IMPROVEMENT OF MECHANICAL PROPERTIES
OF Cu-Ti ALLOYS BY NEW PROCESS

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Introduction

Aging of the supersaturated Cu-Ti alloys was investigated by many workers and this alloys is used commercially as spring. In commercial process, the procedure is as follows:

1. melting
2. casting and forging
3. solution treatment and quenching
4. cold-working
5. prolonged aging

This procedure consists of high energy consumption processes.

By new process (quenching from liquid process), supersaturated crystal solid solution is directly produced. The procedure is as follows.

1. melting
2. quenching from liquid
3. shortened aging

By the new process, Cu-Ti spring alloys are obtained without many pre-treatments (solution treatment, cold-working and prolonged aging) compared with the commercial process. Furthermore, a high concentrated ductile crystal (Cu-10 at% Ti) is produced by the new process. This crystal is more supersaturated, though the solubility limit of titanium is about 5 at% as shown in Fig. 1. The effect of the new process on aging is investigated for Cu-Ti alloys by means of hardness, tensile test and transmission electron microscopy.

Experimental

Cu-Ti alloys were prepared from 99.99% copper and 99.8% sponge titanium in an argon arc furnace. Specimens were prepared by quenching from liquid, which was melted about 1600 K for 100 s under argon atmosphere in an infrared furnace, and the cooling rate was over 10000 K/s to avoid precipitated phase formation. The thickness of specimens was approximately 2 x 10^-4 m. These specimens were aged in a salt bath or in vacuum.

Mechanical properties were investigated by the Vicker's hardness (100 g Lord) and tensile (5.5 x 10^-2 s^-1 strain rate) tests. The changes in microstructure were investigated by electron microscopy and diffraction.

Fig. 1 Cu-Ti phase diagram
Results

Hardness changes for the Cu-Ti alloys which are quenched from liquid and then aged at 673 K are shown in Fig. 2 (ο is Cu-5 at% Ti alloy and  ● is Cu-10 at% Ti alloy.). The result of Cu-5 at% Ti alloys which are produced by commercial process is shown in this figure too (△ is as solution treatment, △ is cold-working (20%) and X is cold-working (50%).).

![Fig. 2 Typical changes in micro-Vicker's hardness of Cu-Ti alloy aged at 673 K.](image)

In the case of commercial process, maximum hardness and rate of hardening are greatly enhanced by cold-working. This enhancement depends on the density of dislocations. This fact was investigated by transmission electron microscopy. Aging-time of maximum hardness is slightly decreased with the increase of cold-work. The main effect of cold-work is enhancement of hardness.

Maximum hardness and rate of hardening are enlarged and aging-time of maximum hardness is shortened by the new process in comparison with the commercial process. Maximum hardness of Cu-5 at% Ti alloy quenched from liquid is equal to that of cold-worked (20%) alloy. Aging time for maximum hardness of the cold-worked (20%) alloy is about 20 times that of quenching from liquid. Consequently, an important feature of the new process is shortened aging of maximum hardness. Furthermore, more supersaturate crystal phase (over solubility limit of Ti) is obtained by the process of quenching from liquid, though the equilibrium solubility limit of titanium concentration is 5 at%, as shown in Fig. 1. Maximum hardness of this crystal phase is equal to that of cold-worked (50%) Cu-5 at% Ti alloy, as shown in Fig. 2 and Table 1. Excess addition of 10 at% Ti induces a large maximum hardness that is equal to cold-work (50%).
One of the most important mechanical properties of the spring is modulus of elasticity. This is obtained by tensile test in this work. The typical type of Cu-10 at% Ti alloys quenched from liquid is shown in Fig. 3. The modulus of elasticity of specimens after aging (1 hr) is about 1.5 times that of as casting specimens. Furthermore, the elongation after aging is about twice as large as before aging.

![Stress-strain curves for Cu-10 at% Ti quenched from liquid.](image-url)
Johnson and Mehl have proposed a quantitative kinetic treatment. This has provided to be a very powerful tool in elucidation of many transformations. This equation is as follows

\[ X = 1 - \exp(-kt^n), \]

where \( X \) is the fraction of transformation, \( k \) is a kinetic constant, \( t \) is the time and the exponent \( n \) is determined by the transformation mode. The parameter \( k \) and \( n \) are determined by plotting \( \log(-\ln(1-X)) \) versus \( \log t \). \( X \) is calculated from hardness in this work. All specimens which are investigated in this work have same exponential value \( (n; 1.7 < n < 2) \) from Fig.4. This result shows that all specimens transformed in the same way and is reconfirmed by Photo.1, Photo.2 and Photo.3.

First we discussed the effect of cold-working in the commercial process. Fig.4 shows the agreement of the logarithmic kinetic constants \( \log(k) \) between the as solution treated and the cold-worked (50\%) alloy. Same results are obtained by transmission electron microscopy, as shown in Photo.1 and Photo.2. Photo.1 shows typical modulated structure of Cu-5 at\% Ti alloys aged for \( 6 \times 10^4 \) s at 673 K. Photo.2 shows modulated structure of Cu-5 at\% Ti alloys which is deformed (50\%) and aged for \( 6 \times 10^4 \) s at 673 K. These photographs show that the wavelength of deformed (50\%) alloy is equal to that of non-deformed alloy.
This result reconfirms the agreement of the rate of transformation between as solution treatment and cold-working (50%). The difference of Photo.1 and Photo.2 is the form of the wavelength. The cold-working (Photo.2) induces irregularity and heterogeneity in modulated structure. These results show that the cold-working before aging does not affect the logarithmic kinetic constants.

Photo.1 Cu-5 at% Ti alloy aged for $6 \times 10^4$ s at 673 K.

Photo.2 Cu-5 at% Ti alloy deformed 50% aged for $6 \times 10^4$ s at 673 K.
In the case of the new process, Photo.3 shows the structure of Cu-5 at% Ti alloy, which is quenched from liquid and then aged for 900 s at 673 K. We can find fine modulated structure and this structure shows the satellite in the electron diffraction pattern. The kinetic constant of the new process is 10 times larger than that of commercial process. This feature is, mainly, induced from difference of mass transport. We suggest that excess vacancy and secondary lattice defects induce the increase of mass transport.

Making a comparison between Cu-5 at% Ti and Cu-10 at% Ti, we understand that the logarithmic kinetic constants depend on titanium concentration. Exponent (n) is about 2, as shown in Fig.4. The mechanism of transformation for Cu-10 at% Ti is as same as that for Cu-5 at% Ti. But the logarithmic kinetic constant increases with concentration of titanium. Calculated temperature of spinodal decomposition (Tc) rises with concentration of titanium. The rise of Tc yields the enlargement of driving force of spinodal decomposition and then the increase of titanium accelerates the spinodal decomposition.

Photo.3 Cu-5 at% Ti alloy quenched from liquid and aged for 900 s at 673 K.

Conclusion

By the new process (quenching from liquid process), supersaturated Cu-Ti crystal solid solution is directly produced without many high energy consumption pre-treatments (solution treatment, cold-working and prolonged aging).

Maximum hardness of the new process is equal to that of cold-work (20%) in Cu-5 at% Ti alloys. Excess addition of 10 at% Ti induces a larger maximum hardness that is equal to that of the cold-worked (50%) alloy. The most important feature of the new process is shortened aging for maximum hardness. The modulus of elasticity of specimens after aging (1 hr) is about 1.5 times that of as casting specimens.

The mechanism of transformation on aging is same spinodal decomposition, but the decomposition rate of the quenched alloys from liquid is larger than that of the commercial produced alloys and also depends on Ti content.

Acknowledgement

The author wish to thank Prof. T. Miyazaki and Dr. H. Mori of Nagoya Institute of Technology for their helps in a part of Electron Microscopy.
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References