Microstructure evolution and aging hardening in a Cu-25Ni-25Mn alloy

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Abstract

The microstructure evolution and mechanical property of Cu-25Ni-25Mn alloy after solution treatment and aging treatment were investigated via TEM observation, XRD analysis and Vickers hardness test. The effect of the NiMn precipitates on hardness and its strengthening mechanism in the Cu-25Ni-25Mn alloy is quantitatively analyzed. The results show that in 450 °C aging process, Ni and Mn precipitate from the copper matrix and form nanoscale NiMn phase particle with a face-centered tetragonal (FCT) structure. The XRD analysis indicates that the NiMn precipitates have a lattice constant of a = b = 0.3693 ± 0.0004 nm, c = 0.3570 ± 0.0006 nm, which is fully coherent with the copper matrix. The precipitation of NiMn phase lead to a precipitation strengthening, which provides significant increase in hardness in the peak-aged Cu-25Ni-25Mn alloy. Compared to the solution treated sample, the hardness of peak-aged sample has been increased by 367 HV. The coherency strengthening and modulus strengthening are the dominant strengthening mechanisms. The hardness increment predicted by coherence strengthening and modulus strengthening mechanism has good consistency with the experiment results.

1. Introduction

Cu-Ni-Mn alloy is a kind of copper-based elastic material with high strength, high elastic modulus and excellent wear resistance. The Cu-Ni-Mn alloys are often used to make molds, elastic components, elastic structural parts, etc, and are widely used in aerospace, electronic appliances, marine ships and other fields [1–3]. As an aging strengthened copper alloy, aging treatment is the main strengthening method for Cu-Ni-Mn alloy to obtain high strength [4]. NiMn phase with FCT structure can be precipitated in Cu-Ni-Mn alloy during aging treatment, thereby causing a significant increase in strength and hardness [5]. For example, the hardness can reach over 450 HV, in Cu-20Ni-20Mn alloy after peak-aging [4].

According to Cu-Ni-Mn ternary phase diagram (Atom content ratio of Ni, Mn is 1) [6], the total solid solubility of Ni, Mn in Cu are with great difference (600 °C, the total solid solubility of Ni, Mn in Cu are 70 at.%; 400 °C, the total solid solubility of Ni, Mn in Cu 10 at.%) under different temperature conditions. Therefore, the Cu supersaturated solid solution is acquired in Cu-Ni-Mn alloys through solution treatment at temperatures above 600 °C; The Ni and Mn atom precipitate out of the Cu supersaturated solid solution, and form the NiMn strengthening phase after annealing at temperatures below 500 °C.

In order to clarify the effect of aging treatment on the mechanical properties of Cu-25Ni-25Mn alloy. The microstructure evolution and mechanical property change of the alloy during the aging treatment is studied in this paper. The influence of precipitated particles on the hardness of Cu-25Ni-25Mn alloy and its strengthening mechanism has been analyzed quantitatively, which provides experimental basis and theoretical support for the process design of high-strength Cu-Ni-Mn series alloy.
2. Materials and methods

Cu-25Ni-25Mn alloy was melted using pure copper (99.95 wt.%) and pure manganese (99.9 wt.%) in a vacuum induction melting furnace. Under the argon atmosphere, the molten metal is poured into a graphite mold to prepare a Cu-Ni-Mn alloy ingot with dimensions of 180 mm × 80 mm × 20 mm. The as-cast ingot was hot rolled at 900 °C, and a plate with a thickness of 5 mm was produced after hot rolling. After the hot-rolled plate was cold rolled to 2 mm, it was heat treated at 900 °C for 1 h followed by water quenching (solution-treatment). Finally, the solution-treated sample is subjected to isothermal aging treatment at 450 °C, and the aging time is 0–120 h.

The hardness of the Cu-Ni-Mn alloy is measured with a 200HVS-5 Vickers hardness tester, the load is 1.96 N, and the load time is 10 s. The number of measurements for each sample is at least 8 times, and the average value is taken.

The microstructure observation is conducted through BMM-90AE metallographic microscope (OM) and FEI Tecnai G2 F20 Transmission Electron Microscope (TEM). TEM sample is prepared through twin-jet electro-polish thinning method. The electrolyte is a mixed solution of 30 vol.% nitric acid and 70 vol.% methanol, and the electrolytic polishing temperature is −40 °C. The lattice constants of the alloy matrix and the second phase are measured by x-ray diffractometer (XRD). The working voltage of the x-ray diffractometer is 40 kV, the tube current is 40 mA, the step size is 0.02 °, and the scanning rate is 10° min⁻¹.

3. Results

3.1. Aging strengthening of Cu-Ni-Mn alloy

Figure 1 is the hardness curve of Cu-25Ni-25Mn alloy after isothermal aging at 450 °C. At the beginning of aging (0–16 h), the hardness increases rapidly with the extension of the aging time. At this time, the alloy hardness increased from 123 HV (solution-treated sample) to 424 HV (sample aged for 16 h), and the hardness increased by ~240%. The hardness of the alloy gradually increases with increasing aging time further, but the growth rate of the hardness decreases significantly. The hardness of Cu-25Ni-25Mn alloy reaches its peak after aging at 450 °C for 40 h, which is about 491 HV. When the aging time exceeds 40 h, the hardness fluctuates within a certain range without significant changes.

3.2. Microstructure evolution of Cu-Ni-Mn alloy during aging process

3.2.1. SEM/TEM analysis

Figure 2 is the microstructure of the solution-treated Cu-25Ni-25Mn alloy at 950 °C. It can be seen that the microstructure of the solid solution alloy is mainly composed of coarse equiaxed grains with an average grain size of ~122 μm. Only a small amount of dislocations can be observed in the TEM image of the solution-treated alloy. It indicates that when the solution treatment is carried out at 950 °C, the Ni and Mn solute atoms in the alloy can be completely dissolved in the copper matrix to form a supersaturated solid solution. At this time, the alloy is mainly composed of a copper matrix phase.

Figure 3 shows the optical micrograph of Cu-25Ni-25Mn alloy aged at 450 °C for different times. The discontinuous precipitation colony is formed at the grain boundary and grows into the grain in the early stage of
After the alloy is aged at 450 °C for 4 h, the volume fraction of discontinuous precipitation colony reaches \( \sim 4.8\% \). With the extension of the aging time, the volume fraction of discontinuous precipitation colony did not change significantly. When the aging time reaches 120 h, the volume fraction of discontinuous precipitation colony in the alloy remains \( \sim 5\% \). It is indicated that the growth process of the discontinuous precipitation colony is suppressed in Cu-25Ni-25Mn alloy during aging at 450 °C.

Figure 4 is the TEM images and corresponding selected area electron diffraction (SAED) pattern of the Cu-25Ni-25Mn alloy after aged at 450 °C. A large number of dispersed nanoscale particles are observed in the matrix of the aged Cu-25Ni-25Mn alloy (figure 4(a)). It indicates that continuous precipitation reaction occurs in Cu-25Ni-25Mn alloy during aging at 450 °C, which results in the formation of dispersed nanoscale NiMn phase particles. With the extension of aging time, the number and volume fraction of NiMn phase gradually increase. When the aging time reaches 120 h, the volume fraction of the second phase particles in the alloy reaches \( \sim 4\% \); at this time, the average particle diameter of the NiMn phase particles can be measured to be \( \sim 4.8\) nm based on a quantitative metallographic analysis technique. The SAED pattern (figure 4(d)) shows two sets of diffraction spots including the FCC structure copper matrix phase with a face-centered cubic (FCC) structure (stronger diffraction spot) and the NiMn phase with a FCT structure (weaker diffraction spot). The superlattice diffraction spots of the NiMn phase indicates that the NiMn phase have an ordered structure. Based on the SAED pattern, the crystallographic orientation relationship between NiMn phase and Cu matrix can be determined as \((220)_{\text{Cu}} // (220)_{\text{NiMn}}, [001]_{\text{Cu}} // [001]_{\text{NiMn}}\). In addition, it can be seen that the discontinuous precipitation colony is composed of lamellar NiMn phase and copper matrix phase (figure 4(c)), the interlamellar spacing of NiMn phase is \( \sim 8\) nm.
3.2.2. XRD analysis

The XRD patterns of solution-treated and aged Cu-25Ni-25Mn alloys are shown in figure 5. Only the diffraction peaks of the FCC structure copper matrix are observed in the XRD diffraction pattern of the solution-treated Cu-25Ni-25Mn alloy, which further confirms that the solution-treated alloy is mainly composed of Cu matrix. Compared with the solution-treated sample, the strong (111) diffraction peak is significantly shifted to higher two-theta values in aged samples. Through the Bragg equation, the lattice constants of the Cu matrix phase in the Cu-25Ni-25Mn alloys can be calculated as shown in figure 6. It is seen that the lattice constant of Cu phase gradually decreases with the increased aging time in aged Cu-25Ni-25Mn alloy. The lattice constant of FCC Cu phase is ∼0.3664 nm. When the aging time reaches 120 h, the lattice constant decreases to ∼0.3650 nm. It is indicated that the precipitation of NiMn phase from the Cu matrix cause the decrease in the lattice constant of the Cu matrix phase.
The diffraction peaks of the FCT NiMn phase are observed in the XRD diffraction pattern of the aged sample (figure 5). In the early stage of aging (4 h), due to the existence of the diffraction peaks of the NiMn phase, the weaker diffraction peaks (such as (002), (002) diffraction peaks, etc) of the copper matrix shifted irregularly. For example, the (002) diffraction peak is shifted to lower two-theta values, while the (022) diffraction peak is shifted to higher two-theta values. When the aging time exceeds 20 h, new diffraction peaks are observed in the \{002\}\textsubscript{Cu} peak and \{022\}\textsubscript{Cu} peak position, implying the existence of NiMn phase. In order to determine the lattice constant of the NiMn phase, the Bragg equation was used to estimate the interplanar spacing of \{002\} and \{022\} planes, and the results are shown in figure 7.

(1) The interplanar spacing of \{002\}\textsubscript{Cu} and \{022\}\textsubscript{Cu} planes can be estimated using the lattice constant of the Cu matrix phase (figure 6). However, the result is significantly different from the interplanar spacing data in figure 7. (2) In the aged Cu-Ni-Mn alloy (aging time \(\geq 20\) h), the interplanar spacing of the \{002\} and \{022\} planes did not change significantly with the increased aging time. It is indicated that the phase producing the \{002\} and \{022\} diffraction peaks has a fixed crystal structure during the aging process. Based on the two points above, it is determined that the two sets of diffraction peaks in the \{002\} and \{220\} peak position are produced by NiMn phase, but not the Cu matrix phase. Therefore, the lattice constant of the NiMn phase can be calculated as \(a = 0.3693 \pm 0.0004\) nm and \(c = 0.3570 \pm 0.0006\) nm. The schematic diagram of the crystal structure of the NiMn phase is shown in figure 8.

4. Discussion

Compared with annealed pure copper (hardness about 31 HV \([7]\), the solid solution Cu-25Ni-25Mn alloy exhibits a higher hardness (\(\sim 124\) HV) as shown in figure 1. That mainly results from the effect of the vacancy, the solution atom and the grain size. (1) the abundant concentration of vacancies are formed due to the quenching, which lead to the increase in strength \([8,9]\). (2) Based on phase diagram \([6]\), Ni and Mn atoms are fully dissolved in the Cu matrix of Cu-25Ni-25Mn alloy after solution treatment at 900 °C. The dissolved Ni and Mn solute atoms can cause lattice distortion on the Cu matrix due to the difference in atomic size and elastic modulus,
which hinders the movement of dislocations, and thus strengthens the alloy [10]; (3) Compared with the annealed pure copper (average grain diameter of about 500 μm), the average grain diameter of the solution-treated Cu-25Ni-25Mn alloy is smaller, which is ~122 μm. According to the Hall-Petch relationship [11], a smaller average grain diameter provides a stronger interface strengthening effect. Therefore, the solution-treated Cu-25Ni-25Mn alloy has a higher hardness than annealed pure copper due to the three factors above. However, the solid-solution strengthening caused by quenched-in vacancies, Ni atoms and Mn atoms have a limited contribution to the hardness and strength, while the grain-boundary strengthening effect is weak in solution-treated sample. Thus, the hardness of the solution-treated Cu-25Ni-25Mn alloy is only ~83 HV higher than that of annealed pure copper.

A large number of the NiMn precipitates with a FCT structure are formed during aging at 450 °C. The precipitation of the NiMn precipitates consumes Ni and Mn atoms, which leads to gradual decrease in the equal amount of solute Ni and Mn atoms in Cu solid solution. Adding Mn in Cu solid solution can cause the increase in lattice constant of the Cu matrix phase, while the adding Ni can cause the decrease in lattice constant of the Cu matrix phase [12, 13]. The lattice constant of the Cu matrix phase gradually decreases due to the precipitation of the NiMn precipitates. It is indicated that the adding Mn in Cu solid solution exhibit a more significant effect on the lattice constant than that of adding Ni.

A significant strengthening (figure 1) occurs in Cu-25Ni-25Mn alloy during aging at 450 °C. The hardness increases from 124 HV (solution-treated sample) to 491 HV after the Cu-25Ni-25Mn alloy being aged for 40 h. The strength and hardness of alloy materials are considered to be the superimposed effect of multiple strengthening mechanisms, including solid solution strengthening, grain boundary strengthening, precipitation strengthening and dislocation strengthening [14-16]. (1) The grain size of Cu-25Ni-25Mn alloy did not change significantly (figures 2 and 3) during aging. (2) The microstructure of aged Cu-25Ni-25Mn alloy is mainly composed of recrystallized grains with low dislocation density. (3) Ni and Mn atoms are gradually precipitated from the matrix. Compared with the solution-treated sample, the solid-solution strengthening effect in the aged alloy is weakened. Therefore, the contribution of solid solution strengthening, grain boundary strengthening and dislocation strengthening to the total hardness increment can be ignored in the aged Cu-25Ni-25Mn alloy.

In addition, both continuous precipitation and discontinuous precipitation occurs in Cu-25Ni-25Mn alloy during aging at 450 °C. Shapiro et al [4, 17] confirmed that the discontinuous precipitation colony has a relatively higher hardness (over 400 HV). However, the volume fraction of discontinuous precipitation colony is small (~0.05) in the aged Cu-25Ni-25Mn alloy. Based on the rule of mixtures [18], a small amount of discontinuous precipitation colony has little effect on the hardness and strength in the peak-aged alloys. Therefore, the aging strengthening of Cu-25Ni-25Mn alloy mainly results from the continuous precipitation of NiMn phase particles.

A large number of spherical second phase particles precipitated from the Cu matrix of the Cu-25Ni-25Mn alloy during aging (figure 4). The average diameter of the particles is about 4.6 nm (figure 4). From SAED pattern (figure 4(d)), it can be seen that the {002} crystal planes of the Cu matrix phase and NiMn phase are parallel. The lattice misfit of the (002) crystal plane are calculated as 0.022 (less than 0.05) [19], which indicates that the matrix phase and the NiMn phase are fully coherent. The nanoscale NiMn phase particles coherent with the matrix can effectively hinder the dislocation motion, and produce significant precipitation strengthening effect [20]. Luca et al [21] found that when the coherent precipitate sizes is small, the precipitation strengthening is controlled by a shearing mechanism. For the shearing mechanism, the strength increase mainly results from the coherency strengthening and modulus strengthening effects caused by the coherent NiMn phase. The coherency strengthening in the Cu-25Ni-25Mn alloy can be estimated by the following model [22]:

![Figure 8. The interplanar spacing / obtained from [200] and [220] peak of the Cu-25Ni-25Mn alloy aged at 450 °C.](image)
\[ \Delta \varepsilon_{coh} = M \chi G \varepsilon (2rf \varepsilon / b)^{1/2}, \]  
(1)

where \( M \) is the Taylor factor, which is 3.1; \( \chi \) is a constant, \( \sim 2.6 \); \( G \) is the shear modulus of matrix phase, \( G_{Cu} = 48.3 \) GPa in Cu alloy \[23\]; \( r \) is the radius of precipitates; \( f \) is the volume fraction of the precipitates; \( b \) is the Burgers vector. The dislocation strain constant \( \varepsilon \) is proportional to the lattice misfit degree \( \delta \), the calculation formula is given as follows \[22, 24\]:

\[ \varepsilon = \delta / [1 + 2G(1 - 2\nu_p) / G_p(1 + \nu_p)], \]  
(2)

where \( \nu_p \) is the Poisson ratio of NiMn phase (\( \sim 0.33 \)); \( G_p \) is the shear modulus of NiMn phase, which is \( \sim 98 \) GPa. The formula for strength increment of modulus strengthening \( \Delta \sigma_{\text{mod}} \) is \[21\]:

\[ \Delta \sigma_{\text{mod}} = 0.0055M(\Delta G)^{1/2}(2f / Gb^2)^{1/2}b(\rho / b)^{3m/2 - 1}, \]  
(3)

where \( \Delta G \) is the modulus mismatch between NiMn phase and copper matrix phase, which is about 49.7 GPa \[25\]; \( m \) is a constant \( \sim 0.85 \). Based on the coherency strengthening and modulus strengthening models, it can be estimated that the contributions of coherency strengthening and modulus strengthening in the peak-aged Cu-25Ni-25Mn alloy are 697 MPa and 449 MPa, respectively. That is, the precipitation strengthening contribution of NiMn phase particles is about 1146 MPa. According to Tabor relationship \[21, 26, 27\], the hardness of Cu-25Ni-25Mn alloy can be shown as:

\[ HV (HV) \approx 3\sigma_y (MPa) / 9.81, \]  
(4)

where \( \sigma_y \) is the yield strength of the alloy. It can be calculated from the formula above that the hardness increase of the peak-aged Cu-25Ni-25Mn alloy caused by the NiMn phase is about 350 HV. It further confirms that the coherency strengthening and modulus strengthening caused by the NiMn phase particles are the main reasons for the aging strengthening in the Cu-25Ni-25Mn alloy.

5. Conclusions

The microstructure evolution and hardness change of Cu-25Ni-25Mn alloy during aging is studied in this paper. The aging strengthening mechanism in Cu-25Ni-25Mn alloy was analyzed. The main conclusions are as follows:

(1) The NiMn phase with an ordered FCT structure is precipitated in Cu-25Ni-25Mn alloy during aging. Its lattice constants are \( a = b = 0.3693 \pm 0.0004 \) nm, \( c = 0.3570 \pm 0.0006 \) nm.

(2) The crystallographic orientation between NiMn phase and Cu matrix in the aged Cu-25Ni-25Mn alloy is \((220)_{Cu} || (220)_{NiMn}, (001)_{Cu} || (001)_{NiMn}\).

(3) The lattice misfit between NiMn phase and Cu matrix in \((002)_{Cu} || (002)_{NiMn}\) is \( \sim 0.022 \), implying that the \((002)_{Cu}\) and \((002)_{NiMn}\) have a completely coherent relation.

(4) The continuous precipitation of nanoscale NiMn phase particles produces significant coherency strengthening and modulus strengthening effects. In the peak-aged Cu-25Ni-25Mn alloy, the nanoscale NiMn phase causes a hardness increase of \( \sim 367 \) HV.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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