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Ordering within precipitates in copper-nickel-titanium alloys

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The precipitation process in alloys containing 4% Ti and 5 to 16% Ni was investigated using transmission electron microscopy, hardness and electrical conductivity measurements. After ageing, spherical γ'-Ni_3Ti precipitates with ordered DO_{22} superlattice were observed in alloys CuTiNi5 to 10 and the $L1_2$ superlattice in the CuTi4Ni16 alloy. With increasing nickel content the size of precipitates decreases; this has only a minor influence on the age hardening. The CuTiNi10 alloy has the best electrical conductivity approaching $18\,m\Omega^{-1}\,mm^{-2}$.

1. Introduction

After thermo-mechanical treatment copper–titanium alloys attain relatively high mechanical properties, approaching those of copper–beryllium alloys [1–3]. The electrical conductivity is however better [4]. The addition of nickel increases the corrosion resistance giving a substantial age hardening effect [5]. Since precipitation of Ni_3Ti provides the hardening effect leaving copper in the solution it was expected that ternary alloys should have better electrical conductivity and corrosion resistance than the binary Cu–Ti alloys. The ageing process in three alloys containing about 4% Ti and different Ni:Ti ratio was investigated by hardness and electrical conductivity measurements and thin foil electron microscopy.

2. Experimental procedure

Alloys containing 4.5 wt% Ti and 5 to 15 wt% Ni were cast in a vacuum induction furnace. The composition of alloys after chemical analysis is given in Table I.

After casting, the alloys were homogenized for 3 h at 900° C in an argon atmosphere. Samples were rolled and sectioned for hardness, conductivity and structure investigations. After solution treatment at 1000° C samples were quenched in water and then aged in a liquid salt bath at a temperature of 680° C. This ageing temperature was chosen as giving significant strengthening in a relatively short time. Thin foils were obtaining using disc polishing at electrolyte containing 33% HNO_3 and 67% CH_3OH. A Philips 301–EM fitted with a goniometer stage was used for the structure investigations.

TABLE I

Alloy	Ti (wt%)	Ni (wt%)	Cu (wt%)
A	4.5	5.0	rest
B	4.5	10.0	rest
C	4.0	16.0	rest

3. Results

Fig. 1 shows hardness changes during the ageing of the alloys investigated. It can be seen that alloys A and B behave in a similar manner reaching a maximum hardness of 175 HB and 168 HB respectively after about 2 min. In alloy C transformations

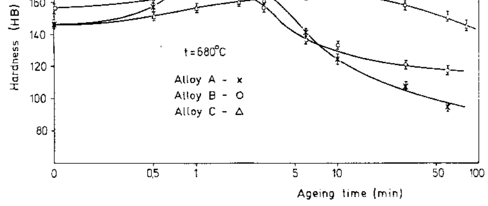

Figure 1 Hardness changes during ageing of A, B and C alloys at 680° C.

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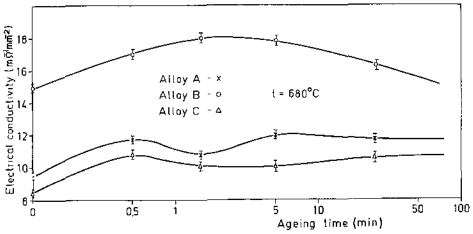

Figure 2 Electrical conductivity versus ageing time at 680° C for A, B and C alloys.

are slower, while the maximum hardness of 162 HB is attained after about 10 min. Results of the electrical conductivity changes during ageing at 680° C are shown in Fig. 2. Alloy B has the best conductivity approaching 18 mΩ^{-1}mm^{-2} after a few minutes. During further ageing a small fall in conductivity can be observed. Alloys A and C have similar conductivity curves. They attain a maximum conductivity of 12 and 11 mΩ^{-1}mm^{-2}, respectively, after about 1/2 min, which is followed by a small depression and a steady value of 10.5 and 11.5 mΩ^{-1}mm^{-2}. Minimum conductivity after about 1 to 2 min corresponds to a maximum hardness.

In order to explain changes of physical and mechanical properties samples were examined in the electron microscope. Fig. 3 shows a set of transmission electron micrographs taken from alloy A, aged for 1.5 min at 680° C. Small precipitates of size 100 to 200 Å show a typical strain field contrast. Diffraction patterns show weak {100}, {110} and {1, 1/2, 0} superlattice spots characteristic of DO_{22} superlattice. Dark field micrographs taken using a (100) superlattice reflection (Fig. 3c) show only some of precipitates in contrast, which indicates that the other variants of ordered domains have been formed in the other precipitates. During further ageing, precipitates grow in size up to about 300 Å (Fig. 4). They show a significant strain field contrast with no well defined interface boundaries or interface dislocations. This indicates that the coherency between matrix and precipitates is preserved. Diffraction patterns show superlattice spots in identical positions as in Fig. 3c, but however of relatively higher intensity. After 25 min of ageing a discontinuous coarsening of precipitates occurs near grain boundaries, as can be seen in Fig. 5. A similar precipitation mechanism was observed in alloy B. Fig. 6 shows a bright field micrograph of a grain of close to [001] orientation as indicated in the diffraction pattern shown in Fig. 6b. An identical pattern of superlattice spots to those obtained from alloy A can be seen. Superlattice maxima are relatively stronger which may indicate a higher degree of order within precipitates of average size less than 100 Å. The size can be measured more accurately in the dark field image taken using the (100) superlattice spot (Fig. 6c). After 25 min of ageing, precipitates grow in size up to about 200 Å as can be seen in Fig. 7. Near grain boundary coarsening of precipitates similar to those observed in alloy A was observed.

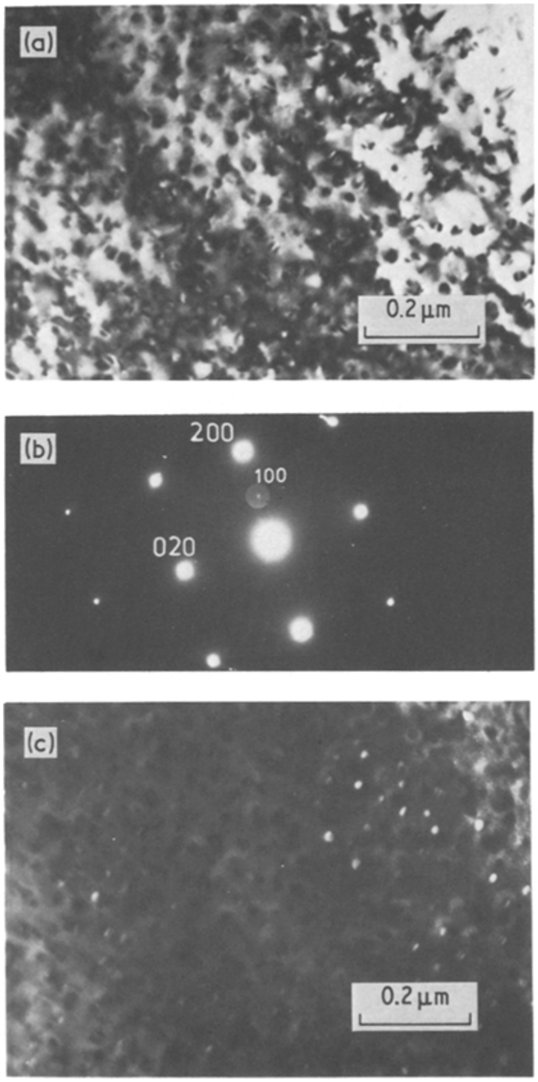

Figure 3 Alloy A aged for 1.5 min at 680° C (a) Bright field image, (b) Electron diffraction pattern, (c) Dark field image taken using (100) superlattice spot.

In alloy C, a stoichiometric relation corresponding to Ni_3Ti, a different type of superlattice, was observed. Fig. 8 shows a transmission micrograph

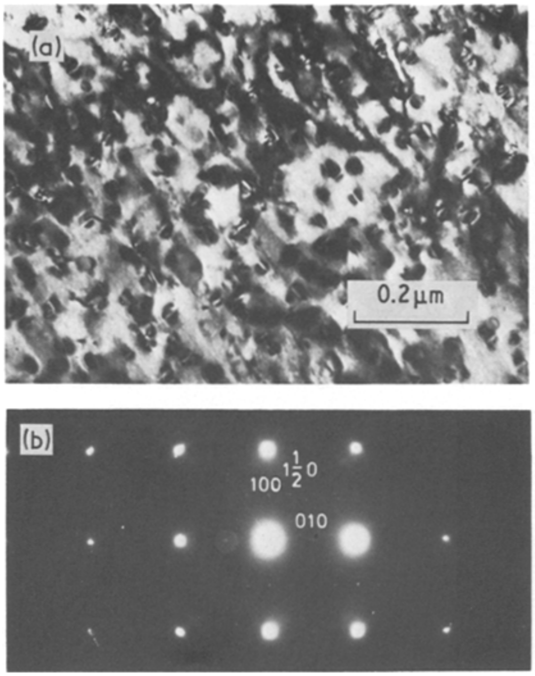

Figure 4 (a) Transmission electron micrograph of alloy A aged for 5 min at 680° C, (b) Electron diffraction pattern.

taken from alloy C, aged for 1.5 min at 680° C. Precipitates are very small and do not exceed a diameter of 50 Å. Diffraction patterns taken from the area shown in Fig. 8a show only a {100} and {110} superlattice maxima; no {1 1/2 0} spots were detected. After 25 min the precipitates grow in size approaching about 100 Å, as can be measured from the dark field micrograph taken using the {100} superlattice spot (Fig. 9). Superlattice maxima are clearly visible after this period of ageing (Fig. 9).

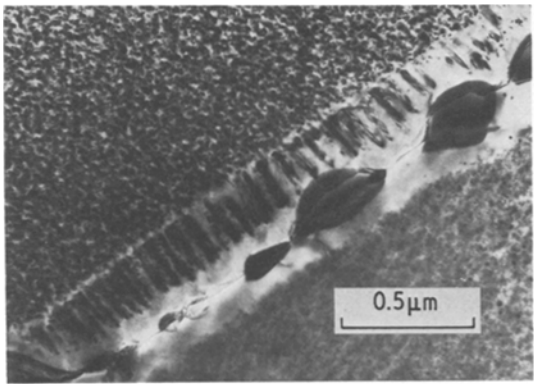

Figure 5 Transmission electron micrograph of alloy A aged for 25 min at 680° C.

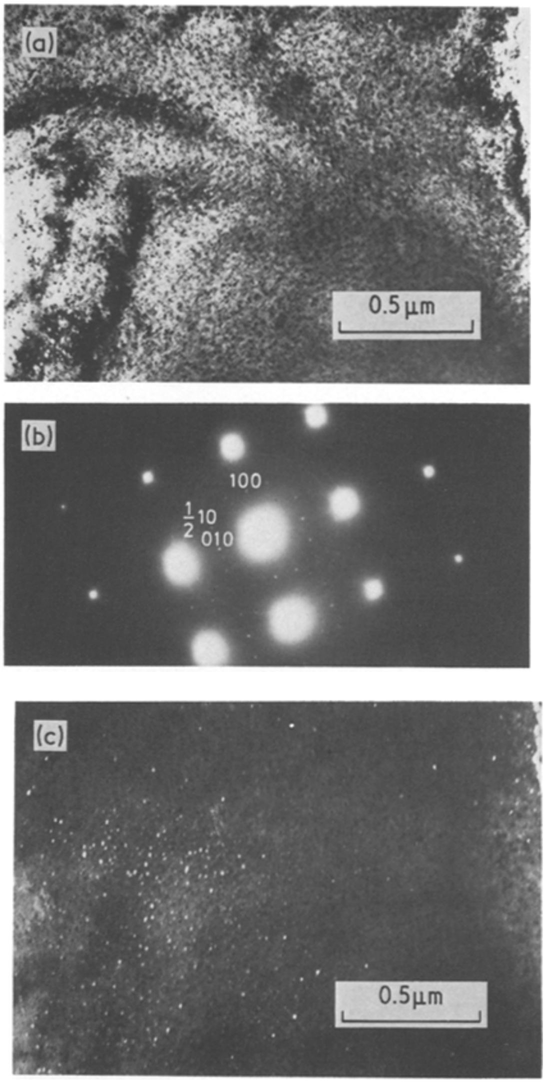

Figure 6 Alloy B aged for 0.5 min at 680° C, (a) Bright field image, (b) Electron diffraction pattern, (c) Dark field image taken using (100) superlattice spot.

4. Discussion and conclusions

The results presented above indicate that spherical γ'-Ni$_3$Ti ordered precipitates (with the same lattice parameter as the matrix) are formed which is in agreement with a previous paper on alloys with higher Ni content [5]. Addition of 5–10 wt% Ni causes a change in character of the superlattice within γ'-Ni$_3$Ti precipitates from L1$_2$ to DO$_{22}$, which is proved by the appearance of additional {1 1/2 0} superlattice reflections. It is highly probable that some Ni atoms in the structure are replaced by Cu atoms which changes the type of superlattice in this compound. With increasing nickel content the size of precipitates, after a

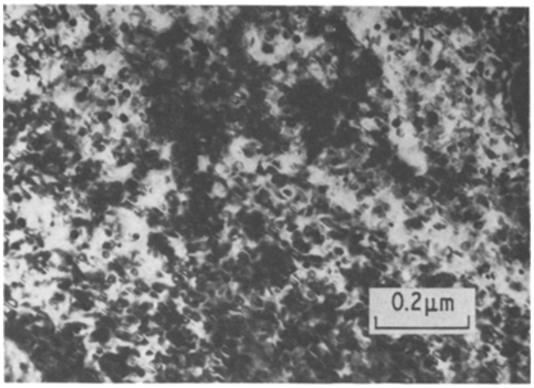

Figure 7 Transmission electron micrograph of alloy B aged for 25 min at 680° C.

given ageing time, decreases. It has however only a weak influence on the age hardening effect because of the close values of the lattice parameters of the matrix and precipitates.

The electrical conductivity of alloys containing nickel is much better than Cu–Ti alloys [5] and similar to that of beryllium bronzes [4, 6]. The strong effect of the conductivity increase in the first stage of ageing corresponds to a different kind of precipitate (excluding copper) in Cu–Ni–Ti alloys, when compared to Cu–Ti alloys. The high conductivity of alloy B is most probably caused by the lowest content of solute atoms in the solution, i.e. the highest content of solute in the precipitates. It may be due to a different stoichiometric ratio Ni:Ti within the precipitates, (i.e. 2:1). This observation agrees with stated change of the character of superlattice within Ni_3Ti precipitates.

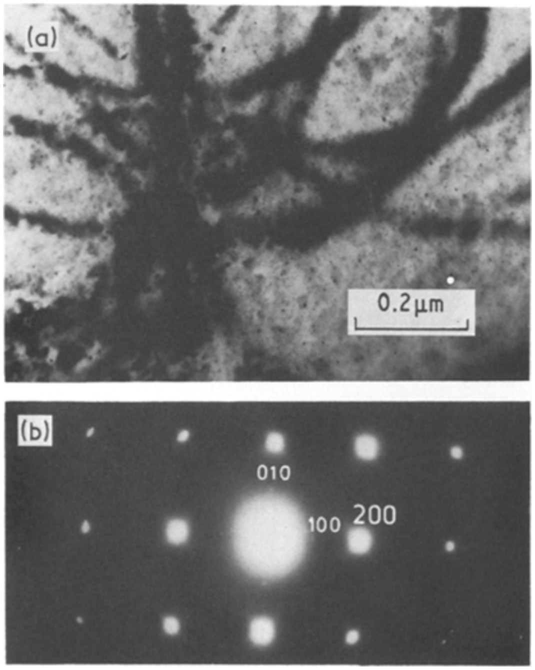

Figure 8 Alloy C aged for 1.5 min at 680° C, (a) Bright field image, (b) Electron diffraction pattern.

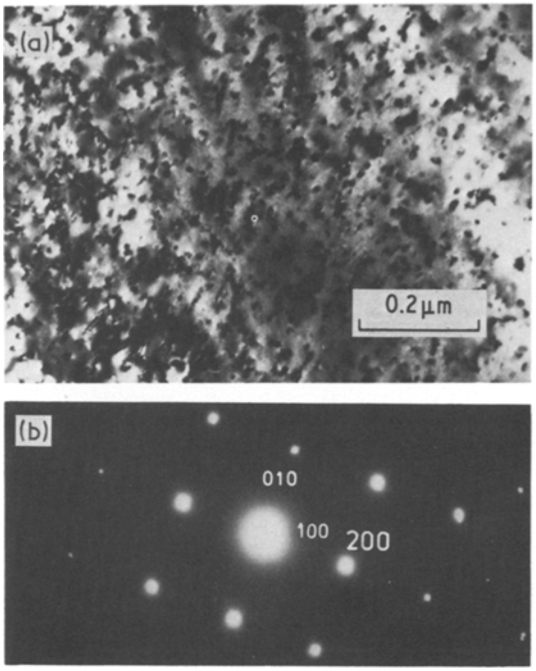

Figure 9 (a) Transmission electron micrograph of alloy C aged for 25 min at 680° C, (b) Electron diffraction pattern.

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