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Grain refinement mechanism of as-cast aluminum by hafnium

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Abstract: The effect of Hf on the grain refinement of as-cast aluminum was investigated using optical microscopy, electron microscopy and X-ray diffraction. The result shows that the grain size of studied alloy decreases effectively with the addition of Hf, Hf can react with Al to form Al_3Hf particles during the solidification, the primary Al_3Hf particles are highly potent nucleants for Al and the nanoscale coherent Al_3Hf particles can inhibit the grain growth by pinning effect. The grain refinement mechanism of studied alloys was verified by the solute theory and the crystallography study, and it can be divided into two distinct types: At low Hf contents, there are no primary Al_3Hf phases to form, the acquired grain refinement is primarily attributed to the constitutional undercooling induced by the Hf solute. At medium and high Hf contents, both Hf solute and Al_3Hf particles contribute to the refinement.

Key words: grain refinement mechanism; aluminum alloy; casting; Hf; Al_3Hf

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1 Introduction

Aluminum and its alloys are attractive engineering materials for structural applications in many industries, because of the low density and good electrical conductivity, good resistance to corrosion, excellent thermal conductivity [1]. The properties of aluminum alloys are governed by many microstructural features including the grain size. Grain refinement of Al alloys is a predominant technique to control the metallurgical characteristics and to improve the soundness of cast alloys, which has been extensively investigated by many researchers for over 80 years [2−5]. It can get a fine equiaxed grain structure of α(Al) through grain refinement, which can eliminate the columnar structure, ensure uniform mechanical properties, improve formability and machinability, reduce casting defects and tearing tendency as well as enhance subsequent mechanical working response [6−11]. Grain refinement also has a significant impact on the aluminum conductors: a fine grain will give rise to high tensile strength based on the fine-grained strengthening theory, but it will increase grain boundary and therefore result in the decrease of electrical conductivity. Thus, it is important to study the mechanism of grain refinement in aluminum conductors.

Several methods have been reported to achieve grain refinement in the final microstructure, such as inoculation, heterogeneous nucleation, solute addition, mechanical agitation [3,10,12,13]. The addition of transition metals or rare earth metals, such as Sc and Zr, can refine the grain of as-cast Al alloys effectively [3,4,6,14]. This is because Zr or Sc can result in the formation of primary Al_3Sc or Al_3Zr phases as well as nanoscale coherent $L1_2$ structured Al_3Sc or Al_3Zr particles, which can behave as potent nucleant particles for Al or inhibit the migration of grain boundary or subboundary, thus will lead to the grain refinement [4,15−17]. The mechanisms of the grain refinement such as the solute theory (the growth restriction factor concept and the relative grain size concept) and the heterogeneous nucleation theory (the crystallographic using the edge-to-edge matching model) have been reported in

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many literatures [3,6,18−24]. It is widely believed that both effective nucleation particles and abundant solutes are indispensable for efficient grain refinement [6,25−28].

Similar to Sc or Zr, Hf can form the nanoscale coherent $L1_2$ structured Al_3Hf precipitate in Al matrix, which has been studied by WU et al [29]. However, up to now, few researches have been investigated in the published literatures about the grain refinement mechanism of as-cast alumnium by hafnium. In the present study, Al−Hf alloys with different Hf addition levels were prepared through conventional casting processes, the grain refinement mechanism was revealed and it can provide experimental evidence to understand the grain refining mechanism in cast metals through inoculation treatment.

2 Experimental

The experimental alloys with different Hf addition levels (0.1%, 0.15%, 0.2%, 0.3%, 0.4%, 0.5% and 0.6%, mass fraction) were prepared by diluting commercially pure aluminum with Al−10.45Hf master alloys (mass fraction, %). The raw materials were melted in a graphite crucible in a resistively heated furnace at 750 °C, after mechanical stirring the melt was cast into an iron water-cooled mould and cooled to room temperature to produce a *d*50 mm × 100 mm ingots. The chemical compositions of the investigated alloys were verified using ICP−MS analysis and listed in Table 1 (all compositions were in mass fraction unless otherwise noted).

Table 1 Compositions of experimental alloys (mass fraction, %)

Sample	Hf	Fe	Si	Cu	Mg	Al
Pure Al	0.001	0.021	0.0085	0.0032	0.0092	Bal.
Al−0.1Hf	0.09	0.047	0.011	0.0037	0.011	Bal.
Al−0.15Hf	0.16	0.034	0.013	0.0062	0.017	Bal.
Al−0.2Hf	0.21	0.022	0.014	0.0091	0.015	Bal.
Al−0.3Hf	0.29	0.048	0.010	0.0058	0.012	Bal.
Al−0.4Hf	0.38	0.025	0.017	0.0085	0.019	Bal.
Al−0.5Hf	0.47	0.041	0.008	0.0046	0.010	Bal.
Al−0.6Hf	0.59	0.062	0.007	0.0074	0.0099	Bal.

Approximately 10 mm sized metallographic specimens were taken from the cast ingots and were mechanically ground, polished by grit paper and then etched by a solution of 1 mL HF, 1.5 mL HCl, 2.5 mL HNO_3 and 95 mL distilled water. After sample preparation, the metallographic structures were characterized by optical microscopy (OM) and using the IPP (Image Pro-Plus) soft to measure the grain sizes. Phase identification was conducted by X-ray diffraction analysis in a SI-MENSD500 full-automatic X-ray diffractometer, operating at 40 kV and 45 A with Cu K_α radiation. Transmission electron microscope (TEM) and scanning electron microscope (SEM) observations were performed with a FEI Tecnai $G^2$20 operated at 200 kV and FEI Quanta-200, respectively. TEM samples were prepared by mechanical grinding specimens to a thickness of 80−100 μm, from which 3 mm diameter disks were punched. The disks were then thinned by twin-jet electro-polishing at ~20 V DC with an electrolyte solution consisting of 30% nitric acid and 70% methanol below −30 °C.

3 Results and discussion

3.1 Macrostructure and microstructure of as-cast aluminum alloys

Figure 1 shows the macrographs of as-cast aluminum grain refined with 0.1%, 0.15%, 0.2%, 0.3%, 0.4%, 0.5% and 0.6% addition level of Hf element, respectively. As illustrated in Fig. 1(a), in the absence of Hf, the aluminum manifests a mixture of complete coarse columnar grain structure at the periphery and coarse equiaxed grains at the center. After adding 0.1% Hf into pure aluminum, the average size of coarse columnar grains and equiaxed grains decrease, as shown in Fig. 1(b). Having a comparison among Figs. 1(c), (d) and (e), it is noted that the columnar grains change to equiaxed grains with the increase of Hf content, and the average grain size is also decreased. When the addition increases to 0.4%, as seen in Fig. 1(f), only fine equiaxed grains are observed. But further increasing the addition level of Hf, equiaxed grain size do not further decrease, as shown in Figs. 1(g) and (h).

The optical microstructures of the as-cast aluminum with different Hf contents are presented in Fig. 2. It can be obviously seen that the grains can be refined dramatically by adding Hf element. Without Hf addition, the average grain size is around 440 μm, with the increasing additions of Hf content from 0.1% to 0.3%, the average grain size decreases continuously from 434 to 251 μm. When 0.4% Hf is added, the average grain size reaches 219 μm, but further increasing the Hf contents from 0.4% to 0.6%, there is no significant improvement in the grain refinement. The smallest grains with the grain size of 196 μm are obtained when the addition reaches 0.6%.

3.2 Determination of relative grain size

The mechanisms of grain refinement such as the solute effect and the heterogeneous nucleation effect