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Investigation of Ca in the Microstructural Evolution and Porosity Analysis of ZK60 Alloy in As-Cast and Extruded Conditions

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ABSTRACT

This research work has been carried out to study the effect of different Ca contents (0.5, 1.0, 1.5, 2.0 and 3.0) on the microstructure and porosity content of ZK60 alloys. The samples were examined by using optical and scanning electron microscopy (SEM) to evaluate the modification efficiency of the alloy with different Ca concentrations. The cast specimens were modified, homogenized and extruded at 350 °C at an extrusion ratio of 12:1. The experimental results showed that the addition of Ca brings about the precipitation of a new phase and refines the as-cast grains. It was also found that the presence of Ca at higher concentrations (>2 wt. %) results in the formation of hard Ca-rich intermetallics segregated in cell boundaries. Hot-extrusion was found to be powerful in breaking the eutectic network and changing the size and morphology of Ca-rich intermetallic phase. By applying the extrusion process and increasing Ca concentration (up to 2.0 wt. %), the porosity percentage decreased from 13.62% to 6.34% and 7.11% to 3.89% for ZK60 and ZK60+3%Ca alloys, respectively.

1. Introduction

The combination of low density and moderate strength makes magnesium (Mg) alloys preferable for applications in which light weight becomes a critical issue, such as applications in the automobile and aerospace industries [1]. The need for weight reduction of structural applications, particularly in the aerospace industry where the implementation of lighter structures is associated with energy saving policies, has led to an increasing interest in the development of lightweight metals over the last years. Magnesium alloy is the lightest structural material with high specific strength, good damping capacity and cast-ability [2-3]. Besides, due to the HCP structure of magnesium, its ductility is relatively poor. In order to achieve more substantial structural applications, it is necessary to develop wrought magnesium alloy products such as rolled sheets, extruded bar and forgings. Compared with aluminum alloys, they have low tensile strength and poor plasticity. Recently, it has been reported [4–8] that rare earth (RE) additions can improve casting characteristics, corrosion resistance and high temperature tensile properties. The effects of RE on the tensile properties of ZK60 alloy have also been studied [9]. For the application of extruded Mg alloys, it is necessary to have not only high strength but also good extrude-ability of materials because the extrusion speed is directly related to productivity. Although ZK60 alloy, which is one of the commercial Mg alloys, has been widely used due to its good combination of strength and ductility, the applications of ZK60 alloy processed by extrusion have

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been very limited due to their low extrusion speed [10], which is attributed to the low incipient melting temperature of ZK60 alloy induced by the low melting temperature of the Mg–Zn phase.

Due to thermally stable $Ca_2Mg_6Zn_3$ intermetallic particles and strong ageing response, Mg-Zn-Ca base alloys show superior creep resistant properties [11-12]. Previous research studies have found that Ca additions in Mg-Zn alloys significantly refine the microstructure, weaken the basal texture and improve the formability [13-15]. In the present work, Mg-6%Zn-0.7%Zr (ZK60) alloys containing different amounts of Ca were produced by extrusion to produce a non-dendritic microstructure. Indeed, the main objective of the current research study is to clarify the role of Ca elements in the formation of precipitates in Mg-Zn-Zr base alloys and to describe microstructural evolution for ZK60-X%Ca alloys.

2. Experimental Procedure

The base material which was used in the current study is a kind of high-strength ZK60 (Mg-6%Zn-0.7%Zr) magnesium alloy. The chemical composition of base ZK60 alloy is listed in Table 1. The alloys were made by melting high-pure magnesium in an electric resistance furnace, and then X%Ca, 6.0 wt. %.Zn and 0.7 wt. % Zr were added under the protection of sulphur hexafluoride SF_6 and CO_2, as a potent and persistent mixture of greenhouse gases. The weight loss of magnesium was selected to be 5%. Zinc and calcium were added as Mg–50 wt. % Zn and Mg–20 wt. % Ca master alloys. The molten alloys were held at 740 °C for 10 min. to ensure the dissolution of all alloying elements. Having been stirred and kept for 40–50 min., the molten alloys were cast into cylindrical ingots at room temperature. Cylindrical castings were cut into billets (30 mm in diameter and 30 mm in height) in order to fit into the extrusion container. These billets were heat treated by high accuracy temperature controlled by electrical resistance furnace (±2 °C). The specimens were homogenized at 350 °C for 12 hrs, and then cooled slowly in the furnace. Afterward, these billets were hot extruded by using the hydraulic press at a ramp speed of 10 mm/s with the extrusion ratio of 12:1 at 350 °C (Fig. 1). The structure of the specimens was studied by optical microscopy (OM). For this purpose, samples were etched in a solution of acetic picral after mechanical polishing. Moreover, the microstructural characteristics and morphologies of the wear surface of the composites were examined by a Vega©Tescan scanning electron microscopy (SEM).

Table 1. Chemical composition of ZK60 primary alloy

Alloy	Si (wt. %)	Al (wt. %)	Fe (wt. %)	Mn (wt. %)	Zr (wt. %)	Zn (wt. %)	Mg (wt. %)
ZK60	0.05	0.05	0.05	0. 1	0.76	6.1	Base

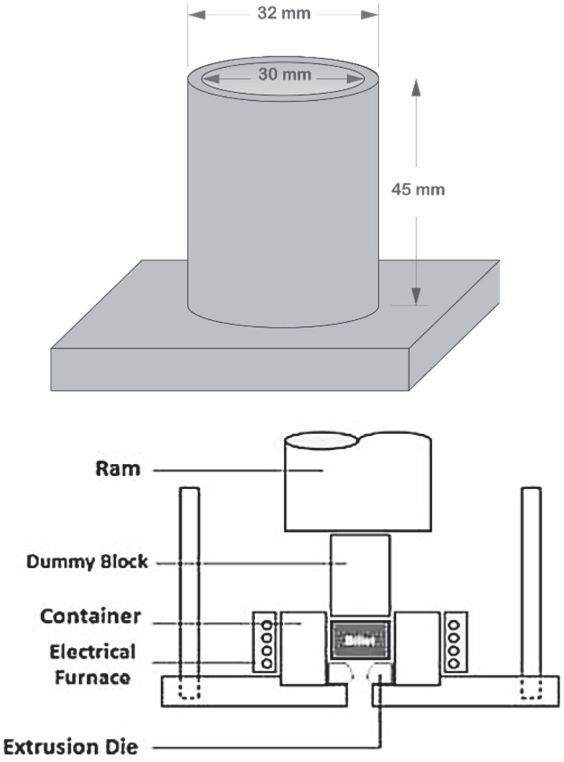


Fig. 1. Schematic of cast iron mold and extrusion die apparatus.

«The bulk density of the cast and extruded specimens was measured employing a proper densitometer, Toledo, Greifensee, Switzerland Mettler, according to the ISO2783 standard test method. Their apparent density was also calculated on the basis of the Archimedes principle. Therefore, the porosity contents were calculated according to the following equation:

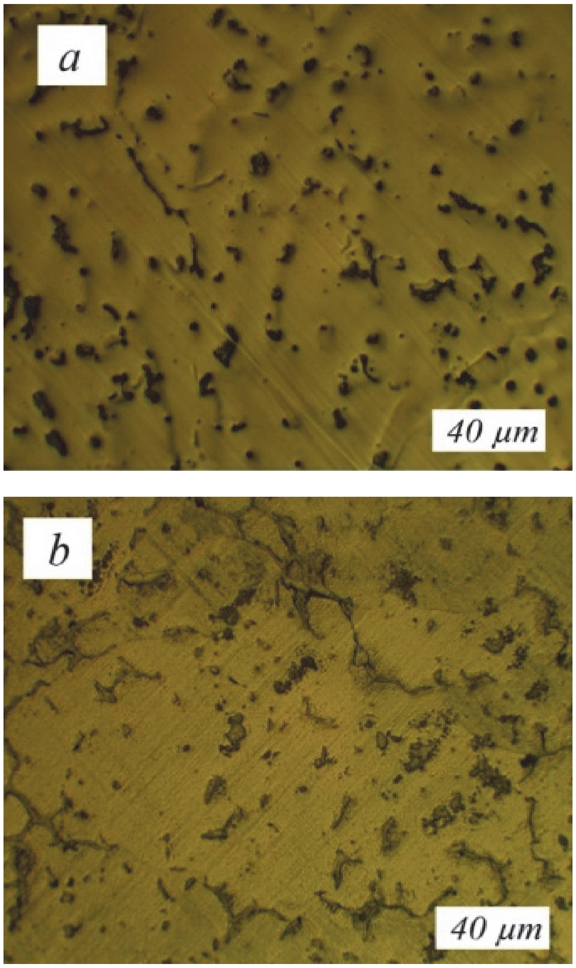
$$\%P = (\rho_{th} - \rho_r)/\rho_{th} \times 100 \quad (1)$$

Where %P is the porosity content, ρ_{th} is the apparent density, and ρ_r is bulk density.»

3 - Results and Discussion

3.1. Microstructural evolution in as-cast condition

The as-cast microstructures of the produced ZK60-X%Ca alloys are displayed in Fig. 2a-d, for the samples containing 0, 0.5, 2 and 3 wt. % Ca respectively. As seen in Fig. 2, the typical microstructure is essentially formed by a homogeneous matrix of α-Mg reinforced by an extensive network of fine grained intermetallic precipitates which congregate along the main α-Mg grain boundaries [17]. In other words, the whole set of as-cast alloys consists of approximately equiaxed alpha-Mg grains with a macro-segregation of the solute element and a network of intermetallic compounds which were mostly precipitated at the grain boundaries. These precipitates are probably formed by the segregation of Zn and Ca elements from the liquid phase during solidification..



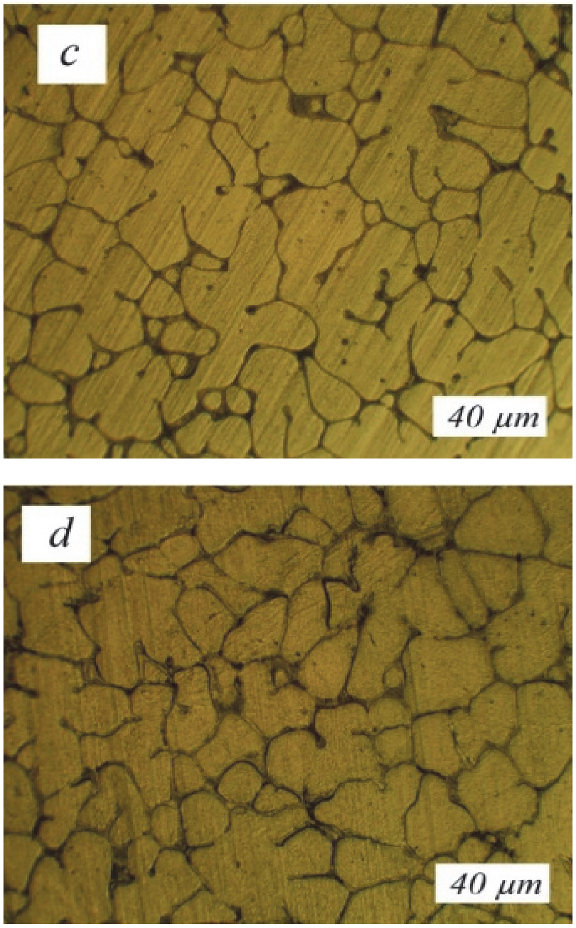
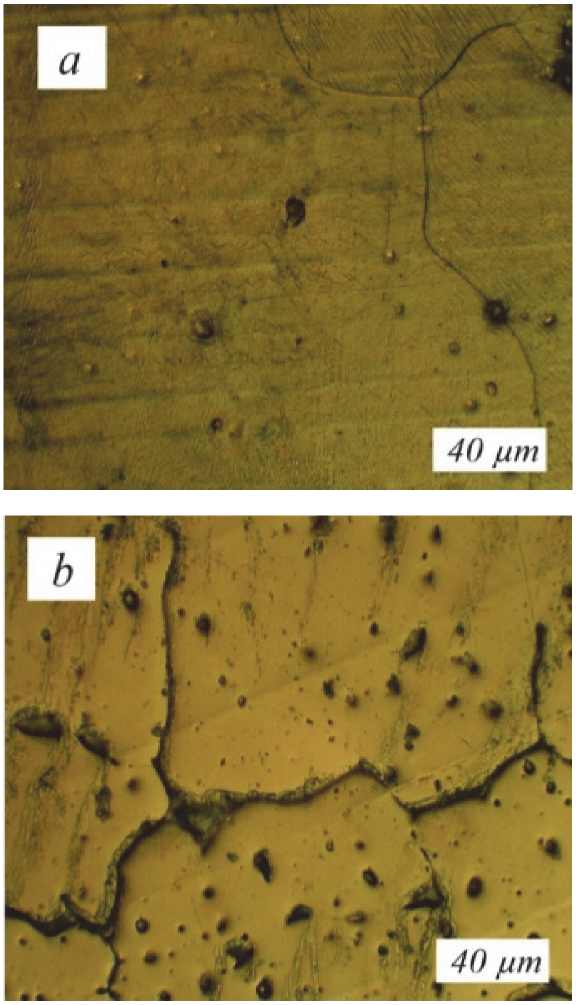


Fig. 2. Optical microstructure of ZK60 alloys before T6 as a function of Ca content (a) 0% (b) 0.5% (c) 2% (d) 1% (e) 3%.

Although the intermetallic phases in the Mg-Zn binary alloys are still controversial, different intermetallic phases were reported in Mg-Zn binary alloys system [18–20], such as Mg_7Zn_3, MgZn, Mg_4Zn_7, $MgZn_2$, Mg_7Zn_3 and Mg_2Zn_{11}. It is worth mentioning that Mg_7Zn_3, distributing in the inter-dendritic region, and Mg_4Zn_7, with a globular shape within α-Mg dendrites, were observed in the as-cast Mg-8Zn alloy [21]. The second phases in Mg-Zn-Ca alloy are commonly Mg_2Ca and $Ca_2Mg_6Zn_3$ which depend on the atomic ratio of Zn/Ca. Adding Ca to Mg-6Zn alloy causes a gradual replacement of Mg-Zn binary compound with $Ca_2Mg_6Zn_3$ ternary compound. Furthermore, different morphologies of intermetallic phases can be identified in the intermetallic network: for example, the fine structured lamellar or acicular phases in base alloy (possibly eutectic Zn component), and a smooth precipitate probably containing Ca elements. It is well known that the Mg–Zn (Mg_4Zn_7) binary phase is the main compound in ZK60 base alloys [19-21]. Because the solid solution of Ca in Mg solid solution is extremely low, the precipitation of Ca-containing intermetallic compounds are easy to be generated in Ca-added alloys. However, the addition of Ca leads to the formation of the ternary Mg–Zn–Ca (Ca_2Mg_6Zn) intermetallic phase instead of the Mg–Zn intermetallic phase. The average grain size of ZK60-X%Ca alloys was determined and found to decrease by increasing Ca content. Table 2 shows the average grain size of ZK60-X%Ca alloys.

Table 2. Average grain size of ZK60+X%Ca casting alloy*s*

Alloy	**ZK60**	**ZK60+ 0.5Ca**	**ZK60+ 0.5Ca**	**ZK60+ 0.5Ca**	**ZK60+ 0.5Ca**
Average grain size (µm)	320	150	120	80	75



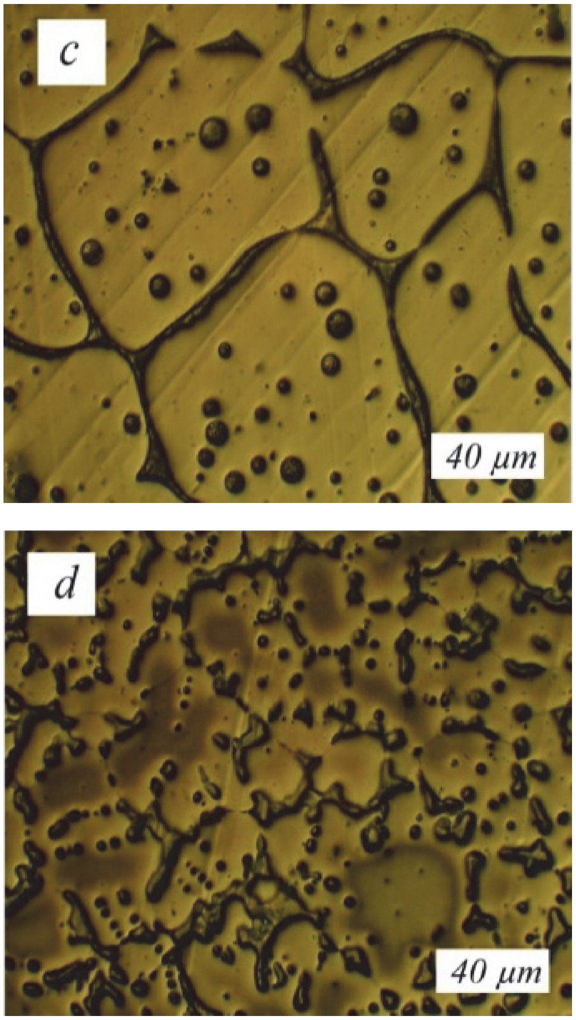
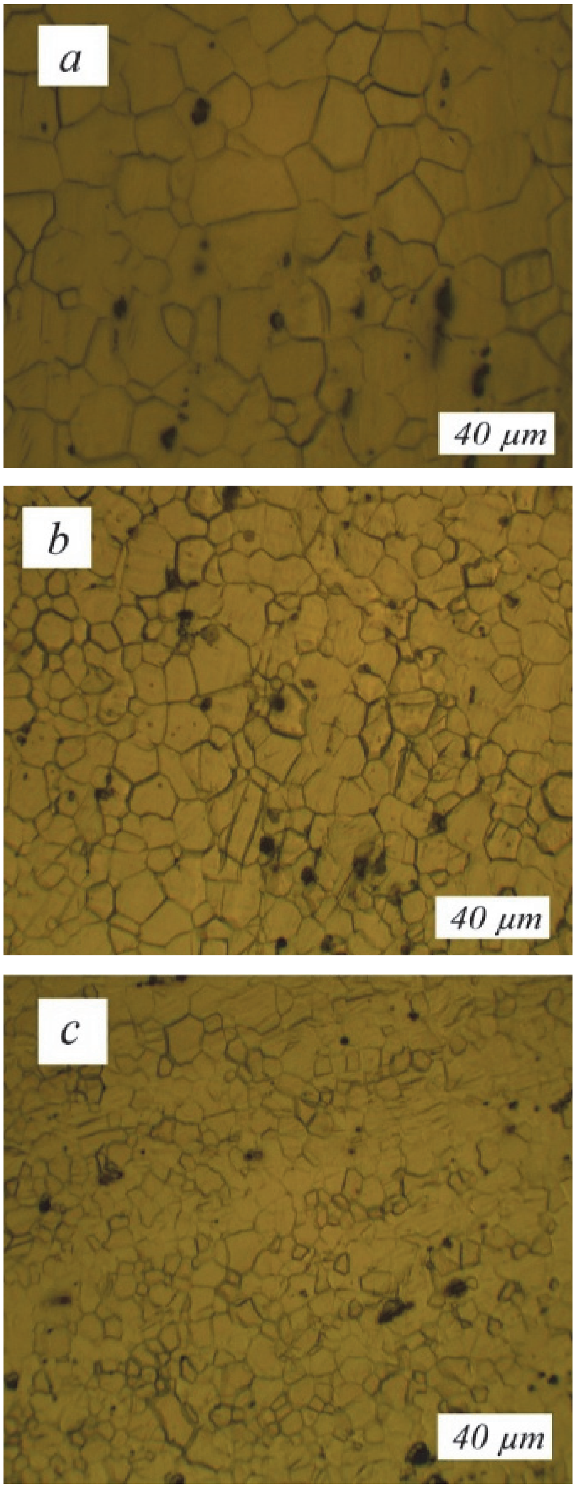


Fig. 3. Optical microstructure of ZK60 alloys after T6 as a function of Ca content (a) 0% (b) 0.5% (c) 2% (d) 1% (e) 3%.

3.2. Microstructural evolution in extruded condition

Figure 3 and Fig. 4 show the optical microstructures of the as-solutionized and as-extruded ZK60-X%Ca alloys. By applying the solutionizing process, the macro-segregation of the as-cast alloys disappeared completely and the volume fraction of the intermetallic compounds decreased slightly. Fig. 4 illustrates the optical microstructure of ZK60-X%Ca alloys in as-extruded condition. The as-extruded of all alloys exhibits a fully recrystallized microstructure with the second phases oriented along the extrusion direction. It is worth mentioning that the average size of ZK60-X%Ca alloys increased slightly by increasing the Ca addition after the extrusion process. The un-dissolved second phases during the homogenization treatment are also oriented towards the extrusion direction. The grain sizes of the recrystallized regions of ZK60-X%Ca alloys are shown in Table 3 respectively.



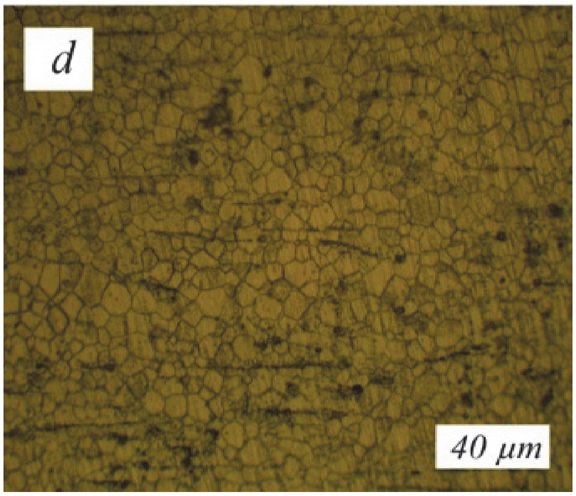


Fig. 4. Optical microstructure of ZK60 alloys after extrusion as a function of Ca content (a) 0% (b) 0.5% (c) 2% (d) 1% (e) 3%.

Table 3. Average grain size of ZK60+X%Ca extruded alloys

Alloy	**ZK60**	**ZK60+ 0.5Ca**	**ZK60+ 0.5Ca**	**ZK60+ 0.5Ca**	**ZK60+ 0.5Ca**
Average grain size (µm)	55	48	35	25	15

During the hot-extrusion process of ZK60-X%Ca alloys, the hard ternary Mg–Zn–Ca (Ca_2Mg_6Zn) intermetallic phases were broken into fragments and rearranged along the extrusion direction (ED), as shown in Fig. 5, which provides the SEM microstructures of the longitudinal section of the as-extruded alloys. The volume fraction of the fragmented phases also increases as the Ca content increases. The ternary Mg–Zn–Ca phases of the as-homogenized ZK60-X%Ca alloys may provide nucleation sites for dynamic recrystallization (DRX) during hot extrusion. The composition of formed intermetallic compounds also varied according to the Ca addition. Table 4 shows the results of the EDS analysis of the as-extruded ZK60-X%Ca alloys. Both the spherical compounds in the grain interior and compound networks along the grain boundaries are comprised of the Mg–Zn–Ca phase with the same chemical composition, as shown in Fig. 5b-c.

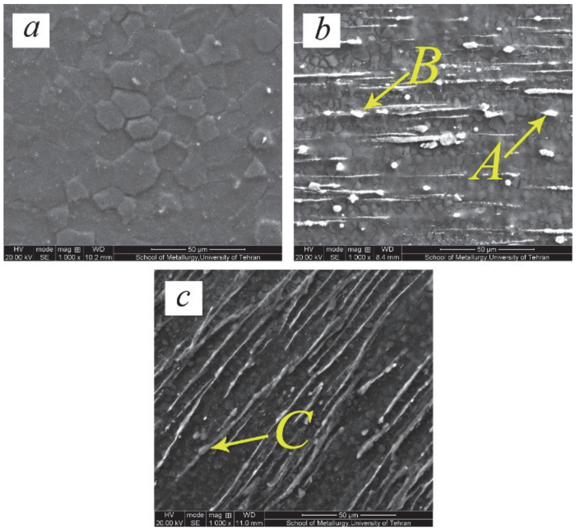


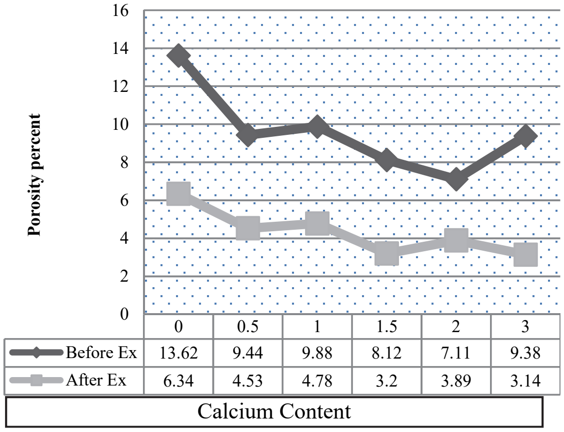
Fig. 5. SEM microstructures of ZK60+X%Ca alloys after extrusion: (a) 0wt.%, (b) 1wt.% and (c) 3 wt.%.

Table 3 Average grain size of ZK60+X%Ca extruded alloy*s*

Alloy with wt. %Ca	**Mg (at. %)**	**Zn (at. %)**	**Zr (at. %)**	**Ca (at. %)**
0.5	73.74	16.73	0.07	9.46
1	71.74	15.73	0.05	12.68
3	68.21	19.76	0.04	9.79

3.3. Porosity analysis

porosity contents decrease as the calcium contents are increased. By increasing the Ca concentration up to 1 percent, the porosity contents start to increase. By applying the extrusion process and increasing the Ca concentration up to 2.0 wt. %, the porosity percentage decreased from 13.62% to 6.34% and 7.11% to 3.89% for ZK60 and ZK60+3%Ca alloys respectively. The formation of porosity in alloys is based on nucleation and growth principle. The nucleation process is usually difficult, but it can be catalyzed by such features as inclusions in the melt or the mold wall. Nevertheless, nucleation will often occur only in the last liquid to freeze when gas super saturation is high. This results in the formation of pores which are effectively trapped in the dendrite mesh and which consequently remain in the solidified casting alloy; however, such pores are most probably caused by inter-dendritic shrinkage; however, the presence of oxides might also suggest a pore formation by an entrained double oxide that was torn apart by shrinkage-induced shear forces [16]. As is observed, the population of porosity decreases significantly after the extrusion process. It is explicable that applying hot extrusion as an effective thermomechanical processing route not only does modify the cast microstructure in respect of the decreasing grain size and second phase distribution, but it also significantly reduces the population of casting defects, i.e. porosity.



	0	0.5	1	1.5	2	3
Before Ex	13.62	9.44	9.88	8.12	7.11	9.38
After Ex	6.34	4.53	4.78	3.2	3.89	3.14

4. Conclusions

In the current research work, the effect of different amounts of Ca on the microstructural evolution and porosity content of ZK60-X%Ca alloys in as-cast and as-extruded conditions has been investigated. The following conclusions are drawn:

1. The addition of high concentrations of Ca to ZK60 base alloy introduces Ca- rich intermetallics, such as $Ca_2Mg_6Zn_3$ phase.
2. Applying the homogenization and extrusion processes introduces fine particles by breaking the eutectic network.
3. The average grain size of ZK60-X%Ca alloys decreased from 60 µm to 15 µm with the Ca addition being increased from 0 to 3.0 wt. % in the as-extruded samples.
4. By increasing Ca contents, the porosity percentage, at first, decreased and then increased. By applying the extrusion process, the porosity content decreased significantly.

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بررسی افزودن درصدهای گوناگون کلسیم بر خواص ریزساختاری و آنالیز تخلخل در حالت ریخته‌گی و اکسترود شده آلیاژ ZK60

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چکیده

در این پژوهش به بررسی افزودن درصدهای گوناگون کلسیم (۰/۵، ۱، ۱/۵، ۲ و ۳) بر ریزساختار و آنالیز تخلخل درحالت ریخته‌گی و اکسترود شده آلیاژ تجاری ZK60 پرداخته شده است. بررسی بهبود ریزساختاری با استفاده از میکروسکوپ نوری، میکروسکوپ الکترونی روبشی انجام پذیرفته است. نمونه‌های ریخته‌گری اصلاح شده و همگن شده در دمای ۳۵۰ درجه سانتیگراد با نسبت اکستروژن ۱۲:۱ اکسترود شدند. نتایج به‌دست‌آمده نشان می‌دهد که افزودن کلسیم موجب تشکیل فازهای جدید و بهبود دانه‌های می‌شود. همچنین حضور کلسیم در غلظت‌های بالاتر (> ۲٪ وزنی) موجب تشکیل ذره‌های بین فلزی غنی از کلسیم در مرزهای سلولی می‌گردد. اکستروژن داغ بسیار مؤثر در شکستن شبکه یوتکتیک و تغییر اندازه و مورفولوژی فازهای بین فلزی غنی از کلسیم بود. با استفاده از فرایند اکستروژن و افزایش غلظت کلسیم (تا ۰/۲ درصد وزنی)، درصد تخلخل برای آلیاژ ZK60 و ZK60+3%Ca به ترتیب از ۱۳٫۶۲ به ۶٫۳۴ درصد و ۷٫۱۱ به ۳٫۸۹ درصد کاهش یافت.

واژه‌های کلیدی: آلیاژ ZK60، ریزساختار، افزودن کلسیم، اکستروژن، آنالیز تخلخل