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Doping Ti to achieve microstructural refinement and strength enhancement in a high volume fraction Y_2O_3 dispersion strengthened Cu

Dengshan Zhou [a, b, *], Xinkai Wang [a], Wei Zeng [c], Chao Yang [d, **], Hucheng Pan [a], Chenguang Li [c], Yujie Liu [a], Deliang Zhang [a, b]

[a] Key Laboratory for Anisotropy and Texture of Materials (Ministry of Education), Northeastern University, Shenyang, 110819, China
[b] Institute of Ceramics and Powder Metallurgy, School of Materials Science and Engineering, Northeastern University, Shenyang, 110819, China
[c] The State Key Laboratory of Metal Matrix Composites, School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai, 200240, China
[d] Shanghai Institute of Applied Physics, Chinese Academy of Sciences (CAS), Shanghai, 201800, China

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A B S T R A C T

In this work, high volume fraction Y_2O_3 dispersion strengthened Ti-free and Ti-doped Cu samples were prepared by mechanical alloying, high temperature heat treatment and powder compact extrusion to study the role of alloying Ti element on microstructures, mechanical properties and electrical conductivity of the extruded samples. It is found that the addition of a small amount of 0.4 wt.%Ti effectively suppresses the coarsening of Y_2O_3 particles during material fabrication, which produces smaller and more uniform oxide particles distributed in a homogeneous ultrafine grained Cu matrix. However, a heterogeneous Cu matrix microstructure, consisting of elongated micrometer-scale Cu grains and equiaxed ultrafine Cu grains, is observed in the Ti-free sample due to significant coarsening of the Y_2O_3 particles. The different microstructural features of the two extruded samples lead to distinctively different mechanical behaviors and electrical conductivities. The energy dispersive X-ray spectrometry elemental and high resolution transmission electron microscopy analysis suggest that the stabilizing mechanisms of the Y_2O_3 particles involve both the segregation of Ti atoms to the surface layers of large Y_2O_3 particles and dissolution of Ti atoms into small Y_2O_3 particles to form complex particles.

1. Introduction

Copper-based materials are promising heat sink materials for high heat flux applications in fusion energy systems [1]. The inherently high thermal conductivity of Cu-based materials can allow them to rapidly remove a great amount of heat generated from plasma. Although the high thermal conductivity is a key physical parameter in such application, both high strength and radiation resistance are also essential in a high heat flux and irradiation environment [2]. Oxide dispersion strengthened (ODS) Cu provides an optimal combination of high conductivity, good strength at intermediate and elevated temperatures, and excellent radiation resistance [2]. The advantages of ODS Cu are also required by materials used as spot welding electrodes and electric contacts [3,4]. Therefore, a high performance ODS Cu is an important engineering materials.

Commercially available ODS Cu that contains a small volume fraction of γ-Al_2O_3 nanodispersoids (normally less than 3 vol.%) is produced by internal oxidization of dilute Cu-Al alloys [5]. In situ formed metastable γ-Al_2O_3 has a highly disordered spinel-type structure and preferentially forms incoherent $\{111\}_{\gamma\text{-alumina}}//\{111\}_{Cu}$ interfaces with the Cu matrix [6]. Yttrium oxide has the closely-related structure of Mn_2O_3, which may allow Y_2O_3 to form different and desirable orientation relationships with Cu [7]. In addition, in comparison with γ-Al_2O_3, Y_2O_3 exhibits a higher thermodynamic stability and lower solubility and diffusivity in Cu [7,8]. Arzt and Wilkinson [9] and Rösler and Arzt [10] proposed that the oxide-matrix interfacial characteristic plays a dominant role in

* Corresponding author. Key Laboratory for Anisotropy and Texture of Materials (Ministry of Education), Northeastern University, Shenyang, 110819, China.
** Corresponding author.
E-mail addresses: zhoudengshan@mail.neu.edu.cn (D. Zhou), yangchao@sinap.ac.cn (C. Yang).

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improving room and elevated temperature mechanical properties of ODS materials. These suggest that Y_2O_3 is superior to γ-Al_2O_3 in producing a high-performance ODS Cu.

Expectedly, increasing the content of oxide dispersoids can improve the strength of ODS materials if the sizes of oxides can be effectively controlled. However, a high volume fraction could promote coarsening of oxides due to short diffusion distance resulting from a high number density of oxides in the matrix. Additionally, large oxide particles at grain boundaries may form once the volume fraction of oxides goes high [11]. These factors are detrimental to the mechanical properties of ODS Cu, and thus weaken their performance. It is clear that the size control of oxides plays a key role in designing a high-volume-fraction ODS Cu.

Prior studies [12–15] suggested that the alloying elements can effectively control the sizes of oxides and increase their thermal stability via facilitating the precipitation and modifying the oxide-matrix interfacial structure. For example, Zhou et al. [13,14] and Han et al. [12] observed that in the Cu-Al_2O_3/Y_2O_3 systems the Ti-doped oxide particles have a smaller average size as compared with Ti-free oxide particles. This favorable stabilizing effect was suggested to be attributed to the segregation of Ti atoms at the Cu/oxide interfaces and their diffusion into the oxide particles. In the development of advanced ODS ferritic steels used as nuclear cladding materials, Ti is an essential element in the formation of complex, stable and small Y_2TiO_5/$Y_2Ti_2O_7$ precipitates [16–18] in the ferritic matrix.

In this work, we report the role of microalloying Ti element on microstructural refinement and strength enhancement of a bulk ODS Cu containing a high volume fraction of Y_2O_3 particles. It is observed that the Ti-doped sample exhibits finer microstructure and higher strength in comparison with the Ti-free sample. The microstructural analysis reveals that the observed microstructure and strength of the Ti-doped sample are correlated with the stabilization of the Y_2O_3 particles by Ti. The observation from this study can guide us to design and develop new ODS Cu materials suitable for applications in extreme conditions.

2. Materials and methods

2.1. Preparation of milled powders

To prepare Ti-free and Ti-doped Y_2O_3 dispersion strengthened (DS) Cu powders with nominal compositions of Cu-5vol.%Y_2O_3 and Cu-5vol.%Y_2O_3-(0.2, 0.4 and 0.8)wt.%Ti, a planetary ball mill (QM-3SP4, Nanjing Nanda Instrument Ltd., China) was used to mill a powder mixture of electrolytic Cu, nano-Y_2O_3 (~30 nm) (Shanghai ST-nano Science and Technology Co., Ltd., China) and TiH_2 (~45 μm) (Beijing Xing Rong Yuan Technology Co., Ltd., China) powders at a high rotation speed of 500 rpm for 12 h. The milling process was continuous and not interrupted during milling. To avoid oxygen contamination during the whole milling stage, the milling vial was loaded with the starting powders and sealed in an argon-filled glove box. A ball-to-powder weight ratio of 5:1 was used, and two different steel balls with diameters of 20 and 16 mm respectively were chosen for the efficient milling. After milling of 12 h, the nanostructured composite powders were produced [14].

2.2. Preparation of bulk samples

Prior to consolidation of different milled powders, 1 h isochronal heat treatment of the milled powders in a temperature range of 300 to 1000 °C was carried out under a vacuum of ~5×10^{-2} Pa in combination with hardness tests to evaluate the thermal stability of the milled powders. The hardness results shown in Ref. [14] exhibit that the hardness values of the annealed samples alloyed with 0.4 and 0.8 wt.%Ti remain almost unchanged even after annealing at a temperature of 1000 °C approaching the melting point of Cu (1084 °C). In this study, we only focus on the samples with the compositions of Cu-5vol.%Y_2O_3 and Cu-5vol.%Y_2O_3-0.4 wt.%Ti and use their 900 °C annealed powders to produce bulk samples.

The interested annealed powders were first pressed into cylindrical powder compacts in air with a 200 tonnage hydraulic press equipped with a glove box. The cylindrical compacts (28 mm in diameter and ~30 mm in height) were then heated rapidly with an induction coil, and extruded into rods with a diameter of 6 mm in an argon-filled glove box at 900 °C. The heated compacts were held at 900 °C for 2min prior to extrusion. The extrusion ratio used was 25:1.

2.3. Microstructural characterization and chemical measurement

An X-ray diffractometer (XRD) (Cu Kα radiation, SmartLab, Rigaku) was used to collect diffraction patterns of the extruded rods. A continuous scanning with an operating voltage and current of 40 kV and 200 mA was carried out to obtain XRD signals at a step of 0.02° and a speed of 4°/min. Based on the Williamson-Hall method [19–22], the dislocation densities in the extruded rods were obtained by performing line profile analysis from the scanned XRD patterns using the following equations

$$\Delta K = \frac{0.9}{D} + \varepsilon K \quad (1)$$

$$\rho = \frac{2\sqrt{3}\left\langle \varepsilon^2 \right\rangle^{1/2}}{Db} \quad (2)$$

where $\Delta K = 2\beta \cos\theta/\lambda$, $K = 2\sin\theta/\lambda$, β is the full width at half maximum (FWHM) of a diffraction peak at a Brag angle of 2θ, λ is the wavelength of the X-ray used, D is the average grain size, ε is the internal elastic strain of the crystalline lattice, ρ is the dislocation density and b is the magnitude of Burgers vector, respectively. A scanning electron microscope (SEM) (Nova NanoSEM 230) with secondary and backscattered electron (BSE) detectors was used to examine the fracture surfaces and oxide particles of the extruded rods. A voltage of 7.5 kV and spot size of 3.5 were employed in SEM examination. The bright field (BF) and high angle annular dark field (HAADF) images showing the sizes and spatial distributions of oxide particles were taken at a camera length of 20 cm/HAADF 2, a spot size of 1.5 nm and an accelerating voltage of 200 kV with a scanning transmission electron microscope (STEM) (JEM 2100F). The electron backscatter diffraction (EBSD, Zeiss, 20 kV) and transmission electron microscopy analysis (JEM 2100F, 200 kV) have been employed to get morphologies and size distributions of Cu grains in the extruded rods. To understand the role of Ti on the fine microstructures of the extruded Cu-5vol.%Y_2O_3-0.4 wt.%Ti rod, the STEM EDS and high resolution transmission electron microscopy (HRTEM) analysis were performed to identify Ti concentrations around large Y_2O_3 particles and chemical compositions and crystal structure of small oxide particles. A normal metallographic preparation method together with vibration polishing was used to prepare the specimens for the EBSD examination. Both STEM and TEM specimens were prepared with twin-jet electropolishing (Struers TenuPol-5) followed by ion milling (Gatan 691). The inductively coupled plasma optical emission spectrometry (ICP-OES) (Optima 8300, PerkinElmer) analysis was conducted to measure the Y, Ti, Fe and Cr elemental contents in the extruded Cu-5vol.%Y_2O_3 and Cu-5vol.%Y_2O_3-0.4 wt.%Ti rods and the measured results were shown in Table 1.