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Processing map and hot deformation mechanism of novel nickel-free white copper alloy

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Abstract: Hot compression test of a novel nickel-free white alloy Cu−12Mn−15Zn−1.5Al−0.3Ti−0.14B−0.1Ce (mass fraction, %) was conducted on a Gleeble−1500 machine in the temperature range of 600−800 °C and the strain rate range of 0.01−10 s^{-1}. The constitutive equation and hot processing map of the alloy were built up according to its hot deformation behavior and hot working characteristics. The deformation activation energy of the alloy is 203.005 kJ/mol. An instability region appears in the hot deformation temperature of 600−700 °C and the strain rate range of 0.32−10 s^{-1} when the true strain of the alloy is up to 0.7. Under the optimal hot deformation condition of 800 °C and 10 s^{-1} the prepared specimen has good surface quality and interior structure. The designed nickel-free alloy has very similar white chromaticity with the traditional white copper alloy (Cu−15Ni−24Zn−1.5Pb), and the color difference between them is less than 1.5, which can hardly be distinguished by human eyes.

Key words: Ni-free white copper alloy; hot compression deformation; constitutive equation; processing map

1 Introduction

Nickel is often used as a key element to produce white copper alloys as it can change the color of copper alloys from red to white [1]. Nickel-containing white copper alloy has been widely used to produce coin, button, zipper, spectacles frame, watchcase, necklace and artwork, due to their silver color, good process ability, favorable cutting performance, fine anti-tarnish property and excellent corrosion resistance [2,3]. However, nickel is harmful to human health, and it may cause allergic by contacting with skin [4−7]. European and American countries have recently forbidden the application of nickel-containing products, and the rule about the content and release amount of nickel in products is getting stricter [8−10]. In order to replace the element nickel, the Japanese YKK Corporation has developed two nickel-free copper alloys, Cu−Zn−Mn and Cu−Zn−Ti [11−13]. They also made analysis on the heat treatment, mechanical property and cracking susceptibility. Only the values of a^* and b^* that present the color degree were used to describe the alloy chromaticity. The third value L^* that denotes the quality of lighting was ignored. In fact, L^* is the key parameter that determines alloy grey scale. Copper alloy has no white in its appearance as L^* drops under 70, no matter how closely a^* and b^* approach zero [14]. Meanwhile, there is no report from YKK about the research on their hot deformability and process technology. Hot deformation is such an important process that completely eliminates the dendrite structure in cast alloy, generates fine and uniform recrystallized grains, and greatly improves the mechanical properties and corrosion resistance of the alloy [15,16].

In this work, the hot deformation process of the designed Cu−12Mn−15Zn−1.5Al−0.3Ti−0.14B−0.1Ce (mass fraction, %) alloy with fine white chromaticity was investigated at different temperatures and strain rates using hot compression simulation. The constitutive

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equation and processing map of the alloy were established and the microstructure evolution during the hot-compression process was characterized.

2 Experimental

The designed Cu−12Mn−15Zn−1.5Al−0.3Ti−0.14B−0.1Ce alloy was prepared by traditional casting method and the traditional nickel white copper alloy (Cu−15Ni−24Zn−1.5Pb) was selected as a reference. The compositions of two alloys are listed in Table 1. The samples were cut into *d*10 mm×15 mm specimens for hot simulation test, which was conducted on a Gleeble−1500 machine at temperatures of 600, 650, 700, 750 and 800 °C and strain rates of 0.01, 0.1, 1 and 10 s^{-1}, respectively. The total hot deformation was 70%. After hot deformation the specimen was quenched by cold water immediately so that the hot deformed structure could be preserved. HP 200 precision color difference instrument was used to test the burnished alloy surface, and CIE1976LAB standard was applied to testing and calculating. Color difference was calculated based on the chromaticity of Cu−15Ni−24Zn−1.5Pb alloy surface, expressed as $\Delta E^*=[(L_d^*-L_w^*)^2+(a_d^*-a_w^*)^2+(b_d^*-b_w^*)^2]^{1/2}$, where L^* is the lightness, a^* is the red-green opponent, b^* is the yellow-blue opponent, subscripts d and w designate the designed sample and the traditional white copper, respectively. The microstructure was observed by a Leica EC3 metallurgical microscope.

Table 1 Compositions of designed alloy and referred alloy

Alloy	Mass fraction/%								
	Mn	Zn	Al	Ti	B	Ce	Ni	Pb	Cu
Cu−12Mn−15Zn−1.5Al−0.3Ti−0.14B−0.1Ce	12	15	1.5	0.3	0.14	0.1	−	−	Bal.
Cu−15Ni−24Zn−1.5Pb	−	24	−	−	−	−	15	1.5	Bal.

3 Results and discussion

3.1 Chromaticity and color difference

Table 2 shows the white chromaticity and color difference results of the designed and referred alloys. It can be seen that the two alloys have very similar white chromaticity. The color difference between them is less than 1.5, which can hardly be distinguished by human eyes.

Table 2 Chromaticity parameters and color differences of designed alloy and referred alloy

Alloy	Chromaticity parameter			Color difference
	L^*	a^*	b^*	ΔE^*
Cu−12Mn−15Zn−1.5Al−0.3Ti−0.14B−0.1Ce	86.45	−0.05	7.14	1.28
Cu−15Ni−24Zn−1.5Pb	87.50	0.26	6.48	−

3.2 Microstructure of as-cast alloy

The typical microstructure of the as-cast Cu−12Mn−15Zn−1.5Al−0.3Ti−0.14B−0.1Ce alloy before hot deformation is shown in Fig. 1, indicating that well-developed dendritic structure can be observed in grains.

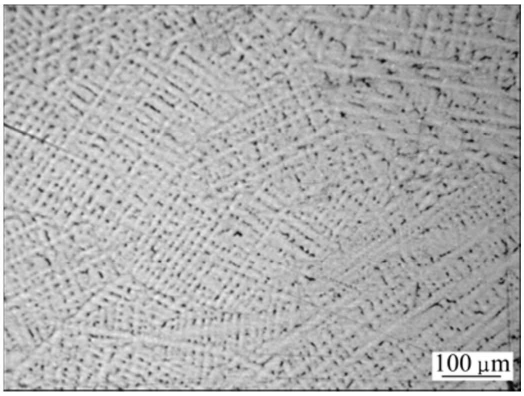

Fig. 1 Initial microstructure of as-cast Cu−12Mn−15Zn−1.5Al−0.3Ti−0.14B−0.1Ce alloy before hot deformation

3.3 Stress−strain behavior

Figure 2 shows the true stress−true strain curves of the designed alloy during hot deformation at different temperatures and strain rates. It can be seen that both deformation temperature and strain rate have great influence on alloy rheological behavior. At the same strain rate, the true stress decreases with increasing deformation temperature; while at the same deformation temperature, the true stress increases with increasing strain rate. Besides, the maximum true stress and the steady true stress both increase with the increase of strain rate and the decrease of deformation temperature, which can be attributed to a process balanced by work-hardening and dynamic recrystallization softening during hot compression. At high deformation temperatures (750−800 °C) and low strain rates (0.01−0.1 s^{-1}), the alloy can obtain enough heat energy or deformation energy. As the work-hardening made the true strain approach its top value, dynamic recrystallization occurred and soon got balanced with work-hardening, keeping the true stress stable [17,18]. Under other conditions, the dynamic recrystallization will not happen or could not happen completely because of insufficient energy, or energy releasing by dynamic recovery. The curves of true stress−strain demonstrated the difficulty to approach a dynamic balance.