Rare Metal Materials and Engineering
Volume 45, Issue 5, May 2016
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com

Cite this article as: Rare Metal Materials and Engineering, 2016, 45(5): 1162-1167.

ARTICLE

Microstructural Evolution and Properties of Aged Cu-3Ti-3Ni Alloy

Liu Jia[1], Wang Xianhui[1,2], Guo Tingting[2], Zou Juntao[1], Yang Xiaohong[1]

[1] *Xi'an University of Technology, Xi'an 710048, China;* [2] *Deakin University, Victoria 3220, Australia*

Abstract: The effect of aging treatment on the microstructure and the properties of Cu-3Ti-3Ni alloy was studied. The microstructure and the precipitated phase were characterized by X-ray diffractometer, scanning electron microscope and transmission electron microscope, and hardness, electrical conductivity and elastic modulus were measured as well. The results show that a number of Ni_3Ti and β'-Cu_4Ti phases precipitate from the Cu matrix after aging treatment. With the increase of secondary aging time, partial alloying elements dissolve into the Cu matrix, and the metastable Cu_4Ti phase transforms into incoherent equilibrium Cu_3Ti phase. The enhanced electrical conductivity is ascribed to the decrease of Ti solubility in the Cu matrix by the formation of the Ni_3Ti and β'-Cu_4Ti precipitates. After an appropriate aging treatment of Cu-3Ti-3Ni alloy, the Ni_3Ti and coherent metastable β'-Cu_4Ti phases precipitate completely, giving rise to the increase of hardness. Aging treatment has no obvious effect on the elastic modulus of Cu-3Ti-3Ni alloy. In the scope of the experiments, the optimal two-step aging treatment parameter for Cu-3Ti-3Ni alloy is to age at 300 °C for 2 h followed by aging at 450 °C for 7 h. The HV hardness, the electrical conductivity and elastic modulus are 1.83 GPa, 31.34 %IACS (International Annealed Copper Standard) and 148.62 GPa, respectively.

Key words: copper alloy; aging; phase transformation; precipitation

Age-hardened Cu-based alloys are indispensable for the electrical connection, high strength springs, electrical contacts, and corrosion and wear resistant materials[1-3], and among them, the Cu-Be alloys exhibit a good combination of electrical conductivity and mechanical properties. However, the anti-stress relaxation property of Cu-Be alloys is poor as used at elevated temperatures[4]. Moreover, Cu-Be alloys are highly sensitive to heat treatment process, giving rise to unstable performances. Furthermore, their toxicity brings about the environmental and health hazards as well. Subsequently, it is of great significance to develop a substituent for Cu-Be alloys. Since Cu-Ti alloys have high strength, hardness and elasticity, good wear resistance, corrosion resistance, workability and weldability as well as high-temperature performance, they have potential as substitutes for Cu-Be alloys. So far, numerous researches on the strengthening mechanism of Cu-Ti alloys have revealed that age hardening takes place by introducing finely dispersed Cu_4Ti particles through heat treatments, but overaging causes the phase transformation from metastable β'-Cu_4Ti to incoherent equilibrium Cu_3Ti phase, significantly decreasing the strength of Cu-Ti alloys[2,5-8]. In comparison with Cu-Be alloys, Cu-Ti alloys have lower electrical conductivity due to the much larger contribution of solute Ti atoms to the electrical resistivity compared to Be atoms[9-11]. It is desired to improve the electrical conductivity of Cu-Ti alloys without deteriorating mechanical strength. Therefore, some attempts have been made to improve the electrical conductivity of binary Cu-Ti alloys by reducing solute Ti atoms in the copper matrix[12-14]. Konno et al.[12] reported that the electrical conductivity of Cu-3 at%Ti alloy with 4 at%Al addition is 6 times larger than that without Al addition, whereas the peak

---

Received date: October 21, 2015
Foundation item: National Natural Science Foundation of China (51201132); Shaanxi Provincial Key Laboratory Research Program (13JS076); Shaanxi Provincial Project of Special Foundation of Key Disciplines (2011HBSZS009); The Pivot Innovation Team of Shaanxi Electrical Materials and Infiltration Technique (2012KCT-25).
Corresponding author: Wang Xianhui, Ph. D., Professor, School of Materials Science and Engineering, Xi'an University of Technology, Xi'an 710048, P. R. China, Tel: 0086-29-82312185, E-mail: xhwang693@xaut.edu.cn

HV hardness decreases from 2.80 GPa to 1.80 GPa. Semboshi et al.[13] revealed that the electrical conductivity of Cu-1 at%Ti alloy by aging in a hydrogen (H_2) atmosphere increased by 140% compared to that of the same alloy aged in a vacuum. The high electrical conductivity is attributed to the formation of TiH_2, which can efficiently remove the Ti solutes from the Cu matrix. However, the hardness of Cu-1 at%Ti alloy drops more rapidly upon aging in the hydrogen atmosphere in comparison to the vacuum aging treatment due to the formation of the brittle TiH_2 phase. Markandeya et al.[14] reported that Cd addition decreases the electrical conductivity of Cu-3Ti alloy though the yield strength and tensile strength increase considerably.

Generally, copper base alloys with good comprehensive properties are solution treated by quenching and subsequent ageing. A number of nano-sized precipitates can be formed in copper matrix through these processes; as a result that the alloy is strengthened and its electrical conductivity is increased. As Ni has a strong affinity with Ti to form Ni_3Ti intermetallic compound which has high melting point, it has a large tendency to push Ti atoms out of copper matrix, decreasing the solid solubility of Ti in the Cu matrix, and thus, it is favorable for the improvement of the properties of Cu-Ti alloys. So far, no literatures have been reported on the effect of Ni addition on the mechanical properties and the microstructure of Cu-Ti alloy. In the present work, the effects of Ni addition and heat treatment on the microstructure and the properties of Cu-3Ti alloy were studied. The microstructure and the phase constituents were characterized by X-ray diffractometer (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM), and the electrical conductivity, the hardness and the elastic modulus were measured as well. The purpose of the present study is to examine the effect of Ni addition on the electrical and mechanical properties of Cu-3Ti alloy, and to shed a light on the aging behavior of Cu-3Ti-3Ni alloy and phase transformation by structural characterization using TEM.

1 Experiment

Button ingots of Cu-3Ti-3Ni alloy were prepared from purity 99.9 wt% electrolytic copper, purity 99.9 wt% titanium and purity 99.9 wt% nickel by arc-melting in an argon atmosphere. Each ingot was melted at least four times to guarantee its homogeneity. The ingots were cut into blocks, and then solution treated at 850 ℃ for 4 h in a SK-G10123K tube furnace, followed by water quenching. Immediately after quenching, the samples were aged at 300 ℃ for 2 h, followed by aging at 450 ℃ for 1, 3, 5, 7 and 11 h in an argon atmosphere (two-step aging). After mechanical polishing, the samples were etched in a solution of 5 g $FeCl_3$, 15 mL HCl and 100 mL distilled water. The phase constituents were determined by a D8ADVANCE X-ray diffractometer operating at 40 kV and 40 mA, Cu-Kα radiation, λ=0.154 06 nm, and microstructure was examined by a JEOL JSM-6700F field emission scanning electron microscope (SEM). The specimens used for TEM observation were cut from the block using an IsoMet 1000 cutting machine and then mechanically polished to obtain 50 μm thick slices. Discs with 3 mm diameter were punched out of these slices and thinned in a M691 ion milling at 4.5 kV. TEM studies were carried out using a JEM-2100HR high resolution transmission electron microscope (HRTEM) with operation voltage of 200 kV. The electrical conductivity was tested in a FQR-7501 eddy conductivity gauge. Hardness measurements were carried out using a HV-1000 Vickers hardness tester under an applied load of 98 N and a holding time of 10 s. The average hardness was obtained from five indentations. The elastic modulus was determined by a G200 Agilent nano indenter, and its value was the average of five measurements.

2 Results and Discussion

2.1 Microstructural characterization

X-ray diffraction analysis was performed to detect phase constituents of as-cast Cu-3Ti-3Ni alloy, and the XRD pattern is shown in Fig.1. According to the X-ray diffraction analysis, as-cast Cu-3Ti-3Ni alloy consists of NiTi phase and Cu matrix. Fig.2 is the microstructure of as-cast Cu-3Ti-3Ni alloy. It can be seen that NiTi phase is uniformly distributed in the Cu matrix.

Fig.3a~Fig.3e show the microstructures of Cu-3Ti-3Ni alloy after various aging treatments. As seen from Fig.3a, the

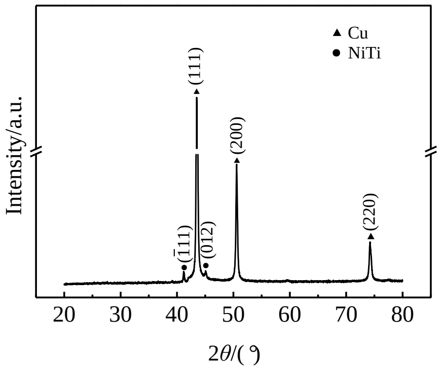

Fig.1 XRD pattern of as-cast Cu-3Ti-3Ni alloy

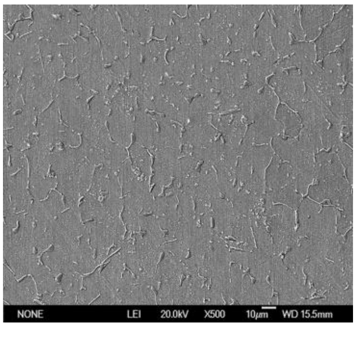

Fig.2 Microstructure of as-cast Cu-3Ti-3Ni alloy

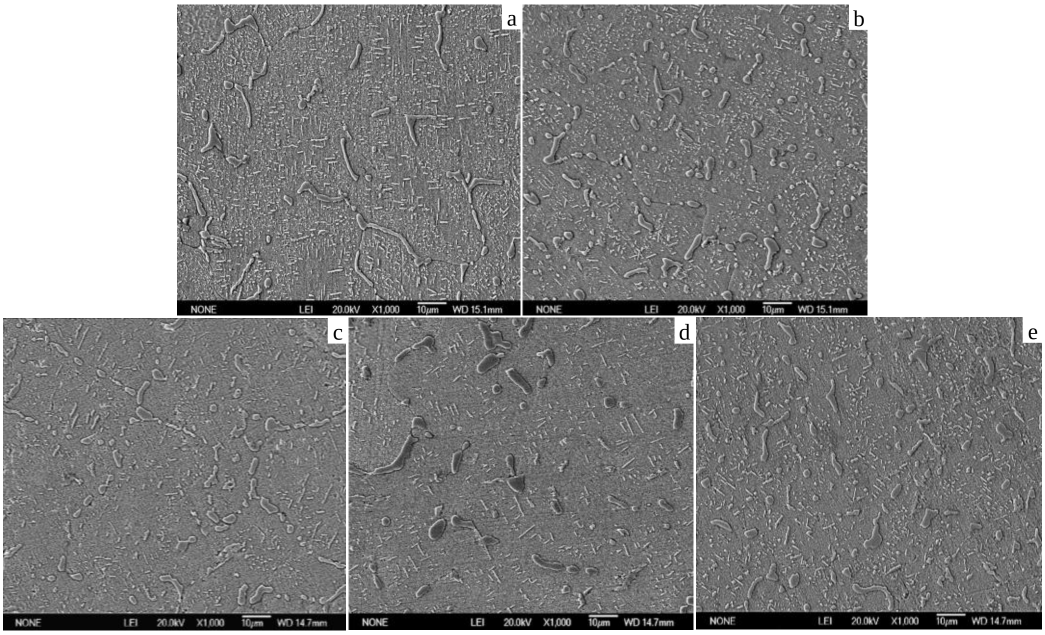

Fig.3 SEM images of Cu-3Ti-3Ni alloy aged at 300 ℃ for 2 h and 450 ℃ for different time: (a) 1 h, (b) 3 h, (c) 5 h, (d) 7 h, and (e) 11 h

secondary phase presents platelet-like and spherical shape after two-step aging at 300 ℃ for 2 h and 450 ℃ for 1 h. After two-step aging at 300 ℃ for 2 h and 450 ℃ for 3 h, the amount of spherical phase decreases, as shown Fig.3b. As seen from Fig.3c, the amount of the spherical phase decreases sharply after two-step aging at 300 ℃ for 2 h and 450 ℃ for 5 h. After two-step aging at 300 ℃ for 2 h and 450 ℃ for 7 h, the spherical phases disappear and the platelet-like phases are distributed uniformly in the Cu matrix (Fig.3d). However, prolonged aging gives rise to the partial dissolution of alloying elements into the Cu matrix and thus some spherical phases increase, as seen in Fig.3e. Fig.4 is an enlarged view of Fig.3e, where the continuous platelet-like phase become discontinuous. In addition, some continuous NiTi phase becomes discontinuous completely.

2.2 TEM observation

In order to determine the precipitated phases of the aged Cu-3Ti-3Ni alloy, two specimens after two-step aging at 300 ℃ for 2 h and 450 ℃ for 7 h, and 300 ℃ for 2 h and 450 ℃ for 11 h were characterized by TEM.

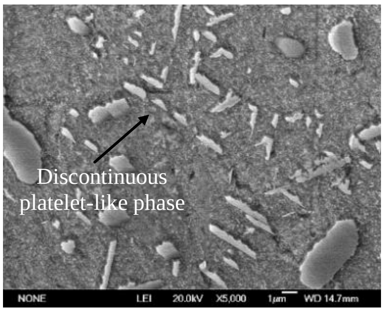

Fig.4 SEM image of Cu-3Ti-3Ni alloy aged at 300 ℃ for 2 h and 450 ℃ for 11 h (enlarged view of Fig.3e)

Fig.5a is a low-magnification bright-field BF TEM image of the Cu-3Ti-3Ni alloy aged at 300 ℃ for 2 h and 450 ℃ for 7 h. As indicated by black arrows in Fig.5a, the platelet-like phase is 1.5 μm in length and 200 nm in width. Fig.5b~Fig.5d are a high-magnification bright field image (BF), a selected area diffraction (SAD) pattern and its schematic diagram, respectively. As demonstrated from Fig.5c and Fig.5d, the tiny precipitated phase is Ni_3Ti with a hexagonal structure of structure parameters: a = 0.5092 nm, b=0.5092 nm, c =0.8297 nm.

Fig.6a is the low-magnification BF image of the same specimen. Apart from the Ni_3Ti precipitates, it is noticed that there are continuous fine precipitates with a length of approximate 100 nm. The corresponding SAD pattern and its schematic diagram are shown in Fig.6b and Fig.6c, respectively. It can be identified that the ordered, metastable and coherent β'-Cu_4Ti precipitate has formed with an orthorhombic structure of structure parameters: a = 0.4530 nm, b=0.4342 nm, c=1.2930 nm.

Fig.7 is the TEM images of Cu-3Ti-3Ni alloy aged at 300 ℃ for 2 h and 450 ℃ for 11 h. Obviously, Fig.7a shows another tiny precipitated phase distributed in the Cu matrix for the same specimen. Fig.7b and Fig.7c are a corresponding SAD pattern and its schematic diagram, respectively. The analysis of SAD pattern indicates that the incoherent fine precipitated phase is Cu_3Ti having an orthorhombic structure with structure parameters: a = 0.545 nm, b= 0.442 nm, c= 0.430 nm as indicated by the black arrow in Fig.7a. It suggests that prolonged aging promotes the phase transformation

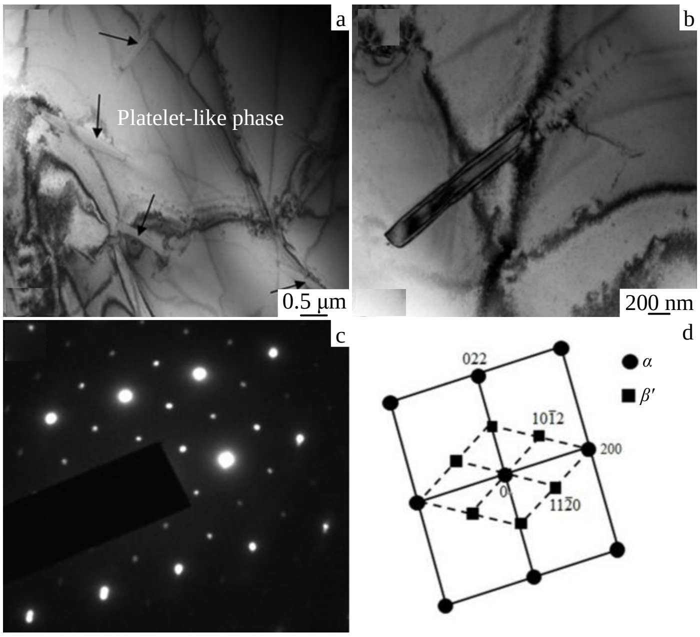

Fig.5 TEM images of Cu-3Ti-3Ni alloy aged at 300 ℃ for 2 h and 450 ℃ for 7 h: (a) low magnification image, (b) BF-TEM image, (c) SAD pattern, and (d) schematic diagram

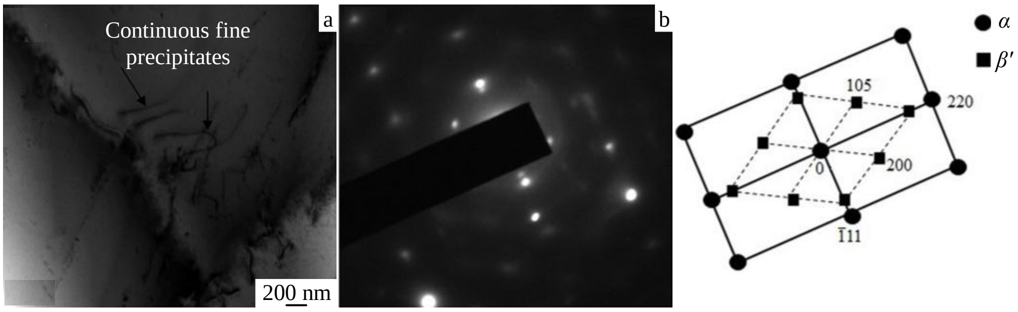

Fig.6 TEM images of Cu-3Ti-3Ni alloy aged at 300 ℃ for 2 h and 450 ℃ for 7 h: (a) low magnification image, (b) SAD pattern, and (c) schematic diagram

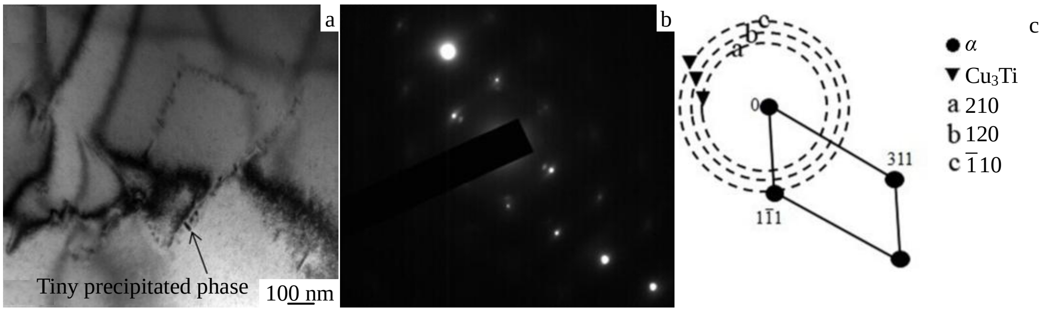

Fig.7 TEM images of Cu-3Ti-3Ni alloy aged at 300 ℃ for 2 h and 450 ℃ for 11 h: (a) low magnification image, (b) SAD pattern, and (c) schematic diagram

from Cu_4Ti phase to Cu_3Ti one. This finding is in good accordance with the result reported by Markandeya et al.[15].

2.3 Hardness and electrical conductivity of Cu-3Ti-3Ni alloy

Fig.8 shows the variation of hardness and electrical conductivity with secondary aging time for Cu-3Ti-3Ni alloy. It is evident that the hardness increases and then slightly decreases with the increase of secondary aging time. At 7 h,

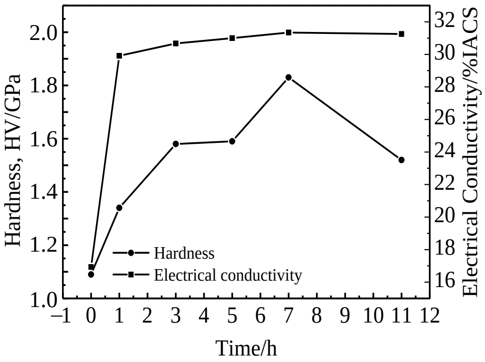

Fig.8 Variation of hardness and electrical conductivity with secondary aging time for Cu-3Ti-3Ni alloy

Cu-3Ti-3Ni alloy reaches its peak HV hardness of 1.83 GPa. This change is closely related to the formation of precipitated phases. At the early stage of aging, the secondary Ni_3Ti and β'-Cu_4Ti phase continuously precipitate from supersaturated Cu matrix. Moreover, β'-Cu_4Ti phase is coherent with the Cu matrix[15]. Thus, the hardness increases progressively till it reaches the peak value. However, further aging gives rise to the partial dissolution of alloying elements into the Cu matrix (see Fig.3e), and the phase transformation from β'-Cu_4Ti to incoherent equilibrium Cu_3Ti (see Fig.7), thus reducing the hardness after aging for above 7 h.

As shown in Fig.8, the electrical conductivity of Cu-3Ti-3Ni alloy rises sharply after two-step aging at 300 ℃ for 2 h and 450 ℃ for 1 h, and then increases slightly with prolonging of secondary aging time. The electrical conductivity can reach up to 31.34 %IACS after aging at 300 ℃ for 2 h and 450 ℃ for 7 h. However, there is a slight decrease in the electrical conductivity if secondary aging time is above 7 h. After secondary aging at 450 ℃ for 11 h, the electrical conductivity of Cu-3Ti-3Ni alloy decreases by 0.29% compared with that of the alloy aged at 450 ℃ for 7 h. This can be explained as follows. Though electrical conductivity is sensitive to a number of microstructural factors including vacancy concentration, solute concentration in the matrix, precipitate size and precipitate volume fraction, the electrical conductivity primarily depends on the solubility of alloying elements in the Cu matrix[16-18]. At the initial stage of secondary aging, Ti and Ni have large supersaturated concentrations in the Cu matrix, so there exist large precipitation kinetics and formation rates of precipitates. Eventually, these solute atoms in the Cu matrix will be greatly reduced by the precipitation of the second phases during aging, which decrease lattice distortion and electron scattering remarkably, increase the electrical conductivity sharply. However, the contents of Ti and Ni elements in the Cu matrix reduce progressively with further aging, and the amount of precipitates decrease correspondingly. Hence, no obvious change occurs for the electrical conductivity. The tiny fluctuation for secondary aging at 450 ℃ for 11 h is probably due to the partial dissolution of alloying elements into the Cu matrix after longer aging time.

Table 1 Elastic moduli of Cu-3Ti-3Ni alloy after various aging treatments

Aging treatment	Elastic modulus/ GPa	Standard deviation
300 ℃ for 2 h/450 ℃ for 1 h	147.76	3.34
300 ℃ for 2 h/450 ℃ for 3 h	147.95	1.89
300 ℃ for 2 h/450 ℃ for 5 h	148.65	3.19
300 ℃ for 2 h/450 ℃ for 7 h	148.62	1.56
300 ℃ for 2 h/450 ℃ for 11 h	150.04	4.35

2.4 Elastic modulus of Cu-3Ti-3Ni alloy

The elastic moduli of Cu-3Ti-3Ni alloy after two-step aging at 300 ℃ for 2 h and 450 ℃ for 1, 3, 5, 7 and 11 h are listed in Table 1. It is seen that the elastic modulus of Cu-3Ti-3Ni alloy after various aging treatments almost keeps constant in the range of the error. It is indicated that aging treatment has no remarkable effect on the elastic modulus of Cu-3Ti-3Ni alloy. This is in good agreement with the conventional viewpoint[19,20]. Generally, it is believed that the elastic modulus of the metallic materials is insensitive to microstructure, alloying elements, heat treatment and cold deformation.

3 Conclusions

1) Ni addition reduces the solute Ti content in the copper matrix, increasing the electrical conductivity.

2) An appropriate aging promotes the precipitation of Ni_3Ti and β'-Cu_4Ti phase, which are beneficial for improving both the electrical conductivity and hardness.

3) Prolonged aging brings about the partial dissolution of alloying elements into the Cu matrix and phase transformation from the metastable Cu_4Ti phase to incoherent equilibrium Cu_3Ti phase, resulting in the decrease of hardness.

4) Aging treatment has no remarkable effect on the elastic modulus of Cu-3Ti-3Ni alloy.

5) In the scope of experiments, Cu-3Ti-3Ni alloy has good combined properties after two-step aging treatment at 300 ℃ for 2 h and 450 ℃ for 7 h. The HV hardness, the electrical conductivity and the elastic modulus reach 1.83 GPa, 31.34 %IACS and 148.62 GPa, respectively.

References

1 Soffa W A, Laughlin D E. *Progress in Materials Science*[J], 2004, 49: 347

2 Nagarjuna S, Srinivas M, Balasubramanian K *et al. Materials Science and Engineering A*[J], 1999, 256: 34

3 Borchers C. *Philosophical Magazine*[J], 1999, 79: 537

4 Liu P, Ren F Z, Jia S G. *Copper Alloys and Applications*[M]. Beijing: Chemical Industry Press, 2007: 110 (in Chinese)

5 Nagarjuna S, Balasubramanian K, Sarma D S. *Materials*

Transactions, JIM[J], 1995, 36: 1058

6 Božića D, Dimčićb O, Dimčića B *et al. Materials Characterization*[J], 2008, 59: 1122

7 Nagarjuna S, Babu U C, Ghosal P. *Materials Science and Engineering A*[J], 2008, 491: 331

8 Markandeya R, Nagarjuna S, Sarma D S. *Materials Characterization*[J], 2005, 54: 360

9 Nagarjuna S, Balasubramanian K, Sarma D S. *Materials Science and Engineering A*[J], 1997, 225: 118

10 Suzuki S, Hirabayashi K, Shibata H *et al. Scripta Materialia*[J], 2003, 48: 431

11 Semboshi S, Konno T J. *Journal of Materials Research*[J], 2008, 23: 473

12 Konno T J, Nishio R, Semboshi S. *Journal of Materials Science*[J], 2008, 43: 3761

13 Semboshi S, Al-Kassab T, Gemma R *et al. Ultramicroscopy*[J], 2009, 109: 593

14 Markandeya R, Nagarjuna S, Sarma D S. *Journal of Materials Engineering and Performance*[J], 2007, 16: 640

15 Markandeya R, Nagarjuna S, Satyanarayana D V V *et al. Materials Science and Engineering A*[J], 2006, 428: 233

16 Feng Y, Wang R C, Peng C Q. *Intermetallics*[J], 2013, 33: 120

17 Guo F A, Xiang C J, Yang C X *et al. Materials Science and Engineering B*[J], 2008, 147: 1

18 Raeisiula B, Poole W J. *Materials Science Forum*[J], 2006, 519-521: 1391

19 Fujiwara K, Tanimoto H, Mizubayashi H. *Materials Science and Engineering A*[J], 2006, 442: 336

20 Kikuchi M, Takahashi M, Okuno O. *Dental Materials Journal*[J], 2006, 22: 64

时效处理对 **Cu-3Ti-3Ni** 合金组织与性能的影响

刘　佳 [1]，王献辉 [1,2]，郭婷婷 [2]，邹军涛 [1]，杨晓红 [1]

(1. 西安理工大学，陕西 西安 710048)

(2. 迪肯大学，澳大利亚 VIC 3220)

摘　要：研究了时效处理对Cu-3Ti-3Ni合金组织与性能的影响。采用X射线衍射仪(XRD)、扫描电子显微镜(SEM)及透射电子显微镜(TEM)对Cu-3Ti-3Ni合金的组织和析出相进行了表征，并对其硬度、导电率和弹性模量进行了测试。结果表明：Cu-3Ti-3Ni合金时效处理后析出 Ni_3Ti 及 β'-Cu_4Ti 相。随着时效时间的延长，部分合金元素回溶于Cu基体，连续的亚稳定 β'-Cu_4Ti 相向不连续的稳定 Cu_3Ti 相转变。Ni_3Ti 相及 β'-Cu_4Ti 相的析出减少了Ti原子的固溶，导致导电率升高。经过合适的时效处理，Cu-3Ti-3Ni合金中的 Ni_3Ti 相及连续的亚稳定 β'-Cu_4Ti 相析出完全，导致硬度升高，但时效处理对合金弹性模量影响不大。在本实验范围内，Cu-3Ti-3Ni合金的最佳时效处理工艺是 300 ℃时效2 h后炉冷，随后450 ℃时效7 h炉冷。Cu-3Ti-3Ni合金的HV硬度、导电率及弹性模量分别是1.83 GPa、31.34 % IACS (国际退火铜标准)及148.62 GPa。

关键词：铜合金；时效；相变；析出相

作者简介：刘　佳，女，1987年生，博士生，西安理工大学材料科学与工程学院，陕西 西安 710048，电话：029-82312185，E-mail: liujia9200920@163.com