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ARTICLE

Effect of High-Pressure Aging Treatment on Microstructure and Properties of Cu-51.15W-0.24Cr Alloy

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Abstract: Aiming at solving the problem of poor strength, low conductivity and thermal conductivity of Cu-W alloys, high pressure aging treatment was conducted to reinforce Cu-51.15W-0.24Cr alloy. The microstructure, hardness, thermal conductivity and conductivity of the alloy after high pressure aging treatment and normal pressure aging treatment were compared. The results show that high pressure aging treatment can increase the compactness of Cu48.61W51.15Cr0.24 alloy, eventually resulting in more dispersed distribution and finer grain size of Cr phase during the aging treatment, and improving the hardness and thermal conductivity of the alloy. After solution treatment at 960 °C for 1 h and aging at 500 °C for 1 h under a pressure of 3 GPa, the hardness, thermal diffusivity and resistivity are determined to be 1540 MPa, 0.5236 $cm^2 \cdot s^{-1}$ and $4.458\times10^{-8}\ \Omega\cdot m$, respectively, which are 17.56% and 10.74% higher than and 4.85% lower than those of alloy under normal pressure, respectively. Therefore, high pressure aging treatment can be an effective way to improve mechanical properties and to reduce resistivity of Cu-51.15W-0.24Cr alloy.

Key words: Cu-51.15W-0.24Cr alloy; high-pressure aging treatment; hardness; thermal diffusivity; resistivity

Cu-W alloys have been widely used as vacuum switch contact materials and resistance welding electrodes owing to their high voltage withstanding stress, good electrical conductivity and resistance to surface welding[1,2]. At present, Cu-W alloys are usually fabricated by liquid phase sintering or infiltration of pre-sintered tungsten skeleton[3]. However, tungsten and copper are almost insoluble, and the melting point and density of tungsten alloy are quite different from those of copper alloy, which makes it difficult to prepare high-density Cu-W alloy[4,5]. Low compactness leads to poor mechanical properties of the alloys, which further restricts their scale application[6]. Therefore, it is of practical significance to improve the compactness of Cu-W alloys, and many methods have been tried. One of the commonly used methods for preparing Cu-W alloy is activated sintering. Although the activator can improve the density of the alloy, unfortunately, the addition of extra elements will deteriorate the thermal and electrical properties of Cu-W alloys[7]. Mechanical alloying is also used to prepare Cu-W alloy with high density and ultrafine grains, but it is difficult to avoid iron impurities due to the use of iron balls and cans, leading to poor thermal conductivity and conductivity[8].

Compared to the above methods, high pressure heat treatment is an effective technique to improve the properties of materials. Because high pressure can reinforce the densification of the material, it has a significant effect on the element diffusion and microstructure transformation during the solid phase transformation[9-12]. Gu et al[13] studied the high-pressure heat treatment on the Cu-Cr alloys, and the results showed that high pressure treatment can improve the compactness of Cu-Cr alloys and reinforce the hardness and compression yield strength. According to above researches, it

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can be seen that high pressure can increase the densification of the material and increase the dislocation density in the metal structure, which makes the strengthening phase precipitated during the aging process more dispersed and finer, thus enhancing the aging strengthening effect and improving the mechanical properties[14-16]. Besides, there are many researches on the application of high pressure treatment for achieving high thermal conductivity or resistivity. For example, Ma et al[17] showed that high pressure treatment can improve the thermal conductivity of CuCr alloy. Ma et al[18] also showed that high pressure treatment can make CuAl alloy compact and increase its thermal expansion coefficient. A previous investigation showed that the thermal expansion coefficient of the Cu-Zn alloy after high pressure treatment can reach the maximum value, which increases by 52.41% in comparison with that of the original Cu-Zn alloy at the same temperature[19]. A recent study showed the electrical conductivity of the CuCrNiAl after high pressure heat treatment is 32.93% higher than that of the original state[20]. Unfortunately, there are few researches on the effect of high pressure heat treatment on the microstructure and properties of Cu-W alloys.

For this reason, the aim of the current study is to investigate the influence of high-pressure aging treatment on microstructure and properties of Cu-51.15W-0.24Cr alloy. The hardness, resistivity and thermal diffusivity were tested by microhardness tester, resistivity tester and thermal constant tester, respectively. The results can provide reference data for understanding the influence of high pressure treatment on the structure and properties of Cu-51.15W-0.24Cr alloy.

1 Experiment

The ingot with the composition of Cu-51.15W-0.24Cr (wt%) was prepared by the infiltration method. The ingot samples were put into a KLX-12B box-type resistance furnace and solution-treated at 960 °C for 1 h, and then cooled by water to room temperature. After that, some samples were aged under high pressure. The high pressure aging was performed in CS-IB type six-anvil high-pressure equipment (Fig. 1) under 3 GPa for 1 h, and the temperatures were 350, 400, 450, 500, 550, 600 °C. Then the samples were held at the optimum temperature for 0.5, 1, 2, 3 h. For comparison, samples aging treated under normal pressure were put in the KL-12D box type electric resistance furnace and the temperature and holding time were as same as those in the high pressure aging.

The microstructure analysis was carried out on Axiovert200 MAT optical microscopy (OM), S-3400N scanning electron microscopy (SEM) and Jeol-2010 transmission electron microscope (TEM). The optical microscope specimens were polished and etched using 3% FeCl$_3$+10% HCl solution. The FM-ARS-9000 microhardness tester (with a load of 50 g for a dwell time of 20 s) and the THV-5 Vickers hardness tester (with a load of 500 g for a dwell time of 20 s) were used to determine the hardness of the constituent phase and the overall hardness of the sample. The samples were shaped into the dimensions of Φ4 mm×10 mm, and then the resistivity was tested on a ZEM-3 resistivity tester. The samples before and after high pressure treatment were shaped into the dimensions of Φ8 mm×1.5 mm, and then the thermal diffusion coefficient was measured by a TC-7000 thermal constant tester. During the experiment, each data was measured at least three times to ensure the reliability.

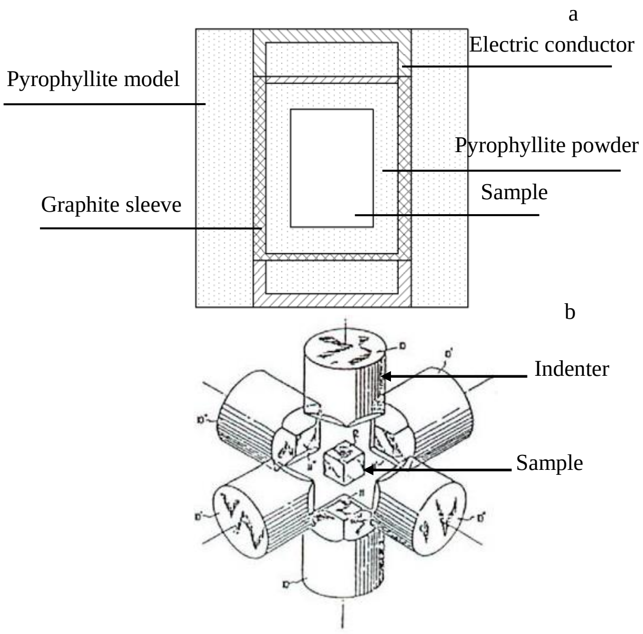

Fig.1 High pressure assembly diagrams: (a) sample assembly diagram and (b) schematic diagram of sample pressure

2 Results and Discussion

2.1 Microstructure

Fig.2 shows the microstructures of Cu-51.15W-0.24Cr alloy treated under different conditions. It can be seen that the as-cast alloy is basically composed of Cu matrix and white irregular W phase. After aging at 500 °C for 1 h under normal pressure and high pressure, the change of microstructure characteristics of the alloys is not obvious. From the SEM observation (Fig. 3), the microstructure of the samples subjected to high pressure aging treatment, compared with that to normal pressure aging treatment, is characterized by the fact that the number of micropores in the Cu matrix is significantly reduced and the compactness is increased. It can also be seen from the SEM morphologies of fracture (Fig. 4) that the fracture morphology of the samples aged under high pressure is denser than that of samples aged under normal pressure aging treatment.

Through TEM observation (Fig. 5), it is clearly found that the matrix of the alloy has a large number of fine precipitated phases after high pressure and normal pressure aging treatments. Meanwhile the precipitates of the sample aged under high pressure are finer than under normal pressure. According to results, the average size of the precipitated phase under normal pressure aging treatment is about 2.14 nm, which is larger than that obtained under high pressure (1.63

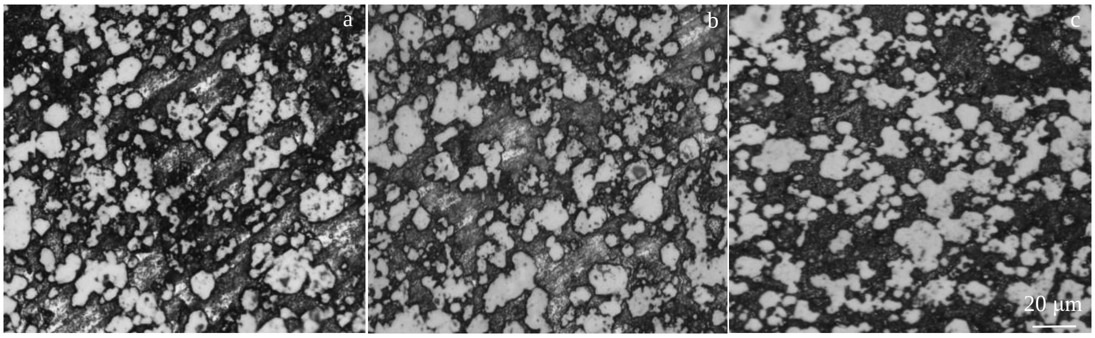

Fig.2 Microstructures of Cu-51.15W-0.24Cr under different states: (a) as-cast, (b) normal-pressure aging treatment at 500 °C for 1 h, and (c) high-pressure aging treatment at 500 °C for 1 h

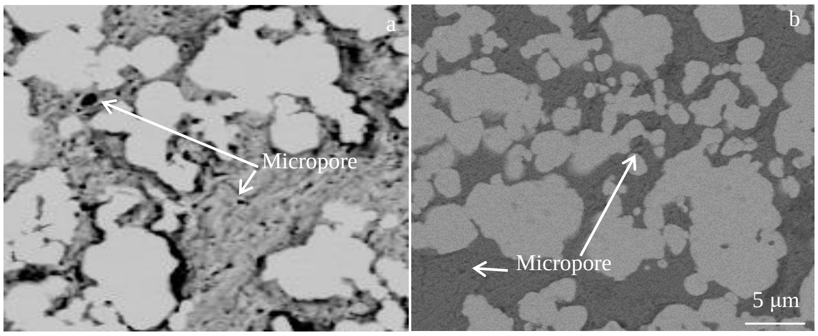

Fig.3 SEM back scattering morphologies of Cu-51.15W-0.24Cr alloy after normal-pressure aging treatment at 500 °C for 1 h (a) and high-pressure aging treatment at 500 °C for 1 h (b)

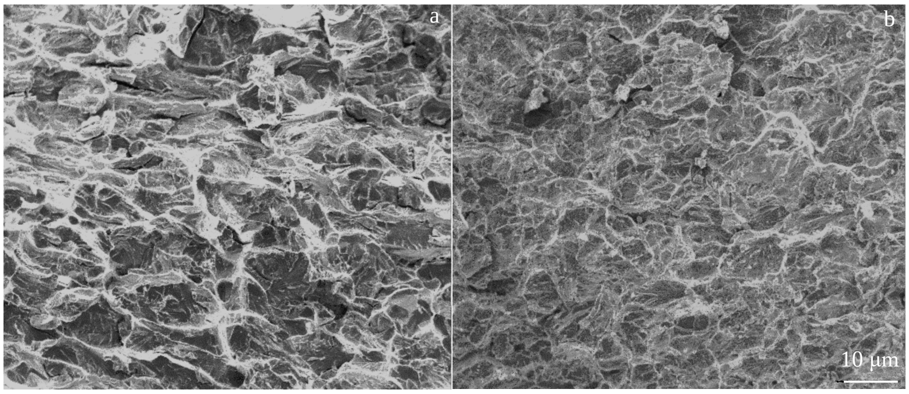

Fig.4 SEM morphologies of fracture of Cu-51.15W-0.24Cr alloy after normal-pressure aging treatment at 500 °C for 1 h (a) and high-pressure aging treatment at 500 °C for 1 h (b)

nm). According to the results of energy spectrum analysis, the content of Cr element in the precipitation phase is relatively high, about 63.12%, so it can be concluded that the precipitation phase is Cr particles.

2.2 Properties

2.2.1 Hardness

Fig. 6 presents the variation of hardness as a function of aging temperature and holding time. It evidences that the investigated samples with high-pressure aging treatment have higher hardness than that with normal pressure aging. Fig. 6a shows that the hardness values in both cases increase rapidly with the rise of aging temperature and approach the highest peak hardness at 500 °C, and then decrease. Fig. 6b shows the change of hardness with aging time. It can be seen that the hardness increases at the beginning of aging treatment and then decreases with the extending of aging time, and reaches

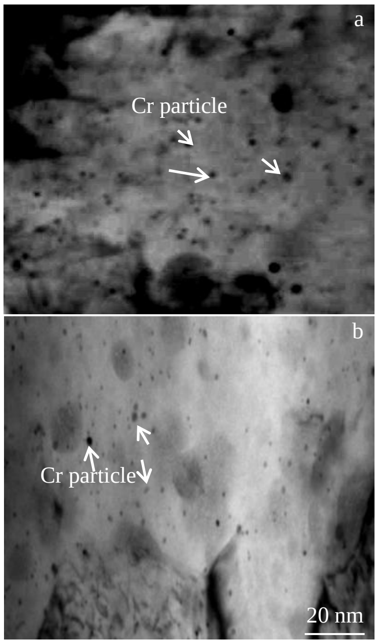

Fig.5 TEM images of precipitates in Cu-51.15W-0.24Cr alloy after normal-pressure aging treatment at 500 °C for 1 h (a) and high-pressure aging treatment at 500 °C for 1 h (b)

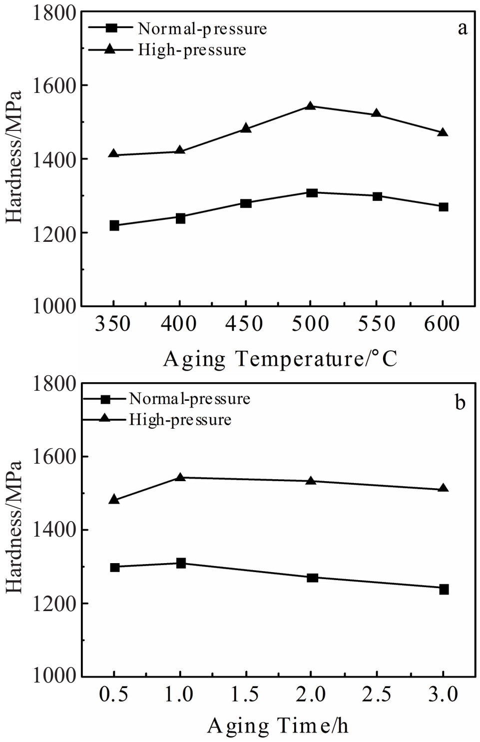

Fig.6 Hardness of Cu-51.15W-0.24Cr alloys: (a) isochronal aging for 1 h and (b) isothermal aging at 500 °C

the peak value after aging treatment for 1 h. Further, the maximum of hardness value of the sample aged at 500 °C for 1 h under high pressure reaches 1540 MPa, which is improved by 26.23% and 17.56% as compared with that of the specimens with solution treatment and normal pressure aging treatment, respectively.

As listed in Table 1, the high-pressure aging treatment can increase the hardness of the Cu matrix and the W phase in the Cu-51.15W-0.24Cr alloy. Therefore, the overall hardness of the alloy is improved.

According to Fig.3, the difference of hardness is attributed to the effect of high pressure, which can eliminate the micropores in the alloy and correspondingly improve the compressive deformation ability and then reinforce the hardness of samples.

At the same time, high pressure can lead to lattice deformation and increase the number of dislocations. High dislocation density provides more effective sites for the precipitation of Cr particles, resulting in increase of the Cr precipitation. In addition, high pressure can suppress the diffusion of atoms, making growth of Cr particles difficult, thereby causing a large number of small size and homogenous spatial distribution particles to precipitate during high-pressure aging (Fig.5). The precipitation strengthening can be described by follows：

$$\tau = 2Gb/r \qquad (1)$$

where τ is the shear stress, G is the shear modulus, b is Burger vector and r stands for the spacing for the intra crystalline particles. The smaller the size of precipitates, the smaller the spacing between precipitates, the greater the stress for dislocations to shear through the precipitates. In addition, dislocation interacts with the precipitate to exert a strong pinning effect. Therefore, obvious precipitation strengthening is obtained during high pressure aging treatment. This explains the reason why the hardness of samples after high pressure aging treatment is higher than that obtained by the normal pressure aging treatment.

It is worth noting that hardness begins to show a decline trend when the aging temperature exceeds 500 °C or holding time is longer than 1 h, and the precipitates begin to grow up and destroy the coherent relationship with the matrix, which leads to the drop of hardness. The results show that the hardness of high pressure aged samples decreases slowly compared to that of atmospheric pressure aged samples, which can be due to the fact that the precipitated Cr particles are not easy to grow under high pressure. This may be related to the suppression of element diffusion by high pressure, which has been verified[21-23].

2.2.2 Resistivity

Fig. 7 shows the variation of resistivity as a function of aging temperature and holding time. It can be seen that electrical resistivity of the alloy with high pressure aging

Table 1 Hardness of Cu matrix and W phase after aging at 500 °C for 1 h (MPa)

Treatment	Cu matrix	W phase
Normal-pressure aging treatment	560	2650
High-pressure aging treatment	930	2910

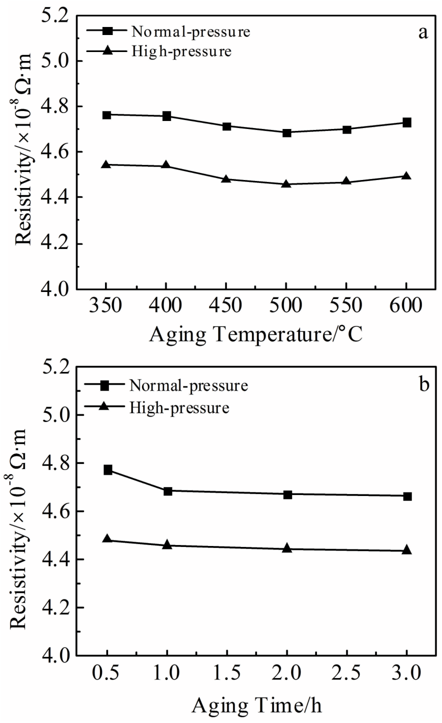

Fig.7 Resistivity of Cu-51.15W-0.24Cr alloys: (a) isochronal aging for 1 h and (b) isothermal aging at 500 °C

treatment is lower than that of atmospheric aging-treated samples. As shown in Fig. 7a, the resistivity of the sample decreases with the rise of temperature and then remains stable, and reaches the minimum value at 500 °C. Fig.7b shows that the resistivity decreases with increasing the aging time at 500 °C for both samples. Further, the resistivity decreases slightly when the aging time is more than 1 h. The sample aged at 500 °C for 1 h under high pressure has the lowest resistivity, with the value of 4.458×10^{-8} Ω·m. Compared with the solution-treated sample (4.967×10^{-8} Ω·m) and the aging-treated sample under the normal pressure condition (4.685×10^{-8} Ω·m), the resistivity decreases by 10.25% and 4.85%, respectively.

2.2.3 Thermal diffusivity

Fig.8 shows the thermal diffusivity of the investigated alloy as a function of aging temperature and holding time. Obviously, the thermal diffusivity of the alloy aged under high pressure is higher than that of the specimens aged under the normal pressure condition. The change trend of thermal diffusivity shows an opposite trend to that of the hardness curve. The thermal diffusivity rises with the increase of aging temperature, then declines slightly and reaches the peak value at 500 °C. As shown in Fig.8b, when the aging time exceeds 1 h at 500 °C, the diffusivity changes slightly and tends to be stable. According to the experimental data, the sample aged at 500 °C for 1 h under high pressure has the highest thermal diffusivity, with the value of 0.5236 cm^2·s^{-1}. Compared with the solution-treated sample (0.4456 cm^2·s^{-1}) and the specimens aged under normal pressure condition (0.4728 cm^2·s^{-1}), thermal diffusivity increases by 17.56% and 10.74%, respectively.

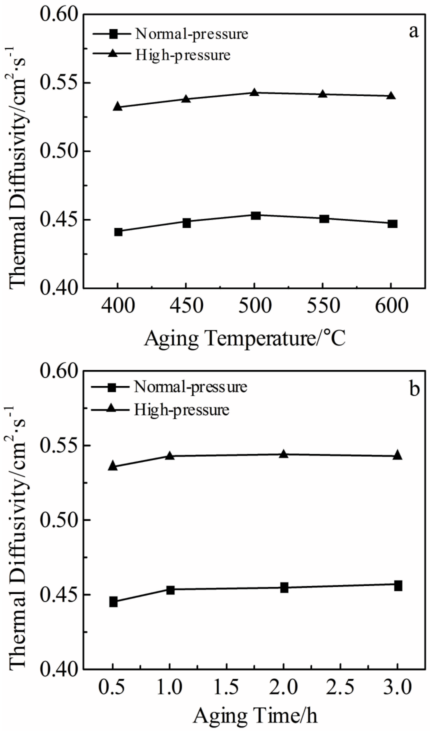

Fig.8 Thermal diffusivity of Cu-51.15W-0.24Cr alloys: (a) isochronal aging for 1 h and (b) isothermal aging at 500 °C

The relationship between conductivity and thermal diffusivity is as follows:

$$\lambda\rho = L'T \tag{2}$$

where λ is the thermal diffusivity of the alloy, ρ is resistivity, L' is the modified Lorentz constant, T is the thermodynamic temperature. There is a negative correlation between resistivity and thermal diffusivity. It is widely accepted that the resistivity and thermal diffusivity of alloys depend on the solute atoms in the matrix. It is well known that the heat conduction and electric conduction are affected by the movement of electrons. It can be easily obtained that the more the solute atoms contained in the solid solution, the stronger the scattering effect on the electrons, the larger the resistivity of the alloy, and the lower the thermal diffusivity. After the solution treatment, due to the large amount of Cr atoms in the Cu matrix, a larger resistivity and a smaller thermal diffusivity of Cu-51.15W-0.24Cr alloy are obtained. After aging treatment, more and more Cr atoms precipitate from the Cu matrix with the increase of aging temperature in early aging stage, eventually resulting in the decline of resistivity and the rise of thermal diffusivity. However, as the aging temperature exceeds 500 °C, some of the Cr precipitates are dissolved in the matrix and eventually result in the uptrend of resistivity and downtrend of thermal diffusivity.

As the holding time is longer than 1 h at 500 °C, the quantity of Cr particles remains basically unchanged, leading to a tendency to maintain stable resistivity and thermal diffusivity. According to SEM images of alloys, the high-pressure aging treatment can reduce the number of micropores in the alloy, thereby reducing the scattering of electrons which is closely related to the micropores. This is also one of the reasons why the thermal diffusivity of the investigated alloy under high pressure aging treatment is higher than that of atmospheric aging treated alloy, and why the resistivity is lower than that of normal pressure aging treated alloy.

3 Conclusions

1) High-pressure aging treatment can improve the mechanical properties and optimize the microstructure of Cu-51.15W-0.24Cr alloy.

2) The Cu-51.15W-0.24Cr alloy, with a hardness of 1540 MPa, thermal diffusivity of 0.5236 cm^2·s^{-1}, and resistivity of 4.458×10^{-8} Ω·m, can be obtained after solution treatment at 960 °C for 1 h and aging at 500 °C for 1 h at a pressure of 3 GPa. As compared with those of normal pressure aging treatment, the hardness and thermal diffusivity increase by 17.56% and 10.74%, respectively, while the resistivity decreases by 4.85%.

3) The improvement of hardness is mainly ascribed to the high pressure, which can increase the compactness of alloy and improve the compressive deformation ability. Additionally, high pressure increases the number of dislocations and makes the Cr particles more dispersed and finer, eventually resulting in a stronger precipitation strengthening effect.

4) After the high pressure aging treatment, the electrical and thermal conductivity can be improved. It indicates that the scattering effect of microstructure on electrons is weakened, which is mainly due to the reduction of micropores in Cu matrix and the improvement of the dispersibility of Cr precipitation.

References

1 Xu L, Yan M, Xia Y *et al. Journal of Alloys and Compounds*[J], 2014, 592: 202

2 Luo Laima, Tan Xiaoyue, Ding Xiaoyu *et al. Rare Metal Materials and Engineering*[J], 2016, 45(8): 1983

3 Zhang Y H, Zhuo L C, Zhao Z *et al. Journal of Alloys and Compounds*[J], 2020, 823: 153 761

4 Amirjan M, Zangeneh-Madar K, Parvin N. *International Journal of Refractory Metals and Hard Materials*[J], 2009, 27(4): 729

5 Qiu W T, Pang Y, Xiao Z *et al. International Journal of Refractory Metals and Hard Materials*[J], 2016, 61: 91

6 Zhou Z J, Kwon Y S. *Journal of Materials Processing Technology*[J], 2005, 168(1): 107

7 Liang S H, Wang X H, Wang L L. *Journal of Alloys and Compounds*[J], 2012, 516: 161

8 Zhou Q, Chen P W. *International Journal of Refractory Metals and Hard Materials*[J], 2015, 52: 137

9 Wu C, Yang S Q, Li Y *et al. Journal of Alloys and Compounds* [J], 2016, 665: 231

10 Wei Z J, Jiang W, Zou C M *et al. Journal of Alloys and Compounds*[J], 2017, 692: 629

11 Guo K Y, Xu C, Lin X P *et al. Transactions of Nonferrous Metals Society of China*[J], 2020, 30(1): 99

12 Ma Yao, Zhou Zhangjian, Tan Jun *et al. Rare Metal Materials and Engineering*[J], 2011, 40(1): 4

13 Gu T, Li J W, Xu F Q *et al. Materials Research Express*[J], 2020, 7(2): 26 505

14 Wang Y H, Xing P D, Wang P *et al. Journal of Alloys and Compounds*[J], 2016, 656: 581

15 Gu T, Xu F Q, Zhao Y H *et al. Materials Research Express*[J], 2019, 6(9): 96 508

16 Chen Y, Liu L, Liu J H *et al. Materials Transactions*[J], 2013, 54(6): 990

17 Ma Y Q, Lin H J, Song D D. *Rare Metals*[J], 2014, 33(3): 293

18 Ma Y Q. *Materials Transactions*[J], 2013, 54(4): 540

19 Chen Y, Liu L, Wang Y H *et al. Transactions of Nonferrous Metals Society of China*[J], 2011, 21(10): 2205

20 Ma Y Q. *Materials Transactions*[J], 2013, 54(5): 725

21 Wei Z J, Wang Z L, Wang H W *et al. Journal of Materials Science*[J], 2007, 42(17): 7123

22 Xu R, Zhao H, Li J *et al. Materials Letters*[J], 2006, 60(6): 783

23 Zhang X Y. *Advanced Engineering Materials*[J], 2001, 3(7): 469

高压时效处理对Cu-51.15W-0.24Cr合金组织和性能的影响

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摘　要：针对Cu-W合金的强度和导热导电性偏低问题，对Cu48.61W51.15Cr0.24合金进行了高压时效处理，并对比了高压时效处理和常压时效处理后合金的微观组织，硬度，热导率以及导电率。结果表明：高压时效处理能增大Cu48.61W51.15Cr0.24合金的致密度，使组织中析出的Cr相更加弥散细小，改善合金的硬度及导热导电性能。该合金经960 ℃/1 h固溶后，再在3 GPa压力下500 ℃时效1 h处理可获得较高的硬度、热扩散系数及较低的电阻率，其值分别为1540 MPa、0.5236 cm^2·s^{-1}和4.458×10^{-8} Ω·m，较相同工艺常压时效处理后的硬度和热扩散系数分别增加了17.56%和10.74%，而电阻率却降低了4.85%。因此，高压时效处理是提高Cu-51.15W-0.24Cr合金力学性能、降低电阻率的有效途径。

关键词：Cu-51.15W-0.24Cr合金；高压时效处理；硬度；热导率；电阻率

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