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Ageing behavior of Cu-15Ni-8Sn alloy prepared by mechanical alloying①

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Abstract: The ageing behavior of the mechanically alloyed Cu-15Ni-8Sn alloy has been studied. Compared with the alloys prepared by casting and rapid solidification, the modulation structure developed during ageing process of those prepared by mechanical alloying is finer and much more uniform, which leads to a higher peak hardness. However, their spinodal decomposition temperature are almost the same. Cold deformation prior to ageing not only accelerates the ageing process but also increases the peak hardness of the alloy.

Key words: Cu-15Ni-8Sn alloys; ageing; mechanical alloying **Document code**: A

1 INTRODUCTION

Cu-Ni-Sn alloys have been considered as possible substitutes for Cu-Be alloys in the manufacture of connectors, spring components and so forth, in the electronics industries because of their outstanding properties such as high strength, high elastic modulus, excellent erosion resistance and high resistance to stress relaxation at elevated temperature[1]. In addition, compared with Cu-Be alloys, the low cost and minor pollution in the preparation process of the alloy have also attracted the increasing attention of many researchers. However, extensive application of the alloy has been hindered by severe segregation of tin during conventional ingot metallurgy process[2]. Mechanical alloying has been considered to be an ideal method to prepare materials with homogeneous fine microstructure[3~4]. In our previously cited work, a Cu-15Ni-8Sn alloy with homogeneous microstructure as well as good mechanical properties has been prepared successfully by mechanical alloying. No segregation of tin has been found in these alloys[5].

Two kinds of phase transformation, i. e., spinodal decomposition and discontinuous precipitation exist during the ageing of the Cu-Ni-Sn alloys[6]. An optimal combination of yield strength and toughness of the alloy can be obtained through artificial ageing treatment with proper temperature and duration. Cold deformation prior to ageing has been found to affect the fracture toughness of the alloy significantly in spite of some existing disputes. Both positive and negative effects have been reported[7,8].

The Cu-15Ni-8Sn alloy prepared by mechanical alloying is characteristic of extremely homogeneous tin distribution, fine microstructure and some fine hard dispersoids induced during the preparation process[5]. Therefore, the ageing behavior of this alloy may differ from the conventional one. In this paper, the ageing process as well as the effects of the prior cold deformation on the mechanically alloyed Cu-15Ni-8Sn alloy is considered.

2 EXPERIMENTAL PROCEDURE

Mechanical alloying of elemental Cu-15Ni-8Sn (mass fraction, %) powder mixture with purity of 99.5 % was carried out for 20 h in a

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QM1-SP planetary type ball milling under an Ar atmosphere. The ball to powder ratio was 15:1, the planetary rotation speed was kept at 230 r/min, the as-milled powder was vacuum degassed at 600 ℃ for 1.5 h, cold pressed under 500 MPa and sintered at 930 ℃ for 1 h in ammonia. Full density of the alloy was achieved through cold rolling of the as-sintered bulk alloy and then solution heat treated at 850 ℃ for 1 h, water quenched. Detail description of the preparation process can be found in Ref. [5]. The alloy after solid solution treatment was either aged directly or cold rolled with a reduction of 80% and aged. Artificial ageing treatments were performed in salt bath at 300 ~ 500 ℃ for different durations.

The progress of ageing was followed using a Rigaku D/max-3B X-ray diffractometer (XRD) with Cu-K_α radiation. A JEM-100CX transmission electron microscope (TEM) was used to examine the morphology of the spinodal structure of the alloy. The Vickers hardness tests were conducted on an HV-50 hardness tester with a load of 50 N.

3 RESULTS

Fig. 1 shows the hardness of the Cu-15Ni-8Sn alloy vs ageing time at different temperatures. It can be seen that: (1) below 400 ℃, the hardness of the alloy increased with the ageing time until reaching a peak value, then decreased; (2) the hardness decreased gradually with increasing ageing time when ageing temperature exceeded 450 ℃ or above; (3) the higher the ageing temperature, the less the time needed to reach the peak hardness.

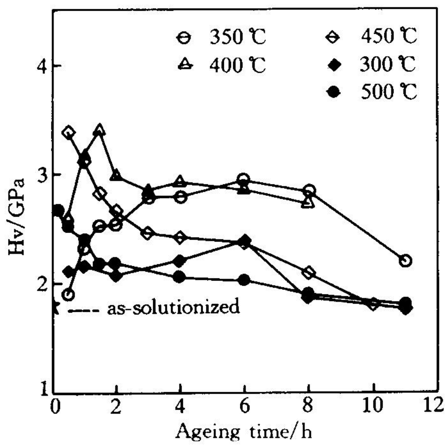

Fig. 1 Hardness variations as a function of ageing time at different temperatures

Fig. 2 illustrates the XRD patterns of the Cu-15Ni-8Sn alloy after aged at 400 ℃ for different durations. The sideband profiles were recorded asymmetrically along (200) and (311) of the Cu-15Ni-8Sn alloy after ageing for 1.5 h. They were more evident in the (111), (220) and (311) peaks of the alloy aged for 4 h and developed to nearly every peaks of the alloy further aged for 8 h.

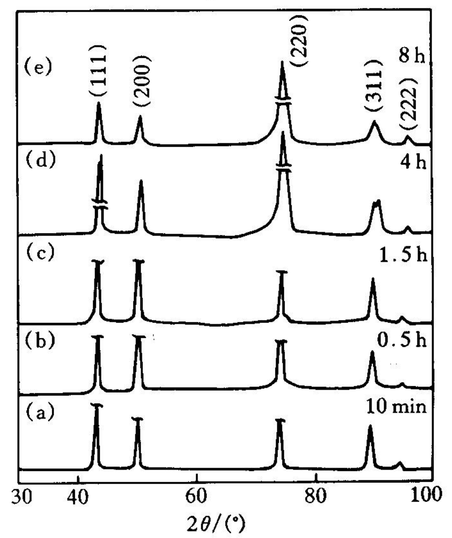

Fig. 2 XRD patterns of mechanically alloyed Cu-15Ni-8Sn alloy aged at 400 ℃ for different durations

The microstructure of the Cu-15Ni-8Sn alloy after aged at 400 ℃ for 1.5 h was investigated by TEM (as shown in Fig. 3). It was evident that the fine scale modulate structure with a wave-length of about 5 nm, which is characteristic of spinodal decomposition, existed in the matrix.

Fig. 4(a) shows the morphology of as-solutionized Cu-15Ni-8Sn alloy. The morphologies of the alloy aged at 400 ℃ for 1.5 h and 4 h are also shown in Fig.4 (b) and (c). After aged for 1.5 h, some discontinuous precipitation were found in the grain boundaries. With the ageing time increased, the amount of these discontinuous precipitation increased gradually and extended from the grain boundaries throughout the matrix.

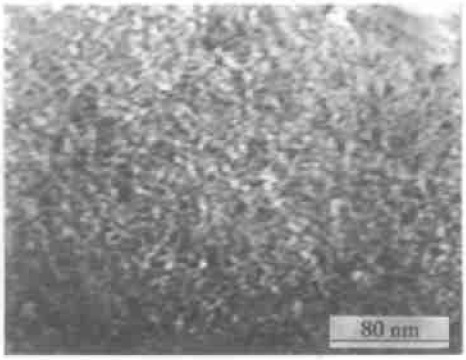

Fig.3 Modulate structure of alloy aged at 400 ℃ for 1.5 h

Fig.5 illustrates the change of hardness as a function of ageing time of the Cu-15Ni-8Sn alloy aged at 400 ℃ with 0 and 80% prior cold rolling. Similar tendency has been found on the prior deformed alloy, except the minor decrease of hardness when aged for 10 min.

4 DISCUSSION

4.1 Ageing progress of mechanically alloyed Cu-15Ni-8Sn alloy

Three stages have been found during the ageing process of the Cu-15Ni-8Sn alloy. In the first stage, spinodal decomposition is the predominant phase transformation. With increasing ageing time, a spinodal structure with repeated Sn-rich region and Sn-deplete region with a wave-length of about 10~100 nm develops[9,10]. The composition modulation in the Cu-Ni-Sn alloys produces a lattice strain modulation due to the larger size of the tin atom, which results in the observed sideband profiles in the XRD patterns (Fig.2). In this stage, the hardness increases with increasing ageing time. On the prolonged ageing time, the wave-length of the modulated structure increases. An intermetallic γ-$(Cu_xNi_{1-x})_3Sn$ with a DO_{22} prototype, in which Cu and Ni are substitutionally interchangeable[9,11], begins to precipitate in the Sn-rich region (Fig.4(b)). These dispersoids attribute to the strength of the alloy through

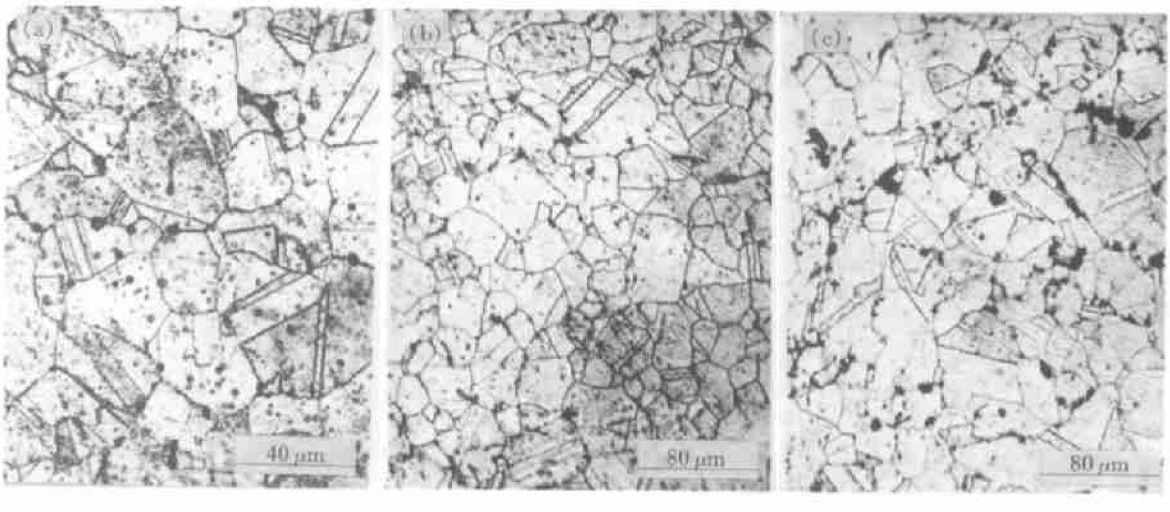

Fig.4 Microstructures of Cu-15Ni-8Sn alloy
(a)—As-solutionized; (b)—Aged at 400 ℃ for 1.5 h; (c)—Aged at 400 ℃ for 4 h

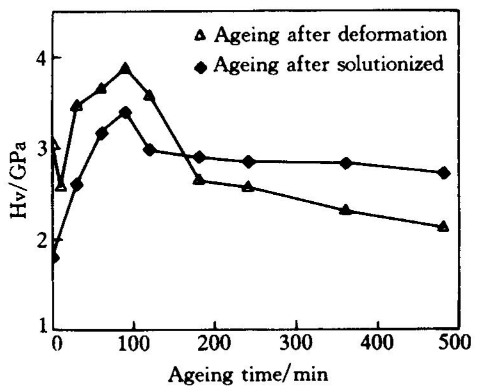

Fig.5 Hardness evolution aged at 400 ℃ with 0 and 80% prior cold rolling

Orowan strengthening mechanism. The hardness of the alloy is further improved and at length reaches a peak value. After aged for 1.5 h, the predominant phase transformation turns to the discontinuous precipitation. The DO_{22} type γ, phase transforms to large, needle-like equilibrium particles with DO_3 prototype[9,11], which develop gradually from the grain boundary to the grain (Fig.4(c)). The coherence relationship between the Sn-rich region and Sn-deplete region is then destroyed, resulting in the disappearance of the strengthening effect and the continuous decrease of the strength and the hardness of the alloy.

The hardness of the mechanically alloyed Cu-15Ni-8Sn alloy aged at 400 ℃ for 1.5 h is 30 ~ 50 Hv higher than that prepared by conventional ingot metallurgy or rapidly solidification. It can be contributed to the fact that the distribution of the tin in the mechanically alloyed Cu-15Ni-8Sn alloy is much more uniform[5], which results the finer and more homogeneous spinodal structure. Meanwhile, the finer hard phase (carbide or oxide) induced by the addition of PCA during ball milling of the elemental powder mixture and finer grains (10 ~ 40 μm) characteristics of mechanical alloying[3,4] not only improves the peak hardness of the alloy during ageing, but also retards the nucleation and growth of the γ equilibrium phase, which rendered the delay of the over-ageing.

In addition, there exists a critical ageing temperature, above which the spinodal decomposition does not occur. The hardness of the alloy decreases gradually with increasing the ageing time[6]. The results in Fig.1 show that the critical ageing temperature is about 400 ~ 450 ℃ for mechanically alloyed Cu-15Ni-8Sn alloy, which is near to those prepared by casting or rapid solidification. When aged at the temperature above the critical ageing temperature, the hardness increases in the early stages due to the existence of the fine dispersoids resulting from the discontinuous precipitation, then decreases continuously with the growth of the dispersoids with the prolonged ageing time.

4.2 Effect of prior cold deformation

Compared with the alloy aged directly after solution treatment, a higher peak hardness of the alloy which experienced cold rolling prior to the ageing treatment has been achieved (Fig.5). Because the strain hardening rate of the Cu-Ni-Sn alloys is high[9] and the ageing temperature of 400 ℃ is supposed not high enough to cause evident recrystallization of the mechanically alloyed Cu-15Ni-8Sn alloy, the increased peak hardness can be attributed to the combined strengthening effects of both ageing and work hardening. Furthermore, the increase of the density of the dislocation and the stored strain energy after cold rolling provides the additional driving force for the spinodal decomposition and the discontinuous precipitation transformations. Therefore, the hardness of the deformed alloy increases at a higher rate than the undeformed one in the early stages of ageing (Fig.5). However, the decreasing rate of the hardness after the peak value is also higher because of the accelerated discontinuous precipitation. After aged at 400 ℃ for 3 h, the hardness of the deformed alloy decreases rapidly from the peak value of 358 Hv to 265 Hv, which is even lower than the undeformed alloy aged at the same condition. It is worth to mention that a decrease of about 46 Hv in the hardness of the deformed alloy is evident when aged for 10 min (Fig.5), which may due to the prominent recovery or internal stress relaxation process of the alloy in the initial stages of ageing treatment.

5 CONCLUSIONS

(1) The ageing process of the mechanically alloyed Cu-15Ni-8Sn alloy involves two different phase transformations, i. e., spinodal decomposition and discontinuous precipitation. The critical temperature, above which the spinodal decomposition does not occur, is estimated to be about 400~450 ℃.

(2) Compared with the alloys prepared by conventional ingot metallurgy or rapid solidification method, the mechanically alloyed Cu-15Ni-8Sn alloy possesses a higher peak hardness (30~50 Hv), which is attributed to the finer grain size, spinodal structure and the homogeneous dispersoids induced by ball milling.

(3) The cold deformation prior to ageing accelerates the ageing process and improves the peak hardness compared to the undeformed alloy.

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