

Modification of the spinodal hardening in a Cu-9 wt % Ni-6 wt % Sn alloy by 0.1 wt % silicon or aluminium addition

JA'AFAR HADI ABBOUD, E. S. DWARAKADASA*

School of Production Engineering and Metallurgy, University of Technology, P O Box 35010, Baghdad, Iraq

Among non-ferrous metallic materials, beryllium-copper and its modifications have been known to develop high strength by a process of precipitation. The fact that these alloys suffer from the disadvantages of high cost, certain property limitations and health hazards during the handling of beryllium, has instigated an extensive search for alternatives. Many new alloys have been successfully developed as substitutes, among which the Cu-Ni-Sn alloys have been shown to develop high strength values [1] surpassing that attainable in the best of the copper-beryllium compositions. Such high strengths have been attributed to the development of a fine modulated structure as a result of a spinodal decomposition. Typically, after suitable mechanical treatment, it has been shown [2] that yield strength values of the order of 1400 MPa can result. However, in these alloys, on overageing, a discontinuous precipitation sets in resulting in an embrittling effect. Critical thermomechanical treatments can, to some extent, offset this defect and improve the ductility at fracture. Easier and more definite ways of improving the strength and ductility would be very desirable. In several aluminium based precipitation hardening alloys it has been shown that an addition of a small amount of a trace element greatly influences the precipitation process in such a way as to result in the elimination of the precipitate-free zones and also grain boundary precipitation. Analogously, an attempt was made to study the influence of adding a small quantity of a quaternary element to a high strength Cu-9 wt % Ni-6 wt % Sn composition on the nature of thermal hardening that occurs due to a spinodal decomposition process. A positive trend was observed in terms of the stabilization of the precipitate structure and absence of softening on long ageing. Results obtained in a preliminary study have been communicated in this paper.

Electrolytic grade copper was melted in a carborundum crucible in a gas fired furnace. Chips of nickel and tin were added well wrapped in copper foil to the molten copper and stirred well to homogenize the melt. To the alloy melt, an equivalent of 0.1 wt % Si or Al was made, also wrapped in copper foil. The trace additions were both made in the elemental form. Three alloys were made for the study whose compositions are given in Table I.

The alloy melt, after allowing for suitable homogenization by stirring, was poured into 15 mm diameter and 250 mm long cast iron moulds. The chill cast ingots were homogenized at 950°C after removing a surface layer of about 0.5 mm to remove contamination and surface defects. The homogenized ingots were forged down in stages down to 1 mm thick strips, which were solution annealed at 950 ± 5°C for 6 h in a vacuum furnace and then water quenched (0°C). Thermal ageing was carried out in thermostatic baths maintained at 390, 400 and 410°C and the process was monitored by hardness measurements in a bench hardness tester to obtain the VHN (Vickers hardness number) of the specimens. At all stages a comparative study was made of the microstructure of the specimens to determine, if any, the influence brought about by the trace additions. It was observed that the presence of the trace element did not change the microstructure at any stage except for a certain amount of grain refinement in both cases of trace additions. For example,

TABLE I Composition of the spinodal alloys made for the investigation

Designation	Composition (wt %)			
	Ni	Sn	Al	Si
Base alloy	9.14	5.76	—	—
S-alloy	8.39	5.80	—	0.15
A-alloy	9.23	5.10	0.13	—

*On leave from the Department of Metallurgy, Indian Institute of Science, Bangalore 560.012, India.

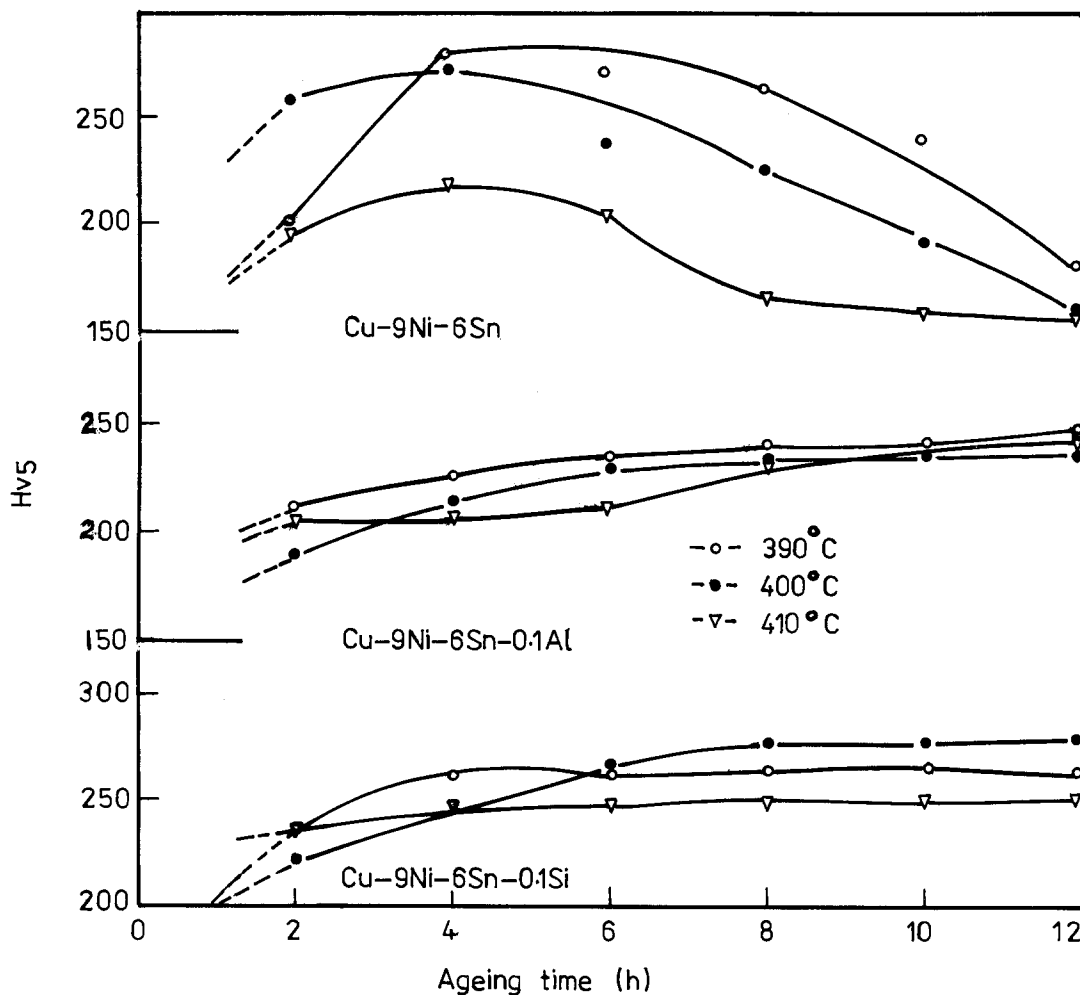


Figure 1 Thermal hardening in Cu-9 wt % Ni-6 wt % Sn alloy with 0.1 wt % Al or Si addition at 390, 400 and 410°C.

in the stage in which the strips were taken for solution treatment, the average grain sizes measured were 60, 40 and 35 μm for the base, S- and A-alloys, respectively. The 6 h solutionizing treatment did not result in any observable grain growth in any of the alloys indicating that the pre-treatment procedure had established a stable grain structure in all the three alloys.

During the pre-treatment, it was qualitatively observed that the alloys containing the trace additions were more easy to forge, and needed less number of stages for being reduced to 1 mm strips compared with that for the base alloy. This was taken to indicate an increased ductility in the alloys with the trace additions.

In Fig. 1 is shown the variation in hardness in the three alloys during thermal ageing at 390, 400 and 410°C. In all the three alloys an initial rapid increase in hardness with ageing time was observed.

In the base alloy, the hardness reached a peak and then, at longer ageing times, the hardness decreased gradually. Hardening was studied for a total period of 15 h. After reaching the peak the hardness continuously decreased during this 15 h period in the base alloy. The behaviour observed in the base alloy is in agreement with earlier findings [1, 2]. It has been shown that the initial hardening is due to a spinodal decomposition process while the softening on overageing is thought to be due to the formation of a grain boundary precipitate of $(\text{CuNi})_3\text{Sn}$. In the Cu-Ni-Sn system this precipitation is observed close to and above the critical spinodal decomposition temperature. In the light of this, in the base alloy, at all the three temperatures of investigation, a reduction in the hardness of the alloy results at long ageing periods indicating that the critical temperature is about 400°C.

Compared with the behaviour in the base alloy, in both the quaternary alloys the hardness gradually increased to a maximum value and after reaching the peak value, it remained nearly the same for the entire 15 h period. The time taken to reach the maximum was slightly longer than that in the base alloy. This is believed to be due to an influence of the trace element atoms on the diffusion of nickel and tin atoms if a vacancy aided mechanism were to be considered. The fact that the hardness did not decrease in the quaternary alloys after reaching the peak is taken to indicate an apparent increase in the critical spinodal temperature brought about by the trace addition. This is also seen from the fact that in the quaternary alloys the hardness curves for all the three ageing temperatures were very close to each other, while in the base alloy ageing temperature had an observable influence on the level of hardness. The constancy in the maximum hardness in the alloys was taken to indicate a stabilization of the spinodal decomposition product and the prevention of the onset of the discontinuous precipitation reaction. If this were true, the quaternary alloys would exhibit a larger amount of fracture ductility than that observed in the base alloy. In preliminary tests [3] this fact has been confirmed. Also SEM (scanning electron microscopy) observations [4] of tensile fractures indicate a change from a purely intergranular fracture in the base alloy to a mixed type intergranular-transgranular failure. The latter fractures exhibit the presence of extensive dimples indicative of ductility. The tensile strength of the alloys, however, did not show any significant increase. It may be noted that the slightly smaller

value of hardness in the A-alloy was traced to the smaller tin content of the alloy (3).

The result presented herein demonstrates the possibility of overcoming embrittlement in high strength spinodal Cu-Ni-Sn alloys by recourse to trace element additions. These alloys are being presently studied further by TEM (transmission electron microscopy) to determine the influence of the trace element addition on the morphology of the spinodal decomposition. Results will be published in due course.

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