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Effects of Ca addition on the microstructure and mechanical properties of AZ91magnesium alloy

WANG QUDONG, CHEN WENZHOU, ZENG XIAOQIN, LU YIZHEN, DING WENJIANG, ZHU YANPING, XU XIAOPING
The State Key Laboratory of Metal Matrix Composites, Shanghai Jiaotong University, Shanghai 200030, People's Republic of China
E-mail: wangqd@hotmail.com

M. MABUCHI
National Industrial Research Institute of Nagoya, Hirate-cho, Kita-ku, Nagoya 462-8510, Japan

The effects of Ca addition on the microstructure and mechanical properties of AZ91 magnesium alloy have been studied. The results show that the Ca addition can refine the microstructure, reduce the quantity of $Mg_{17}Al_{12}$ phase, and form new Al_2Ca phase in AZ91 magnesium alloy. With the Ca addition, the tensile strength and elongation of AZ91magnesium alloy at ambient temperature are reduced, whereas Ca addition confers elevated temperature strengthening on AZ91 magnesium alloy. The tensile strength at 150°C increases with increasing Ca content. The impact toughness of AZ91magnesium alloy increases, and then declines as the Ca content increases. The tensile and impact fractographs exhibit intergranular fracture features, Ca addition changes the pattern and quantity of tearing ridge, with radial or parallel tearing ridge increasing, tensile strength, elongation and impact toughness reduce.

1. Introduction

Magnesium alloys have been widely used in automobile, electronics and aerospace industries due to their low density, high specific strength and specific stiffness, superb damping capacity, excellent machinability and good castability [1]. However, only a small amount of research and development has been carried out on them in comparison with that for aluminum alloys. The restrained application of magnesium alloys is attributable to: the ignition and combustion of the alloys during melting and casting, the complicated process of melting and their relatively poor elevated temperature properties and corrosion resistance [2].

It was found that small addition of Ca to a magnesium alloy can increase its strength and corrosion resistance [3, 4], but addition of Ca above 1% decreases the strength and elongation of the Mg-Ca binary alloy [5]. Additionally, Ca addition improves the elevated temperature properties of magnesium alloys [6], but also promotes hot tearing [7]. Small addition of Ca can refine the grain size, disperse Mg_2Si [2], and break down the dendritic morphology of the Mg_2Si into round and well-distributed small particles [8]. On the other hand, the addition of Ca is also effective for prevention of ignition and oxidation of the magnesium alloy during melting [9, 10]. Researchers in Japan are making efforts to fabricate ignition-proof magnesium alloys containing Ca [11–14]. At present, new types of industrial magnesium alloys containing Ca have been developed [15], and Mg-Al-Ca ternary alloys with ultrahigh tensile strength (as high as 500 MPa) have been fabricated via rapidly solidified powder metallurgy [16]. However, research concerning the effects of Ca on magnesium alloys is still limited. AZ91 magnesium alloy is the most widely used magnesium alloy to date, so the effects of Ca on the microstructure and mechanical properties of AZ91 are examined.

2. Experimental

The present alloys were prepared using AZ91 alloy ingots and the metal Ca. Table I shows the chemical compositions of the alloys. The melting was carried out in a 20 kg resistance crucible furnace, and Ca was added at 600–650°C. The melt of the magnesium alloy was refined at 720–730°C and then held for 20 min before pouring. A cover flux was added before charging and during melting to prevent ignition.

Ambient temperature tensile specimens with a diameter of 16 mm were cast in a metal mould. The same specimens were machined to manufacture double threaded tensile specimens with a diameter of 5 mm, which were used for elevated temperature tensile tests as same as before [17]. Impact specimens without notch were cast to $10 \times 10 \times 70$ mm in a metal mould and used to test the impact toughness of the alloys at ambient temperature. The ambient and elevated temperature tensile tests were carried out on a SHIMADZU AG-100KNA materials testing machine at a tensile speed of 1 mm/min. The impact toughness was measured using an XJJ-50J impact testing machine. The microhardness was measured using an MHT-1 microhardness tester under a 10-g load. Brinell hardness was measured using

TABLE I Chemical compositions of used alloys (wt%)

	Al	Zn	Mn	Ca	Be	Fe	Cu	Si	Ni
AZ91	8.12	0.923	0.142	—	0.00067	0.0148	<0.004	0.0607	0.0042
AZ91 + 0.5Ca	7.95	0.887	0.165	0.40	0.00052	0.0099	<0.004	0.0549	<0.0017
AZ91 + 1.0Ca	7.67	0.828	0.173	0.98	0.00046	0.0125	<0.004	0.0513	<0.0017
AZ91 + 2.0Ca	7.33	0.839	0.172	1.92	<0.00027	0.0130	<0.004	0.0503	0.0032

a 69-6 optical hardness tester under a load of 62.5 kN, a pressure head diameter of 2.5 mm and a loading time of 30 ± 2 s.

Metallographic specimens were prepared for microstructural analyses from cross sections of the calibrated parts of the ambient temperature tensile specimens. The phases in the specimens were identified by means of a D/MAX-IIIA X-ray diffractometer. The tensile and impact fractographs were obtained in PHILIPS SEM515 and S520 scanning electron microscopes (SEMs). The compositions of the phases were analyzed quantitatively using an energy-dispersive spectroscopy (EDS) facility attached to the S520 SEM.

3. Results and discussion

3.1. The effects of Ca addition on the microstructure

Fig. 1 shows the effects of Ca addition on the microstructure of AZ91. It is evident that the Ca addition refines the dendrite cell size. The cell size and the size of $Mg_{17}Al_{12}$ phases on grain boundaries in the alloys decrease with increasing Ca content. With the addition of Ca, the $Mg_{17}Al_{12}$-Mg co-operative eutectic has a reduced quantity or disappears and a new Al_2Ca phase (light gray, also identified by EDS) is formed. On increasing Ca content in AZ91, the amount of the $Mg_{17}Al_{12}$ phase decreases while the amount of Al_2Ca phases increases, and the Al_2Ca phase tends to distribute reticularly along cell boundaries.

As just noted, Al_2Ca phase is formed on Ca addition, but no Mg_2Ca formed in the specimens. Fig. 2 shows the result of X-ray diffraction analyses of AZ91 + 2.0Ca alloys. The microhardnesses (HV) of $Mg_{17}Al_{12}$, Al_2Ca and the matrix are 102–114, 77–85 and 59–70 kg/mm^2, respectively.

It was found that the addition of Ca decreases the quantity of the $Mg_{17}Al_{12}$ phase. This result is due to the following reasons: (1) the solubility of Ca in magnesium at room temperature is very low; (2) no Mg_2Ca phase is formed by Ca addition (verified by the X-ray diffraction analyses); (3) one unit (in mass) of Ca will consume 1.35 units (in mass) of Al when the Al_2Ca phase is formed (computed by the molecular formula).

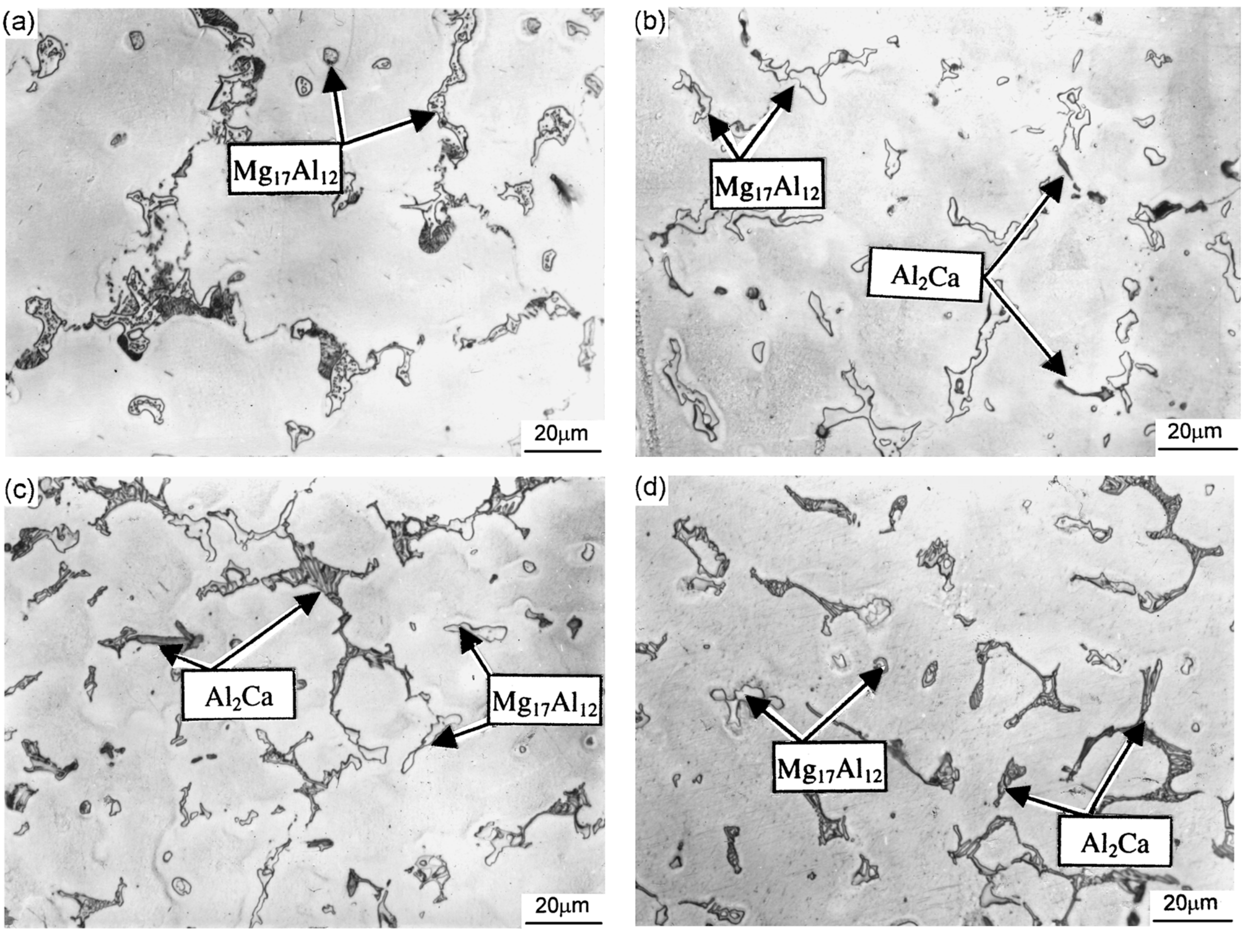

Figure 1 Effects of Ca addition on the microstructure of AZ91 alloy. (a) AZ91, (b) AZ91 + 0.5Ca, (c) AZ91 + 1.0Ca, (d) AZ91 + 2.0Ca.

TABLE II Effects of Ca addition on mechanical properties of AZ91 alloy

	25°C		100°C		150°C		
Alloy	σ_b (MPa)	δ (%)	σ_b (MPa)	δ (%)	σ_b (MPa)	δ (%)	A_k(J)
AZ91	162.0	2.1	132.2	3.4	102.2	7.8	13.3
AZ91 + 0.5Ca	157.2	2.0	130.0	3.3	106.6	7.2	14.5
AZ91 + 1.0Ca	152.3	1.8	128.0	3.5	110.0	7.0	19.5
AZ91 + 2.0Ca	147.4	1.7	131.0	3.2	112.0	6.8	13.0

σ_b: tensile strength, δ: elongation, A_k: impact toughness.

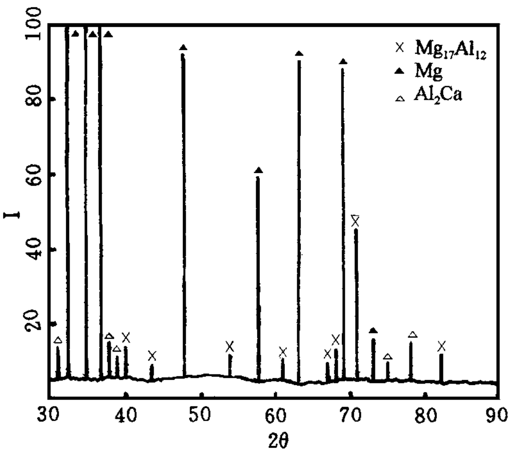

Figure 2 Result of X-ray diffraction analyses on AZ91 + 2Ca alloy.

3.2. The effects of Ca addition on the mechanical properties

The influences of Ca addition on the tensile properties of AZ91 are shown in Figs 3–5 and Table II. The ambient temperature tensile strength and elongation to fracture of AZ91 decrease with increasing Ca content (Fig. 3). When temperature increases, the tensile strength and elongation at 100°C change a little; at 150°C, the tensile strength of AZ91 increases with increasing Ca content while elongation decreases slightly. Table II shows an arresting result. When temperature is at 25°C, 100°C, 150°C, the tensile strength of AZ91 is 162.0 MPa, 132.2 MPa, 102.2 MPa, respectively. When temperature increases from 25°C to 100°C, 150°C, the tensile strength of AZ91 reduces with 29.8 MPa, 59.8 MPa, respectively. With Ca content increasing, the reduction of tensile strength of Mg alloys resulting from temperature elevating declines. When temperature increases from 25°C to 100°C, 150°C, the reduction of tensile strength of AZ91 + 2.0Ca is just 16.4 MPa, 35.4 MPa, respectively.

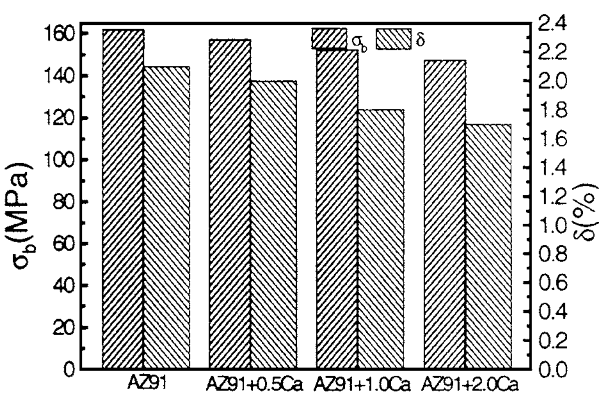

Figure 3 Effects of Ca addition on the ambient temperature tensile properties. σ_b: tensile strength, δ: elongation.

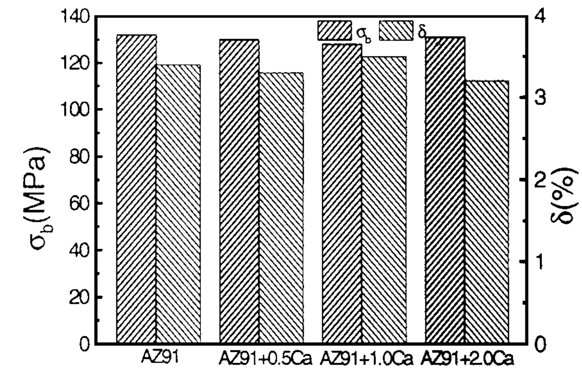

Figure 4 Effects of Ca addition on the tensile properties at 100°C. σ_b: tensile strength, δ: elongation.

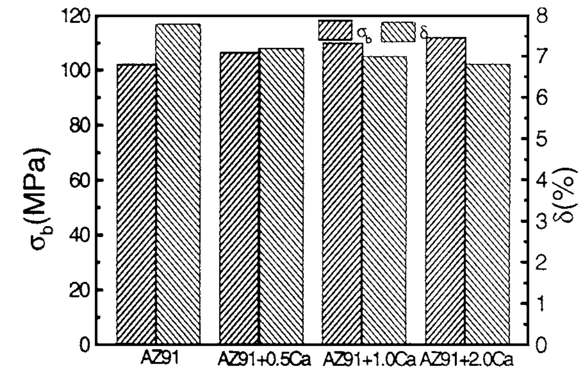

Figure 5 Effects of Ca addition on the tensile properties at 150°C. σ_b: tensile strength, δ: elongation.

As discussed above, the addition of Ca forms a new Al_2Ca phase and decreases the quantity of the $Mg_{17}Al_{12}$ phase. However, due to the low strength of the Al_2Ca phase and its reticular distribution along cell boundaries, which is harmful to mechanical properties. As a result, when Ca content increases, the ambient temperature tensile strength and elongation are impaired.

The mechanical properties of AZ91 alloy decrease rapidly at temperatures above 100°C (Figs 3–5). This behavior is attributed to the fact that magnesium alloys undergo creep mainly by grain-boundary sliding, and the main strengthening phase is $Mg_{17}Al_{12}$ in AZ91, which has a low melting point (437°C) and poor thermal stability. $Mg_{17}Al_{12}$ phase can readily coarsen and soften at the temperatures exceeding 120–130°C, and does not serve to pin the grain boundaries. In addition, $Mg_{17}Al_{12}$ has a cubic crystal structure incoherent with the *h.c.p.* magnesium matrix, which leads to the fragility of $Mg/Mg_{17}Al_{12}$ interface [17]. All of the above lead to the poor elevated temperature tensile properties of AZ91 alloy (Figs 4 and 5, Table II).

Addition of Ca to AZ91 formed Al_2Ca precipitation in the alloy. Al_2Ca has much high melting point (1079°C) and thermal stability [18]. On the other hand, the amount of $Mg_{17}Al_{12}$ reduces after Ca addition. As a result, sliding of grain boundaries and growth of cracks were effectively prevented at elevated temperatures, the reduction of tensile strength of Ca containing Mg alloys resulting from temperature elevating declines, even tensile strength at 150°C increases with Ca content increasing (Fig. 5), and obvious elevated temperature strengthening effect was obtained. However, large amount of reticular Al_2Ca formed along cell boundaries when excessive Ca was added cuts apart the alloy matrix, which results in the decrease or a little change of elevated temperature tensile strength and elongation with Ca content increasing (Figs 4 and 5)

Fig. 6a through (c) shows the fractographs of the ambient temperature tensile specimens with different Ca content. Fig. 6a shows that plastic deformation is limited in AZ91 alloy, which exhibits intergranular fracture features with some secondary cracks (see arrowheads at A) on it. Additionally, the dimpled quasi-cleavage fracture is also observed in some parts (Fig. 6a, at B of middle), there are some small cleavage steps in the quasi-cleavage dimples, which are connected by the tearing ridges of different size. With Ca addition into AZ91, the tearing deformation zone (at C in Fig. 6) enlarges, and the orientation of tearing ridges becomes more obvious, but fractographs retain intergranular fracture features. In Fig. 6b, the orientation of tearing ridges is a little random, in Fig. 6c, the tearing ridges behavior radial patterns (arrowheads indicate the radial direction). Radial patterns result from shear deformation and fast tearing with low energy when crack comes to critical size. Cracks propagate along the radial direction of tearing ridges. At this time, the macroscopically plastic deformation is very small, it is a kind of brittle fracture macroscopically, but there is a lot of plastic deformation in microscopically local area. As a result, the tensile strength and elongation reduce with Ca content increasing (Fig. 3).

The effects of Ca on the impact toughness of AZ91 are shown in Fig. 7 and Table II. The impact toughness

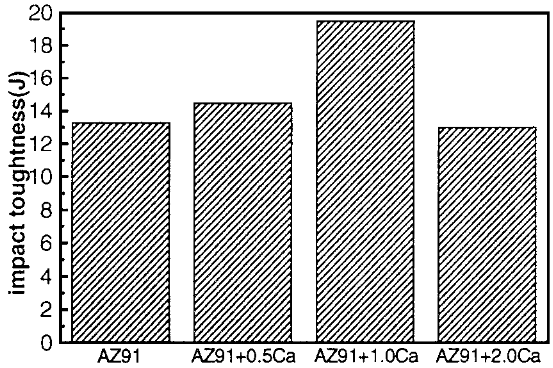

Figure 7 Effects of Ca addition on the impact toughness of AZ91 alloy.

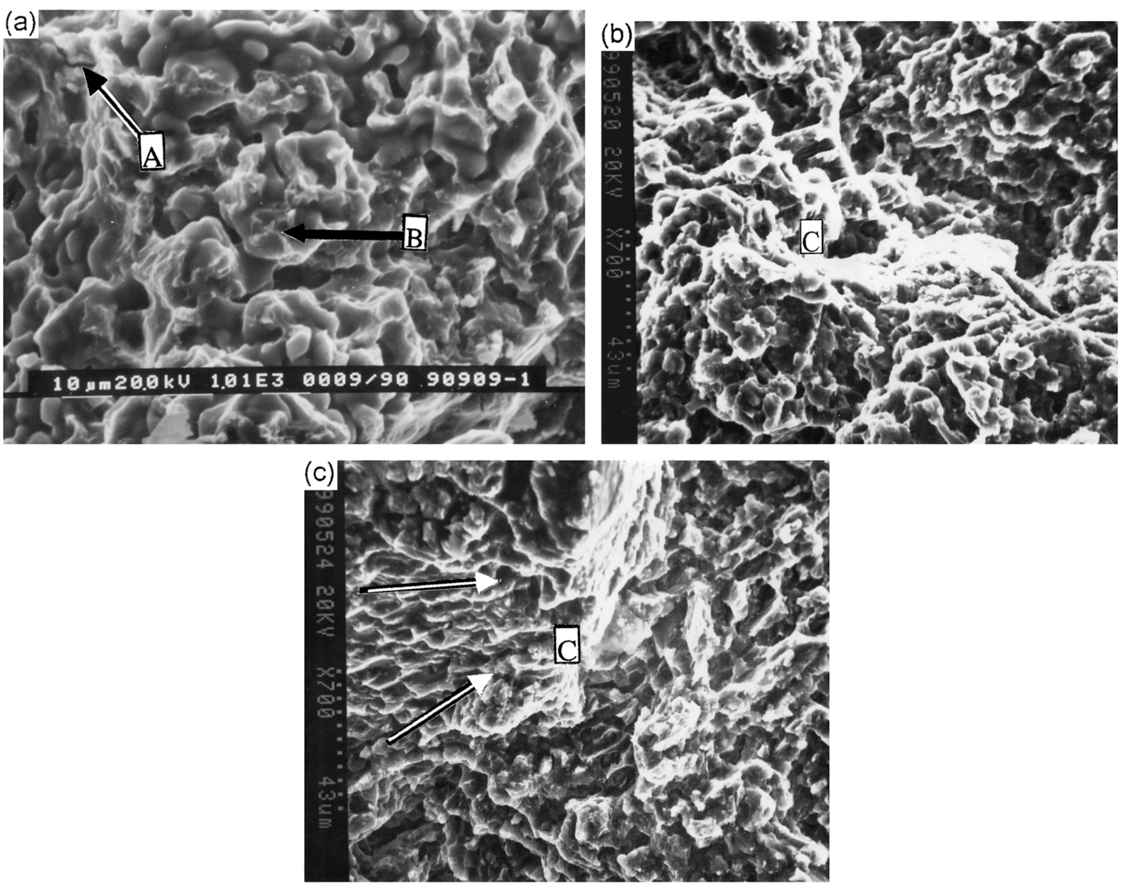

Figure 6 Effects of Ca addition on the tensile fractographs of AZ91 at ambient temperature. (a) AZ91, (b) AZ91 + 0.5Ca, (b) AZ91 + 2.0Ca.

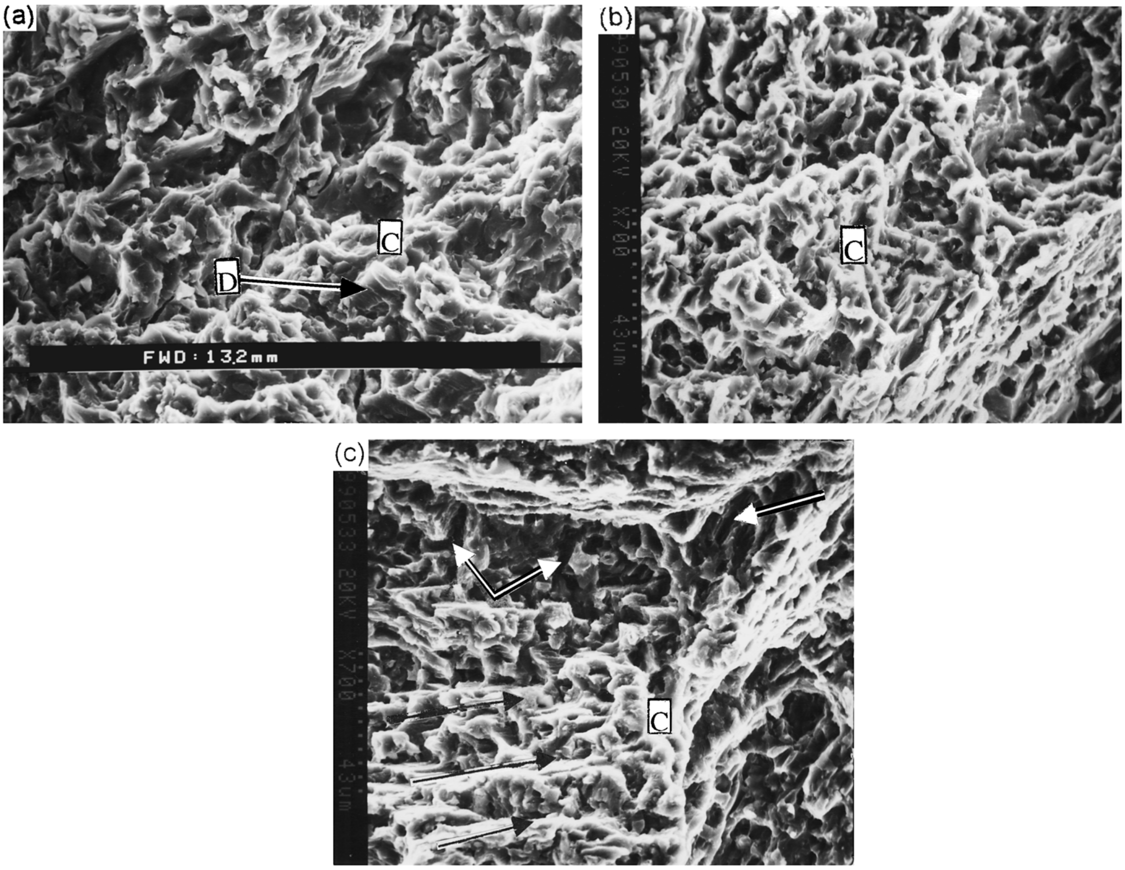

Figure 8 Effects of Ca addition of the impact fractographs of AZ91 alloy. (a) AZ91, (b) AZ91 + 0.5Ca, (b) AZ91 + 2.0Ca.

increases from 13.3J (AZ91) to 19.5J (AZ91 + 1.0Ca) and decreases to 13.0J (AZ91 + 2.0Ca) with increasing Ca content. The improvement of impact toughness by small addition of Ca ($\leq$1.0wt%) is considered to be due to the refinement of the cells and of the $Mg_{17}Al_{12}$ phase on cell boundaries. When Ca content is above 1.0wt%, the increasing amount of Al_2Ca compound that reticularly distributes along cell boundaries causes a drop in the impact toughness.

Fig. 8a–c shows the effects of Ca on the impact fractograghs of AZ91. They behavior in different intergranular fracture patterns. Fig. 8a shows that the impact fractograph of AZ91 has more cleavage steps (at D in Fig. 8a) and tearing ridges (at C in Fig. 8) than its tensile fractograph. Fig. 8b shows that the grain cells are refined and the amount of tearing ridges increases with 0.5wt%Ca addition, but there is not orientation for tearing ridges. At this time, impact toughness increases. Fig. 8c shows that tearing ridges behavior radial even parallel patterns(black arrowheads indicate the tearing direction), which results from fast tearing with low energy when crack comes to critical size. Some sunken pits remain after interface decohesion between compound phase/matrix (see white arrowheads in Fig. 8c). As a result, the impact toughness reduces again.

4. Conclusions

The following results were obtained from the present investigation:

1. Ca addition to AZ91 magnesium alloy refines the dendrite cell size and the $Mg_{17}Al_{12}$ phase. With Ca addition, a new Al_2Ca phase is formed and the amount of the $Mg_{17}Al_{12}$ phase decreases. The Al_2Ca phase has an increasing tendency of reticular distribution along cell boundaries with increasing Ca content.

2. The ambient temperature tensile strength and elongation of AZ91 both decrease with increasing Ca content. However, with Ca content increasing, the reduction of tensile strength resulting from temperature elevating declines, and the tensile strength at 150°C increases with increasing Ca content.

3. The impact toughness of AZ91 magnesium alloy increases firstly, and then declines as the content of Ca increases.

4. The tensile and impact fractographs of the studied magnesium alloy exhibit intergranular fracture features. For tensile fractographs, tearing ridges behavior more obvious radial patterns and their amount increases with Ca content increasing, which reduces the ambient temperature tensile strength and elongation. For impact fractographs, the amount of tearing ridges without orientation increases first, and then tearing ridges behavior radial or parallel patterns with Ca content increasing, which leads to impact toughness increasing first, and then reducing with Ca content increasing.

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