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Microstructure and properties of heavily deformed Cu-Ag-Ce *in situ* nano-filamentary composite

ZHANG Xiao-hui(张晓辉)[1], YAN Lin(闫 琳)[1], NING Yuan-tao(宁远涛)[2]

(1. Grikin Advanced Materials Co. Ltd., General Research Institute for Nonferrous Metals, Beijing 100088, China;
2. Kunming Institute of Precious Metals, Kunming 650221, China)

Abstract: Abstract: The microstructure and properties of heavily deformed Cu-Ag-Ce *in situ* nano-filamentary composite were studied in this paper. As cast, copper matrixes were dendritic and Ag-rich phases, some of which present spheroidizing tendency, were embedded in Cu dentritic arms. After heavily deforming, Ag-rich phases develop into fibers: the thick fibers with a size of more than 50 nm and the thin ones with a size of less than 30 nm. Strengthening of Cu-Ag-Ce *in situ* nano-filamentary composite could be divided into two stages and the combination of different strength and conductivity could be obtained through controlling reducing area, intermediate heat treatment and stabilizing treatment. The results revealed that heavily deformed Cu-Ag-Ce *in situ* nano-filamentary composite had high strength (>1.5GPa) and high conductivity(>65% IACS).

Key words: heavily deformed alloy; copper-silver alloy; nanometer fibers; high-strength and high conductivity materials

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1 Introduction

In recent years, the high-strength and high-conductivity copper alloys produced by the co-deformation of two-phase structure using heavily deforming have been studied[1-5]. According to the crystal type, the materials are divided into Cu-b.c.c. (body centered cubit, such as Nb, Fe, Cr) type and Cu-f.c.c. (face centered cubit, for example Ag) type. Previous study[7] indicates that Cu-Ag alloy containing less 6% (mass fraction) silver is single phase Cu, the other alloys with more than 6%(mass fraction) Ag contain two phases: copper-rich and silver-rich solid solutions. Tensile strength has nearly relation to Ag content[1]: at the same reduction, tensile strength increases with increasing Ag content. For example, at a reduction of 96%, the strengths are 947 MPa for 8% Ag(mass fraction), and 1050 MPa for 24% Ag(mass fraction)[1]. But this can reduce the conductivity and increase the cost. The solidification rate has some effects on mechanical and electrical properties, and the more rapid solidification rate is, the more early tensile strength can reach[13]. In a few previous studies[8-10], to obtain higher strength at lower reduction or Ag content was investigated by adding the third element, such as Nb, Cr, Zr or C. The rare earth has special physical and chemical property which can fine crystal, increase mechanical property and re-crystallization temperature[11,12]. However the research about Cu-Ag-RE (Rare Earths) is rarely reported.

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Biography: ZHANG Xiao-hui(born in 1975), Male, Engineer, Master.

In this study, Cu-Ag-Ce *in situ* filamentary composite was produced, by using cerium as an additive element, and the properties and microstructure are investigated.

2 Experimental

Electrolytic copper, high pure silver and cerium, with the purity of 99.95%, 99.99%, 99.9% separately, were used to prepare Cu-Ag-Ce alloy, in which the content of sliver was 10% (mass fraction) nominal component and that of cerium was 0.1% (mass fraction) with additional one.

The experimental route and the methods to test mechanical and electrical property were the same as previous studies[13,14]. The alloy with a diameter of 3.0 mm was rolled to foils (about 5 μm thick), then the foils were electropolished by MTP—1 electropolishing machine using a 20% nitric acid in ethanol mixture. The centers of them are less then 500 nm in thickness. The samples were observed by TEM (Transmission Electron Microscope) using a Hitachi H—800. The alloy for XRD (X-Ray Diffraction) was determined whether there was cerium oxide or other phases.

3 Results and discussion

3.1 Microstructure

The scanning electron micrograph of Cu-Ag-Ce *in situ* composite is shown as Fig. 1. The alloy contains two phases: the copper matrixes (the darker phases) were fir-tree like, and silver-rich phases (the lighter ones), presenting reseau- or dot-like, are embedded in the dentrite-arms. The content of cerium is 0.04% by the fix quantify spectral analysis. The phases with cerium or cerium oxide were not found by XRD results, maybe because Ce is solutionized in Cu-rich and Ag-rich phases. As cast, Ag-rich phases of Cu-10Ag-0.04Ce present spheroidizing comparing to the Cu-10Ag *in situ* filamentary composite, which maybe relates to component undercooling due to adding of the Ce. After heavily deforming, microstructure of Cu-10Ag-0.04 Ce develops into filamentary structure, as shown Fig. 2(a). The microstructure consists of three phase: copper-rich phase (the matrix, the lighter regions, indicated by 'A'), the thick Ag-rich filaments(or lamellae, indicated by 'B') with a size of more then 50 nm, and thin Ag filaments (less then 30 nm, indicated by 'C'). The dislocation structure is not found in many fields of the samples, as shown in previous study of Hong[15]: as the filament spacing decreases with the deformation increasing, the dislocation density between filaments also decreases. According to the diffraction pattern from the area containing the Cu-matrix and Ag filament, as shown in Fig. 2(b), Cu-matrixes and Ag filaments have the same crystal orientation: $(\bar{1}11)_{Cu} \parallel \bar{1}11)_{Ag}, [110]_{Cu} \parallel [110]_{Ag}$.

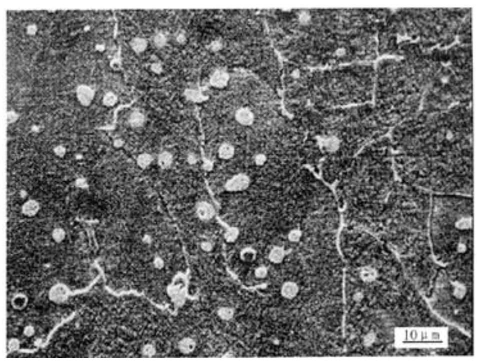
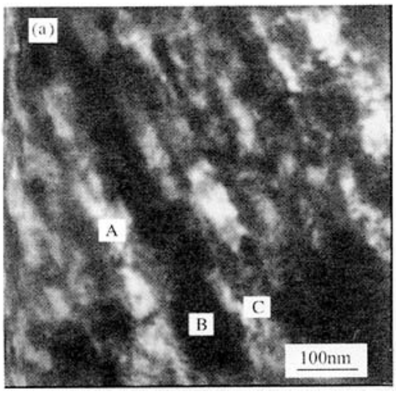


Fig. 1 Microstructure (seen by backscattered electrons) of the Cu-10Ag-0.04Ce *in situ* filamentary composite as cast

3.2 Mechanical property

Fig. 3 shows the dependence of tensile strength of Cu-Ag-Ce *in situ* nano-filamentary composite on true strain. Tensile strength increases slowly with the increasing of the reduction of area, when the true strain η (draw ratio, $\eta = \ln(A_0/A)$, where A_0 and A are the initial and final cross sectional areas, respectively) is less then 8.4. Howev-



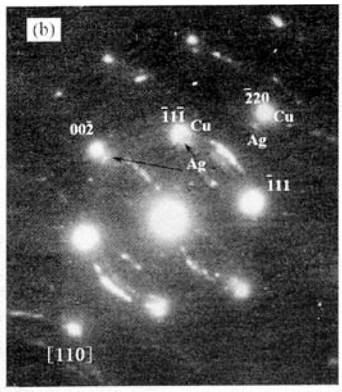


Fig. 2 TEM bright field image (a) and the diffraction pattern (b) of Cu-10Ag-0.04Ce *in situ* nano-filamentary composite

er, it increases quickly while true strain η is greater. The point (speaking exactly, should be a range) where the increasing degree of tensile strength changes is named strengthening turning point. It relates to such factors as solidification rate, alloy component and intermediate heat treatment (abbreviated as IHT)[13]. The strengthening turning points with different Ag contents were shown as Table 1. The strengthening turning points shift forward (or becomes smaller) with increasing of Ag content, and is up to a minima while silver reaches cutectic point. The point shifts forward after adding the cerium, which is due to the spheroidizing of Ag-rich phases and refining of crystals because rare earth cerium is added. Previous studics[13,14] reveal the strengthening Cu-Ag *in situ* filamentary composite is divided into two stages: at the first stage dislocation strengthening is dominant, at the second stage interface strengthening is main. The investigation[16] for TEM indicate that at a fibre diameter of about 55 nm the dislocation density reaches a maxima and decreases rapidly with increasing degree of deformation and decreasing fibre diameter.

Table 1 The strengthening turning point of the different alloys

Alloys	Strengthening turning point η_p	References
Cu-72% Ag	6.0	[7]
Cu-35% Ag	7.5	[7]
Cu-15% Ag	≥8.0	[7]
Cu-10% Ag	9.5	[13]
Cu-10Ag-0.04Ce	8.4	this study

Fig. 4 was the curves of tensile strength dependent on true stain with different heat treatment. Tensile strength of the alloys with different heat treatment increase with the reduction of areas, seen as the Fig. 3. Tensile strength of the alloy with IHT is higher than that of the alloy with non IHT, and that of the alloy with two times is the highest. Tensile strength can be raised after IHT, which consists in precipitation of fine silver fibers. They enhance the precipitation-strengthening and interface-strengthening of the second strengthening stage.

3.3 Comprehensive property

Influence of IHT on comprehensive property of Cu-Ag-Ce *in situ* nano-filamentary composite was shown as Fig. 5. Tensile strength and conductivity of said materials increase after the IHT. After two

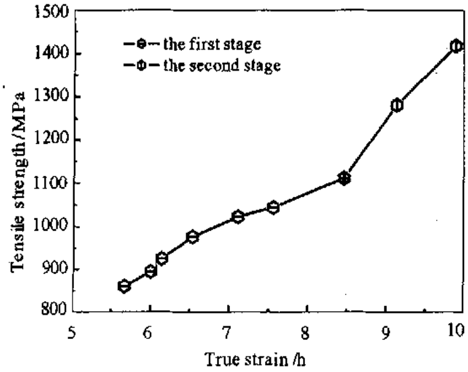


Fig. 3 Tensile strength as a function of true strain for Cu-10Ag-0.04Ce *in situ* nano-filamentary composite

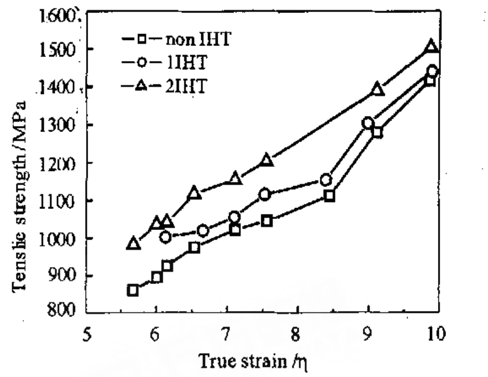


Fig. 4 Tensile strength as a function of true strain for Cu-10Ag-0.04Ce with varying IHT

times IHT, tensile strength of Cu-Ag-Ce *in situ* nano-filamentary composite is up to 1.5 GPa, and 65.9% IACS (International Annealed Copper Standard, 100%IACS = 1.7241$\mu\Omega$ cm) for conductivity while true strain (equals to 9.88. It is well-known that tensile strength is in opposition to conductivity. Why can IHT increase tensile strength and conductivity? The resistivity of *in situ* composite is divided into four parts[15]: $\rho=\rho_{pho}+\rho_{dis}+\rho_{int}+\rho_{imp}$, where ρ_{pho} is the resistivity contribution from phonon scattering, which is dependent on temperature, ρ_{dis} is dislocation scattering, ρ_{int} is interface scattering, and ρ_{imp} is the impurity scattering. For the same material, ρ_{pho} and ρ_{imp} are constant at room temperature. So ρ_{dis} and ρ_{int} relate to IHT. Cu-Ag-Ce *in situ* composite recover after IHT. The microstructure changes hardly during the recovering, however, interior defects decrease. On the other hand, fine Ag fibers precipitate during heat treatment, which decrease solid solubility of silver in copper matrix and crystal scattering arose by them. This is a precondition that increases conductivity for subsequent deformation, at the same time, these fine Ag precipitations contribute greatly on increasing of tensile strength.

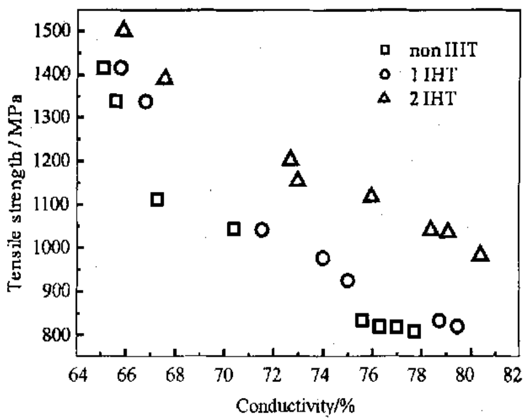


Fig. 5 Tensile strength as a function of conductivity for Cu-10Ag-0.04Ce with varying IHT

4 Conclusion

(1) Cu-10Ag-0.04Ce *in situ* nano-filamentary composite, with high strength (1.5 GPa) and high conductivity (65.9%IACS), was produced by using the technology combining heavily deforming and intermediate heat treatment.

(2) Although the content of cerium is very low, some Ag-rich phases is spheroidized. After heavily deforming, Ag-rich phases develop into fibers or lamellas: the thick Ag-filaments or lamellas with size of more than 50 nm, the thin ones with size of less than 30 nm.

(3) Strengthening of Cu-10Ag-0.04Ce *in situ* nano-filamentary composite is divided into two stages, and there is a turning point (or narrow range) between them. Dislocation multiplication is the main factor

for strength increasing at the first stage, and abundant interfaces at the second stage.

(4) Strength and conductivity increase after IHT and later working, which attributes to the precipitation of Ag. The matrixes are refined and crystal scattering is decrease because of precipitating of Ag.

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