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## High Temperature Hardness of Lead-free and Composite Solders

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# High Temperature Hardness of Lead-free and Composite Solders

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Solder joints in microelectronic devices are frequently operated at an elevated temperature in service. They also experience plastic deformation caused by temperature excursion and difference in thermal expansion coefficients. Deformed solders can go through a recovery and recrystallization process at an elevated temperature, which would alter their microstructure and mechanical properties. In this study, to predict the changes in mechanical properties of Pb-free solder joints at high temperatures, the high temperature microhardness of several Pb-free and composite solders was measured as a function of temperature, deformation, and annealing condition. Solder alloys investigated include pure Sn, Sn-0.7Cu, Sn-3.5Ag, Sn-3.8Ag-0.7Cu, Sn-2.8Ag-7.0Cu (composite), and Sn-2.7Ag-4.9Cu-2.9Ni (composite). Numbers are all in wt.% unless specified otherwise. Solder pellets were cast at two cooling rates (0.4 and 7 °C/s). The pellets were compressively deformed by 30 % and 50 % and annealed at 150 °C for 2 days. The microhardness was measured as a function of indentation temperature from 25 to 130 °C. Their microstructure was also evaluated to correlate with the changes in microhardness.

*Key word*: Pb-free solder, microstructure, high temperature microhardness, mechanical deformation, recrystallization

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## INTRODUCTION

Recently the world-wide, active R&D efforts in industry, universities and national laboratories have made considerable progress for a full transition toward lead-free soldering technology.[1-6] However, our knowledge on lead-free solders is still at an infant level compared to lead-containing solders. Especially the fundamental questions regarding the microstructure-property relations and mechanical behaviors of Pb-free solders during thermo-mechanical processes are not fully understood yet.

In this study, the microhardness of several Pb-free and composite solders were investigated to predict the changes in mechanical properties of Pb-free solder joints under the similar working conditions of electronic devices. Solder joints are often subjected to varying temperatures and plastic deformations caused by the mismatch in coefficients of thermal expansion.[7] This could lead to thermal fatigue failure of solder joints, which is a critical long-term reliability issue to be solved for the successful transition to Pb-free solder technology. The continuing trend of miniaturization of electronic packages demands solder joints smaller in dimension and volume, and heat dissipation more difficult due to high power requirements. This situation would produce even more severe stress and deformation in the solder joints used for high performance electronic systems. Deformed solders can go through a recovery and recrystalization process at an elevated temperature. The recrystallization temperature of pure Sn is reported to be below room temperature.[8]

The microstructure-property relations of several Pb-free solders have been investigated to understand the microstructural changes during thermal and mechanical processes of Pb-free solder joints. The microstructure of reflowed solder joints is known to be mainly controlled by the solidification process of a molten solder. The solidification conditions of solder joints are often determined by the heat dissipation from an electronic package. The microstructure of solder joints can be also changed by the thermo-mechanical conditions of the package in service. The microstructure evolution in solder joints upon thermomechanical stressing is, therefore, difficult to predict because complex interactions between the solidified microstructure and thermal/mechanical variables are expected.

In this study, the microstructure-property relations of several Pb-free and composite solders were investigated by measuring the microhardness of Pb-free solders at an elevated temperature and correlating them to the changes in their microstructures of plastically deformed and annealed solder alloys.

## EXPERIMENTAL PROCEDURES

High temperature microhardness of Pb-free and composite solders were measured at an elevated temperature (between 25 and 130 °C) as a function of cooling rate, deformation, and annealing condition. Solder alloys investigated include pure Sn, Sn-0.7Cu, Sn-3.5Ag, Sn-3.5Ag-0.7Cu, Sn-2.8Ag-7.0Cu (composite), and Sn-2.7Ag-4.9Cu-2.9Ni (composite). Two binary and one ternary solders are eutectic. To reproduce the microstructures and mechanical properties observed in Pb-free solder joints, the cooling rate, ingot size, and reflow conditions of cast alloys were carefully controlled. A graphite mold having multiple cavities was employed to cast each solder alloy into a small pellet of 0.200" in diameter and 0.125" in height. Pb-free solders were reflowed at 250 °C for 2 min and solidified at a cooling rate of 0.4 and 7 °C/sec. A typical cooling rate employed in a conventional reflow process of the printed circuit board assembly line is 0.5-1.0 °C/sec. The composite solders were produced by adding an excess amount of Cu or Ni into near-ternary eutectic Sn-Ag-Cu alloys and subsequently rolling the cast alloy ribbon to break down Cu-Sn or Ni-Sn intermetallic compounds into fine disperson. The fabrication process of composite solders was described in detail in the previous publication[9].

A compressive deformation of about 30 and 50 % was applied using a slow crosshead speed (0.1 mm/min) to minimize any heterogeneous deformation in the solder pellet. To study the effect of heat treatment, as-cast and/or deformed solder pellets were subjected to an annealing treatment at 150 °C for 48 h in nitrogen gas.

To evaluate high temperature hardness, a solid-state heating device was attached to a specimen holder, where heat was supplied to the bottom of a solder pellet. A modified base plate of the hardness tester was also heated externally to maintain a uniform temperature of a test sample during indentation. The microhardness test was performed using a 50 g setting. The Vickers hardness number (VHN) was reported as an average value of 20 indentations or more. The metallographic samples were obtained by cross sectioning a solder pellet into two halves and mounting them to reveal the internal surface parallel to the direction of compressive deformation. To reveal the solder microstructure clearly, the Sn matrix was lightly etched in a solution of 5% $HNO_3$, 3% HCl and 92% $CH_3OH$ for several seconds. The microstructures of the deformed and annealed solder pellets in their central area were metallographically examined.

## RESULTS AND DISCUSSION

### Microstructure of As-Cast Solders

The microstructures of as-cast alloys with different cooling rates (0.4 and 7 °C/sec) are shown in Fig.1. For pure Sn, a large grain structure is observed in the as-cast condition. The dendritic growth morphology of the β-Sn crystal structure is unique in as-cast Sn-Cu, Sn-Ag, and Sn-Ag-Cu alloys, while no dendritic structure is observed in the pure Sn either as-cast or deformed. For Sn-0.7Cu, Sn dendrites are dispersed uniformly in the matrix of the Sn-Cu eutectic structure in the as-cast condition. For Sn-3.5Ag, Sn dendrites are well developed along a certain direction in the matrix of the Sn-Ag eutectic microstructure in the as-cast condition. For Sn-3.8Ag-0.7Cu, Sn dendrites of smaller arm spacing than Sn-Cu or Sn-Ag are surrounded by the Sn-Ag-Cu eutectic structure. For the composite solders of Sn-Ag-Cu and Sn-Ag-Cu-Ni, small $(Cu,Ni)_6Sn_5$ intermetallic particles, which were initially formed as the primary intermetallic compound dendrites and crushed into fine particles by in-situ process,[9] are dispersed uniformly in the matrix of the Sn-Ag-Cu(-Ni) structure. These reinforcing IMC particles promote a fine-grained microstructure, because the particles act as a nucleation site, as well as a barrier of gain boundary movement. The effect of cooling rate on the Sn dendrite structure was not so significant for the slow vs fast cooling condition. Therefore, the fast cooled solders are only chosen for the evaluation of deformation, annealing, and high temperature hardness.

Figure 2 shows the microstructure after annealing (150 °C, 48 h) for each solder (bottom six), compared with the as-cast condition (top six). For Sn and Sn-0.7Cu, a large grain structure is noted, which is possibly as a result of recrystallization and grain growth during annealing. Sn-Ag, Sn-Ag-Cu, and composite solders maintain the casting structure that is composed of dendritic primary Sn and eutectic structure. Large proeutectic $Ag_3Sn$ plates, reported in Sn-Ag or Sn-Ag-Cu solidified at a slow cooling rate,[10] are not observed here in Sn-3.5Ag and Sn-3.8Ag-0.7Cu alloys as-cast or annealed, which were solidified at a relatively higher cooling rate, 0.4–7 °C/sec.

### Microstructure of Deformed Solders

Typical microstructures of six different alloys with a compressive deformation of 30 % (top six) are shown in Fig. 3. The annealed microstructures of each corresponding alloy upon heat treatment at 150 °C for 48 h after 30 % deformation are also shown in Fig. 3 (bottom six). For pure Sn, there is no sign of the plastic deformation accumulated in the as-deformed condition, but a fully recrystallized microstructure is noticed for all levels of deformation. No significant change in grain size is detected in the pure Sn as a function of plastic deformation. This is consistent with the hardness measurement to be discussed in the next section.

For Sn-Cu, a large grain structure is observed after deformation and annealing. Due to the large amount of plastic deformation, the Sn dendrite structure observed in the as-cast condition is significantly deformed and aligned along the direction perpendicular to the direction of loading. Upon annealing at 150°C for 48 h, the deformed microstructure has undergone a recrystallization process to yield equi-axed grains of random orientation. For Sn-Ag and Sn-Ag-Cu, the initial dendritic structure was more persistent to exist in the deformed and annealed condition.

For Sn-Ag-Cu(-Ni) composite solders, due to the reinforcement of fine $(Cu,Ni)_6Sn_5$ particles, the recrysatalllization was much retarded in comparison to the monolithic solders under an equivalent condition of deformation and annealing. The recrystallized microstructure of composite solders was finer than the monolithic alloys.

Microhardness Measurement

Table 1 and 2 summarize all the microhardness results obtained in this study as a function of alloy composition, cooling rate, compressive deformation, annealing and indentation temperature. They are also graphically shown in Figs. 4 and 5.

The room temperature hardness of Pb-free solders in as-cast, deformed and annealed conditions are described in Fig. 4. In general, the microhardness of Pb-free solders increase as the amount of alloying elements increases from pure Sn to Sn-Cu to Sn-Ag to Sn-Ag-Cu to composite solders. As the amount of deformation increases up to 50%, an increase in hardness due to strain hardening effect is clearly shown in the case of Sn-Ag, Sn-Ag-Cu and composite solders, but not much in pure Sn and Sn-Cu.  Upon annealing at 150 °C for 48 h, an appreciable reduction in hardness was noted for each alloy group. Interestingly, the hardness reduction in the annealed solders was more drastic in the heavily deformed alloys as shown in Fig. 4.  This may be explained by the fact that a heavily deformed solder has a more strain energy stored than a lightly deformed one, providing a higher driving force for the process of recrystallization and grain growth, and resulting in more reduction in hardness compared to a lightly deformed solder. Table 1 compares the effect of cooling rate on the hardness; slow cooling (0.4 °C/s) vs fast cooling (7 °C /s). For the range of cooling rate examined, the microhardness values were not significantly affected by the different cooling rate for each alloy group.  This is consistent with the microstructural observation made with the slow vs fast cooled samples.

The changes in microhardness of Pb-free solders are illustrated in Fig. 5 as a function of indentation temperature with the as-cast and annealed samples. The microhardness of each alloy steadily decreases as the indentation temperature increases from room temperature to 130 °C. The hardness difference between the as-cast and annealed samples becomes less significant when the indentation temperature becomes higher for each alloy.

As reported previously,[11] it is confirmed that the hardness of Sn-rich Pb-free solders strongly depends on the amount of alloying elements, such as Cu, Ag, and Ni. These alloying elements are responsible to produce Sn-containing IMC particles in the eutectic microstructure or as a proeutectic phase. Since the volume fraction of the eutectic microstructure in the interdendritic region of the as-cast alloys generally increases in order of Sn-0.7Cu, Sn-3.5Ag, Sn-3.5Ag-0.7Cu, Sn-2.8Ag-7.0Cu (composite) and Sn-2.7Ag-4.9Cu-2.9Ni (composite), the trend of the hardness increase among these soldes is well understood. In the case of composite solders, the primary reinforcing IMC particles further harden the solder matrix. In the annealed solders, the hardness reduction could be explained by coarsening of IMC particles within the eutectic microstructure in addition to the recrystallization and grain growth process.

It is interesting to note the hardness changes of Sn-Ag-Cu vs Pb-Sn as a function of indentation temperature in Table 1. The hardness number of Sn-Ag-Cu becomes higher than Pb-Sn as the temperature increases, even though Pb-Sn has a higher hardness number at room temperature. This hardness reversal can be understood in terms of its homologous temperature (indentation temperature / melting temperature). Because Pb-Sn has a lower melting temperature than Sn-Ag-Cu, its homologous temperature is higher at the same indentation temperature. Figure 6 shows the microhardness changes of solders as a function of homologous temperature. The hardness reduction at a higher indentation temperature is influenced by their melting temperature and homologous temperature, more significantly in the low melting temperature solder. Solders of a higher homologous temperature at the same indentation temperature show more reduction in hardness compared to solders of a lower homologous, as the case of Pb-Sn vs Sn-Ag-Cu. For composite solders, the melting temperature of solder matrix is nearly the same as Sn-Ag-Cu, however the decrease in hardness is relatively small as the indentation temperature increases. This fact supports that a composite solder is a good candidate for the high temperature applications.

## SUMMARY

High temperature hardness of several Pb-free and composite solders was measured in terms of alloying composition, cooling rate, plastic deformation, and annealing condition. From this study, the following conclusions are drawn.

- The microstructure and microhardness of Pb-free and composite solders were significantly influenced by the alloy composition, plastic deformation and annealing condition, but not much by the range of cooling rate examined (0.4 to 7C/sec).

- The recrystallization and grain-growth processes were observed in the deformed and annealed Sn-rich solders depending on plastic deformation or annealing condition. The pure Sn has undergone the recrystallization and grain growth even at room temperature during plastic deformation.

- The annealing of as-cast and deformed Sn-rich solders at 150°C for 48 h has produced a considerable reduction in hardness. For Sn-Ag, Sn-Ag-Cu, and composite solders, more plastic deformation has caused more reduction in hardness during the annealing process, while no dependence was observed for Sn and Sn-Cu.

- The microhardness of Pb-free and composite solders steadily decreases as the indentation temperature increases from room temperature to 130C. The hardness difference between the as-deformed and annealed samples becomes less significant when the indentation temperature becomes higher for each alloy.

- The hardness of composite solders was higher than monolithic Pb-free solders in all conditions, and decreases more slowly as the indentation temperature increases. The reinforcing fine IMC particles promote a fine-grained microstructure more stable for the deformation and annealing process

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Table 1. Microhardness of solders as s function of cooling rate and indentation temperature.

| | | Pure Sn | Sn-Cu eutectic | Sn-Ag eutectic | Sn-Ag-Cu eutectic | Pb-Sn eutectic | Sn-Ag-Cu composite | Sn-Ag-Cu-Ni composite |
|---|---|---|---|---|---|---|---|---|
| 25°C | fast cooling | 6.8 | 11.1 | 14.1 | 15.6 | 17.3 | 17.9 | 18.9 |
| | slow cooling | 5.6 | 10.4 | 12.7 | 14.6 | 16.6 | 17.2 | 18.7 |
| 60°C | fast cooling | 5.7 | 10.2 | 11.9 | 13.3 | 13.9 | 14.7 | 16.4 |
| | slow cooling | 5.1 | 9.8 | 10.9 | 12.7 | 13.9 | 13.8 | 16.1 |
| 100°C | fast cooling | 4.9 | 8.5 | 9.8 | 11.8 | 10.5 | 11.2 | 13.3 |
| | slow cooling | 4.8 | 8.3 | 9.5 | 11.8 | 10.4 | 11.2 | 13.4 |
| 130°C | fast cooling | 4.2 | 6.9 | 7.9 | 9.1 | 9.1 | 10.3 | 10.8 |
| | slow cooling | 4.2 | 7.1 | 7.6 | 9.5 | 8.8 | 10.2 | 10.5 |

Table 2. Microhardness of solders as s function of indentation temperature, deformation, and annealing.

| Indent Temp. | | amount of deformation | pure Sn | Sn-Cu eutectic | Sn-Ag eutectic | An-Ag-Cu eutectic | Sn-Ag-Cu Composite | Sn-Ag-Cu-Ni Composite |
|---|---|---|---|---|---|---|---|---|
| 25 oC | deformation | 0% | 6.8 | 11.1 | 14.1 | 15.6 | 17.9 | 18.9 |
| | | 10% | 7.8 | 13.7 | 15.4 | 17.1 | 19 | 20 |
| | | 30% | 7.1 | 12.8 | 14.8 | 17.3 | 19.3 | 20.6 |
| | annealing | 0% | 6.6 | 8.2 | 12.7 | 12.3 | 14.9 | 15.3 |
| | | 10% | 6 | 8.7 | 12.2 | 13.2 | 15 | 15.3 |
| | | 30% | 6.5 | 9.2 | 10.7 | 11 | 12.2 | 13.4 |
| 60 oC | deformation | 0% | 5.7 | 10.2 | 11.9 | 12.7 | 15.7 | 16.4 |
| | | 10% | 6.2 | 11.9 | 12.4 | 14.8 | 16.4 | 17.2 |
| | | 30% | 6 | 11.1 | 12.1 | 14.9 | 16.6 | 17.5 |
| | annealing | 0% | 5.8 | 7.7 | 11.1 | 10.8 | 12.6 | 13.1 |
| | | 10% | 5.5 | 8.1 | 10.7 | 11.4 | 12.6 | 13.3 |
| | | 30% | 5.9 | 8.4 | 10.3 | 9.8 | 11.1 | 12.2 |
| 100 oC | deformation | 0% | 4.9 | 8.5 | 9.8 | 11.8 | 13.2 | 14 |
| | | 10% | 4.8 | 9.3 | 10.2 | 13.1 | 13.6 | 14.4 |
| | | 30% | 4.8 | 9 | 9.9 | 12.8 | 13.5 | 14.6 |
| | annealing | 0% | 4.7 | 7.2 | 9.4 | 11.3 | 12.2 | 12.7 |
| | | 10% | 4.6 | 7.7 | 8.9 | 12.1 | 12.1 | 12.5 |
| | | 30% | 4.8 | 7.6 | 8.8 | 11.5 | 11.3 | 11.9 |
| 130 oC | deformation | 0% | 4.2 | 6.9 | 7.9 | 9.1 | 11.2 | 11.8 |
| | | 10% | 4.3 | 7.2 | 8 | 9.7 | 11.4 | 12 |
| | | 30% | 4.4 | 7.1 | 8 | 9.8 | 11.2 | 12 |
| | annealing | 0% | 4.1 | 6.2 | 7.2 | 8.5 | 9.7 | 10.4 |
| | | 10% | 4.1 | 6.6 | 6.8 | 9.2 | 9.8 | 10.2 |
| | | 30% | 4.1 | 6.6 | 6.9 | 9.1 | 9.5 | 9.9 |

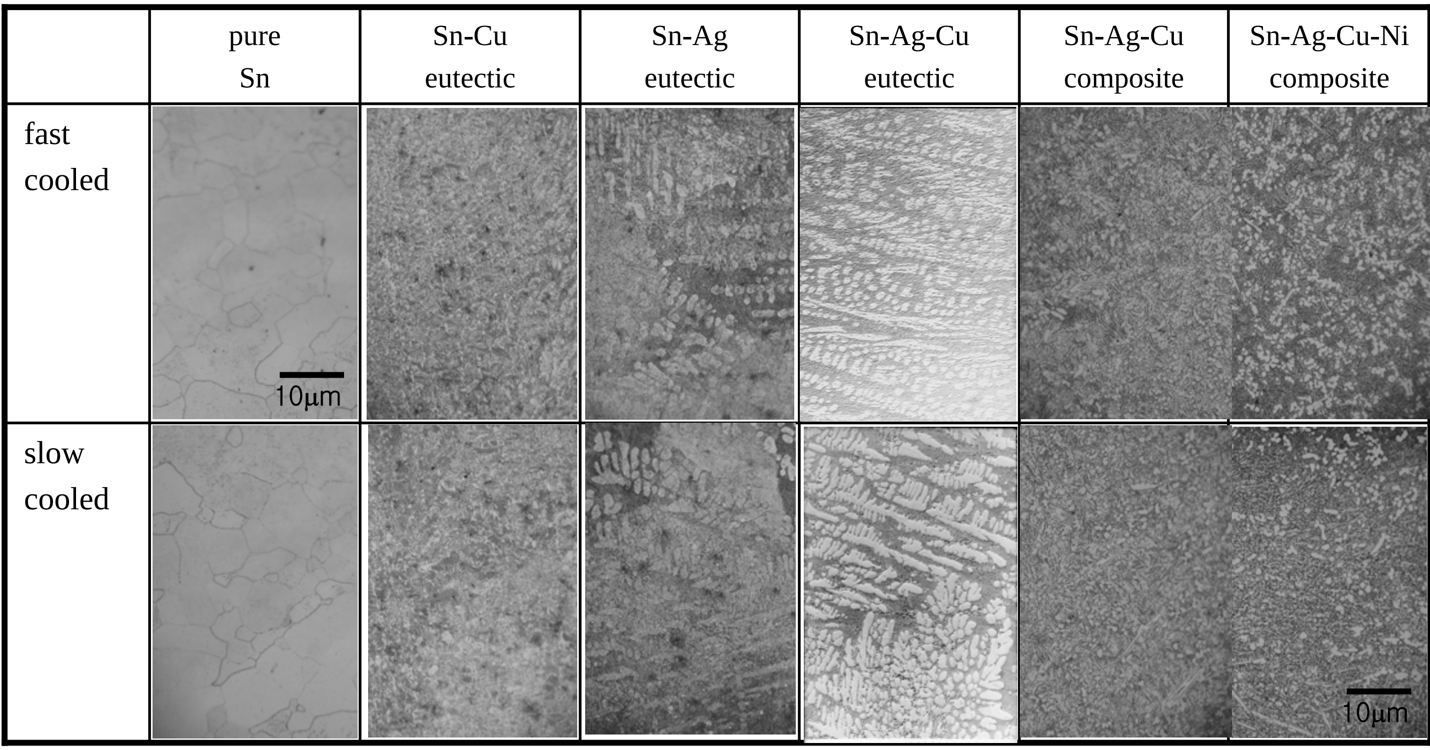


Fig. 1. Micrographs of Sn and Sn-rich lead free solder alloys in the as-cast condition with fast cooling rate (top 6) and slow cooling rate (bottom 6).

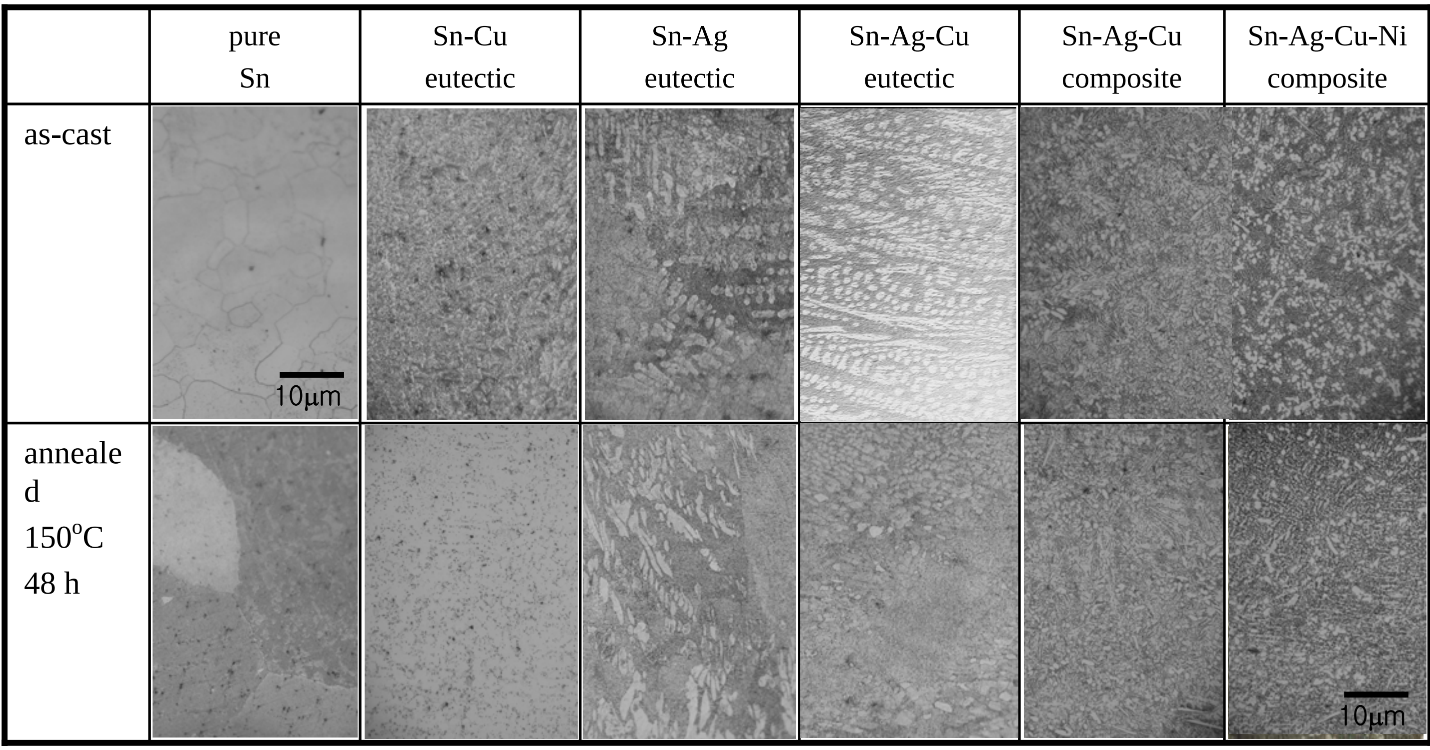


Fig. 2. Micrographs of Sn and Sn-rich lead free solder alloys in the as-cast condition (top 6) and after annealing at 150 °C, 48 h (bottom 6).

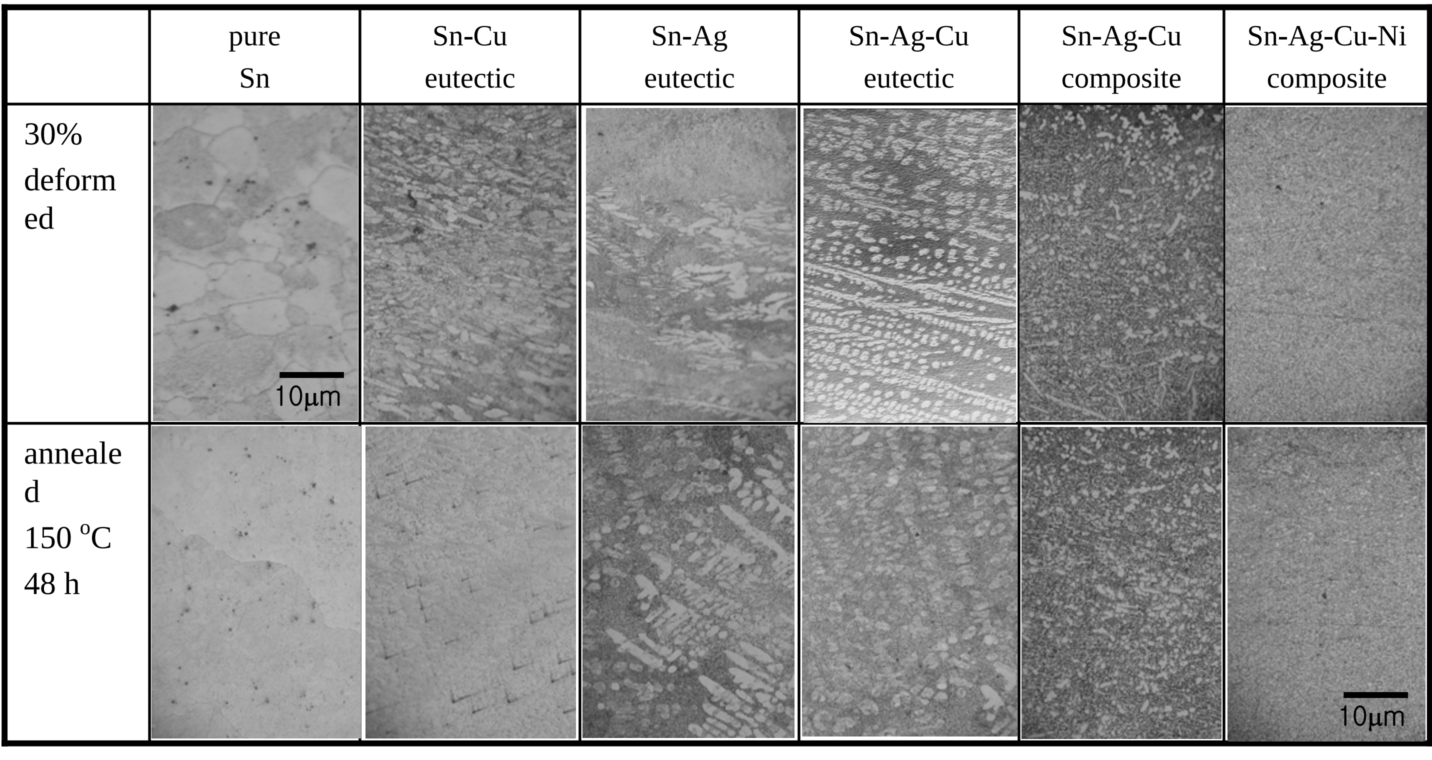


Fig. 3. Micrographs of Sn and Sn-rich lead free solder alloys 30 % deformed (top 6) and annealed at 150 °C, 48 h (bottom 6).

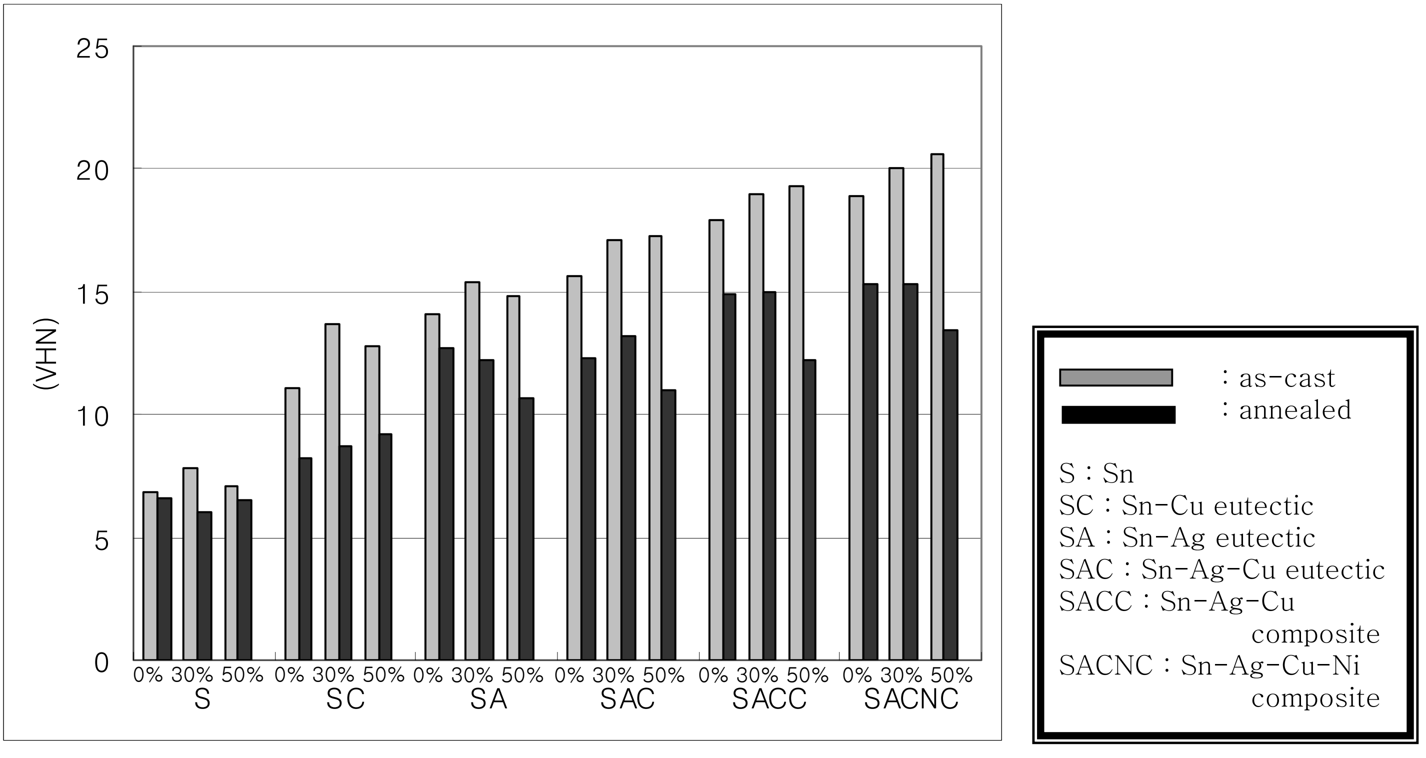


Fig. 4. The microhardness (VHN) measurement of solders as a function of alloy composition, plastic deformation, and annealing. For each group, the hardness bars are arranged in order of the amount of deformation (0, 30, 50 %).

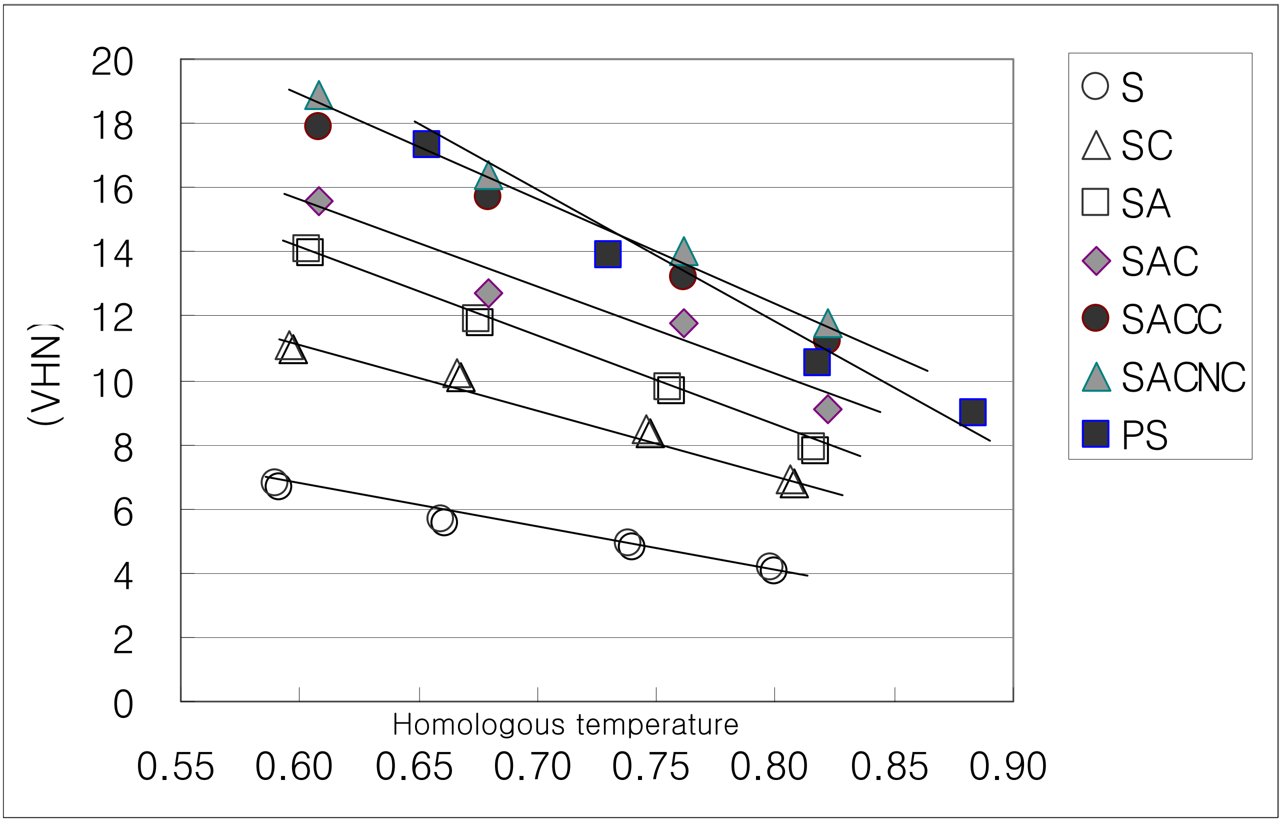


Fig. 6. Microhardness (VHN) changes of as-cast solders as a function of homologous temperature and alloy composition.

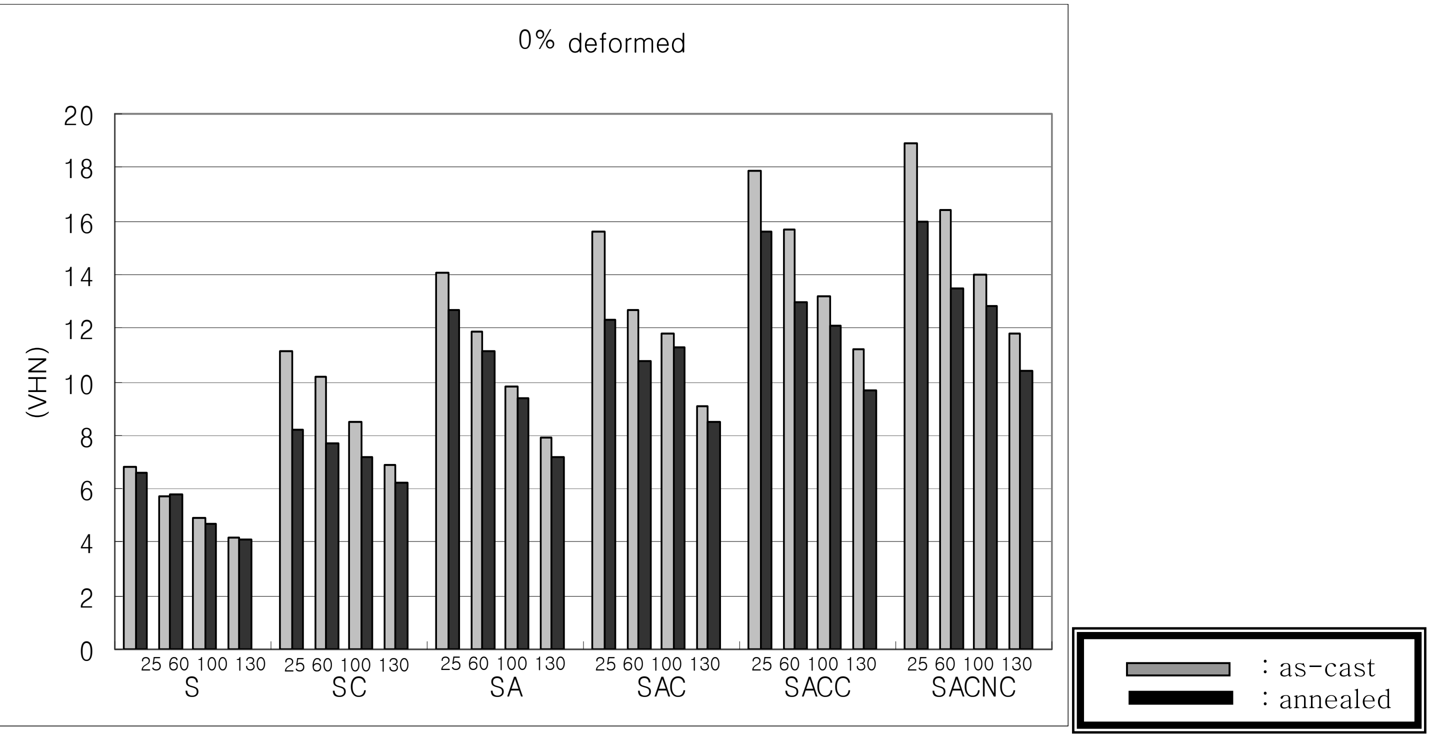


Fig. 5. The microhardness (VHN) measurement of solders as a function of alloy composition, indentation temperature, and annealing. For each group, the hardness bars are arranged in order of indentation temperatures (25, 60, 100 and 130 °C)