the ultimate strength of the specimens tested. The intermetallics did act to decrease the total elongation to failure, especially at 20°C and -196°C . The intermetallics also increased the work hardening rate at -196°C . Decohesive failure occurs between the intermetallic rods and the solder matrix at -196°C . At 20°C the solder matrix can flow around the intermetallics during straining but a stress is still present on the intermetallics causing them to cleave. At 125°C the intermetallics have little or no effect on the mechanical properties of the bulk solder.

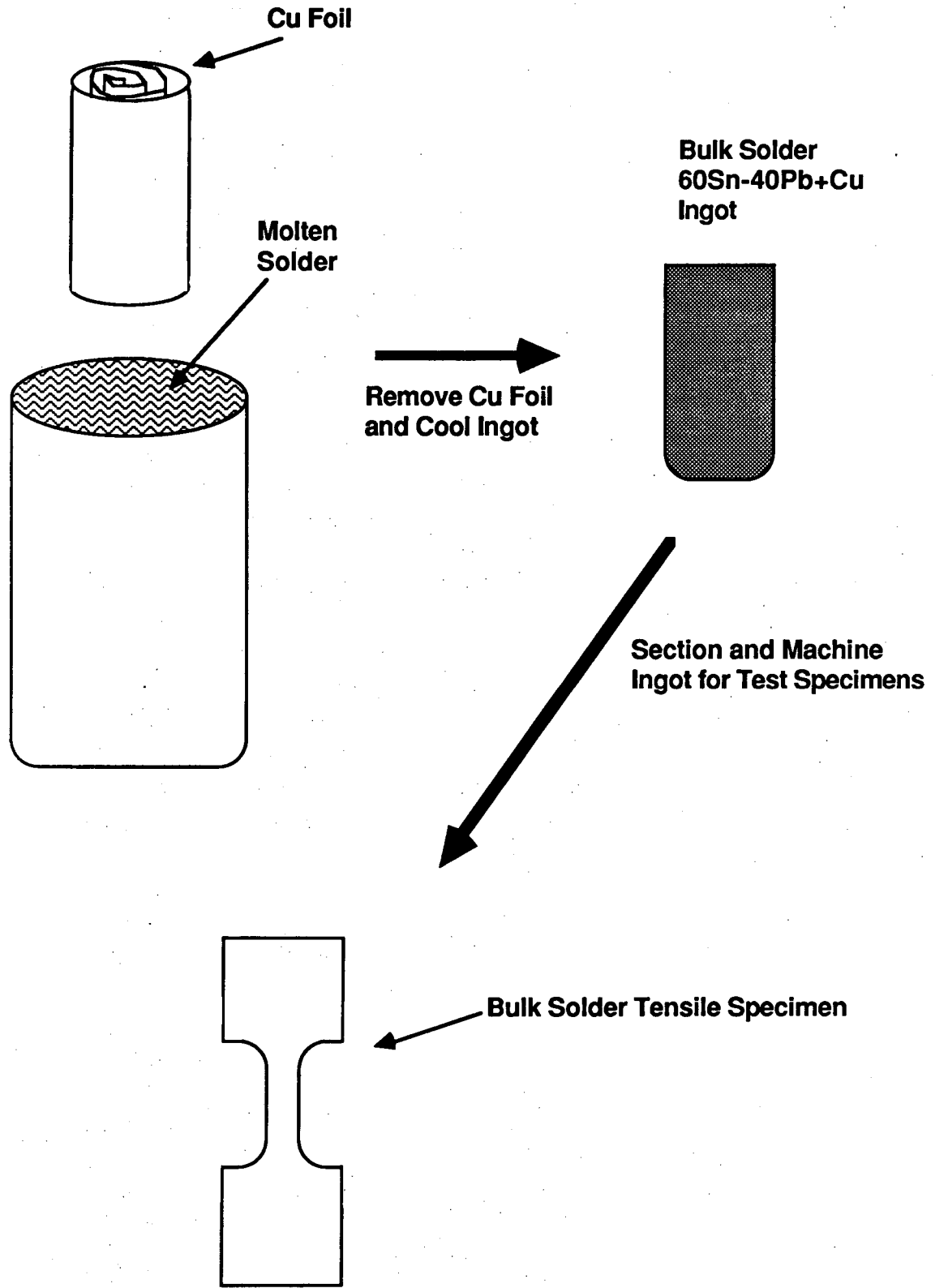
The presence of the intermetallic rods in bulk solder is detrimental to the mechanical properties, especially at low temperatures. The rods act as nucleation sites for failure either by cleavage or interfacial separation in bulk solder. This indicates that the intermetallic rods would have adverse effects on solder joints that undergo deformation.

ACKNOWLEDGEMENTS

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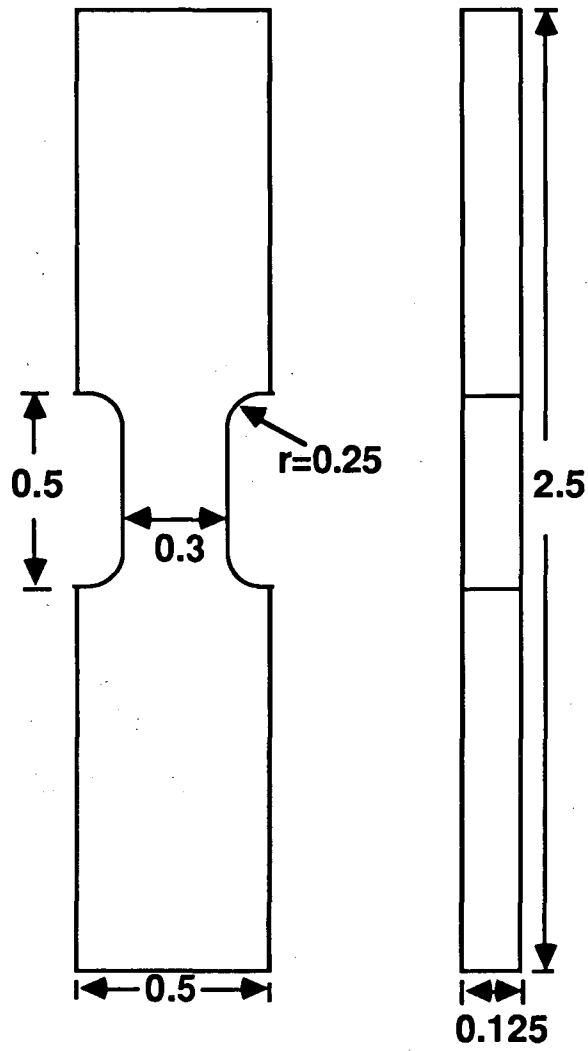
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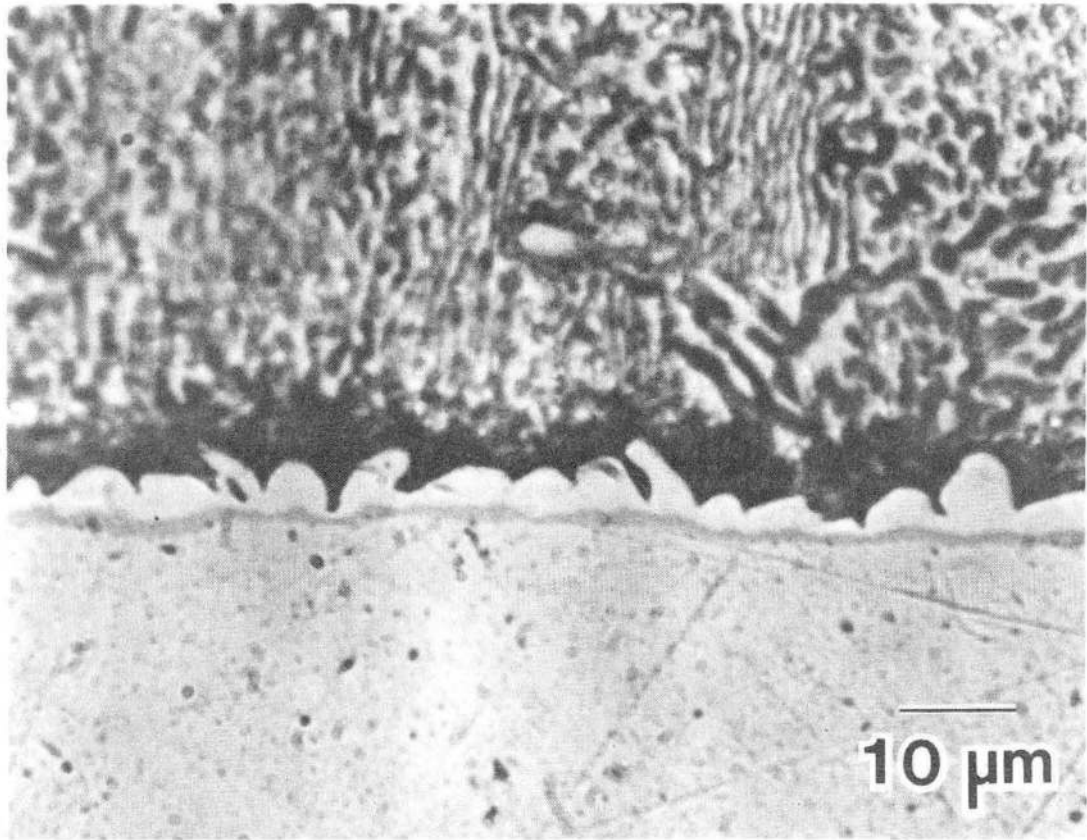
Fig. 1 Processing method used to manufacture bulk ingots of 60Sn-40Pb with Cu-Sn intermetallics.



Dimensions in inches

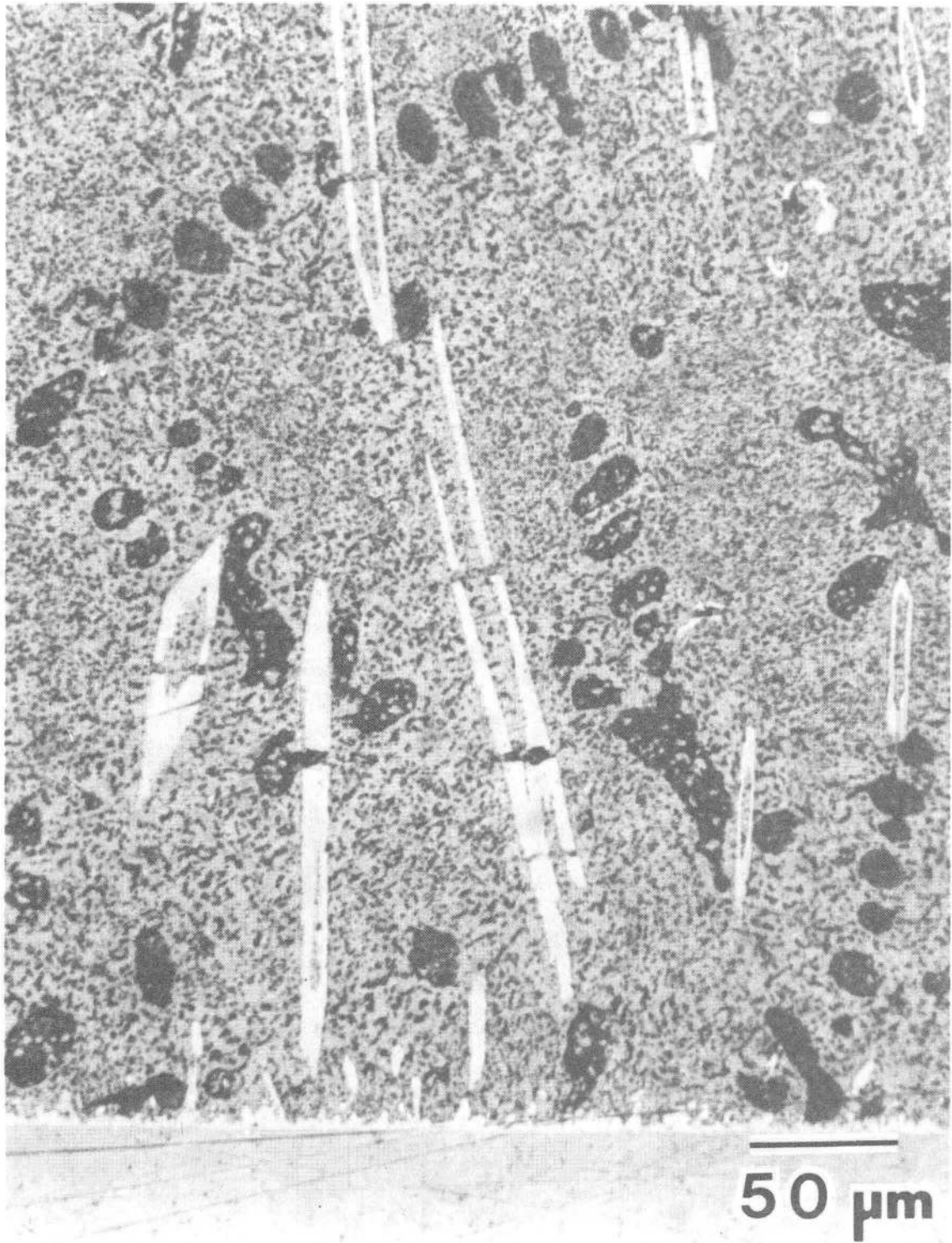
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Fig. 2 Tensile specimen used to test bulk solder.



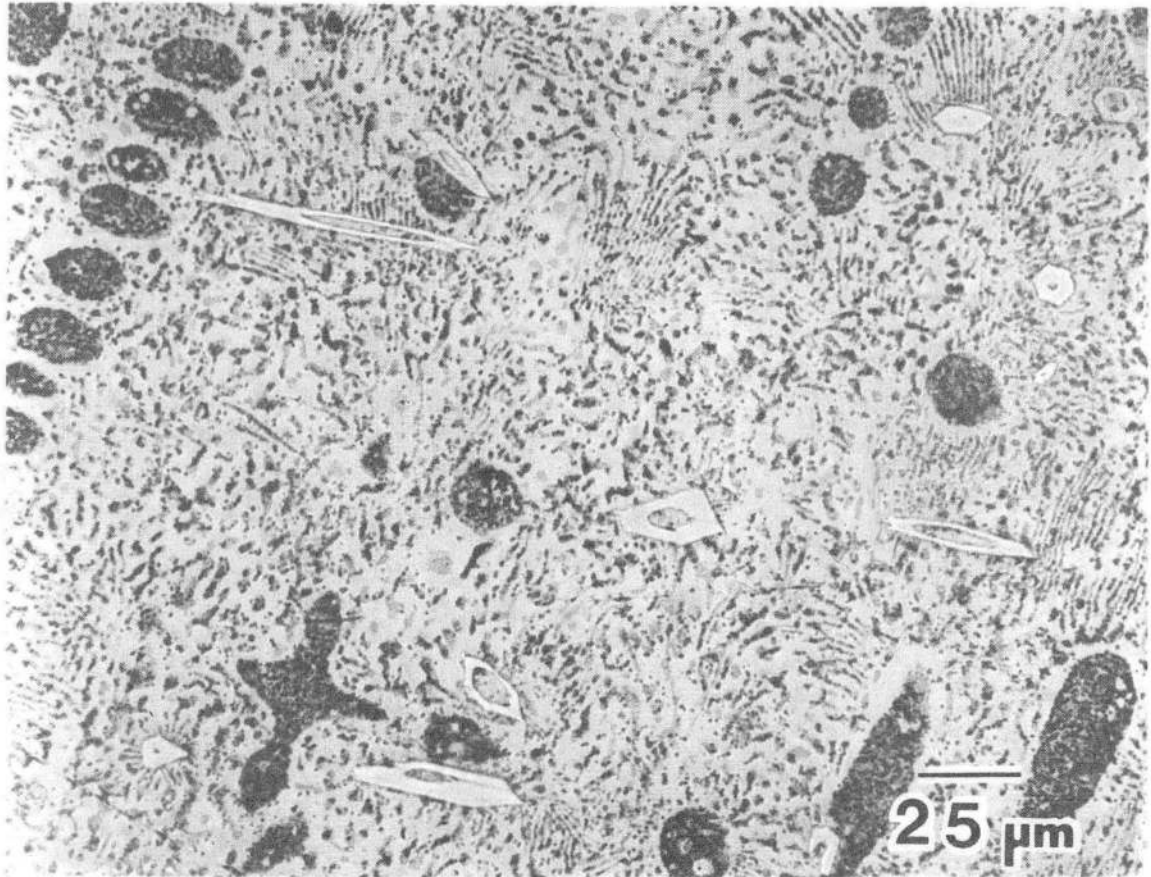
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Fig. 3 Optical micrograph of 60Sn-40Pb solder on Cu.
Intermetallic phases present are Cu_3Sn adjacent to the Cu
and Cu_6Sn_5 adjacent to the solder.



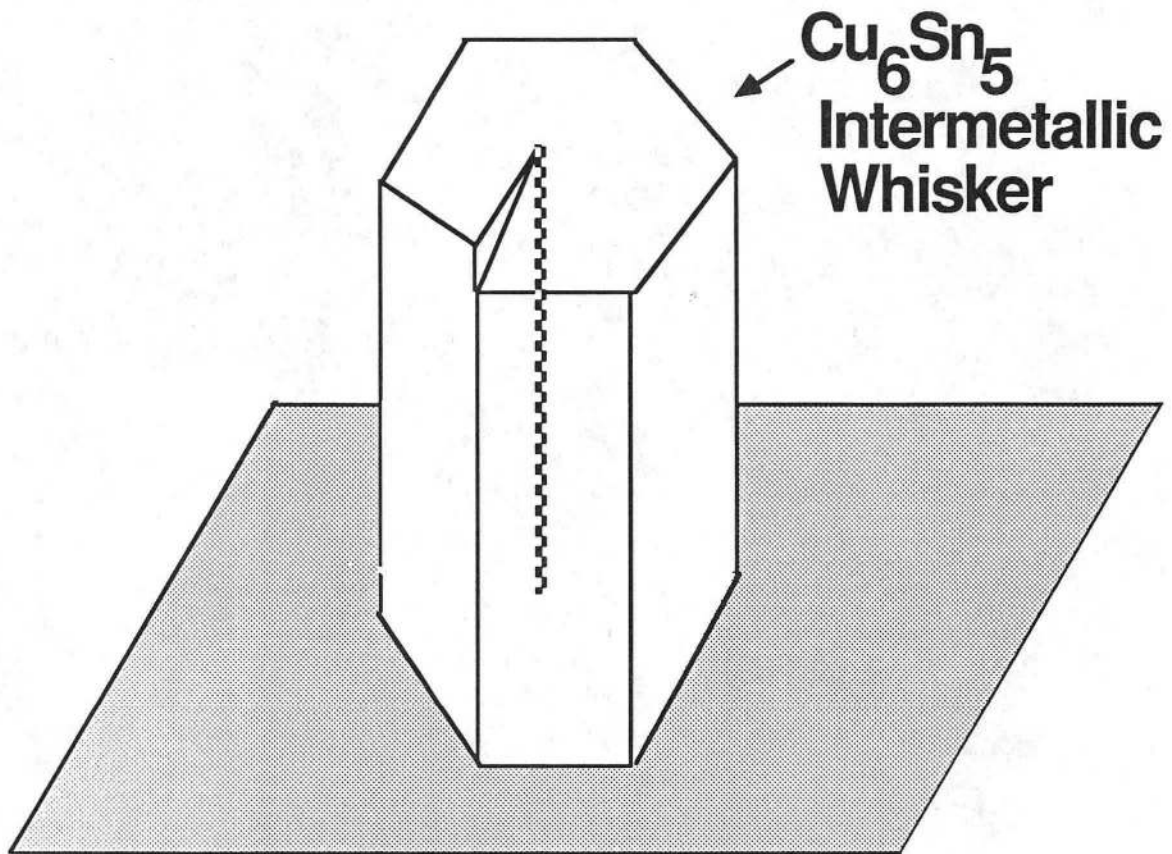
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Fig. 4 Optical micrograph of Cu_6Sn_5 rods present in the bulk solder of the 60Sn-40Pb solder/Cu joint.



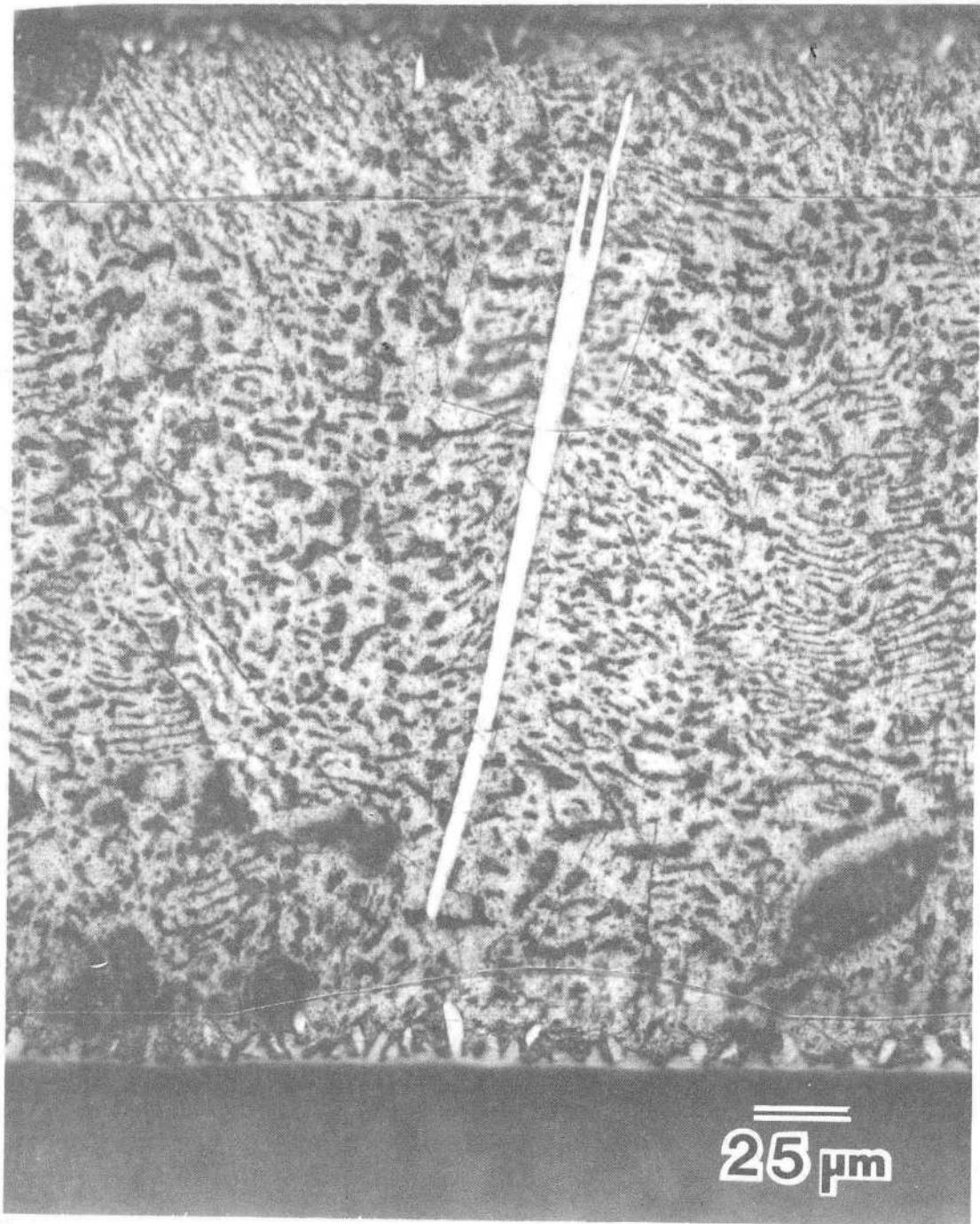
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Fig. 5 Optical micrograph of Cu_6Sn_5 intermetallic rods present in the bulk solder of the 60Sn-40Pb solder/Cu joint. The unusual shapes are observed by cutting the rods through varying sections during polishing.



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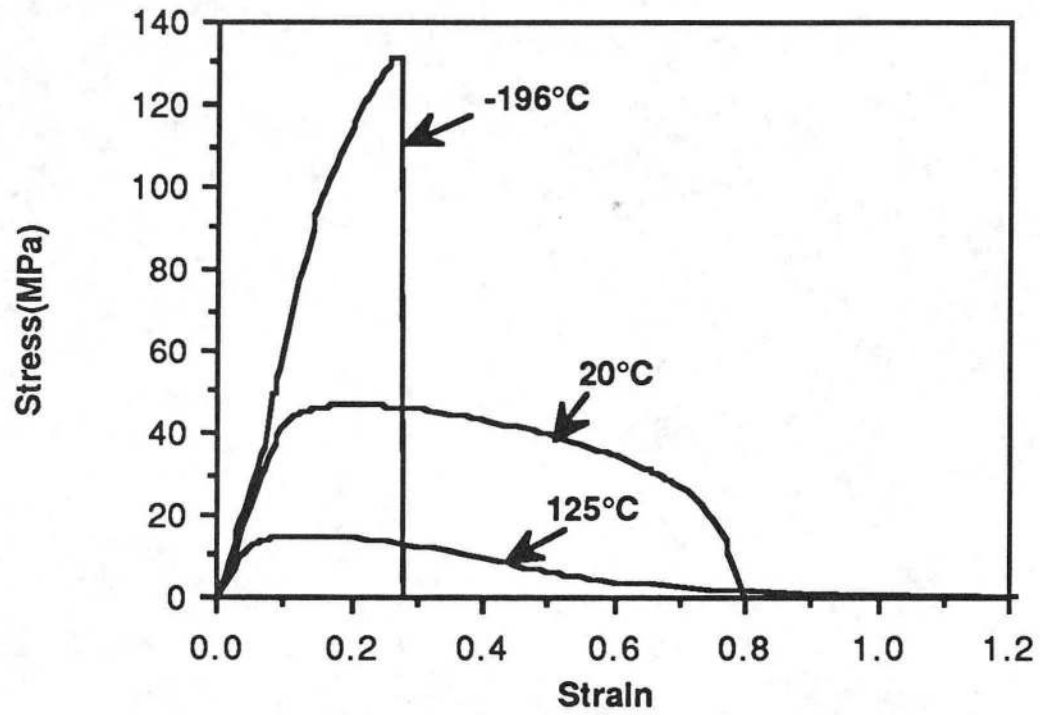
Fig. 6 Schematic diagram illustrating the growth of the intermetallic rods using the proposed screw dislocation ledge mechanism model.



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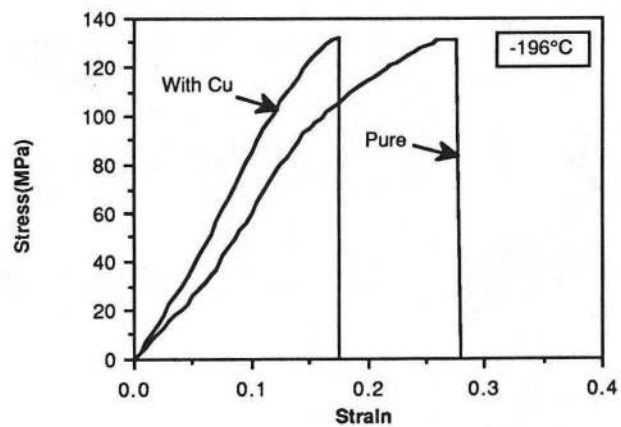
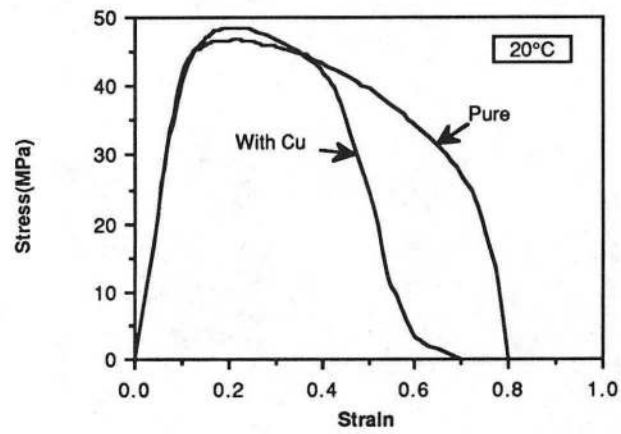
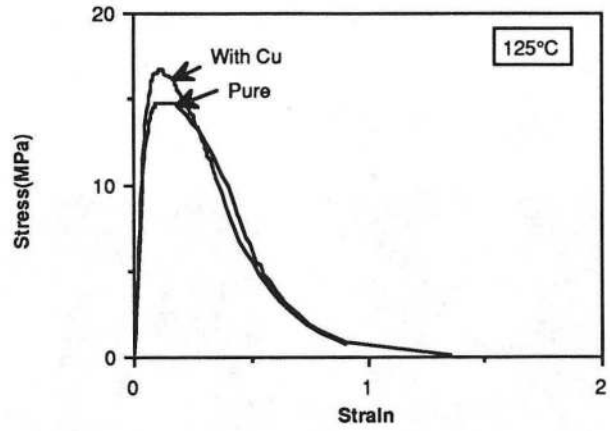
Fig. 7 Optical micrograph of a Cu_6Sn_5 intermetallic rod in a 60Sn-40Pb solder/Cu joint.

Pure 60Sn-40Pb



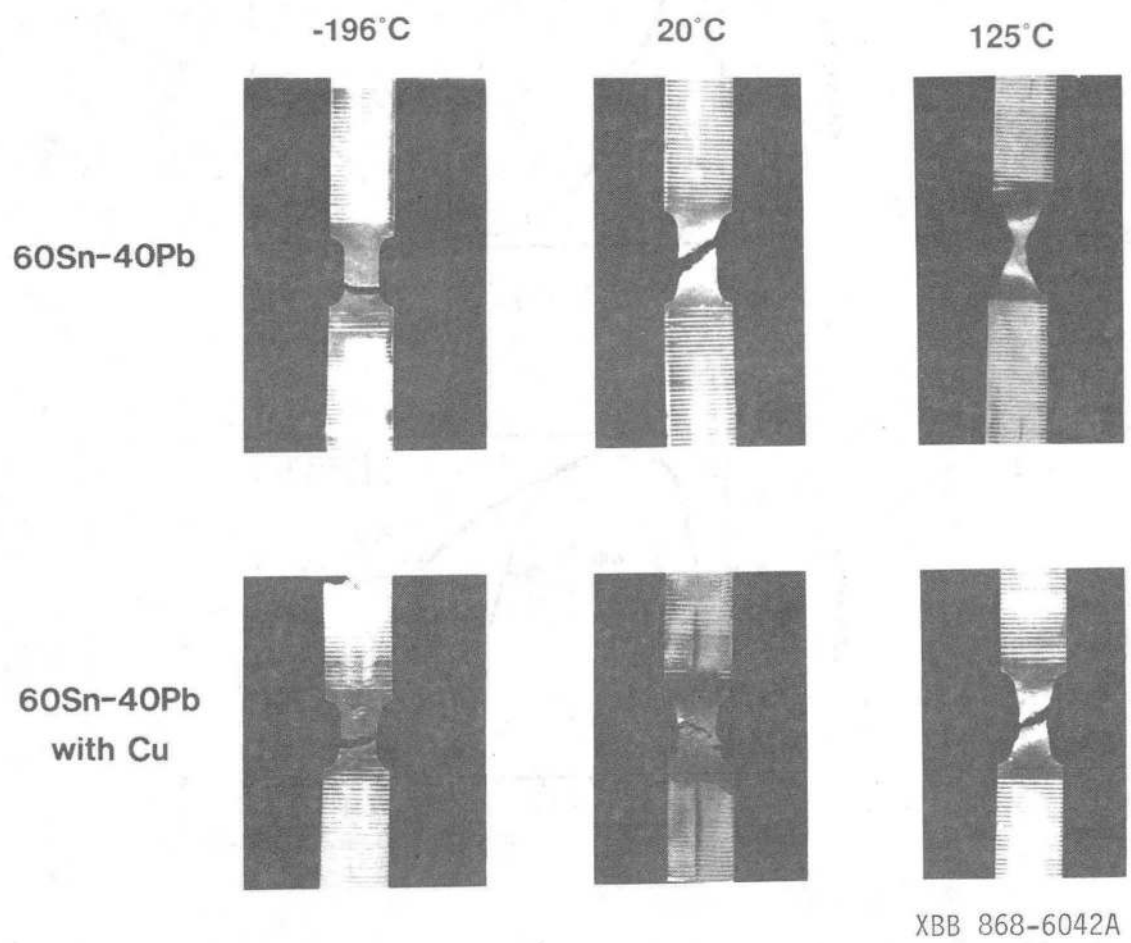
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Fig. 8 Stress vs. Strain plots for pure 60Sn-40Pb solder tested at 125°C, 20°C, and -196°C.



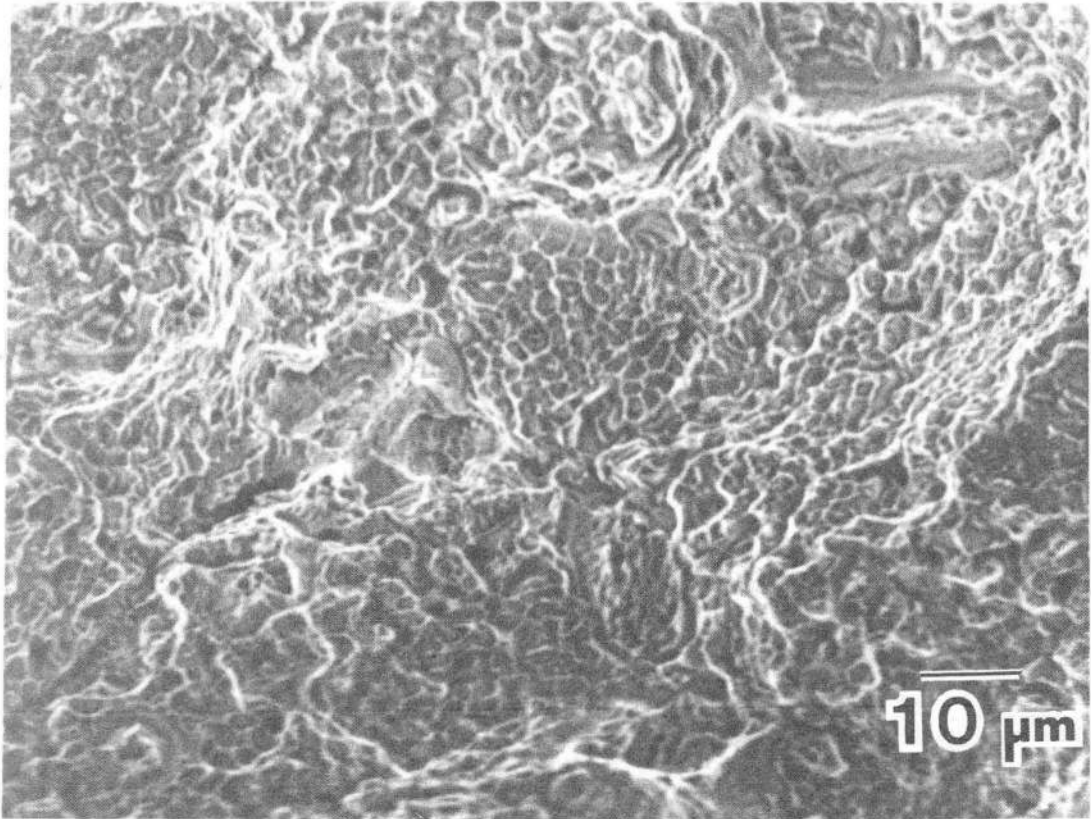
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Fig. 9a-c Stress vs. Strain plots for 60Sn-40Pb with Cu-Sn intermetallics, and pure 60Sn-40Pb for the three temperatures tested. The "pure" curve represents 60Sn-40Pb and "with Cu" represents 60Sn-40Pb with Cu⁶Sn⁵ intermetallic rods present.



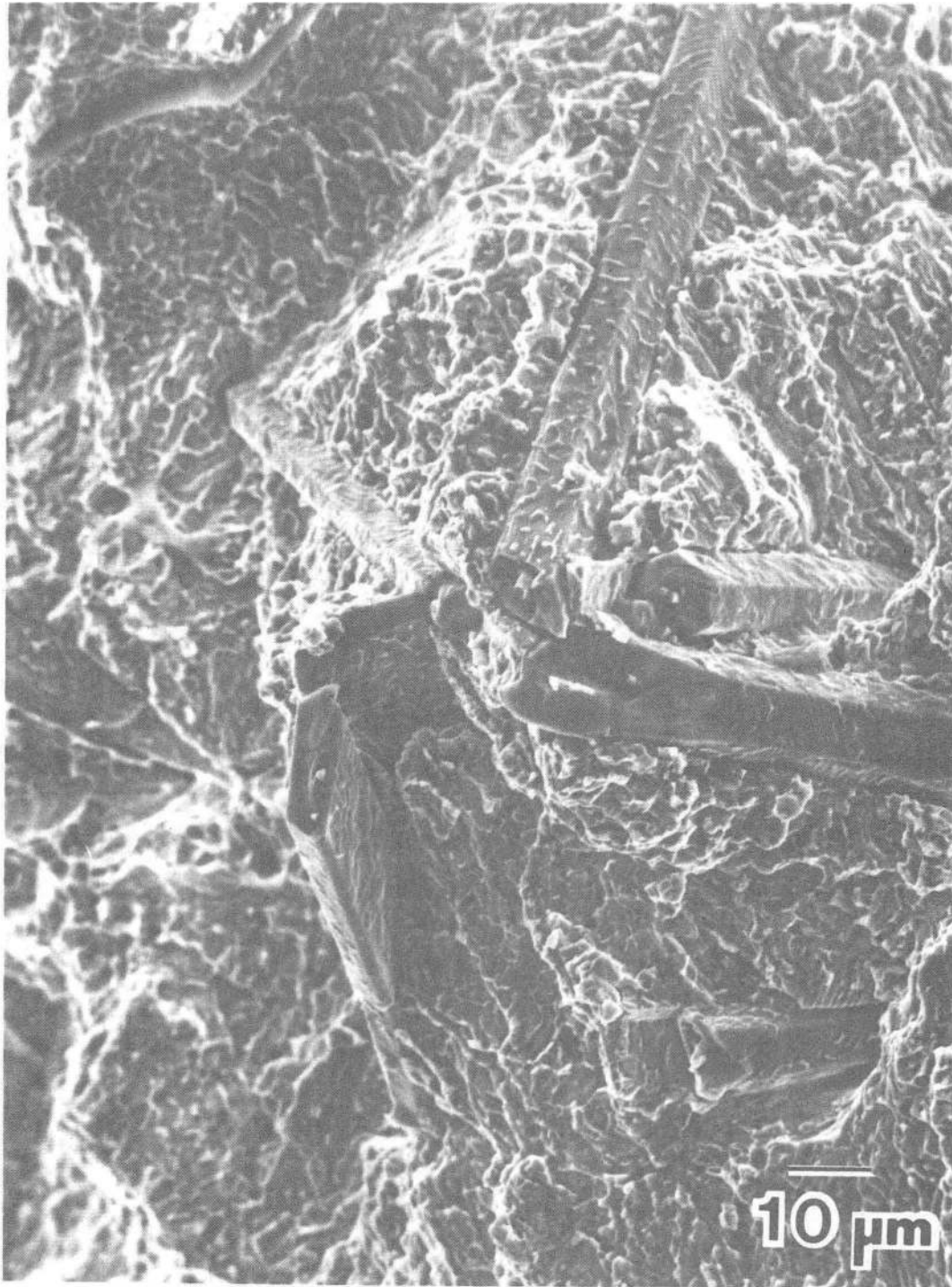
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Fig. 10 Macrographs of failed solder samples tested in tension.



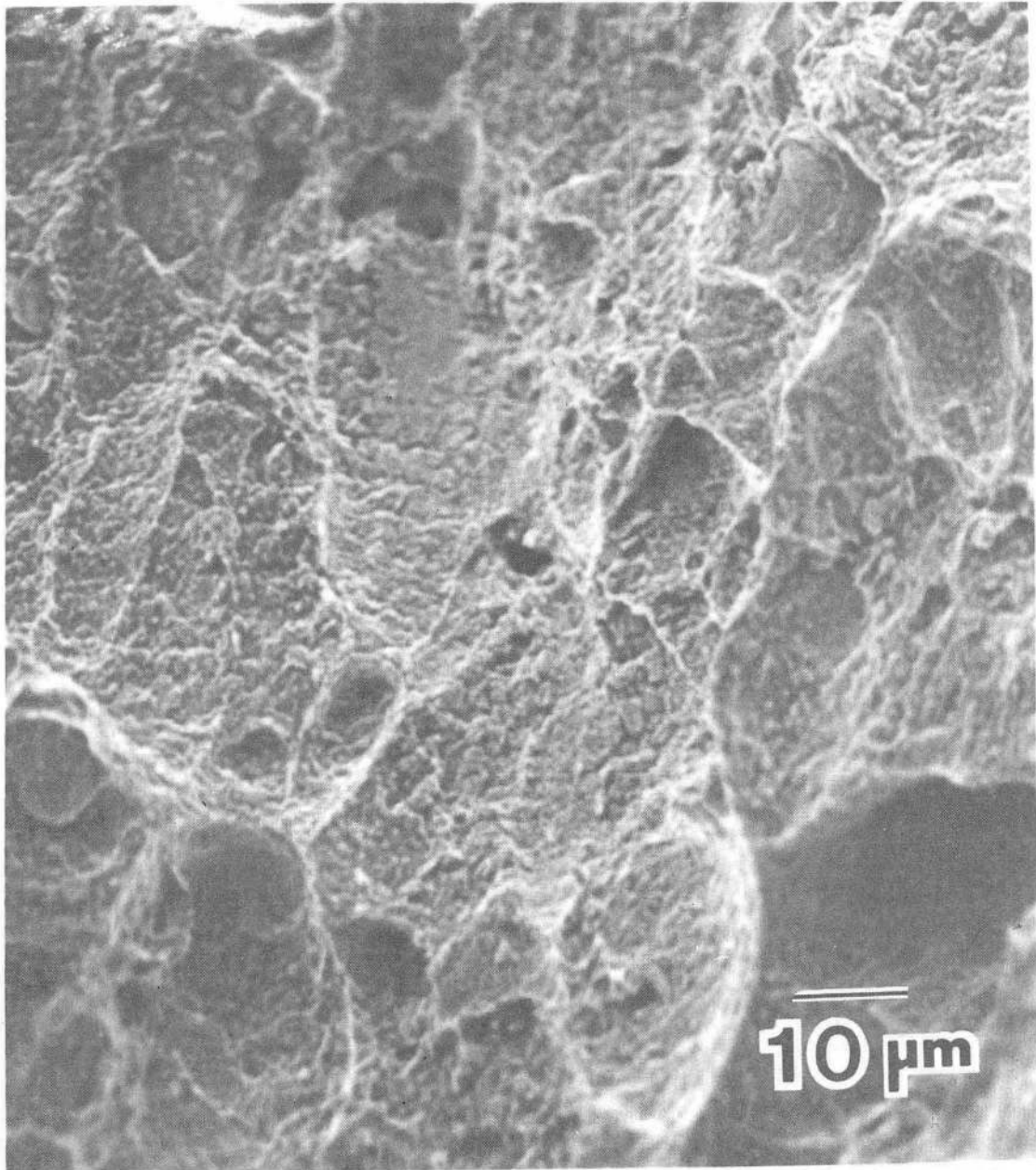
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Fig. 11 SEM fractograph of pure 60Sn-40Pb solder failed at -196°C .



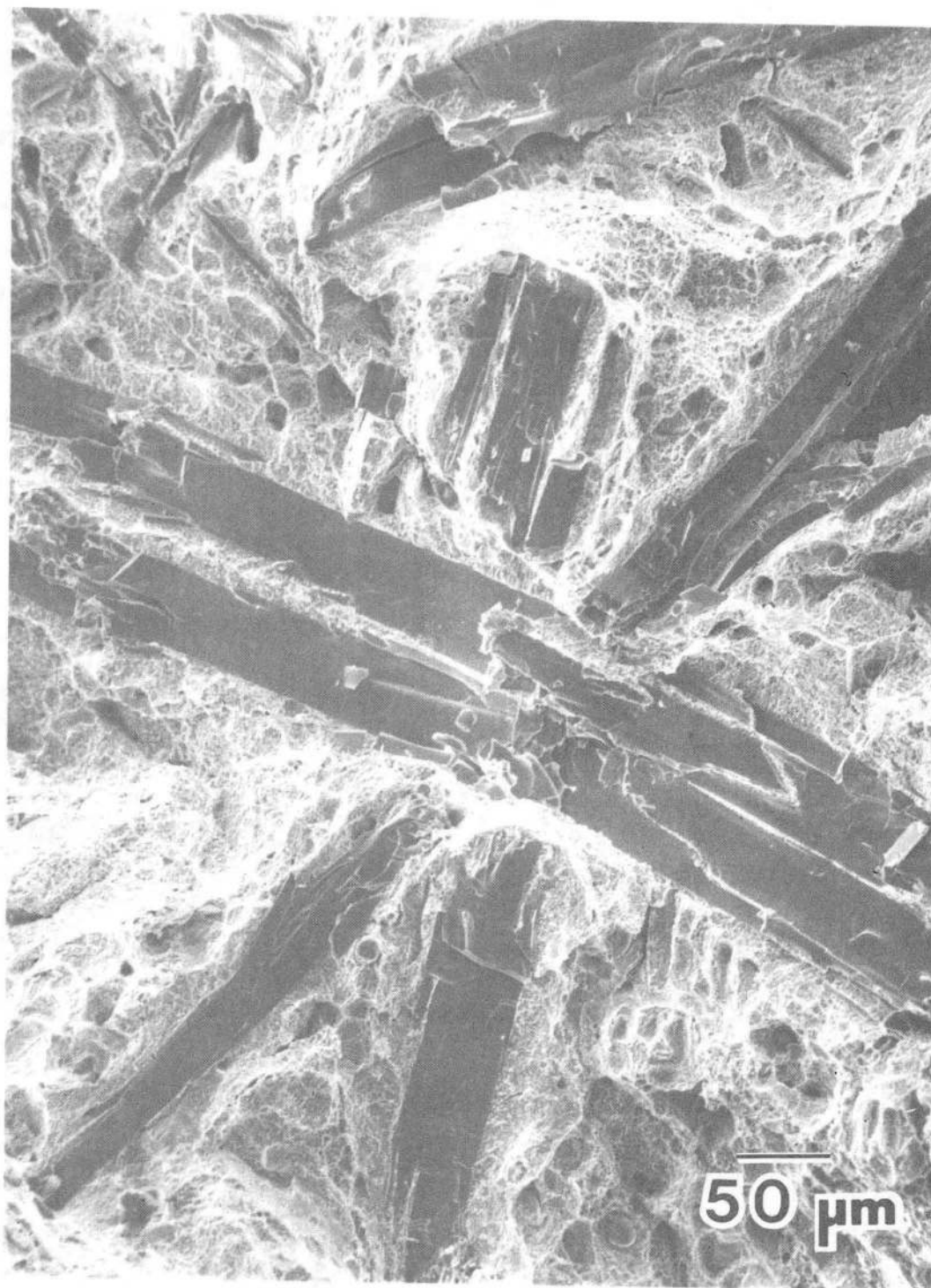
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Fig. 12 SEM fractograph of 60Sn-40Pb with intermetallics failed at -196°C .



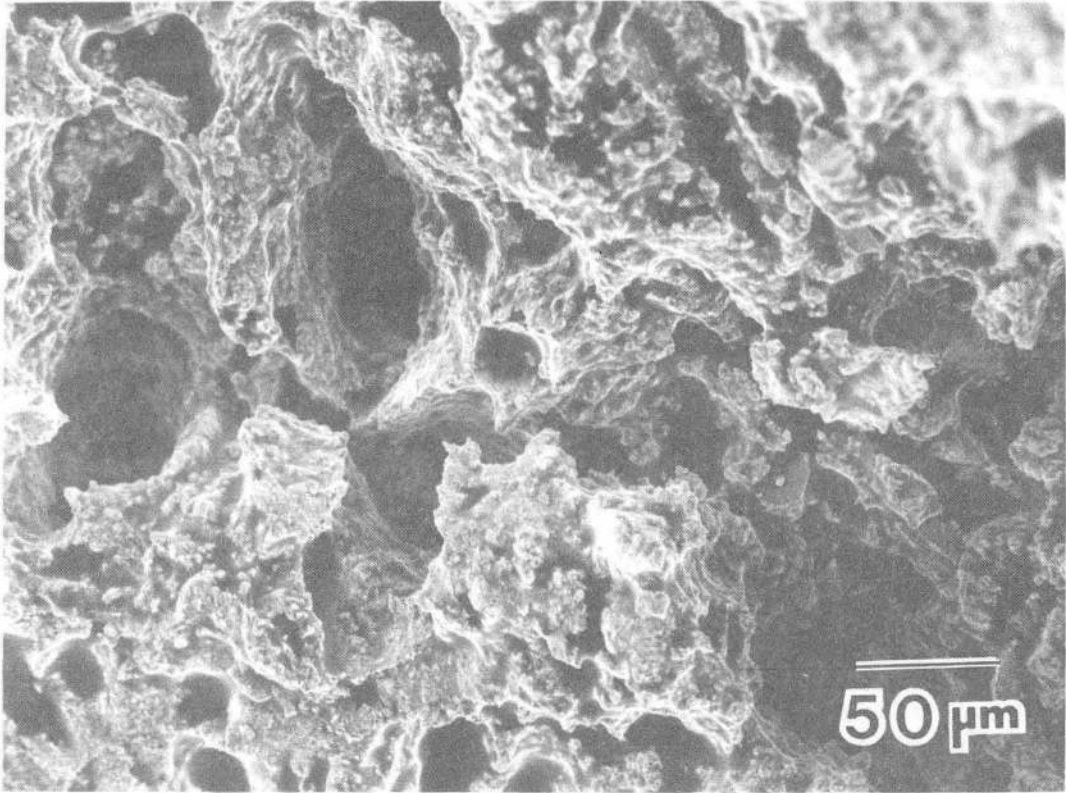
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Fig. 13 SEM fractograph of pure 60Sn-40Pb solder tested at 20°C.



XBB 868-6254

Fig. 14 SEM fractograph of 60Sn-40Pb with intermetallics failed at 20°C.



XBB 868-6036

Fig. 15 SEM fractograph of 60Sn-40Pb with intermetallics tested at 125°C.

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