Effect of Li_2O Addition on Crystallization Behavior of $\text{CaO-Al}_2\text{O}_3\text{-MgO}$ Based Inclusions

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The crystallization behavior of $\text{CaO-Al}_2\text{O}_3\text{-MgO}$ oxide powder which is one of the major non-metallic inclusions in Al-killed steel was systematically examined in the present study. 33mass% CaO –62mass% Al_2O_3 –5mass% MgO and 30mass% CaO –57mass% Al_2O_3 –5mass% MgO –8mass% Li_2O glass powders were heat-treated at 1073–1673 K for 8–512 s under air.

$\text{CaO-Al}_2\text{O}_3\text{-MgO}$ glass was found to be crystallized immediately after the heat treatments. Moreover, it was revealed that the addition of Li_2O accelerated the crystallization of the glass powders, and controlled aggregation of crystal particles. Additionally, the indentation hardness of crystallized glasses after 512 s heat-treatments was investigated by using a nano-indenter. The addition of Li_2O had the effect of lowering the hardness of samples, which indicates that Li_2O would improve the deformation behavior of aluminate based inclusions.

KEY WORDS: crystallization; TTT diagram; aluminate; hardness; deformation.

1. Introduction

The required level of cleanliness of steel has become stricter year by year. It is well known that non-metallic inclusions will degrade the quality of clean steel especially regarding mechanical properties and workability. Thus, numerous efforts have been made to control the composition of the non-metallic inclusions in molten steel^{1–6)} and the morphology of inclusions in solid phase steel.^{7–11)}

The behavior of non-metallic inclusions in solid phase steel has been investigated mainly for Si-killed steel. Ohshiro *et al.* reported that control of the composition of the inclusions to make them easily deformable during hot rolling was effective in improving the reliability of high fatigue spring steel.⁹⁾ Kimura *et al.* investigated the behavior of inclusions during hot rolling and cold drawing,¹⁰⁾ and concluded that the fracture probability of oxide inclusions can be predicted from Young's modulus and mean atomic volume of the oxides that was introduced by them. Shiraiwa *et al.* investigated crystallization behavior for the $\text{MnO-Al}_2\text{O}_3\text{-SiO}_2$ and $\text{CaO-MnO-Al}_2\text{O}_3\text{-SiO}_2$ systems and the deformation behavior of non-metallic inclusions in solid steel. They determined the softening temperature for glassy state inclusions, and concluded that non-metallic inclusions were deformable when hot rolling processes were carried out at higher temperatures than their softening point.¹¹⁾

The crystallization behavior of oxides which include SiO_2 has been investigated not only for the application in the control of inclusions. For example, Asayama *et al.* investigated

phase transformation of cordierite glass ($2\text{MgO-2Al}_2\text{O}_3\text{-5SiO}_2$) to α -cordierite to optimize the condition for the cordierite ceramics production.¹²⁾ Mizuno *et al.* investigated the crystallization behavior of mold flux ($\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-Na}_2\text{O-F-MgO}$).¹³⁾ As mentioned above, numerous investigations have been carried out on silicate glasses for various purposes. However, crystallization behaviors of aluminate systems were not investigated in detail because of the experimental difficulty whereby aluminate glass immediately crystallizes as a consequence of its weak network structure.

The purpose of the present study is to control the morphology of non-metallic inclusions in Al-killed steel, which consists of oxides without SiO_2 as Al_2O_3 , $\text{MgO-Al}_2\text{O}_3$, and $\text{CaO-Al}_2\text{O}_3\text{-MgO}$. Then, the effect of Li_2O addition on the crystallization behavior of $\text{CaO-Al}_2\text{O}_3\text{-MgO}$ system was systematically investigated. Additionally, the indentation hardness of crystallized glasses was measured.

2. Experimental Procedure

2.1. Sample Preparation

Chemical compositions in mass% of sample oxides employed in the present study are shown in **Table 1**, which are plotted in the phase diagram of $\text{CaO-Al}_2\text{O}_3\text{-MgO}$ system¹⁴⁾ shown in **Fig. 1**. The composition of both samples are in the Alkemade triangle of $\text{CaO-Al}_2\text{O}_3$, $3\text{CaO-2Al}_2\text{O}_3\text{-MgO}$ and MgO .

Reagent grade CaCO_3 , Al_2O_3 , MgO , and Li_2CO_3 powders

Table 1. Chemical composition (mass%).

CaO	Al ₂ O ₃	MgO	Li ₂ O
33	62	5	—
30	57	5	8

Fig. 1. Phase diagram of CaO–Al₂O₃–MgO system. Solid circles indicate the slag compositions employed in the present study.

were weighed to form given compositions (cf. Table 1) and mixed in a mortar. The powder mixtures were placed in a Pt crucible and melted in a SiC electric resistance furnace at 1 873 K. After that, the sample melts were quenched on a polished copper plate. These quenched glasses were ground into a powder and the powder size was controlled to 30–50 μm by using a stainless sieve.

2.2. Heat Treatment for Crystallization

Heat treatments of glass powders were carried out by using a SiC electric resistance furnace in air. One g of the sample glass powder was put in a Pt crucible, and the crucible inserted in the furnace which was preheated to 1 073–1 673 K. The temperatures were measured by using an R-type Pt–Rh thermocouple placed under the crucible. After 8–512 s holding, the samples in the Pt crucible were water-quenched.

2.3. Characterization

Phase identification was conducted by a X-ray diffractometer (XRD, Rotaflex Ru-200, Shimadzu Corporation) using Cu–K α radiation for CaO–Al₂O₃–MgO glasses, and Co–K α radiation for CaO–Al₂O₃–MgO–Li₂O glasses. The crystallinity of samples was determined in accordance with XRD internal standard method, which employed Si as a standard substance.

The morphology of precipitated crystalline phases was observed by using a scanning electron microscope (SEM, JSM-5600, JEOL). Specimens for the SEM observation were prepared as follows. Heat-treated sample powder was fixed in an acrylic tube with resin, then polished progressively using SiC paper and diamond paste. The polished surface of samples was chemically etched with 4.6 mass% HF aqueous solution for 90 s to make the observation easy. The

Fig. 2. XRD diffraction patterns of CaO–Al₂O₃–MgO glass after heat treatment at 1 273 K for various holding time. **Fig. 3.** XRD diffraction patterns of CaO–Al₂O₃–MgO glass after heat treatment at various temperature for 512 s.

dimensions of the crystal particles precipitated were measured by image analysis on the SEM micro-images.

Measurement of indentation hardness was conducted by using a nano indenter (Nano Indenter XP, MTS) to investigate deformation behavior of the crystalline inclusions. Before the measurements, the sample powder was fixed with resin, then the change in the indentation hardnesses of several crystallized powders of each sample were measured. The hardness was calculated with the load on the indenter and the displacement from the surface of a single particle of crystallized glass.

3. Results and Discussion

3.1. Crystallization Behavior

Figure 2 shows, as an example, X-ray diffraction patterns of the CAM heat-treated at 1 273 K for various holding times. These results indicated that the CAM glass crystallized progressively with holding time, which similar tendencies were found in other samples.

Figure 3 illustrates X-ray diffraction patterns of the CAM heat-treated at several temperatures for 512 s. After 512 s heat-treatments, the CAM glass powders were found to be crystallized with holding time. In addition, after heat-treatments above 1 573 K, another crystalline phase (12CaO·7Al₂O₃) was detected, which did not correspond

with the equilibrium phases ($\text{CaO} \cdot \text{Al}_2\text{O}_3$, $3\text{CaO} \cdot 2\text{Al}_2\text{O}_3 \cdot \text{MgO}$ and MgO) of the CAM.

Many investigations have been carried out regarding the stability of $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ phase in the Al_2O_3 – CaO system.^{15–17} Among them, Nurse *et al.* concluded that the $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ phase was not stable under strictly anhydrous conditions, however was stabilized by the presence of moisture.¹⁵ The glass samples in the present study was heat-treated under air atmosphere that had not been treated with any dehydration systems, which indicated that the presence of moisture would be the reason for the formation of $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ phase.

Figure 4 reveals X-ray diffraction patterns of the CAML heat-treated at several temperatures for 512 s. The CAML glass similarly crystallized after 512 s heat-treatments with holding time, however the crystalline phases precipitated were $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ and $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3$, which was independent of the holding temperatures in the range of 1273–1523 K.

3.2. TTT Diagrams

The results of XRD analysis described above are summarized in TTT diagrams of crystallization. **Figure 5** shows the TTT diagram of the CAM glass. The solid curves in Fig. 5 indicate the crystallinity which was determined by the XRD

Fig. 4. XRD diffraction patterns of CaO – Al_2O_3 – MgO – Li_2O glass after heat treatment at various temperature for 512 s.

Fig. 5. TTT diagram on crystallization of CaO – Al_2O_3 – MgO glass with crystallinity curves.

internal standard method. As can be seen in Fig. 5, with the heat-treatments at temperatures above 1273 K, the crystallization started after a very short holding time of less than 100 s. Moreover, the crystallinity increased with the holding time, and the rate of crystallization increased with the holding temperature.

It is well known that, in silicate systems, glassy phases are easily obtained. In other words, crystallization does not occur easily, which is attributed to the low diffusivity due to the rigidly bonded silicate networks $(\text{SiO}_4^{4-})_n$. The crystallization rate of the aluminate based inclusions in the present study was significantly higher than that of silicate based inclusions in the previous investigation,³⁾ which is responsible for the structure of aluminate melts without rigid networks as silicate melts.

The TTT diagram of the CAML glass is shown in **Fig. 6**. As shown in Fig. 6, the crystallinity curves of the CAML glass were placed in a shorter holding time region than that of the CAM glass. These results indicate that the addition of Li_2O will accelerate the crystallization of CaO – Al_2O_3 – MgO system, which might be attributed to the fact that Li_2O would lower the viscosity of aluminate melts.

3.3. SEM Observation

Figures 7 and 8 reveals SEM images of the chemical etched surface of the CAM and the CAML glasses heat-treated at given temperatures. The morphology of precipitated crystal grains was found to be spherical in both glasses, and the crystal grains can be seen to precipitate in the entire region of the glass powder. Moreover, the crystal grains precipitated in the CAM glass formed aggregates, which resulted in large grains. However, it should be noted that the size of crystal grain precipitated in the CAML glass was found to be much finer than that of the CAM glass, which is attributed to the fact that the crystal grains would not aggregate.

Figures 9 and 10 indicate the mean grain size of crystal precipitated in the CAM and the CAML glasses as a function of the holding time, respectively. As can be seen in Fig. 9, the grain size of crystals in the CAM increased up to several micrometers with the holding time. In contrast, as can be seen in Fig. 10, the grain size of crystals in the CAML did not reveal significant increase with the holding time. The sizes of the crystal grains were consequently less than $0.2 \mu\text{m}$. These results clearly suggest that the addition of

Fig. 6. TTT diagram on crystallization of CaO – Al_2O_3 – MgO – Li_2O glass with crystallinity curves.

CaO-Al₂O₃-MgO heat treated at 1273 K

CaO-Al₂O₃-MgO heat treated at 1673 K

Fig. 7. SEM images of etched surface of CaO-Al₂O₃-MgO glass after heat treatments.

CaO-Al₂O₃-MgO-Li₂O heat treated at 1273 K

CaO-Al₂O₃-MgO-Li₂O heat treated at 1573 K

Fig. 8. SEM images of etched surface of CaO-Al₂O₃-MgO-Li₂O glass after heat treatments.

Fig. 9. Mean grain size of precipitated crystal in CaO–Al₂O₃–MgO glass as a function of holding time at given temperature.

Fig. 10. Mean grain size of precipitated crystal in CaO–Al₂O₃–MgO–Li₂O glass as a function of holding time at given temperature.

Fig. 11. Indentation hardness of CaO–Al₂O₃–MgO based inclusions as a function of displacement from the surface.

Li₂O can suppress the aggregation of the crystal grains in the CaO–Al₂O₃–MgO system.

3.4. Deformation Behavior

Figure 11 reveals the hardness of the CAM and the CAML glasses heat-treated at 1573 K for 512 s, namely 100% crystallinity samples. As shown in Fig. 11, although the hardness of the CAM glass increased to 10 GPa, in contrast, the hardness of the CAML glass is less than 3 GPa with the displacement. The difference in the hardness is attributed to the grain size in the crystallized glass particle mentioned in Figs. 9 and 10, and represents the difference in deformation resistance of crystallized glass. Consequently, these results obtained in the present study suggest that the addition of Li₂O can significantly improve the plastic deformability of aluminate based inclusions.

4. Conclusions

The crystallization behavior of 33mass%CaO–62mass%Al₂O₃–5mass%MgO and 30mass%CaO–57mass%Al₂O₃–5mass%MgO–8mass%Li₂O glass were systematically investigated. In addition, the indentation hardness that corresponds to the deformability of inclusion was measured on the selected samples.

Although the crystallization rate of the CAM glass was significantly larger than that of silicate glasses, furthermore the addition of Li₂O clearly accelerated the crystallization of the CaO–Al₂O₃–MgO system and suppressed the formation of aggregates. Consequently, the CAML glass generated the finer crystal grains after heat-treatments, which resulted in a lower indentation hardness than that of the CAM glass.

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