Phase Diagram for the System CaO-Al₂O₃-ZrO₂

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Phase equilibria in the system CaO-Al₂O₃-ZrO₂ were studied to optimize nozzle composition for tundishes that are used in continuous casters of steel, by identifying the composition that minimizes clogging. Mixtures of CaO, Al₂O₃, and ZrO₂ with various compositions were equilibrated at 1873 and 1773 K and then quenched into water. X-ray diffraction analysis was used for phase identification, and electron probe microanalysis was employed to measure chemical compositions. On the basis of these and previous results, the eutectic and peritectic lines have been estimated. Based on the phase diagram, the optimal nozzle composition is CaO-saturated CaZrO₃.

I. INTRODUCTION

In recent years, Al₂O₃ agglomeration onto a tundish nozzle has been a serious problem for the continuous casting process of steel. Nozzle clogging by agglomerated Al₂O₃ gives rise to a nonuniform flow of molten steel in the mold, plus defects in products from large Al₂O₃ inclusions, which separate from the clogged nozzle. Moreover, nozzle consumption must be minimized to remain competitive in the current global economy. Thus, prevention of nozzle clogging has received considerable attention.

Several investigations on the mechanism of the clogging and its prevention have been reported. Ogibayashi has reviewed the factors that influence clogging, as follows: (1) deoxidation method, (2) cleanliness of steel, (3) Ar gas injection through a nozzle, (4) steel temperature, and (5) nozzle composition. In particular, nozzle materials that react with Al₂O₃ and form a low-melting slag have attracted growing interest. CaO or CaO-ZrO₂ has been proposed as nozzle materials. Since the CaO nozzle is not chemically stable in the metallurgical operation, CaO-ZrO₂ has been considered a more promising material. For practical use of the CaO-ZrO₂ nozzle, wettability of molten steel and the mechanism of Al₂O₃ agglomeration have been studied. Formation of a CaO-Al₂O₃-ZrO₂ molten slag should be taken into account for a better understanding of the nozzle clogging phenomena and to identify optimal chemical compositions for the nozzle. Therefore, knowledge of thermodynamic properties for the CaO-Al₂O₃-ZrO₂ system, such as the phase diagram and activities, are essentially required at molten steel temperatures.

The phase diagram of the CaO-Al₂O₃-ZrO₂ system was first reported by Berezhnoi and Kordyuk. They determined a single-phase region of the liquid and the stoichiometric composition of the ternary compound as Ca₇Al₁₃ZrO₁₈ (C₇A₁₃Z) with melting point 1823 K. Espinosa and White, however, reported that the ternary compound is Ca₁₁₃Al₁₁₂ZrO₅₅ (C₁₁₃A₁₁₂Z₅₅) and that it decomposes into CaZrO₃ (CZ) plus liquid by a peritectic reaction at 1813 ± 10 K. In addition, the single-phase region of liquid presented by Espinosa and White was much larger than that by Berezhnoi and Kordyuk. Thus, there is a significant discrepancy between the two reports. Bannister reported the solid-phase equilibria of the system determined from the study on an oxygen sensor using stabilized ZrO₂. Some of the present authors reported the liquidus composition of the ternary compound as Ca₇Al₁₃ZrO₁₈ saturated with the CaO and CZ phases at 1873 K. Sakai and Suito determined the two liquidus compositions doubly saturated with the CaO and CZ phases at 1873 K. There is, however, considerable doubt in Sakai and Suito’s results as to establishment of equilibrium, since they used Al₂O₃, CaO, and ZrO₂ crucibles, which may react with the liquid phase at the interfaces.

Other subsystems of CaO-Al₂O₃-ZrO₂ have been investigated by the following researchers: Liddle and Brett reported on the CaAl₂O₄ (CA)-CZ system; on the CaO-Al₂O₃ system, Nurse et al. concluded that CA and CA₂ are incongruently melting compounds; Lea and Desch, however, reported that these compounds melt congruently. The CaO-ZrO₂ system was studied by Stubicanc, and the eutectoid transformation temperature was revised based on the results of the activity measurements by Tanabe and Agata. On the Al₂O₃-ZrO₂ system, some results are summarized in the SLAG ATLAS. Thus, although phase diagrams are currently available for some subsystems, the ternary phase diagram of the CaO-Al₂O₃-ZrO₂ system is not well established. The aim of the present study is to experimentally determine the equilibrium phase relations of the ternary system at 1873 and 1773 K. The present study is to experimentally determine the equilibrium phase relations of the ternary system at 1873 and 1773 K. First, the phase relations are approximately estimated based on the previously described studies and presented in Figure 1. The compositions of single-phase regions are experimentally determined for the liquid phase, cubic and tetragonal ZrO₂ solid solutions, and ternary compound. The melting reaction of CA and the relation between the phase diagram and the activity of CaO are also discussed. Consequently, based on the results of the phase diagram obtained, the optimal composition of the nozzle is discussed.
Phase equilibria were studied by using the synthesized compounds mixed with Al₂O₃, CaO, or ZrO₂ as starting materials. The initial compositions are listed with the experimental procedures in Table II and presented as the open squares in the tentative phase diagram shown in Figures 1(a) and (b). Mixtures were pressed into tablets of 10-mm diameter and 3-mm thickness with a load of 213 MPa. The tablets were contained in a platinum crucible, whose diameter and wall thickness were 15 and 0.05 mm, respectively; then suspended at a uniform temperature region in a LaCrO₃ resistance furnace. All experiments were carried out in air. The temperature of the furnace was controlled within ±1 K, and the temperature of the sample was measured using a Pt·30 pct Rh-Pt·6 pct Rh thermocouple, which was very close to the sample. In order to promote reactions, the samples were first heated at higher temperatures than the experimental temperature by 20 to 50 K for 85 to 792 ks. Samples were subsequently equilibrated at the experimental temperature for 86 to 1440 ks and then quenched in water. On quenching, liquid was readily retained as glass so that the phase assemblage existing at the equilibration temperature was evidently frozen in the samples. The phases existing in the samples were identified by XRD. The chemical composition of each phase was measured by an electron probe microanalyzer (EPMA) with an accelerating voltage of 20 kV and a probe current of 10 nA. The glasses and crystalline phases in the quenched samples provide the liquidus and the solidus compositions at the equilibration temperature.

Sintered Al₂O₃ (Al₂O₃ 5 99.5 mass pct, SiO₂ 5 0.1 mass pct, CaO 5 0.2 mass pct, and MgO 5 0.09 mass pct), stabilized ZrO₂ (ZrO₂ 5 93.4 mass pct, SiO₂ 5 0.1 mass pct, Al₂O₃ 5 0.8 mass pct, CaO 5 5.52 mass pct, MgO 5 0.1 mass pct), and single-crystalline CaO were used as standard samples for quantitative analysis by EPMA. The ZAF correction procedure was applied. Since all experiments were carried out in air, the nitrogen content in the quenched samples was measured with a LECO* oxygen-nitrogen determinator. The nitrogen content in samples was 0.24 mass pct at most, and therefore, the effect of nitrogen on the phase diagram is considered negligible.

**III. RESULTS**

**A. Equilibrium Phase Relations at 1873 K**

Attainment of an equilibrium should be confirmed by approaching an equilibrium state from different initial states, e.g., undersaturated and supersaturated states. However, in the case of the solid oxides system, it takes a considerably long time to attain an equilibrium state from an undersaturated state because of slow diffusion. Therefore, in the present study, samples were forced to be heated first at higher temperature than aimed temperature by 20 to 50 K to promote reactions and then kept at aimed temperature with different time periods, as mentioned in Section II. This allows samples to approach an equilibrium from a supersaturated state. Time dependence of chemical compositions and microstructures was examined for quenched samples. From