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Effect of RE elements on the structure and impact toughness of sand-cast Zn–12%Al alloy

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Abstract

The effect of rare earth (RE) elements on the structure and impact toughness of sand-cast Zn–12wt.%Al (ZA-12) alloy was investigated systematically as the content of mischmetal (Ce + La > 75 wt.%) was varied. RE elements appear mostly in the form of clusters between the primary β dendrites or at the boundary of the eutectic η phases in faceted compounds, and in small amounts in the core of the primary β dendrite or in the eutectic η phases in the form of a solid solution. The secondary dendrite arm spacing (DAS_{II}) of the primary β dendrites decreases and the eutectic β phase changes from rods to short rods or granules with increasing RE content. The RE elements, and particularly the RE compounds, absorb the Fe impurity in the alloy. The impact toughness of sand-cast ZA-12, whether as-cast or heat-treated, tends to increase as the content of the RE elements increases, and is about twice that of the RE-free alloy at around 0.12 wt.% RE. It is suggested that the improvement of the impact toughness is related to the refinement of the grain size and the absorption of the Fe impurity by the RE elements in the alloy.

1. Introduction

Three types of gravity cast ZnAl alloys, Zn–8wt.%Al (ZA-8), Zn–12wt.%Al (ZA-12) and Zn–27wt.%Al (ZA-27), have been shown to have high competitiveness in the search for improved materials. However, their applications are limited because of the low ambient temperature toughness [1]. In order to improve the toughness of cast ZnAl alloys, some workers [2, 3] have adopted an enhanced cooling rate technique to refine the grain size and homogenizing heat treatments to enhance the decomposition of the supersaturated solid solution and the solid phase transformation, and have found that Pb and Fe impurities are harmful to the toughness of the alloys. Other workers [4–7] have added Ti, B, Zr, etc. to ZnAl alloys, which leads to refinement of the grain size, changes in the structural morphology and a substantial improvement in the ductility. The toughness of alloys is usually increased by an improvement in the ductility. However, the effect of additional elements on the structure and toughness of ZnAl alloys has not been investigated in detail, particularly in ZA-12 [6].

Rare earth (RE) elements have high chemical activity. It was shown in investigations of aluminium alloy [8] that RE elements can purify the melt, improve the foundry characteristics, modify the structure and increase the ambient or elevated temperature mechanical properties. As the primary α phase of ZnAl alloys is a Zn-containing aluminium-based solid solution, it is expected that RE elements in ZnAl alloys will have similar effects to that in aluminium alloys. Several studies [4–7] have indicated that RE elements in ZnAl alloys remove the impurities and refine the grain size. For this reason, it is possible to increase the toughness of ZnAl alloys using RE elements.

In this study, we investigate the modification, due to RE elements (cheap mischmetal), of the structure of sand-cast ZA-12 and the interaction of the RE elements with the Fe impurity. The effect of RE elements on the impact toughness is examined.

2. Experimental procedures

2.1. Alloy and melting

The binary ZnAl phase diagram is shown in Fig. 1 [9]. Chemical analysis of the ZA-12 alloy gives 11.99 wt.% Al, 0.77 wt.% Cu and 0.017 wt.% Mg. Mischmetal was added in various amounts: 0.00, 0.04, 0.08, 0.12 and 0.16 wt.%.

Melting of the alloy was carried out in a medium-frequency induction furnace. Commercially pure Mg (99.5%) was used to prepare the alloy. The melting procedure for the alloy followed that given by Gervais *et al.* [10]. When the alloy had melted and its temperature

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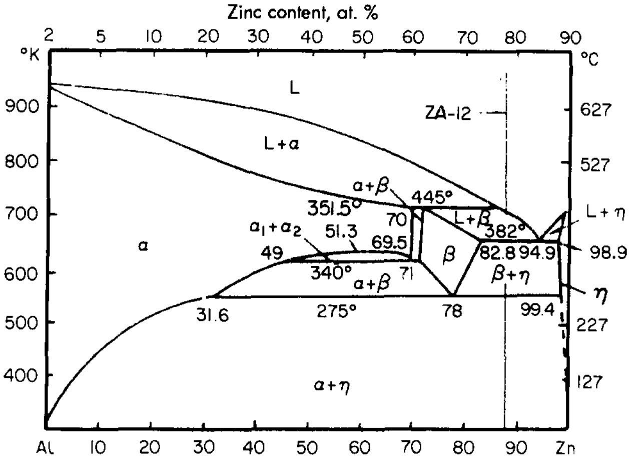

Fig. 1. Binary Zn–Al phase diagram [9].

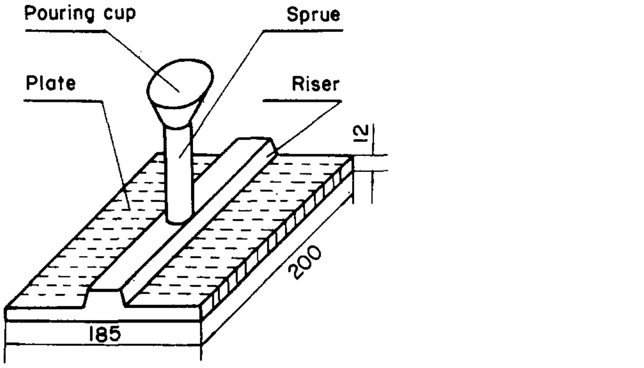

Fig. 2. Schematic diagram of the plate casting for impact specimen.

had risen to 650–700 °C, a certain quantity of the melt was transferred to a preheated ladle. Al–10%RE master alloys were added in batches to the melt in the furnace, and the same quantity of the melt was poured into the ladle immediately after each addition of master alloy; thus alloys were obtained having the same fundamental composition but different RE contents.

2.2. Casting and heat treatment

The mould pattern employed for studying the structure and impact toughness is shown in Fig. 2. The module of the riser, $(V/A)^2$, exceeds that of the plate by 1.2 [11]. The broken lines represent the cutting positions for the impact toughness specimens, which ensures a consistent solidification condition for each impact specimen. The pouring temperature was 500 °C and the demoulding time was 30 min [12]. The influence of the heat treatment temperature on the toughness [2] was examined by treating the specimens for 30 min at different temperatures (100, 180, 250 and 320 °C) in an electric resistant furnace, followed by cooling in the furnace.

2.3. Metallographic and property examinations

The metallographic and fractographic observations were made by scanning electron microscopy (SEM). Electron microprobe analysis was performed on a JSE-35 EDAX-9100 microprobe. The dendrite arm spacing (DAS_{II}) of the primary dendrites was randomly measured by light microscopy, and averaged over 50 locations in each specimen. All the specimens analysed were taken from the centre of the impact specimens, and etched in an alcohol–4% HCl solution. The 10 mm×10 mm×55 mm un-notched Charpy impact specimens were machined following the broken lines in Fig. 2. Each impact value represents the average of five to seven specimens.

3. Results and discussion

3.1. Formation of RE compounds in the alloy

RE elements appear mostly as RE compounds which are distributed in the alloy in the form of clusters (Figs. 3(a) and 3(b)). Large particles of RE compounds are found between the primary β dendrites (Fig. 3(a)). Small particles of RE compounds are present at the boundary between two eutectic η phases (Fig. 3(b)). Their dimensions, which were roughly estimated, vary in the range 1–10 μm. The large particles have a faceted morphology, whereas the small particles seem to be more spherical. As shown in Table 1, these particles are rich in Zn and Al, and contain 3.5 wt.% La and 12.0 wt.% Ce. The Fe content in the particles exceeds the average Fe value of the alloy which is in agreement with previous work [5]. These particles were suggested to be intermetallic compounds [13]. According to electron microprobe analysis (Table 1), the chemical formula is Zn_8Al_7RE which corresponds to 48 at.% Zn, 42 at.% Al and 6 at.% RE.

Small amounts of RE elements form a solid solution in the core of the primary β dendrites and in the eutectic η phase. The dendrite core contains 0.40 wt.% La and 0.63 wt.% Ce, whereas the eutectic η phase contains 0.19 wt.% La and 0.32 wt.% Ce. La and Ce in the solid solution coexist with a relatively high Fe content.

3.2. Effect of RE elements on the structure

The structure of sand-cast ZA-12 is modified and refined by RE elements. When the RE content is increased to 0.16 wt.%, DAS_{II} is reduced from 24.30 μm to 19.63 μm (Fig. 4) which agrees with the results of Skenazi *et al.* [4] and Luo *et al.* [5], confirming the refining effect of RE elements. It can be seen in the as-cast structure of the RE-free alloy (Fig. 5) that the eutectic β phases are chiefly present in rods. According to the ZnAl alloy phase diagram (Fig. 1), the volume

TABLE 1. Electron microprobe analysis of the phases present in sand-cast ZA-12

Alloy	Phase	Zn (wt.%)	Al (wt.%)	Cu (wt.%)	La (wt.%)	Ce (wt.%)	Fe (wt.%)
RE-free	Dendrite core	66.39	32.64	0.94			–
	Dendrite shell	67.22	31.42	1.15			0.21
	Eutectic η phase	94.17	4.31	1.74			–
	Eutectic β phase	70.29	28.46	1.17			–
0.12 wt.% RE	Dendrite core	62.99	34.59	1.18	0.40	0.63	0.21
	Dendrite shell	84.32	13.38	2.09	–	–	–
	Eutectic η phase	89.74	7.23	2.35	0.19	0.32	0.18
	Eutectic β phase	81.51	16.06	2.34	–	–	–
	RE compound	65.71	15.85	1.65	3.49	11.89	1.40

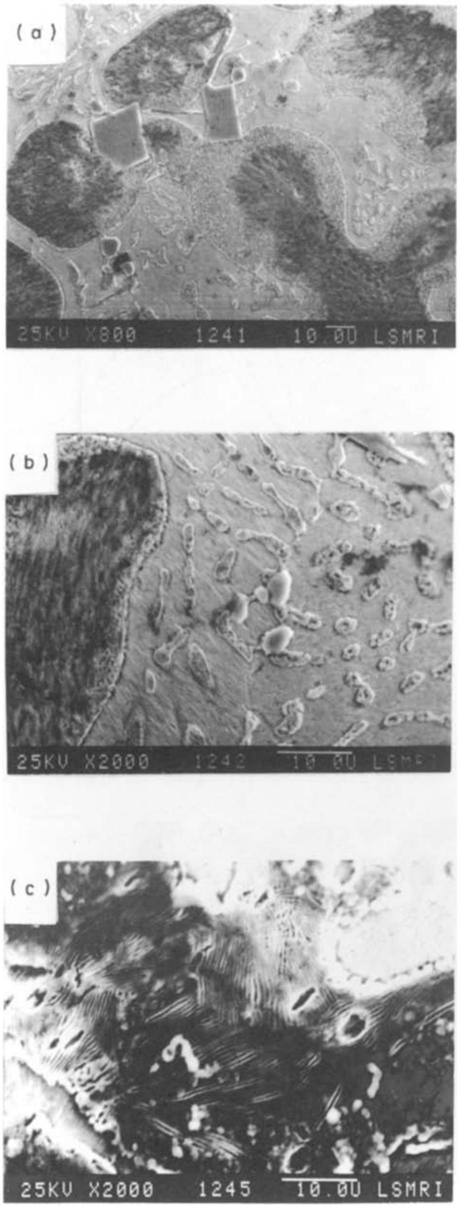

Fig. 3. Scanning electron micrographs of sand-cast Za-12–10.12wt.%Re: (a, b) as cast; (c) 320 °C for 3 h, furnace cooling.

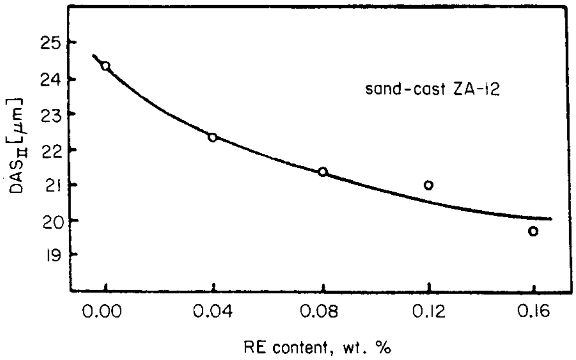

Fig. 4. Effect of RE elements on DAS$_{II}$ of sand-cast ZA-12.

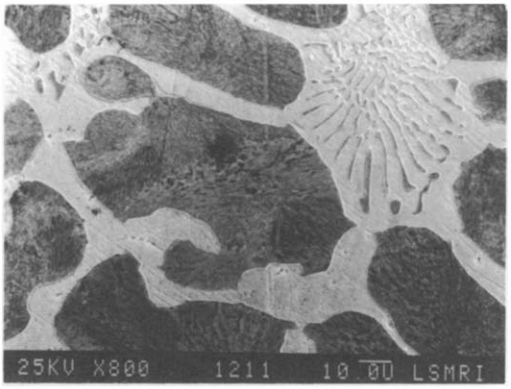

Fig. 5. Scanning electron micrograph of as-cast, sand-cast RE-free ZA-12.

fraction of the eutectic β phase is about 29% and less than $1/\pi$, which reaches the condition for the formation of rods, so giving the morphology shown in Fig. 5. However, with the addition of RE elements, the eutectic β phase takes the form of short rods or granules (Figs. 3(a) and 3(b)), indicating a change in the solidification process. This observation is supported by a study on the growth of eutectic carbides in white cast iron of the chromium family in which Liang and Su [14] reported that the length of the carbides was shortened with an increase in RE elements. It is supposed that the microsegregation of RE elements during solidification of the alloy results in constitutional supercooling which partially remelts the dendrite [15]. Furthermore, the structural examination shows that the volume fraction of the eutectic β phase tends to decrease with increasing RE content.

RE elements intensify the microsegregation of the primary β dendrites and lower the Al content of the eutectic β phase. As indicated in Table 1, the shell of the dendrite contains 13.38 wt.% Al which is much different from the core (34.59 wt.% Al) where the RE content reaches 0.12 wt.%. The eutectic β phase contains 16.06 wt.% Al, which is much lower than the Al content of the RE-free alloy (28.46 wt.% Al). If the alloy contains RE elements, a much thicker shell of primary β dendrite appears in the granular eutectoid colonies, while the core is present in lamellar form (Fig. 3(a)); the lamellar eutectoid structure prevails in the primary dendrites of the RE-free alloy (Fig. 5). It is clear that this difference is related to the microsegregation within the primary dendrite. Owing to dendrite microsegregation, enhanced by the addition of RE elements, the much thicker shell of primary dendrite is supersaturated within the $(\beta+\eta)$ phase region, which leads to the precipitation of secondary η phase (η_{II}) with decreasing temperature. Once the temperature falls below the eutectoid point, the shell forms a granular eutectoid structure through nucleation and growth on the η_{II} particles, while the core becomes lamellar as a result of the absent η_{II} nucleus. After homogenization at 320 °C for 3 h, the particles dissolve into the primary dendrites and dendrite microsegregation is reduced because of atomic diffusion. During subsequent furnace cooling, the lamellar eutectoid structure forms throughout the primary dendrite, while the granular eutectoid structure almost disappears (Fig. 3(c)).

RE elements, particularly RE compounds, absorb the Fe impurity (Table 1). The ZnAl alloys are highly sensitive to Fe. Needles of $FeAl_3$ will appear if the Fe content exceeds 0.05 wt.% and the toughness and ductility of ZnAl alloys will be reduced [3]. The Fe atoms can be absorbed when RE elements exist in the primary dendrite or in the eutectic η phase. Fe absorption is particularly effective when RE elements form faceted RE compounds which can accommodate a high Fe content (up to about 1.4 wt.%), thus decreasing the opportunity for Fe to form $FeAl_3$ needles. Although the RE compounds may be brittle, the faceted morphology has much less effect on the toughness than the needle morphology of the $FeAl_3$ compounds.

It should be noted that separate eutectics exist in the alloy whether it contains RE or not (Figs. 3(a) and 5). The separate eutectics form because the eutectic β phase nucleates readily and grows around the primary dendrite in the narrow space between the primary dendrites and the secondary dendrites. This phenomenon has been described previously [16].

3.3. Effect of RE elements on the impact toughness

It is shown in Fig. 6 that the impact toughness of sand-cast ZA-12 varies with the addition of RE elements for different heat treatments. Whether as-cast or heat-treated, the impact toughness tends to increase with the addition of RE elements and is about twice that of the RE-free alloy when the RE content reaches around 0.12 wt.%. The fracture surfaces in the RE-free as-cast alloy are present in a quasi-cleavage manner, showing flat facets and thin stretching lines in the surrounding facets (Fig. 7). This indicates that less ductile tearing is associated with the fracture of the RE-free alloy. The fracture surfaces of the RE-containing as-cast alloy mainly show many fine dimples (Fig. 8), which suggests that the ductile deformation of these microregions contributes to the improvement in the impact toughness. RE elements refine the primary

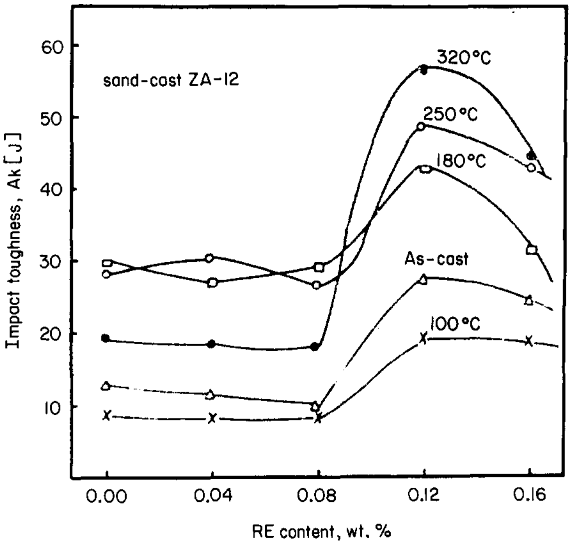

Fig. 6. Effect of RE elements on the impact toughness.

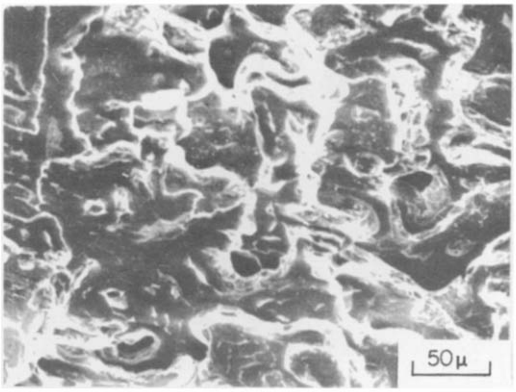

Fig. 7. Scanning electron fractograph of as-cast, sand-cast RE-free ZA-12.

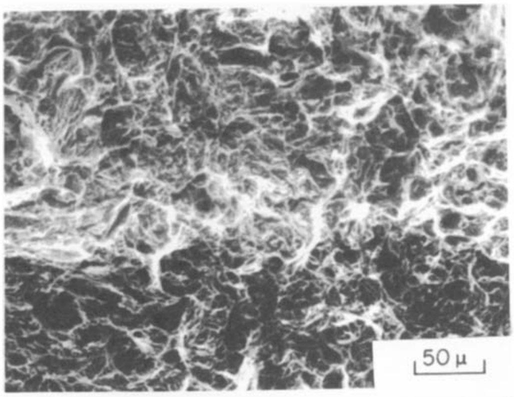

Fig. 8. Scanning electron fractograph of as-cast, sand-cast ZA-12–0.12wt.%RE.

dendrites and the eutectic β phase. Consequently, a high strain energy is needed for fracture because of a change in fracture mode from interdendritic (brittle) to transdendritic (ductile) [2]. In addition, the Fe content of ZnAl alloys has a large effect on the impact toughness [3]. RE elements and RE compounds absorb large amounts of Fe, which decreases the amount of $FeAl_3$ needles, resulting in an improvement in the impact toughness. These two aspects are considered to be the main reasons for the increase in the impact toughness. However, microcracks on the fracture surface in Fig. 8 can be seen, which are associated with the brittle nature of the RE compounds. Excessive addition of RE elements, for example over 0.16 wt.%, will cause the impact toughness to decrease. Furthermore, microshrinkage was discovered on the fracture surfaces of all specimens, which limits the improvement in the impact toughness [3].

4. Conclusions

(1) Most of the RE elements in sand-cast ZA-12 alloy form faceted RE compounds which are distributed in the form of clusters between the primary β dendrites or at the boundary of the eutectic η phase. A few exist in the form of a solid solution in the core of the primary β dendrite or in the eutectic η phase.

(2) RE elements shorten the DAS_{II} of the primary dendrites and change the eutectic β phase from long rods to short rods or granules. RE elements enhance the microsegregation of the primary β dendrite and affect the morphology of the eutectoid structure.

(3) RE elements, particularly RE compounds, absorb the Fe impurity in ZnAl alloys.

(4) Whether as-cast or heat-treated, the impact toughness of sand-cast ZA-12 tends to increase with an increase in RE content. When the RE content reaches 0.12 wt.%, the impact toughness is twice that of the RE-free alloy. The improvement is due to the RE elements which refine the grain size and absorb the Fe impurity in the alloy.

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