論 文

Mechanical Behavior and Microstructure Evolution during Semi-Solid Squeeze Cast Processing of Ignition-Proof Mg-Zn-Ca-Zr Alloy

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Abstract

The mechanical behavior and microstructural evolution in the ignition-proof Mg-Zn-Ca-Zr alloy produced by the semi-solid squeeze casting are clarified and the mechanical properties are also compared with those of squeeze cast Mg-Zn-Ca-Zr alloy. The tensile strength and elongation increase slightly as the solid fraction depending on temperature decreases, while the 0.2% proof stress decreases. The size of primary crystal increases with increasing holding time. The tensile strength and 0.2% proof stress of the semi-solid squeeze cast Mg-Zn-Ca-Zr alloy decrease as the size of primary crystal increases, indicating the dependence of strength on the size of primary crystal. The elongation of the semi-solid squeeze cast Mg-Zn-Ca-Zr alloy is two times as large as the squeeze cast Mg-Zn-Ca-Zr alloy and the tensile strength is unchanged despite the growth of primary crystal, resulting from the refining of the melted αMg phase and the brittle eutectic compound as well as the reduction of solidification shrinkage and porosities. (Received September 10, 1997)

1. Introduction

Importance of magnesium and its alloys has been recognized as a light-weight high specific strength material, which can cope with the recent energy and environmental problems. However, it is very dangerous to produce magnesium alloys in the air due to the ignition during melting and casting. This is a critical obstacle which disturbs magnesium alloys in their industrial applications. We reported[1, 2] that the combined addition of calcium and zirconium was effective for the ignition prevention of magnesium alloys during melting and casting. In addition, the semi-solid state forming processes that has recently received a considerable attention as a technique giving several potential benefits[3] are suitable to safe production of magnesium alloy. The subsequent target which we should hit is to apply such the "ignition-proof magnesium alloys" to the semi-solid state forming processes for the improvement of mechanical properties.

The aim of this work is therefore to investigate the mechanical behavior and microstructure evolution in the ignition-proof Mg-Zn-Ca-Zr alloy produced by semi-solid forging and to clarify the influence of semi-solid forged structure on mechanical properties.

2. Experimental Procedures

2.1 Preparation of materials

The alloy for semi-solid forging in this work was made up from pure magnesium, calcium, zinc with purities of 99.9mass%, 99.5%, 99.9% respectively, together with Mg-65%Zr master alloy. The melting was carried out under the mixed gas atmosphere of SF_6 (25%) and CO_2(75%) at 1073K. The melt was poured into a mold preheated to 573K and was squeeze-cast under an applied low pressure of 25 MPa and a plunger speed of 22 mm/s in order to prepare the sound alloy. Consequently, the alloy with a height of 60mm and a diameter of 55 mm were obtained. Based on the result reported previously[4], the calcium and zirconium with content higher than 1% were added to produce alloy with very fine spherical structure. The Mg-6.0%Zn-2.0%Ca-1.5%Zr alloy(wt%) was machined to ingot with a height of 20 mm and a diameter of 55 mm. A hole with a depth of 15 mm and a diameter of 3.5 mm was drilled through the ingot for thermocouple. The schematic illustration of apparatus and fabrication method of ignition-proof Mg-Zn-Ca-Zr alloy using semi-solid forging are shown in Fig. 1. The alloy was set

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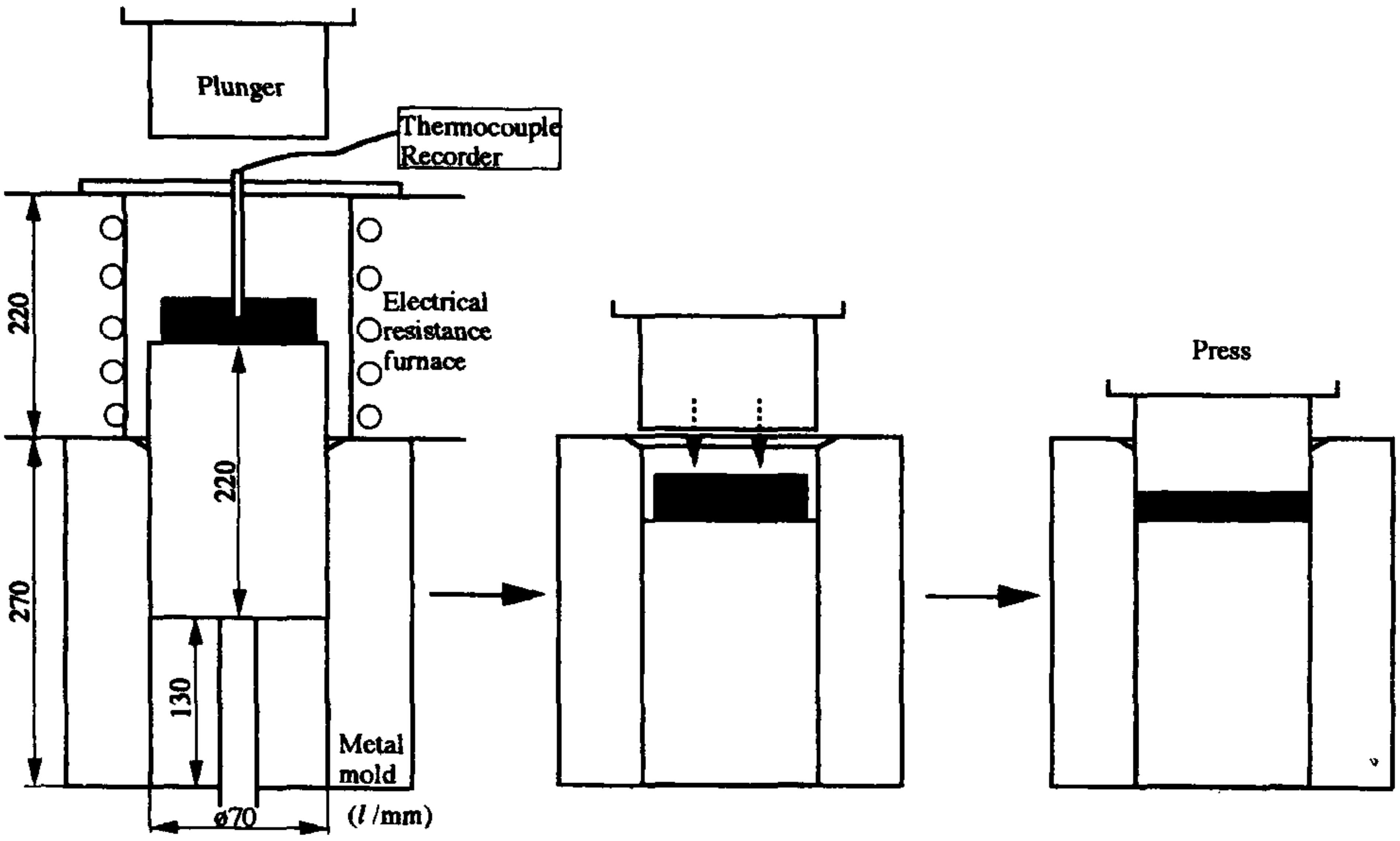

Fig. 1. Schematic illustration showing fabrication apparatus and process of Mg-Zn-Ca-Zr alloy by semi-solid squeeze casting.

on the mold and was heated to objective temperature by an electrical resistance furnace. The temperature was measured by a recorder with a thermocouple put into the hole of alloy. The temperature distribution in alloy was investigated in advance. As a result, the heating time of 1.8ks was taken in order that the temperature between inside and outside in alloy might be constant at the objective temperature. The injection (objective) temperatures in Mg-6.0%Zn-2.0%Ca-1.5% Zr alloy were 868K and 883K. After the electrical resistance furnace was got rid of at the injection temperature, the alloy was solidified under pressure of 100 MPa applied immediately. A pressure time was 200s and a plunger speed was 80 mm/s.

2.2 Tensile test

The tensile test specimens with a diameter of 3.6 mm and a gauge length of 14mm were machined from the obtained materials. Displacements(strains) of the specimens were measured using both a pair of strain gauges which were attached on the gauge section in parallel and a clip gauge which was set between the inner surfaces of the specimen's grips. The tensile test was carried out under a constant strain rate condition of 6×10^{-4}/s at 298K. At least three specimens were tested to obta in the value of elastic modulus, 0.2% proof stress, tensile strength and elongation. In the present study, tensile strength is comparable to fracture strength.

2.3 Analysis of microstructure

The microstructure of Mg-Zn-Ca-Zr alloy produced by squeeze casting was observed by an optical microscope (OM). And the microstructure of semi-solid squeeze cast Mg-Zn-Ca-Zr alloy was also observed by an OM in order to investigate the influences of temperature, heating time and holding time on the microstructure.

The solid fraction was obtained from the volume fraction of primary crystal which exists as solid phase in the semi-solid state. The image analysis system was used for the measurement of volume fraction of primary crystal dictating the nominal temperature of injection, size and size distribution of primary crystal in the Mg-Zn-Ca-Zr alloy varied during holding isothermally in the semi-solid state. The volume fraction and size distribution of primary crystal were calculated from the area of primary crystal obtained by a charge-coupled device camera(CCD). Under an assumption that the primary crystal was spherical, the size of primary crystal was obtained.

The fracture surface and the microstructure of the longitudinal section near the fracture surface were observed by a scanning electron microscope and an optical microscope to examine fracture behavior.

3. Results & Discussion

3. 1 Influence of temperature and holding time on semi-solid squeeze cast microstructure

The typical microstructures and block shape molded product of Mg-Zn-Ca-Zr alloy produced by semi-solid forging under the condition of holding time of 40 min at 883K are shown in Fig. 2. The alloy reveals very fine structure of spherical grains with an average grain size of 23 μm. The white particles in the cast structure of alloy are primary α-Mg crystals while the black continuous areas between primary crystals are the eutectic structure. The microstructure of semi-solid squeeze cast Mg-Zn-Ca-Zr alloy consists of the ripened primary Mg crystal, eutectic compound[4] and refined primary crystal in the eutectic area.

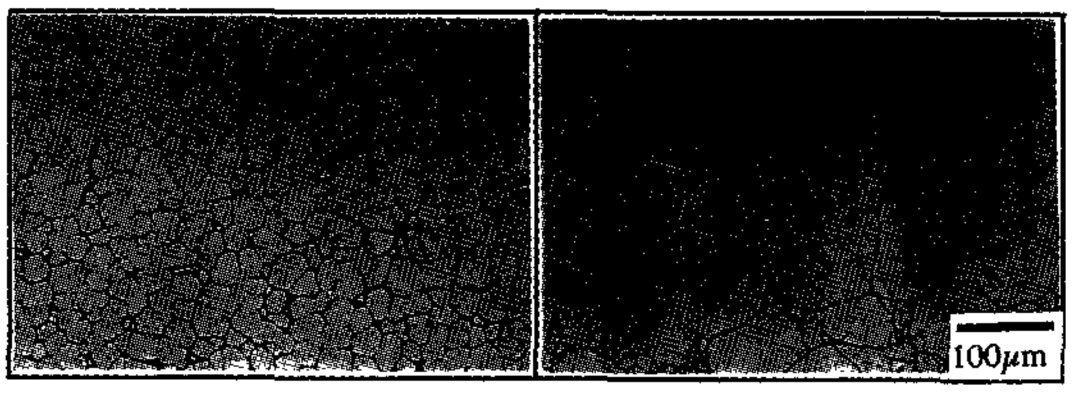

Fig. 2. Microstructures of a) prematerial and b) semi-solid squeeze cast Mg-Zn-Ca-Zr alloy produced at holding time of 40 min and 883 K.

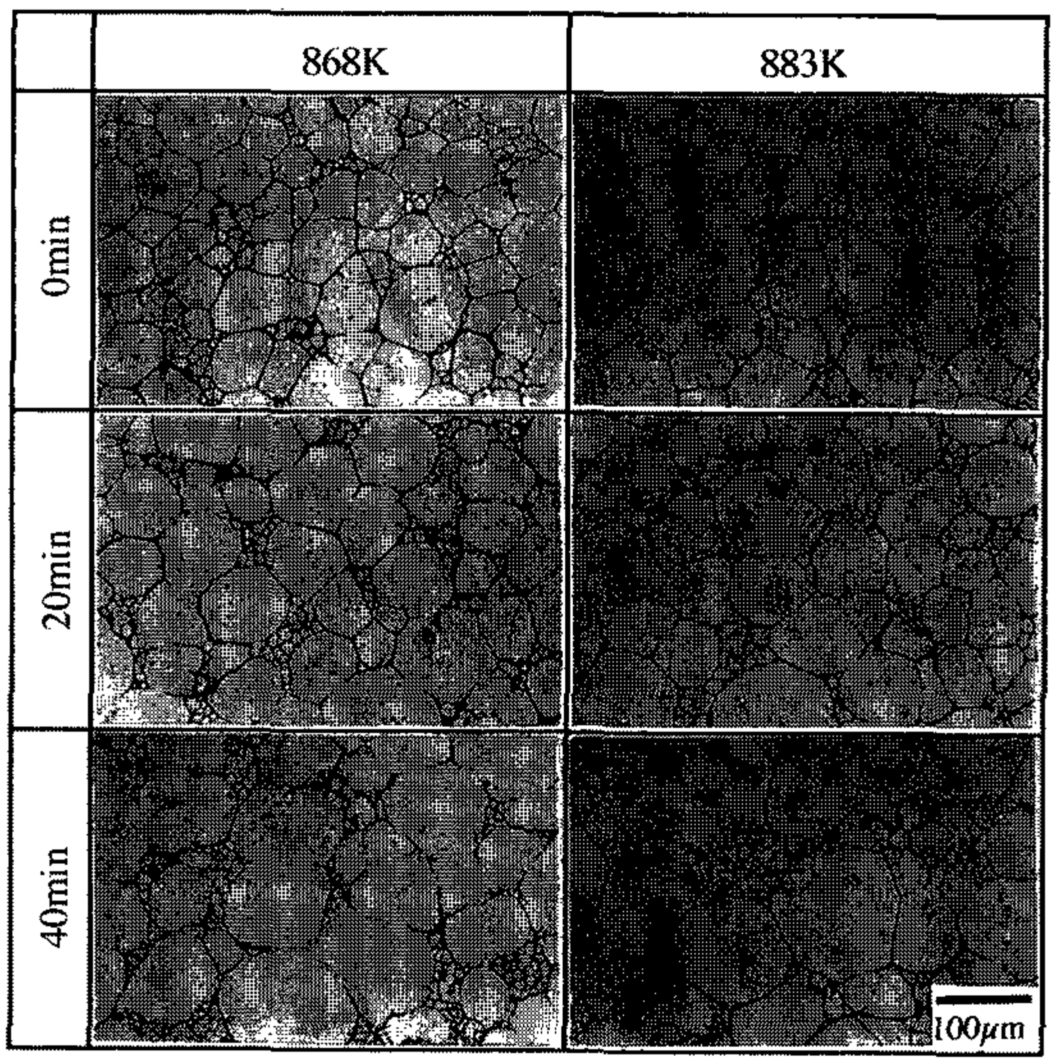

Fig. 3. Influence of holding time of microstructure of semi-solid squeeze cast Mg-Zn-Ca-Zr alloy at 868 K and 883 K.

The influence of holding time on microstructure in the Mg-Zn-Ca-Zr alloy held at 868K and 883K is shown in Fig. 3. With increasing holding time and temperature in the semi-solid state, the number of primary crystal decreases. The primary crystals coarsen and become more spherical with increasing holding time. At 868K and 883K, some αMg phase melts. After solidifying from the semi-solid temperature, the melted αMg phase appears as very fine equiaxed dendrites in the eutectic area or very fine dendrites grown out from the primary crystals. And the microstructure of refined brittle eutectic is also shown in fracture surface of Fig. 12 as notch-steps that are smaller than that in the squeeze cast alloy.

The influence of heating temperature and holding

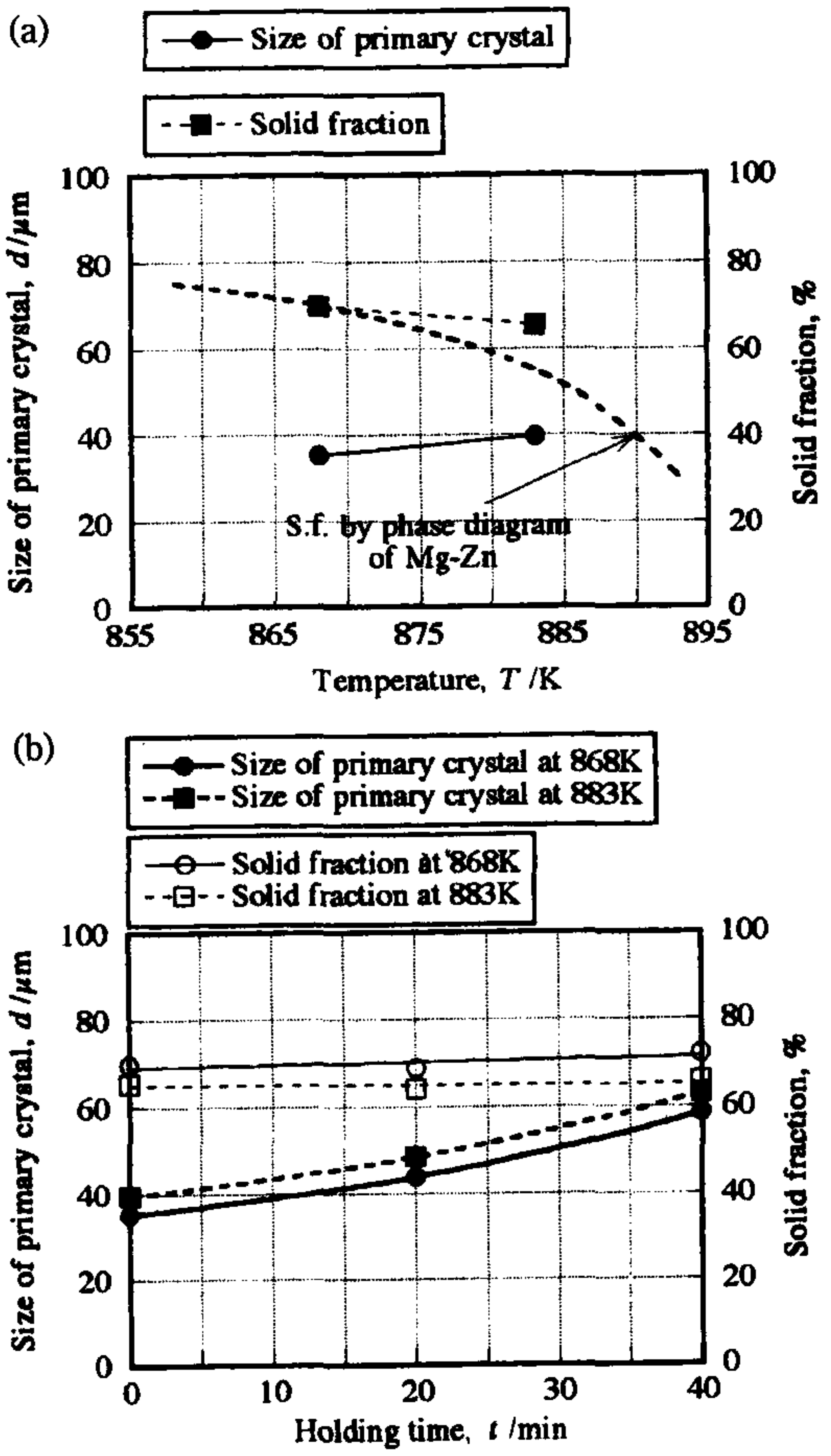

Fig. 4. Influence of a) temperature and b) holding time on size of primary crystal and solid fraction in semi-solid squeeze cast Mg-Zn Ca-Zr alloy.

time on size of primary crystal and solid fraction are shown in Fig. 4a) and b) respectively. The solid fraction that is compared with the solid fraction calculated from phase diagram of Mg-Zn decreases slightly with increasing temperature. The solid fraction is almost no changed with increasing holding time because the solid fraction is determined by temperature. The size of primary crystal increases slightly despite the same heating time as temperature increases but markedly increases as holding time increases. On the other hand, the form factor F, defined as $F=4\pi A/L^2$ (A=Area and L=Circumference) of alloy having spherical primary crystals is 0.64. The form factor at 883K and 868K are approximately 0.70 and 0.67 respectively indicating spherical particles.

A study on coarsening of primary crystal in the semi-solid state has been conducted by many researchers. Ostwald ripening(LSW theory) [5-8] and coalescence ripening [8-10] dominate the growth of primary crystal. The LSW theory is expressed in terms of the cube of the average particle radius to vary linearly with time as following equation :

$$R^*(t)-R^*(0)=Kt \qquad (1)$$

where $R^*(t)$ is the average particle radius at time t, $R^*(0)$ is the average radius at time t=0 when the system has reached a steady state distribution. K is the coarsening rate constant for growth by ostwald ripening when the volume fraction of coarsening phase is nearly zero. However, the equation (1) is also applied in case of that the volume fraction is not zero. The increase of the average particle size also follows the $R^*\propto t$ kinetics by equation (1) under the assumption that the rate determining step of coalescence is diffusion of solute atoms in the liquid. Actually, it is very difficult to clarify the effects of ostwald and coalescence ripening operating independently because the growth of primary crystal in the semi-solid state is taken place by ostwald and coalescence ripening at the same time.

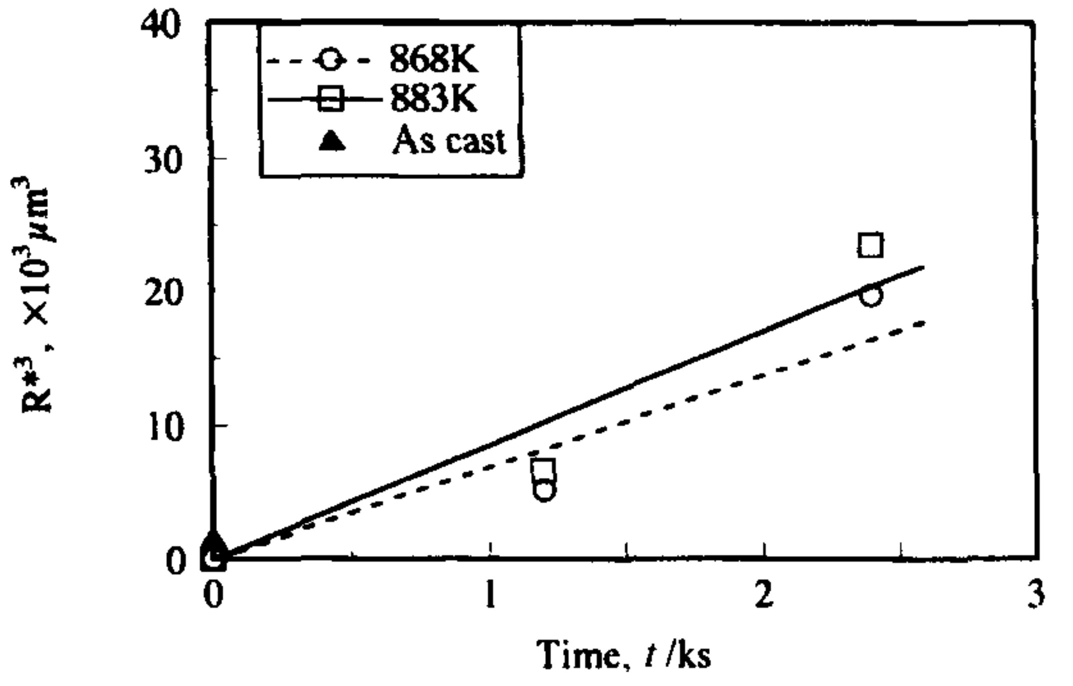

Fig. 5. Plot of R* as a function of coarsening tme t in the semi-solid state by the microstructure evolution in Mg-Zn-Ca-Zr alloy produced by semi-solid squeeze casting.

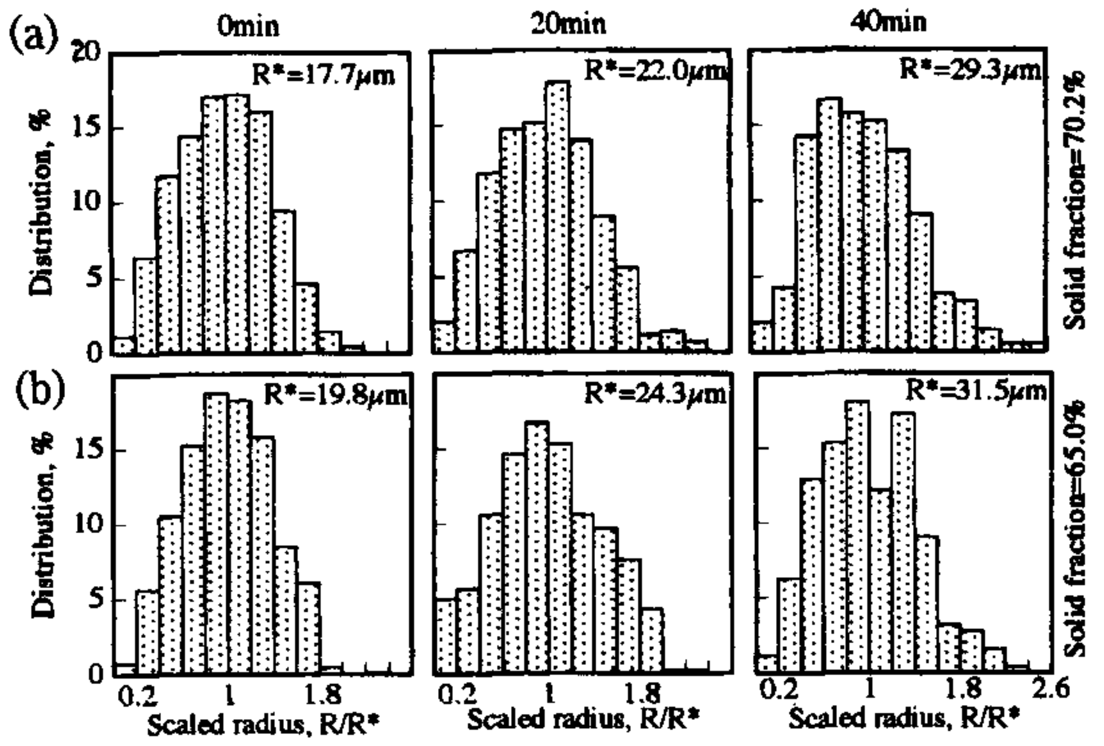

Fig. 6. Primary crystal radius distribution of Mg-Zn-Ca-Zr alloy after isothermal ripening at different temperatures and coarsening times in the semi-solid state; a) 868 K and b) 883 K.

The growth kinetics of primary crystal in the Mg-Zn-Ca-Zr alloy at 868K and 883K follow a $R^*\propto Kt$ law as shown in Fig. 5. The straight lines are fit to equation (1). In the semi-solid squeeze cast Mg-Zn-Ca-Zr alloy, many large grains formed by coalescence of grains are observed. Figure 6 shows the size distributions of primary crystal in the Mg-Zn-Ca-Zr alloy and illustrates the effects of holding time(coarsening time) and temperature. With the lapse of coarsening time, the distribution between 0.4 and 1.4 of R/R* broadens. This is considered as the result from growth by coalescence ripening. In the early coarsening stage ostwald ripening plays a large role in the coarsening of primary crystal in the Mg-Zn-Ca-Zr alloy. However, coalescence ripening rather than ostwald ripening dominates the coarsening of primary crystal in the semi-solid state with the passage of coarsening time.

3.2 Tensile properties of semi-solid squeeze cast Mg-Zn-Ca-Zr alloy

The influence of temperature on tensile properties of the Mg-Zn-Ca-Zr alloy produced by semi-solid forging

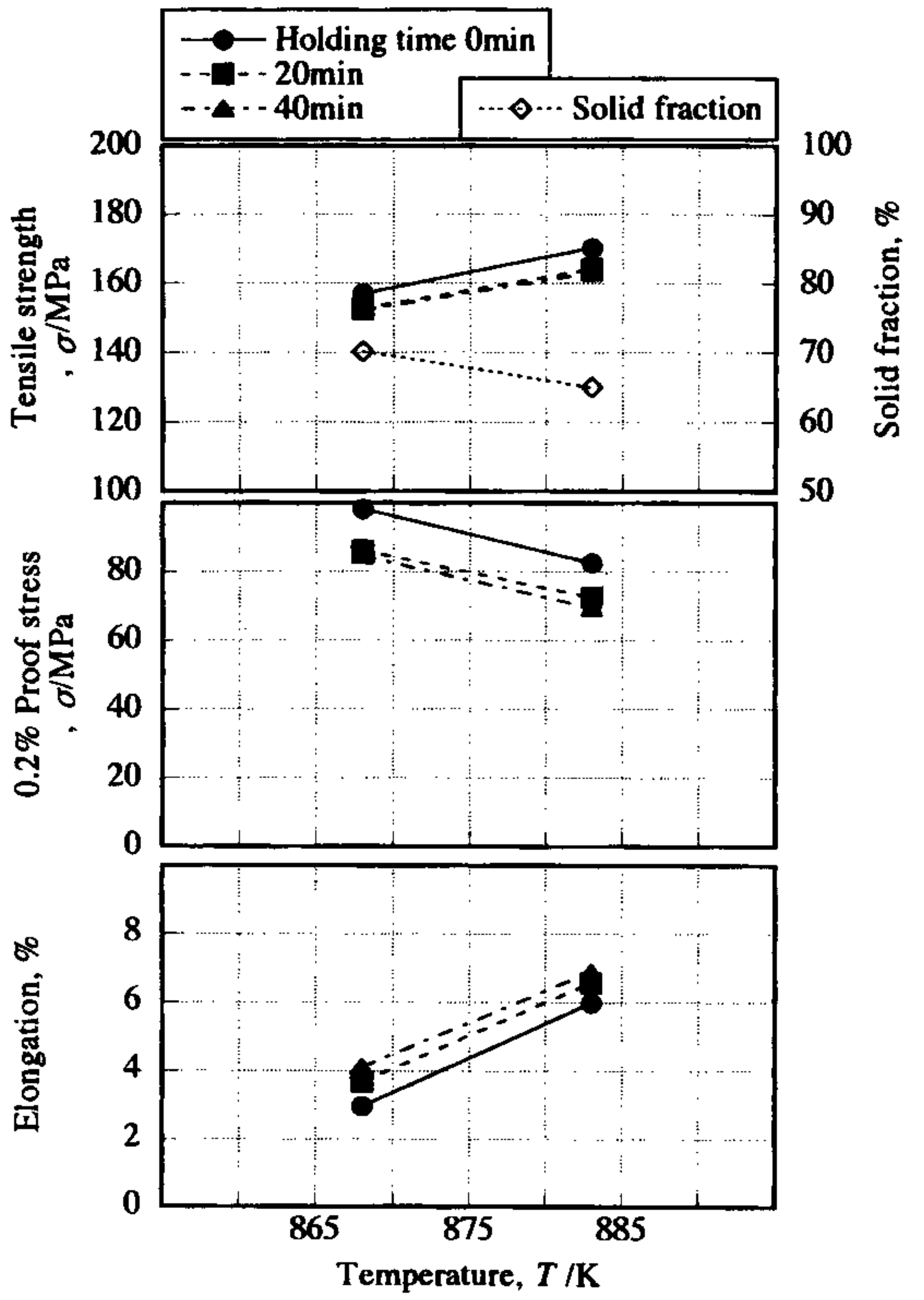

Fig. 7. Relation between tensile properties and solid fraction with increasing temperature in semi-solid squeeze cast Mg-Zn-Ca-Zr alloy.

is shown in Fig. 7. The tensile strength and elongation increase with increasing temperature (decreasing solid fraction) and the 0.2% proof stress decreases. The increase of tensile strength and elongation results from the followings that the αMg phase changing into the very fine equiaxed dendrites in the eutectic area and the very fine dendrites grown out from the primary crystals at high semi-solid temperature is more than that at low semi-solid temperature, because the refined αMg phase prevents the propagation of crack passing through the intergrains. In contrast, the decrease of the 0.2% proof stress depending on the solid fraction is due to the following that there are a lot of primary crystals, i.e., grain boundaries which prevent the dislocation motion, in high solid fraction compared with low solid fraction. Namely, at different temperature (solid fraction), the proof stress is mainly affected by the αMg phase which is solid in the semi-solid state and the refined αMg phase has an large effect on the tensile strength and elongation.

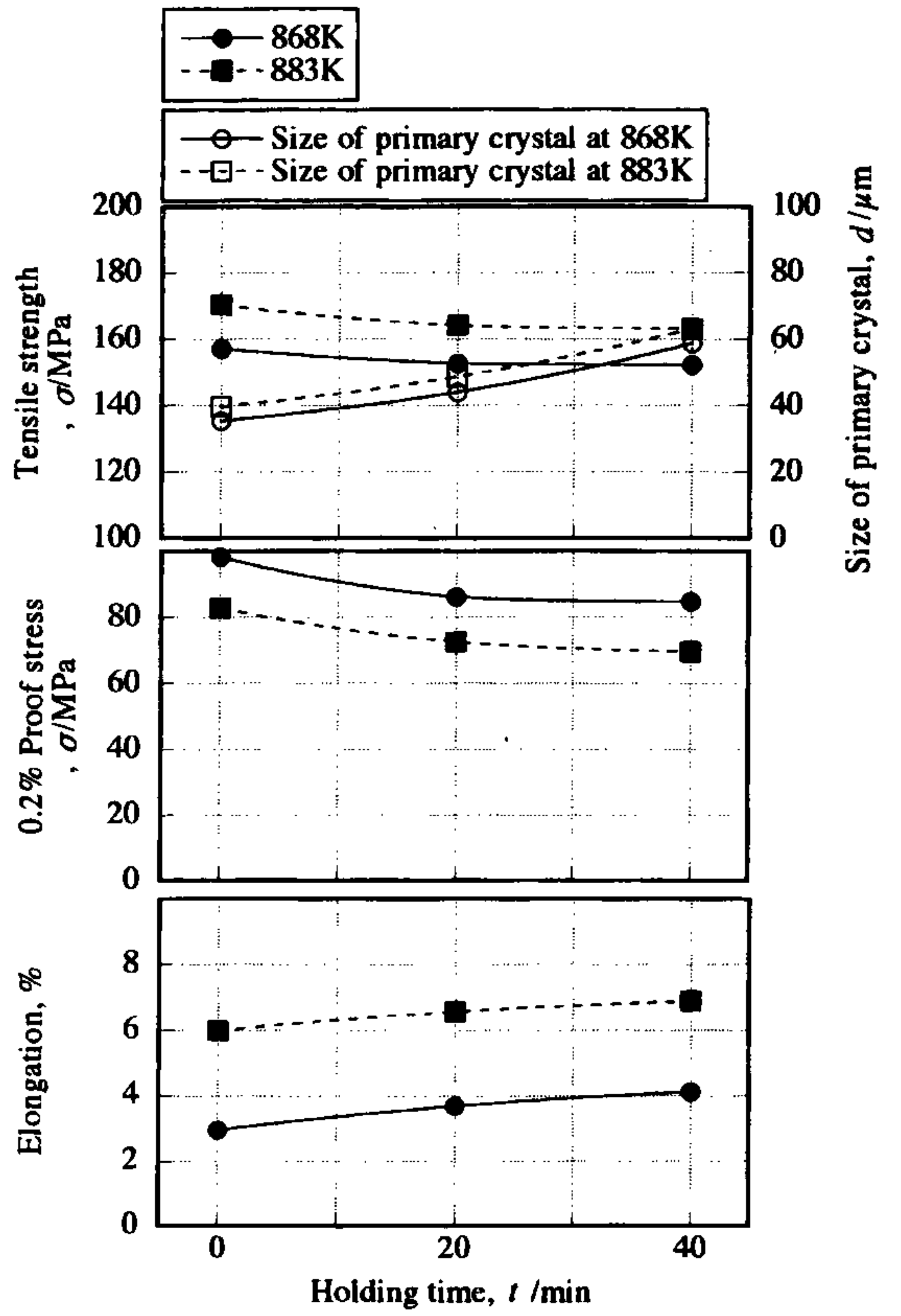

Fig. 8. Relation between tensile properties and size of primary crystal with increasing holding time in semi-solid squeeze cast Mg-Zn-Ca-Zr alloy.

Figure 8 shows the influence of holding time on relation between tensile properties and size of primary crystal in the semi-solid squeeze cast Mg-Zn-Ca-Zr alloy. The tensile strength and 0.2% proof stress of the Mg-Zn-Ca-Zr alloy held at 868K and 883K decrease with increasing holding time, i.e., increasing size of primary crystal. However, the elongation increases as the size of αMg phase increases at 868K and 883K. The 0.2% proof stress varies linearly with a reciprocal of square root of the size of primary crystal as shown in Fig. 9. It is for this reason that the grain boundaries act as an obstacle to dislocation motion. In the semi-solid squeeze cast Mg-Zn-Ca-Zr alloy, the relation between the 0.2% proof stress and the size of primary crystal follows the Hall-Petch relation[11],

$$\sigma_y = \sigma_i + k_y d^{-1/2} \tag{2}$$

where σ_y is yield stress, d is grain size, σ_i refers to the average yield stress of a single crystal and is det-

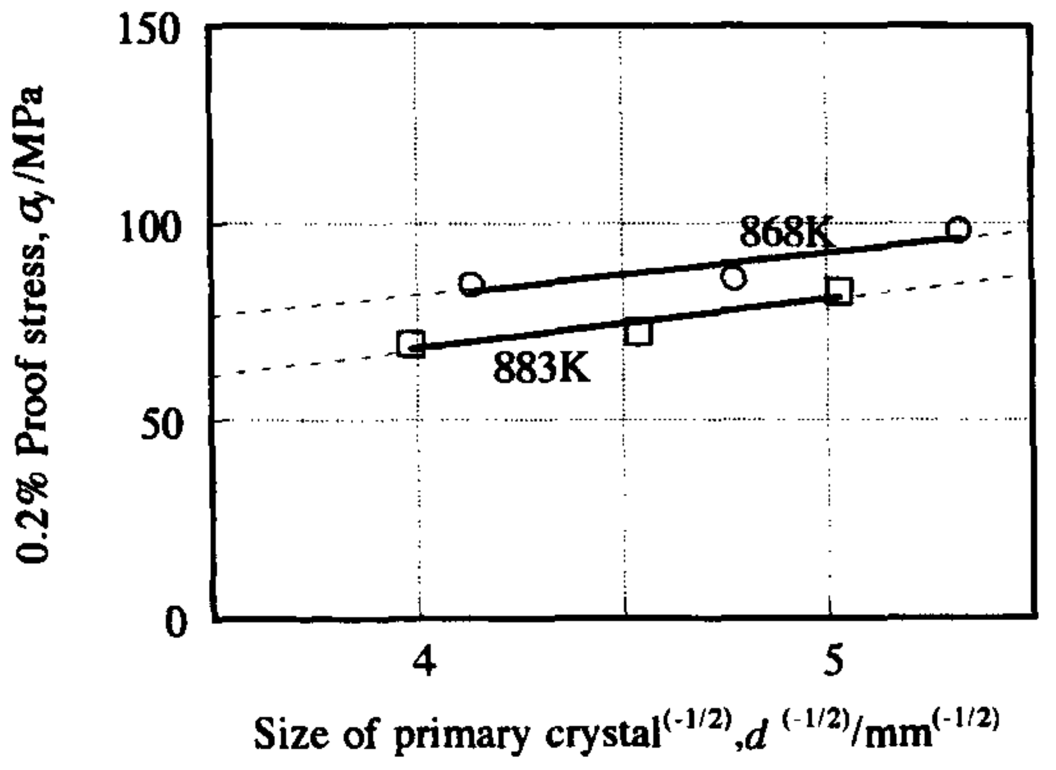

Fig. 9. Relation between size of primary crystal and o.2% proof stress of semi-solid squeeze cast Mg-Zn-Ca-Zr alloy.

ermined by all the operative strengthening mechanism except grain boundary strengthening and ky is a complex parameter that determines the effectiveness of grain boundaries in raising the yield stress. In this work, the increase of the size of αMg phase which is solid in the semi-solid state has large effect on the decrease of tensile strength and 0.2% proof stress as holding time increases at constant solid fraction. In fact, the effect of both the area of remelted region and the size of rapid solidified structure should be considered to clarify accurately the mechanical behavior of semi-solid cast magnesium alloys. Nevertheless, the result shown in Fig. 9 indicates that the size of αMg phase existing as solid in the semi-solid state must be a dominant factor playing an significant role in the mechanical behavior. However, the effect of α Mg phase on the strength will become smaller with become smaller with decreasing solid fraction (increasing the liquid fraction). In other words, the dependence of strength on size of primary crystal will disappear and the graph shown in Fig. 9 will lie down.

The microstructures in the vicinity of fracture surface an SEM images of fracture surface in the Mg-Zn-Ca-Zr alloy produced at different holding time and temperature are shown in Fig. 10. The fracture of the semi-solid squeeze cast Mg-Zn-Ca-Zr alloy takes place intergranularly. The difference of fracture behavior in the Mg-Zn-Ca-Zr alloy produced under different conditions of holding temperature and time is not obvious. The fracture surfaces show the intergranular fracture of the semi-solid squeeze cast Mg-Zn-Ca-Zr alloy. The bumpiness in fracture surface corresponds to the size of grains in microstructure in the vicinity of fracture surface and becomes large with the lapse of time. In the fracture surface of the Mg-Zn-Ca-Zr alloy held at 883K for 40min, the small bumpiness corresponding to very fine structure solidified rapidly from semi-solid temperature is observed between large bumpiness.

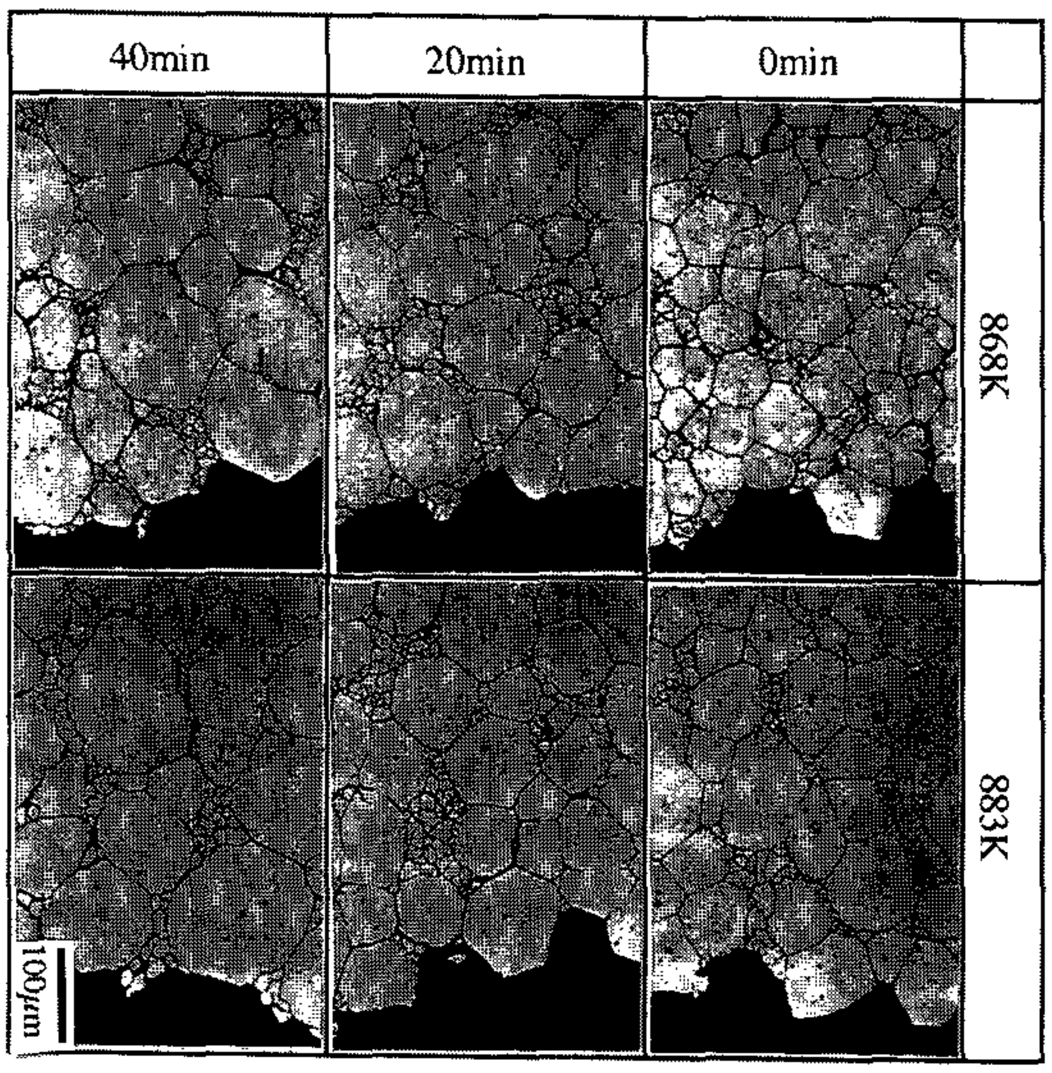

Fig. 10. Microstructures in the vicinity fo fracture surface in semi-solid squeeze cast Mg-Zn-Ca-Zr alloy produced at different holding time and temperature.

3.2 Comparison of tensile properties between squeeze cast Mg-Zn-Ca-Zr alloy and semi-solid squeeze cast Mg-Zn-Ca-Zr alloy

The tensile properties of semi-solid squeeze cast Mg-Zn-Ca-Zr alloy held at 883K for 0min that were the highest among the semi-solid squeeze cast Mg-Zn-Ca-Zr alloy ingots produced at various conditions, were compared with those of squeeze cast Mg-Zn-Ca-Zr alloy produced under conditions a plunger speed of 22 mm/s and pressure of 100 MPa[4].

The comparison of tensile properties in the Mg-Zn-Ca-Zr alloy ingots produced by squeeze casting and semi-solid squeeze casting are shown in Fig. 11. The tensile strength between squeeze cast alloy and semi-solid squeeze cast alloy is almost same, but the 0.2% proof stress decreases in semi-solid squeeze cast alloy. However, the elongation of the semi-solid squeeze cast alloy is two times as large as that of the squeeze cast

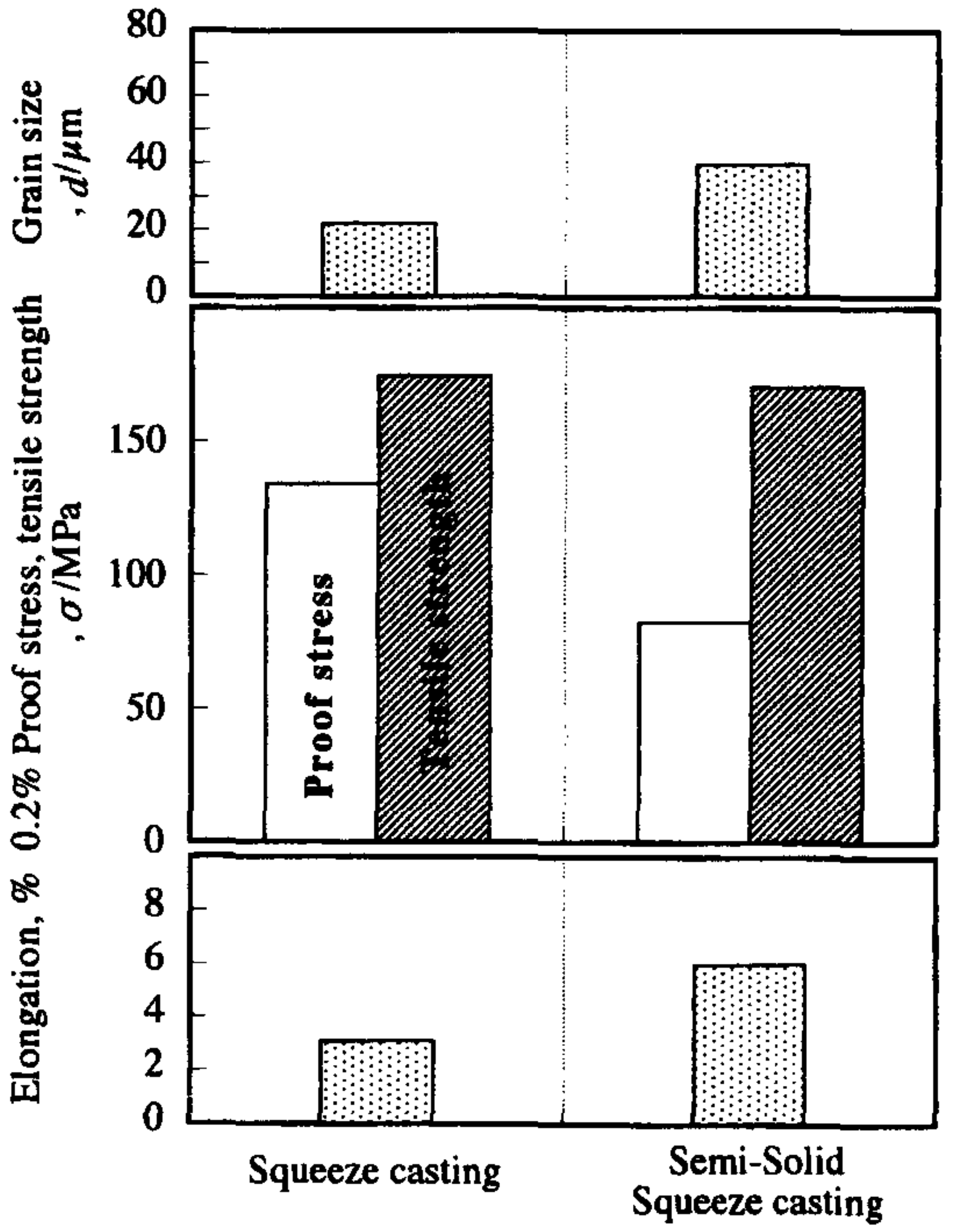

Fig. 11. Crain size, tensile strength, 0.2% proof stress and elongation of Mg-Zn-Ca-Zr alloys produced by squeeze casting and semi-solid squeeze casting.

alloy. The unchanged tensile strength despite the coarsening of primary crystal and the improved elongation result from not only the refining of the melted αMg phase and the brittle eutectic compound dissociated in the semi-solid state but also the reduction of solidification shrinkage and porosity. The decrease of 0.2% proof stress is caused by the marked increase of the size of primary crystal because grain boundary acts as an obstacle to the dislocation motion, i.e., the grain size strengthening contributes largely to the strain hardening.

The microstructures in the vicinity of fracture surface and SEM images of fracture surface in the Mg-Zn-Ca-Zr alloy ingots produced by squeeze casting and semi-solid forging are shown in Fig. 12. The microstructures in the vicinity of fracture surface in the Mg-Zn-Ca-Zr alloy ingots produced by squeeze casting and semi-solid forging reveal intergranular fracture. In particular, the fracture in the semi-solid squeeze cast Mg-Zn-Ca-Zr alloy ingot occurs with passing through the refined eutectic region which is liquid in the semi-solid state. Accordingly, the refining of the eutectic structure must be one of factors giving rise to the improvement of tensile strength and elongation. The fracture surfaces also show intergranular fracture surface with bumpiness corresponding to size of grains in the microstructures in the vicinity of the fracture surface. The bumpiness in the semi-solid squeeze cast Mg-Zn-Ca-Zr alloy is lager than that of the squeeze cast Mg-Zn-Ca-Zr alloy due to the coarsening of primary crystal in the semi-solid state. In the fracture surface of the semi-solid squeeze cast Mg-Zn-Ca-Zr alloy, notch-steps showing the area of refined brittle eutectic are smaller than that in the squeeze cast Mg-Zn-Ca-Zr alloy.

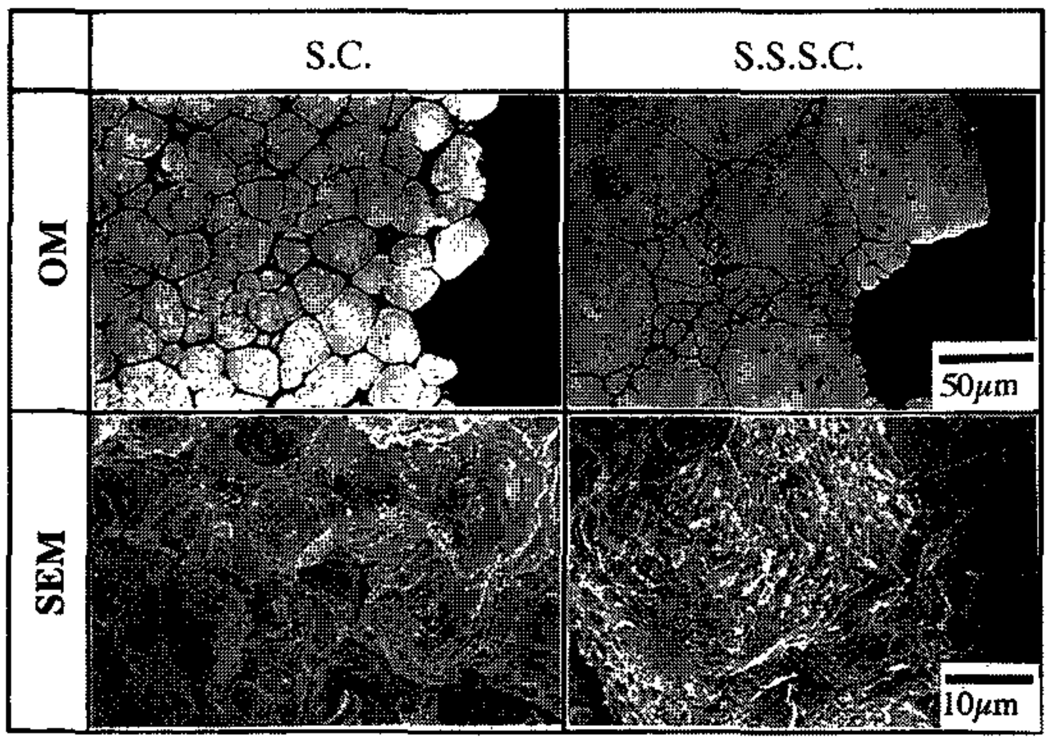

Fig. 12. Microstructures in the vicinity of fracture surface and SEM images of fracture surface in Mg-Zn-Ca-Zr alloys produced by squeeze casting and semi-solid squeeze casting.

4. Conclusions

The ignition-proof Mg-Zn-Ca-Zr alloy was produced by semi-solid forging. The mechanical behavior and microstructure evolution of the ignition-proof Mg-Zn-Ca-Zr alloy during the semi-solid state were investigated. The mechanical properties were compared with those of Mg-Zn-Ca-Zr alloy produced by squeeze casting.

The increase of semi-solid temperature gives rise to the slight increase of size of primary crystal and the decrease of solid fraction. The size of primary crystal increases with increasing holding time, the growth kinetics of primary crystal in the ignition-proof Mg-Zn-Ca-Zr alloy at 868K and 883K follow a $R^* \propto Kt$ law.

The decrease of solid fraction accompanying the increase of the refined region gives rise to the increase of tensile strength and elongation, while the 0.2% proof stress decreases. The tensile strength and 0.2% proof stress of the ignition-proof Mg-Zn-Ca-Zr alloy produced by semi-solid forging at 868K and 883K decrease as the size of primary crystal increases, indicating that the strength depends on the size of primary crystal. But, the elongation increases as the size of primary crystal increases. The semi-solid squeeze cast Mg-Zn-Ca-Zr alloy produced at 883K without holding shows the most excellent tensile properties among the others.

The elongation of the semi-solid squeeze cast Mg-Zn-Ca-Zr alloy is two times as large as the squeeze cast Mg-Zn-Ca-Zr alloy and the tensile strength is unchanged despite the growth of primary crystal. This results from the refining of the melted αMg phase and the brittle eutectic dissociated during the semi-solid state as well as the reduction of solidification shrinkage and porosities.

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