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Effects of lanthanum addition on microstructure and mechanical properties of as-cast pure copper

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Abstract: As-cast Cu-La alloys with La contents in the range of 0–0.32 wt.% were fabricated by vacuum melting method. The effects of La on microstructure and mechanical properties of as-cast pure copper were investigated using optical microscopy (OM), scanning electronic microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and tensile test. The results showed that La had obvious effects on the solidification microstructure and the grain refinement of as-cast pure copper. With the increase of La content, the ultimate tensile strength, the yield strength and the microhardness increased gradually, but the elongation increased first and then decreased while La content exceeded 0.089 wt.%. The improvement of mechanical properties was attributed to the effect of grain refinement strengthening, solid solution strengthening, second phase strengthening and purifying. However, excessive adding La would deteriorate the elongation owing to the excessive Cu_6La phases.

Keywords: as-cast pure copper; La; microstructure; mechanical property; rare earths

It is well known that rare earth (RE) elements have been widely used as addition elements to improve the properties of ferrous metals[1], aluminum and magnesium alloys[2,3].

At the same time, the lanthanum (La) element has also been frequently used in metals, such as aluminum alloys and magnesium alloys. It is reported that the La addition in the Al-Mg-Si-Zr alloy led to a less precipitation hardening effect by forming compounds with Si. Meanwhile, the tensile strength of the Al-Mg-Si-Zr alloy with La addition was deteriorated. The thermal-resistant properties and electrical conductivity of the alloy with La addition were enhanced[4]. According to Ref. [5], microstructure of eutectic silicon of A356 alloy with 1.0 wt.% La was well refined. The La addition in A356 alloy led to the elongation improvement and had no effects on the tensile strength. Peng et al. found that the addition of La to the Mg-Gd-Zr alloy could lead to the reduction of the dendrite arm spacing of the as-cast alloy and result in an slight improvement in the mechanical properties and age hardening response[6]. Golmakaniyoon et al. found that the volume fraction of eutectic phases increased with the increase of La content, which gave rise to the increase of the creep resistance and the shear strength of Mg-6Zn-3Cu alloy[7]. La had also shown beneficial effects on copper and Cu-based alloys.

It has been reported[8] that La addition in Cu-Te-La alloy led to the formation of La-rich compounds. The compounds that assemble on the grain boundary can prevent grains from growing up. Thus, the grain refinement results in the improvement of the strength of the copper alloy. Xie et al. suggested that the lattice parameter of copper rich solid solution would increase with increasing amounts of La elements in the Cu-Cr-La alloy. And the precipitation of the secondary phase produced by La added gave rise to the increase of the strength of Cu-Cr-La alloy[9].

Nevertheless, it is uncertain that La has effects on the microstructural evolution of copper and Cu-based alloys, and the strengthening mechanism in copper and Cu-based alloys with La addition is not clear. The objective of this research was to investigate the influence of La-rich second-phase particles on the microstructure and mechanical properties of as-cast pure copper. Furthermore, the strengthening mechanism of pure copper with La addition was discussed. Finally, the optimal content of La in pure copper was determined.

1 Experimental

The electrolytic copper 99.97% in purity and the metallic lanthanum 99.99% in purity were melted in a vacuum induction furnace. The La contents of 0 wt.%, 0.030 wt.%, 0.051 wt.%, 0.100 wt.%, 0.200 wt.% and 0.320

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wt.%, enwrapped by pure copper foils, were added into the molten copper bath through the loader at about 1180 ºC after the pure coppers were completely melted. The molten alloys were poured into the mould preheated to about 300 ºC to obtain the cylindrical ingots. Table 1 shows the chemical composition of alloy.

The La content in pure copper was determined by a plasma emission spectrometer (IRIS Advantage 1000 ICP-AES). The microstructure was observed by a ZMEF4A optical microscope (OM) and an SSX-550 scanning electron microscope (SEM). The compositions of every phase were determined by a SHIMAJZU energy dispersive spectrometer (EDS). X-ray diffraction (XRD) was performed with Cu Kα radiation to analyze the crystal structure. The microstructure and second-phase particles were also characterized by a Tecnai G2 transmission electron microscope (TEM). Tensile tests were performed on a Zwick Z050 machine at ambient temperature and a tensile rate of about 1 mm/min. Hardness of the samples was tested by a Vickers hardness tester under the load of 300 g and holding 15 s. The fractography was observed by SEM. The size of grains in these specimens was determined by using linear intercept method. The average size of second phases was determined by using backscattered electrons images and an image analysis software.

2 Results and discussion

2.1 Effects of La addition on microstructure of as-cast pure copper

Fig. 1 shows the backscattered electrons (BSE) morphology of as-cast pure copper with different La contents. The presence of two phases with different colors can be observed. The white spherical phases are RE-rich particles, and the gray phases are copper matrix. It is well known that the atomic radius of La is larger than that of Cu. It is hard to form substitution solid solution between La and Cu elements. Therefore, the solid solubility of La elements in pure copper is very low. When La is added into the copper, minor fraction of La can be soluble in copper. However, major fraction of La reacts with Cu and forms La-rich second-phase particles.

In order to accurately determine the size of second-phase particles in the matrix, several BSE images with a

Table 1 Chemical composition of alloy

Alloy	P content/ ppm	Ni content/ ppm	Ag content/ ppm	Sb content/ ppm	Si content/ ppm	Pb content/ ppm	S content/ ppm	La content/ wt.%	Cu content/ wt.%
$0^{\#}$	1.22	2.39	9.27	2.83	19.08	10.94	6.38	N.D.	Bal.
$1^{\#}$	1.46	3.15	11.15	2.90	6.30	1.17	4.62	0.022	Bal.
$2^{\#}$	1.33	2.69	10.95	2.93	5.15	1.00	5.03	0.040	Bal.
$3^{\#}$	1.17	2.68	9.72	2.85	4.23	1.16	5.02	0.089	Bal.
$4^{\#}$	1.46	1.88	10.77	2.88	3.88	1.00	4.94	0.180	Bal.
$5^{\#}$	1.16	3.58	7.08	2.84	1.00	1.05	4.70	0.320	Bal.

N.D.: Not detected

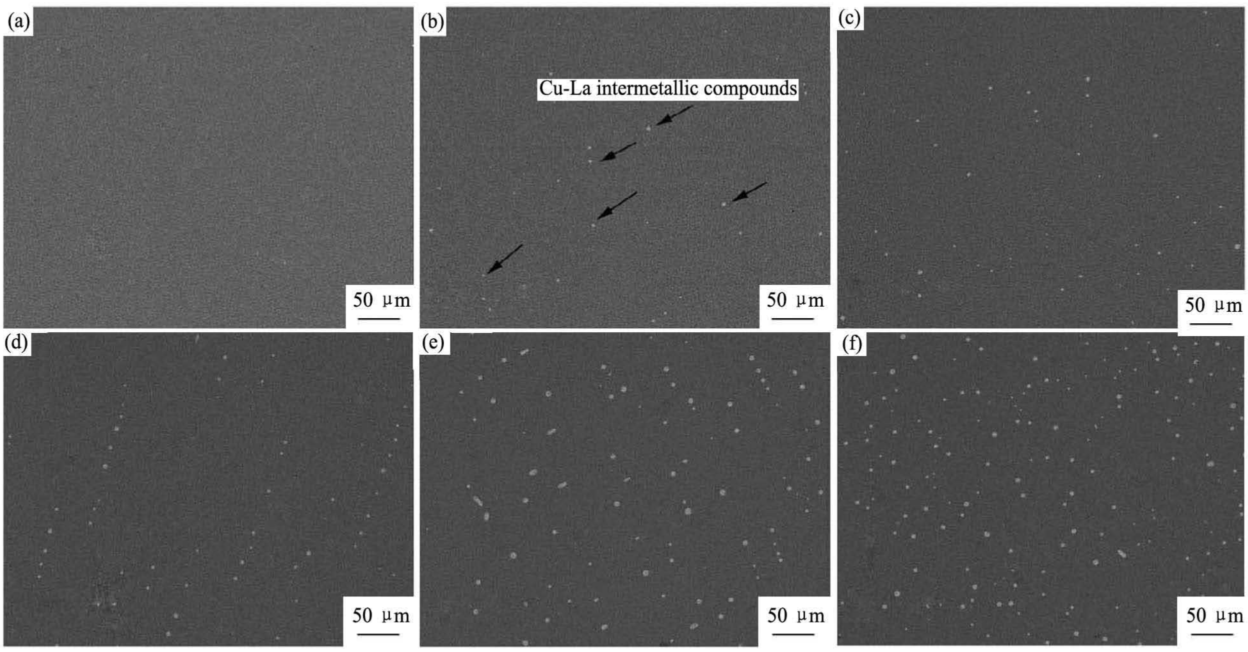

Fig. 1 Backscattered electron images of as-cast pure copper with different La contents
(a) $0^{\#}$ (La=0%); (b) $1^{\#}$ (La=0.022%); (c) $2^{\#}$ (La=0.040%); (d) $3^{\#}$ (La=0.089%); (e) $4^{\#}$ (La=0.180%); (f) $5^{\#}$ (La=0.320%)