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Effect of ZrO_2 on the alkali feldspar–aluminosilicate interface

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The contact angles of the alkali feldspars containing 0, 4, 8 and 12 vol % ZrO_2 on the aluminosilicate substrate were measured by sessile drop method. During the heating from 1350 to 1520° C and the holding at 1350° C, the contact angles were generally increased with increasing ZrO_2 content. 8 vol % ZrO_2 in the melt drop was very effective to raise the contact angles and 12 vol % ZrO_2 was barely sufficient to maintain the contact angles at around 90° or larger at elevated temperatures. The SEM micrographs indicated that ZrO_2 particles were scattered throughout the drop and also located in the interface between the drop and substrate. The dissolution of the substrate by liquid feldspar and the diffusion of ZrO_2 in the substrate were also observed. The cause of the increase in contact angle with increasing ZrO_2 content are discussed.

1. Introduction

Contact angle $\theta = 90°$ is defined as the boundary between nonwetting ($\theta > 90°$) and wetting ($\theta < 90°$) [1]. In ceramics, most efforts were made to enhance wetting behaviour for a good adhesion between metal and ceramic such as metal brazes for use with oxides, sintering with a reactive liquid [1], and metal glass sealing [2], etc., but there are few references in the literature dealing with enhancing nonwetting behaviours.

Sliding gate systems for steel ladles are important for the smooth operation of continuous casting and secondary steelmaking. Pan and Ko [3] explored the mineralogical aspects and melting behaviours of commercial packing sands for the sliding gate systems and identified feldspar, specifically microcline as a constituent of the packing sands; the wetting/nonwetting transition temperature of liquid feldspar on silica was proposed as a criterion for the selection of feldspars for use in packing sands and larger contact angles at temperature were preferred by Lee and Ko [4]; the validity of the proposal was subsequently confirmed by Chien *et al.* [5].

Higher steel temperatures and a longer holding time in the steel ladle are the current trends of steelmaking. The availability of natural feldspars in commercial scale for use in packing sands production could be unreliable in future because the alkali feldspars containing $> 12\% K_2O$ and $< 2\% Na_2O$ are generally suitable for the current packing sands production [4]. Consequently, it appears to be feasible to develop a synthetic feldspar to substitute natural feldspars if a higher contact angle is required at a given temperature to meet the severer environment in steelmaking.

The purpose of the present work was to investigate the wetting behaviours of mixtures of alkali feldspar and zirconia by the sessile drop technique. Zirconia was chosen due to its high surface energy [6] and chemical inertness with molten glasses [7].

2. Experimental details

2.1. Materials

Mixtures of natural alkali feldspar and zirconia containing 0, 4, 8 and 12 vol% ZrO_2 were prepared. Sizes of feldspar and zirconia were below 75 μm. The chemical analysis of the feldspar and zirconia is given in Table I.

2.2. Apparatus

A 1600° C high temperature heating microscope* was used to observe and record the evolution of

*Heating microscope type 1-A, Leitz Co., D-6330 Wetzlar, W. Germany.

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TABLE I Chemical analysis of alkali feldspar and zirconia

Type	Feldspar (wt %)	Zirconia* (wt %)
SiO_2	66.78	
Al_2O_3	18.86	
Fe_2O_3	0.11	
Na_2O	8.85	
K_2O	3.26	
CaO + MgO	0.56	0.15
ZrO_2		98.5

*Monoclinic ZrO_2, product no. Z296p8086A, Atomergic Chemical Corp., Plainview, New York, USA.

melting of a specimen. The microscope was equipped with a built-in camera and a screen from which the profile changes of a specimen during heating and holding can be clearly viewed.

2.3. Procedure

A pellet 3 mm high by 3 mm diameter was formed by hand press. Then the pellet was placed on a flat fireclay substrate (60% Al_2O_3)† in the microscope, and heated at a rate of $10°C\,min^{-1}$. Dimensional and contact angle changes against temperature were closely observed during the heating and holding. Profiles of a melt drop at temperature intervals were taken through the built-in camera and contact angles determined by measuring from the photographs.

The tested specimens were cut cross sectionally. Scanning electron microscopy‡ (SEM) and X-ray mapping‡ (XRM) were conducted for an investigation of microstructural changes of the melt drops and fireclay substrate.

The melt drop containing 8 vol% ZrO_2 was quenched in the water after 1 h holding at 1350° C. The SEM micrograph indicated that ZrO_2 existed as particles in the drop during the contact angle measurement.

3. Results and discussion

Fig. 1 shows the temperature dependence of the contact angle for melt drops from 1300 to 1520° C, and Fig. 2 gives the time dependence of the contact angle for the same drops at 1350° C. As can be seen, the contact angles decreased with increasing temperature for all the melt drops except the one containing 12 vol% ZrO_2, but the contact angles for the melt drops containing 4 and 8 vol% ZrO_2 maintained a constant value with increasing temperature from 1440 and 1400° C, respectively; during holding at 1350° C, the contact angles also decreased with increasing time for all the melt drops except the one containing 12 vol% ZrO_2, but the contact angles for the melt drops containing 4 and 8 vol% ZrO_2 again maintained a constant value after 35 and 25 min holding at 1350° C, respectively; the contact angles for the melt drop containing 12 vol% ZrO_2 increased slightly with increasing temperature during

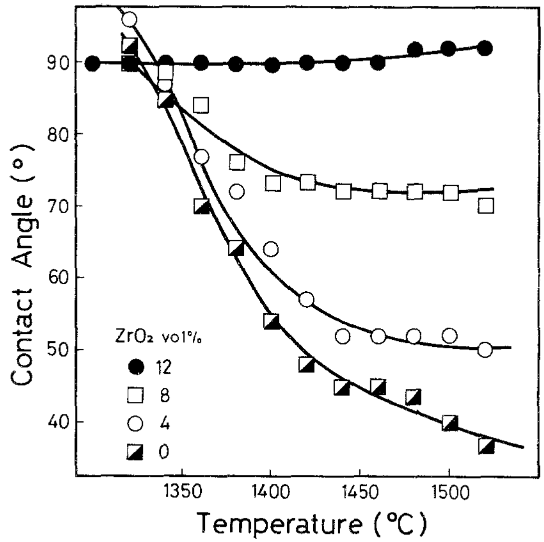

Figure 1 Temperature dependence of contact angle between feldspar and 60% Al_2O_3 aluminosilicate substrate.

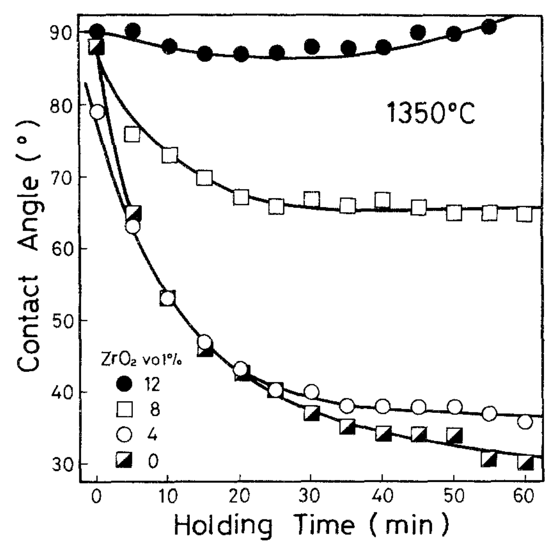

Figure 2 Time dependence of contact angle between feldspar and 60% Al_2O_3 aluminosilicate substrate.

†Fireclay plate no. 580544, Leitz Co., D-6330 Wetzlar, W. Germany.
‡Scanning Electron Microscope, type Autoscan, ETEC Corp., Hayward, California 94545, USA.

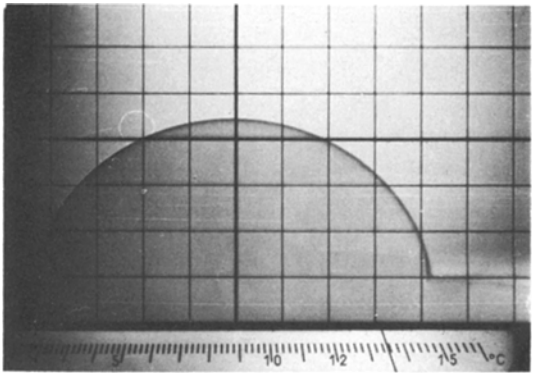

Figure 3 Profile of the feldspar melt drop containing 8 vol % ZrO_2 after 60 min holding at 1350° C.

heating, but decreased and then increased slightly during holding at 1350° C. Apparently, 8 vol % ZrO_2 in the melt drop is quite effective to raise the contact angle. Moreover, 12 vol % ZrO_2 in the melt is barely sufficient to maintain contact angles around 90° or larger. The wetting behaviours of alkali feldspar on the fireclay substrate and silica, respectively, are very close as reported by Pan and Ko [3]. Consequently, the synthetic alkali feldspars containing > 4 vol % ZrO_2 should be a substitute for natural feldspars if higher steel temperatures and longer holding times are required for steel ladle operation in connection with continuous casting in the future.

Fig. 3 shows the profile of the melt drop containing 8 vol % ZrO_2 at 1350° C. The SEM micrograph (Fig. 4a) for the same drop revealed that ZrO_2 particles were scattered throughout the drop and the dissolution of the fireclay substrate by the liquid feldspar occurred. The corresponding XRM micrograph (Fig. 4b) showed the diffusion of ZrO_2 from the melt drop into the substrate. The SEM micrograph at higher magnification (Fig. 5a) indicated that the periphery of ZrO_2 particles is round, and the corresponding XRM micrograph (Fig. 5b) also showed that ZrO_2 appears in the void of ZrO_2 assemblies. The solution of ZrO_2 particles in the melt is suggested. The SEM micrograph (Fig. 4a) also revealed that bubbles appeared in the interface between the melt drop and the substrate. The bubbles also appeared elsewhere in the melt. The evaporation of alkali vapour was related to the formation of bubbles in glasses containing alkali feldspars [8]. Apparently, alkali bubbles nucleated and grew at the solid–liquid interface and then moved upward. The present work observed that bubbles appeared regardless of whether the drop contained ZrO_2 or not.

Surface energy is an additive property [6] and

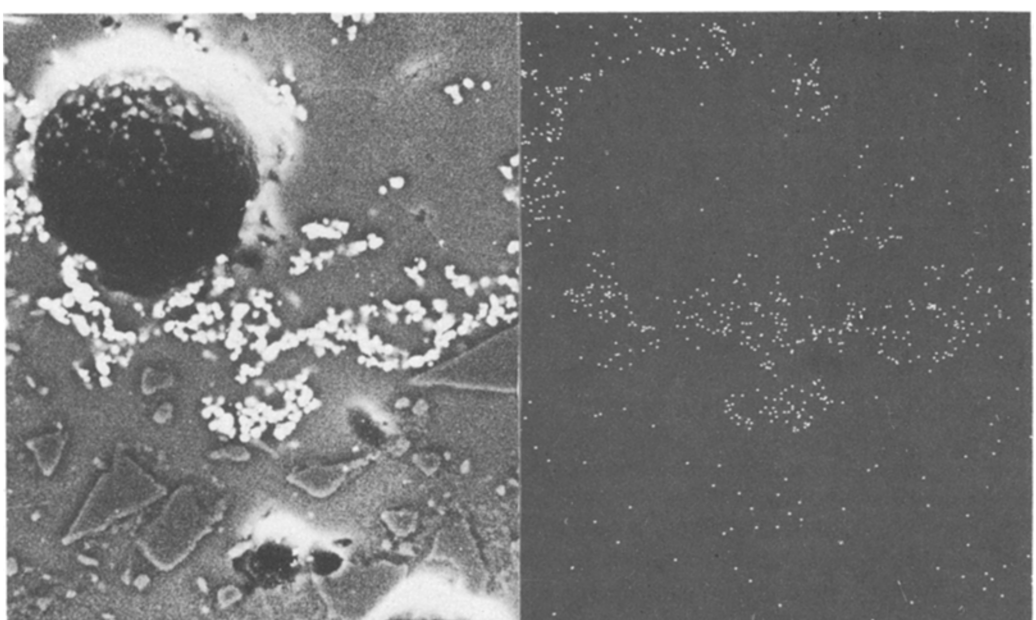

Figure 4 SEM and XRM micrographs for the melt drop as shown in Fig. 3, (a) SEM, (b) XRM, ($ZrK\alpha$).

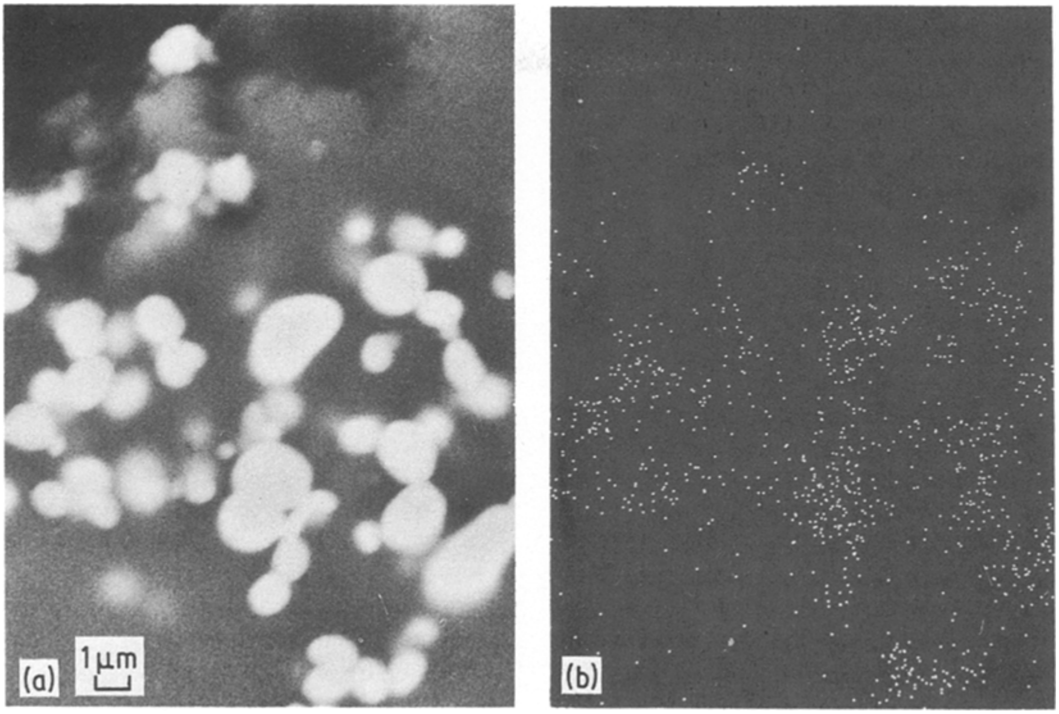

Figure 5 SEM and XRM micrographs for the melt drop as shown in Fig. 3 at higher magnification, (a) SEM, (b) XRM, (Zr*K*α).

ZrO_2 has a much higher surface energy in comparison with silicate glasses [6]. Consequently, the feldspar melt drop with ZrO_2 has a higher surface energy than that without ZrO_2, and the higher the ZrO_2 content, the higher the surface energy in the melt drop. As shown in Figs. 1 and 2, and the contact angles are consistently larger than 90° for the drop containing 12 vol % ZrO_2 during the later stages of contact angle measurement. It appears that this was possible only when the solid–liquid interface energy was increased at the time of measurement. The solid–liquid interface energy appears to be raised when feldspar melt drops contain ZrO_2, and the interface energy increases with increasing ZrO_2 content.

The contact angle is governed by interface energy as given by Young's equation [9]:

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}$$

where θ is the contact angle, γ_{sv} is the solid–vapour interface energy, γ_{sl} is the solid–liquid interface energy, and γ_{lv} is the liquid–vapour interface energy. It can be seen that $\cos\theta$ is decreased and hence θ is increased by a raising of γ_{lv} or γ_{sl}. This possibly explains the effect of ZrO_2 on the alkali feldspar–aluminosilicate interface as observed by the present work.

4. Summary and conclusions

1. The contact angles of the alkali feldspars containing 0, 4, 8 and 12 vol % ZrO_2 on the aluminosilicate substrate were measured by the sessile drop method.

2. During heating from 1350 to 1520° C and holding at 1350° C, the contact angles were generally increased with increasing ZrO_2 content.

3. 8 vol % ZrO_2 in the melt drop was very effective to raise the contact angles and 12 vol % ZrO_2 was barely sufficient to maintain the contact angles around 90° or larger at elevated temperatures.

4. The SEM micrographs indicated that ZrO_2 particles were scattered throughout the drop and also located in the interface between the drop and substrate. The dissolution of the substrate and the diffusion of ZrO_2 in the substrate were also observed.

5. The increase in contact angle with increasing ZrO_2 content is possibly caused by a raising of the liquid–vapour or solid–liquid interface energy.

Acknowledgement

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