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Relationships between structure and hardness developed during the high temperature ageing of a smart Cu-based alloy

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Smart shape memory alloys are used industrially due to their novel properties. Copper-based shape memory alloys are strongly influenced by ageing treatments which involve microstructural changes. The present work has been carried out on a CuZnAlCo alloy which has been aged at 400, 500 and 600 °C for time durations ranging from 5 min to 12 h. Hardness measurements have been performed and the microstructural evolution has been determined by electron microscopy. The results show that microstructural changes are strongly dependent on the ageing temperature and time. A maximum hardness of 300 $Hv_{0.2}$ has been obtained after ageing treatments. Equilibrium α and γ phase and non-equilibrium phases (β or martensite) are present in the alloy depending on the ageing temperature and the ageing time. The maximum hardness has been associated with the presence of the α and γ phases.

1. Introduction

Smart shape memory alloys are used as engineering components because of their particular properties, e.g., shape memory effect (SME), pseudoelasticity and two way shape memory effect (TWSME).

Amongst the different kinds of shape memory materials which have been studied those based on copper are of particular significance because of their low cost. Since shape memory properties of smart Cu-based alloys are a consequence of the presence of the β phase or martensite and, as these two phases are metastable, the properties of these alloys are strongly influenced by ageing treatments at low or high temperatures.

Takezawa and Sato found, when ageing at moderate temperatures Cu–Zn–Al alloys with a low electron to atom concentration ($e/a < 1.46$), the presence of a bainitic structure which formed after an incubation period. At a higher electron to atom concentration, γ_2 precipitation occurred during ageing [1–3]. Wu and Wayman (4) have also found β_3 or γ precipitates when ageing a Cu–25.80% Zn–3.68% Al alloy at 250 °C for 10 min.

A considerable amount of work has been carried out on the shape memory properties of Cu–Zn–Al and Cu–Al–Ni alloys [5–7]. However, these alloys have become more and more complicated as a result of the addition of other elements, e.g., Mn and Ti elements which improve the shape memory properties (CANTIM alloys) [8] and also elements to give grain refinement (Co and Zr) [9].

A certain amount of work has been carried out to study the ageing processes that take place in these alloys. The present authors have studied the isothermal ageing phenomena at low ageing temperatures ($T_{\text{ageing}} \leqslant 300$ °C) [10] and the athermal ageing by differential scanning calorimetry (DSC) of a Cu–Zn–Al–Co [11], where Co was added as a grain refining element [12].

The present study is concerned with the ageing phenomena occurring at high ageing temperatures ($T_{\text{ageing}} \geqslant 400$ °C) on a Cu–Zn–Al–Co alloy.

2. Experimental procedure

An ingot of Cu–20.2 wt % Zn–6.6 wt % Al–0.7 wt % Co was obtained by melting the pure metals in a sealed quartz tube 14 mm in diameter. The ingot was homogenized at 850 °C for 12 h. Semicircular samples 5 mm thick were cut from the ingot for further heat treatment and examination.

All the samples were heated into the β field at 850 °C for 15 min and then water quenched to room temperature. Individual samples were then heated, in an electric furnace, at 400, 500 and 600 °C for 5, 10 and 15 min and 1, 6 and 12 h.

Vickers microhardness measurements were made at a load of 200 g on each of the samples using a Leitz Wetzlar Durimet instrument. Eight measurements were carried out, on each sample, and the average obtained. The changes in the microstructure were determined by scanning electron microscopy (SEM) using an ISI SS60 microscope (20 kV) equipped with an energy dispersive X-ray spectrometer (EDS) which was used for microanalysis ($Z > 4$) and transmission electron microscopy (TEM) using an Hitachi H-800-MT instrument (200 kV).

3. Results and discussion

The original structure of the alloy, after water quenching from 850 °C and prior to the ageing treatment, is shown in Fig. 1. It had a completely twinned martensitic structure with the presence of dendritic and polyhedric cobalt precipitates [13]. Transmission electron microscope studies carried out in previous work [14] also revealed the existence of small cobalt precipitates with an average size of 50 nm.

The change in hardness with ageing time and temperature is shown in Fig. 2. It can be seen that there is a rapid increase in hardness, at low ageing times (5 min) for all the ageing temperatures studied. A maximum of 300 $Hv_{0.2}$ was found for the sample aged at 400 °C for 10 min. Longer ageing times produce a decrease in the hardness.

On increasing the ageing temperature, the maximum is achieved at shorter times but this maximum is lower than that found for 400 °C which is characteristic of a diffusion controlled age hardening system. Longer ageing times, for the temperatures studied, resulted in softening and the hardness returned to the original value for the unaged alloy.

Comparing these results with those obtained previously [10], it is clear that a maximum hardness of 300 $Hv_{0.2}$, which is nearly double the original as quenched hardness, is achieved by ageing the alloy. These changes are brought about as a result of complex structural changes during ageing as the alloy moves into different stability fields.

The sample aged at 400 °C for 10 min is shown in Fig. 3. The equilibrium phases $\alpha + \gamma$ are present in the fully transformed sample. This structure is associated with the maximum hardness.

However, at this ageing temperature, the equilibrium phase diagram shown in Fig. 4 would indicate that the phases present should be $\alpha + \beta + \gamma$. At 400 °C for a short time, during the reheating process the original martensite decomposes, at temperatures within the range 100–300 °C, to give $\alpha + \gamma$ as the temperature rises to 400 °C. There would appear to be insufficient time for the α and γ phases to react to form the β phase, that is to say equilibrium is not achieved.

Longer ageing times allow the sample to achieve equilibrium and the β phase forms, but on quenching from this temperature, the β phase transforms martensitically, as is shown in Fig. 5, giving a final structure $\alpha + \gamma +$ martensite. The β phase transforms martensitically because it has the same composition as that of the original β phase in the alloy. Small γ precipitates are also present in the alloy, see Fig. 6, with an average size of 25–40 nm. These precipitates contain some Co [13].

The presence of martensite, obtained from quenching of the β phase, which has formed at 400 °C, is associated with a slow decrease in the hardness to the original as quenched value as would be expected.

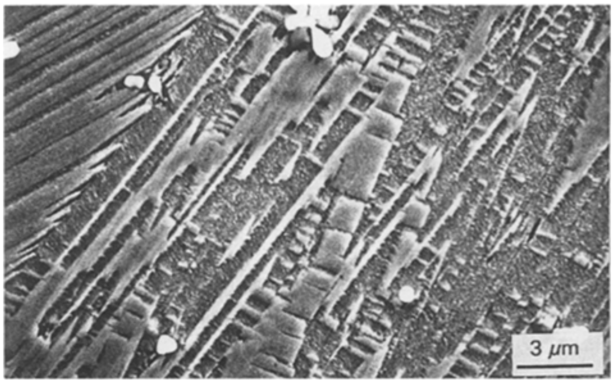

Figure 1 Twinned martensitic structure of the original as quenched sample.

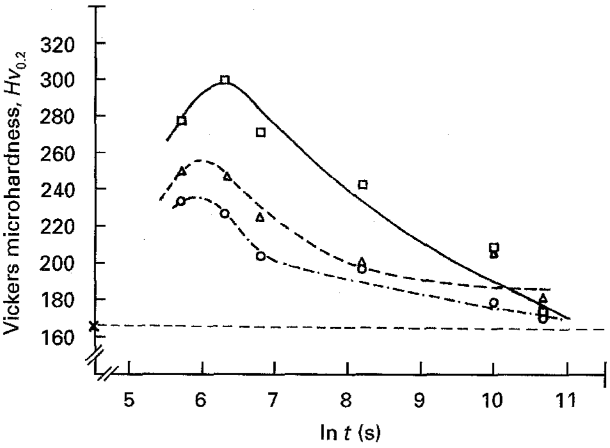

Figure 2 Hardness Vickers values of the aged samples. The temperatures investigated were (□) 400 °C, (△) 500 °C, (○) 600 °C and (×) the as quenched material.

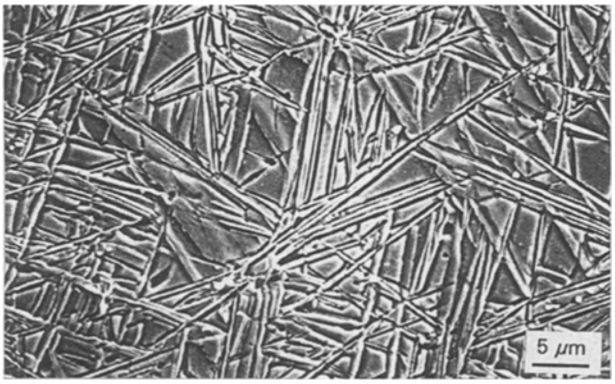

Figure 3 Microstructure of the alloy aged at 400 °C for 10 min.

A higher ageing temperature (500 °C) places the sample in the $\alpha + \beta$ fields, as shown in Fig. 4. A similar structure, as that found for the sample aged at 400 °C for 10 min, is found, for the sample aged for 5 min at 500 °C as is shown in Fig. 7. As γ is no longer the stable phase, there is a smaller quantity of $\alpha + \gamma$ phases obtained by decomposition of the original martensitic phase, when compared with the sample aged at 400 °C. After ageing at 500 °C, a large quantity of α phase is nucleated at the grain boundaries of the prior β phase and Widmanstatten α forms inside the β grains. Long ageing times allow the alloy to achieve equilibrium when $\alpha + \beta$ phases are present, with twins being formed in the α phase as is shown in Fig. 8. The remaining β matrix has a higher Al and Zn content, in comparison with the original composition, because the α phase which forms becomes richer in copper, thus, the β matrix is stabilized and does not transform

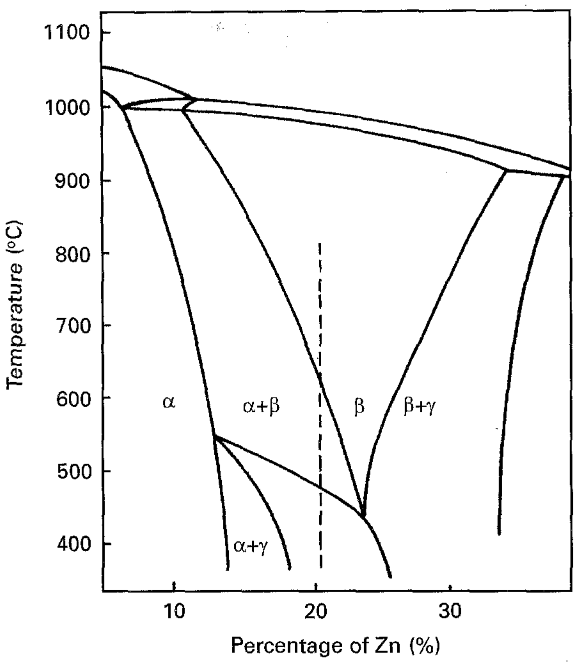

Figure 4 Vertical section at 6.6 wt % Al of the ternary Cu–Zn–Al diagram.

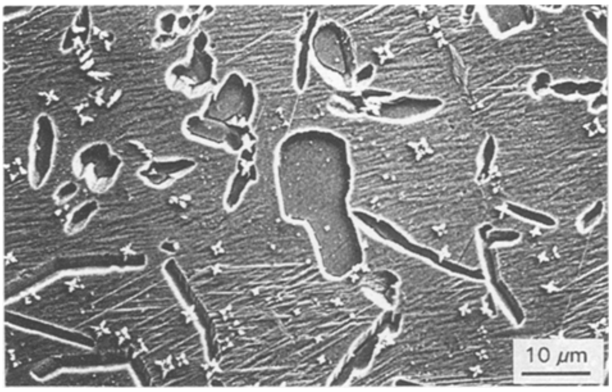

Figure 5 Equilibrium α + γ phase in a martensitic matrix for the sample aged at 400 °C for 12 h.

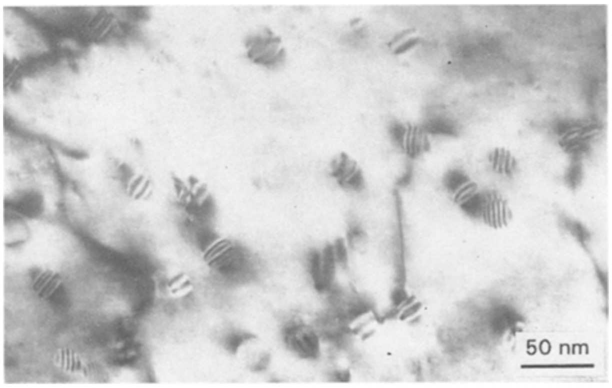

Figure 6 Transmission micrograph showing γ precipitates obtained from the same sample of Fig. 5.

martensitically on quenching from the ageing temperature at the end of the ageing treatment.

Small γ precipitates are still present in the β phase after ageing at 500 °C for 12 h, as is shown in Fig. 9. The particles have an average size of 80–100 nm. These precipitates are produced in the first stage of decomposition [10] and it seems that they do not transform back into β, until the second stage of decomposition, when the α and β phases have transformed to their equilibrium compositions.

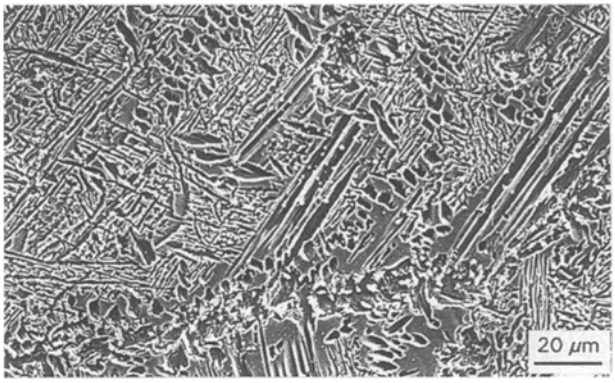

Figure 7 Microstructure of the sample aged at 500 °C for 5 min.

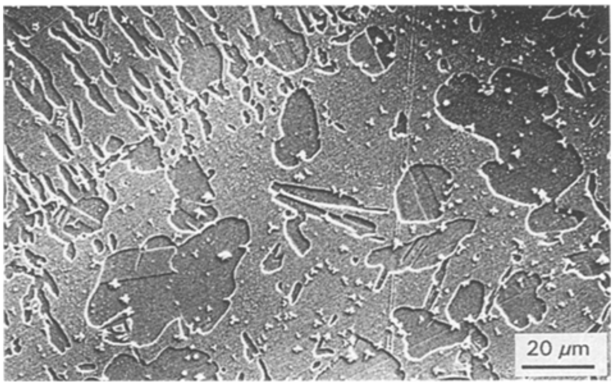

Figure 8 α and β phase present in the sample aged at 500 °C for 12 h.

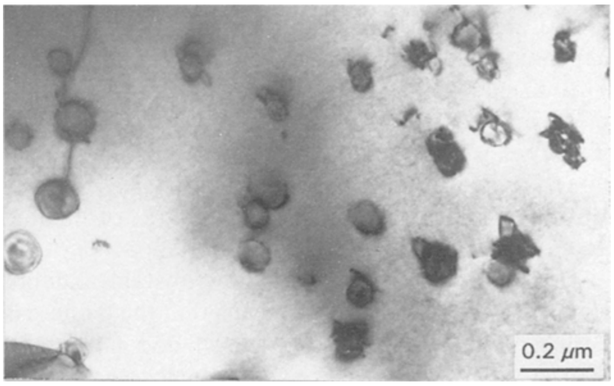

Figure 9 γ precipitates surrounded by tangle dislocations.

The structure of the sample aged at 600 °C for 12 h is shown in Fig. 10. The α phase is present together with a martensitic structure which corresponds to the transformed β matrix. The equilibrium phase diagram, Fig. 4, shows that the structure of the alloy at the ageing temperature is still α and β, as in the case of 500 °C. However, at 600 °C there is less α phase in the structure. This means that the stable β phase at 600 °C may have a nominal composition close to the original one which then allows, the β phase, to transform martensitically on quenching.

The presence of the martensite or the β phase, on ageing, involves a decrease in the hardness, until it reaches nearly the original value.

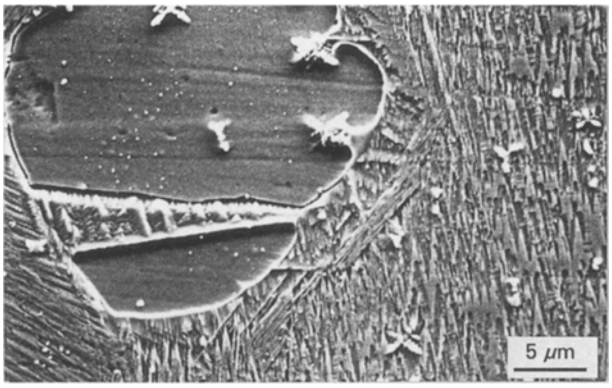

Figure 10 Martensitic structure with α phase present in the sample aged at 600 °C for 12 h.

4. Conclusions

1) A maximum of 300 $Hv_{0.2}$ is achieved for an alloy of Cu–20.2 wt % Zn–6.6 wt % Al–0.7 wt % Co when ageing for 10 min at 400 °C. Increasing the ageing temperature or the time, or both, brings about a decrease in hardness to the original as quenched hardness.

2) The final microstructure of the aged alloy is strongly dependent on the ageing temperature, but not as strongly dependent upon the ageing time. The sequence can be summarized as follow:

i) Low ageing times, independently of the ageing temperature, produces the equilibrium phases $\alpha + \gamma$ with the presence of small γ precipitates, although the equilibrium phase diagram shows $\alpha + \beta + \gamma$ at 400 °C or $\alpha + \beta$ at 500 and 600 °C.

ii) Long ageing times produce different structures depending on the ageing temperature.

a) At 400 °C, the $\alpha + \gamma$, obtained from the decomposed matrix at low ageing time, transforms back into β, giving an $\alpha + \gamma + \beta$ structure with small γ precipitates. On quenching, the β matrix transforms martensitically leading to a final structure containing $\alpha + \gamma$ + martensite + small γ precipitates.

b) At 500 °C, the α phase is now in stable equilibrium with the β phase. That means that the β phase is enriched in Al and Zn. The enriched β does not exhibit a martensitic transformation on quenching back to room temperature.

c) At 600 °C, $\alpha + \beta$ are the stable phases. However, since less α phase is present at this temperature than at 500 °C, a depletion of Al and Zn in the β matrix produces almost the original composition. Thus, on quenching from this temperature the β transforms martensitically to give a final structure of α + martensite + small γ precipitates.

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