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Effects of temperature-gradient-induced damage of zirconia metering nozzles

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Abstract: The effects of temperature-gradient-induced damage of zirconia metering nozzles were investigated through analysis of the phase composition and microstructure of nozzle samples. The analysis was carried out using X-ray diffraction and scanning electron microscopy after the samples were subjected to a heat treatment based on the temperatures of the affected, transition, and original layers of zirconia metering nozzles during the continuous casting of steel. The results showed that, after heat treatment at 1540, 1410, or 1300°C for a dwell time of 5 h, the monoclinic zirconia phase was gradually stabilized with increasing heat-treatment temperature. Moreover, a transformation to the cubic zirconia phase occurred, accompanied by grain growth, which illustrates that the temperature gradient in zirconia metering nozzles affects the mineral composition and microstructure of the nozzles and accelerates damage, thereby deteriorating the quality and service life of the nozzles.

Keywords: temperature gradient; zirconia metering nozzles; mineral composition; microstructure; damage mechanism

1. Introduction

Partially stabilized zirconia (PSZ) has become one of the most important refractories in the metallurgy industry because of its high refractoriness, remarkable fracture toughness, and good resistance to thermal shock, corrosion, and scouring [1–3]. At present, PSZ is frequently used as a starting material for metering nozzles [4]. During the continuous casting of steel, a metering nozzle provides a reasonably steady and smooth flow of molten steel [5]. If the metering nozzle cannot tolerate the strong mechanical and chemical attacks from the molten steel and slag, the quality of steel products will be degraded or the casting process may fail. Therefore, the mechanism of damage to a zirconia metering nozzle during continuous casting of steel must first be elucidated to extend the service life of metering nozzles.

A used metering nozzle can be divided into original, transition, and affected layers according to the degree of infiltration of molten steel and slag. Previous studies on the damage mechanism of PSZ metering nozzles have revealed that infiltration of SiO_2 from steel slag causes the destabilization of zirconia [6–7]. SiO_2 and stabilizing agents (CaO, MgO, and Y_2O_3) form low-melting phases [8]; meanwhile, the cubic zirconia (c-ZrO_2) or tetragonal zirconia (t-ZrO_2) phase transforms to the monoclinic zirconia (m-ZrO_2) phase, which is related to the formation of microcracks [9]. Therefore, from the original to the affected layer, the degree of stability should theoretically decrease because the contents of the c-ZrO_2 and m-ZrO_2 phases decrease and increase, respectively. However, in our previous work [10], we found that the degree of stability did not gradually decrease from the original to the affected layer; the change was actually irregular, as shown in Fig. 1. Thus, other factors might have affected the mineral phase of the zirconia metering nozzle.

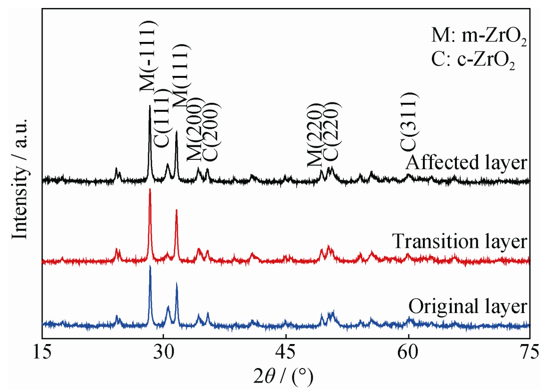

Fig. 1. X-ray diffraction (XRD) patterns of the layers in a used zirconia metering nozzle.

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PSZ has a low thermal conductivity and is an ideal starting material for components that require low heat loss [11]; however, low thermal conductivity causes an obvious temperature gradient in a metering nozzle during the continuous casting of steel. In our previous works, we used the ANSYS software to obtain the temperatures of the original, transition, and affected layers during continuous casting through finite element analysis of the temperature field distribution for a zirconia metering nozzle [12]. In this paper, the metering nozzle samples were heat treated at different temperatures (1300, 1410, and 1540°C, corresponding to the original, transition, and affected layers, respectively) to simulate the casting environment and the mineral composition and microstructure of the samples were subsequently characterized. The effects of the temperature-gradient-induced damage to the zirconia metering nozzle were investigated thoroughly. The main factors that led to the damage of the zirconia metering nozzle during continuous casting were identified.

2. Experimental method and process

Two kinds of zirconia metering nozzles from different refractory factories were used in this investigation. Sample A was acquired from Anyang Special Refractories Factory, and sample B was acquired from Shanghai Jinru New Material Technologies Co., Ltd. The chemical composition and the physical characteristics of the samples are listed in Tables 1 and 2, respectively. Heat treatments were carried out at 1300, 1410, and 1540°C with a dwell time of 5 h in a high temperature creep furnace. The mineral phase composition was determined by X-ray diffraction (XRD; D/MAX 220). Microstructures were observed by scanning electron microscopy (Quanta 200).

Table 1. Chemical composition of zirconia metering nozzles wt%

Sample	ZrO_2	MgO	CaO	Y_2O_3	SiO_2	Al_2O_3	TiO_2
A	92.29	2.22	1.34	0.66	2.30	1.02	0.17
B	96.22	2.69	0.11	0.13	0.44	0.30	0.11

Table 2. Physical performance of zirconia metering nozzles

Sample	Density / ($g·cm^{-3}$)	Porosity / %	Compressive strength / MPa
A	5.08	5.76	542
B	5.28	5.53	536

3. Results and discussion

3.1. Phase compositions

The XRD patterns of samples A and B after heat treatment are shown in Fig. 2.

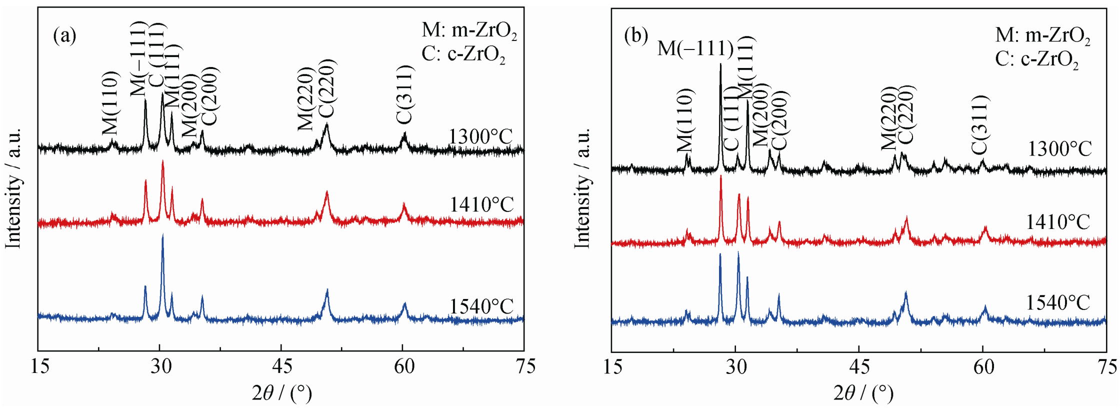

Fig. 2. XRD patterns of the heat-treated zirconia samples: (a) sample A; (b) sample B.

Fig. 2 shows that samples A and B are both composed of $m\text{-}ZrO_2$ and $c\text{-}ZrO_2$ phases. Increasing heat-treatment temperature caused the diffraction peak intensity of the (111) crystal plane of the cubic phase to increase and that of the (111) and (−111) crystal planes of the monoclinic phase to decrease. The volume fraction of the monoclinic phase V_m in the samples was obtained using Eq. (1) [13–14]:

$$V_m = \frac{I_m(-111) + I_m(111)}{I_m(111) + I_m(111) + I_c(111)} \quad (1)$$

where I_m is the intensity of the monoclinic phase peak and I_c is the intensity of the cubic phase peak.

The calculated results are shown in Fig. 3.

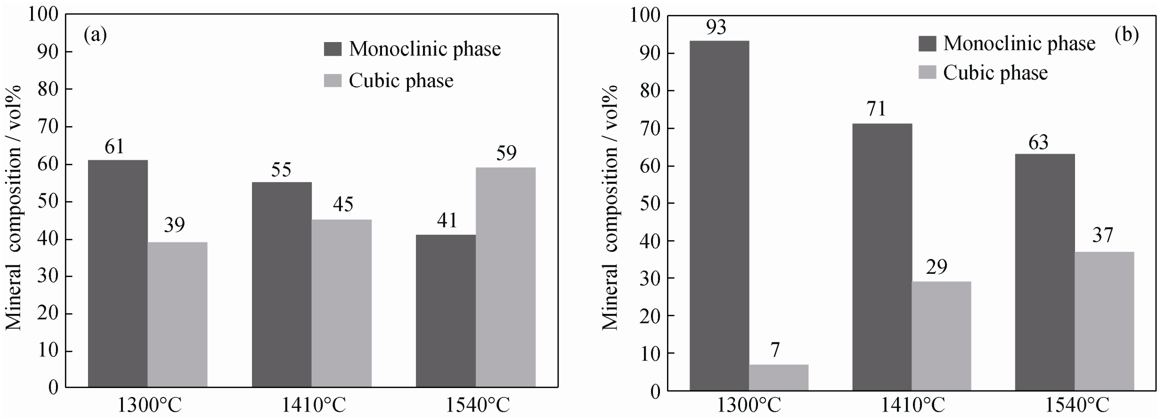

Fig. 3. Volume fractions of the monoclinic and cubic zirconia phases: (a) sample A; (b) sample B.

Fig. 3 indicates that different heat-treatment temperatures affect the mineral phase of zirconia metering nozzles. During the continuous casting of steel, the monoclinic phase was gradually stabilized and a transformation to the cubic phase occurred from the original to the affected layer under the effect of temperature gradient.

3.2. Microstructure

Fig. 4 shows the microstructures of the samples after heat treatment.

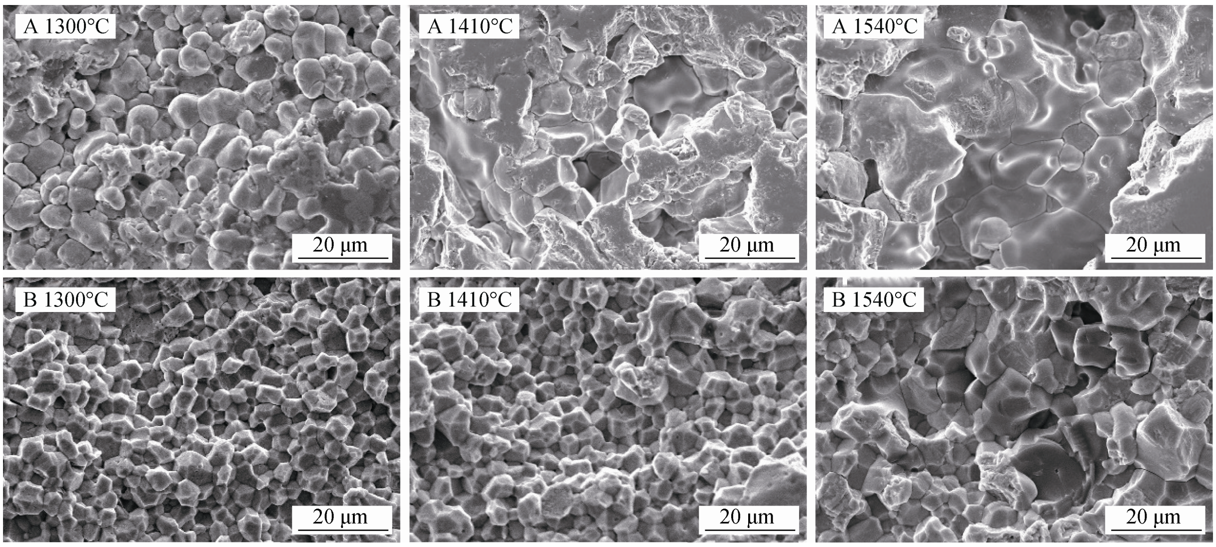

Fig. 4. Microstructures of the heat-treated zirconia samples.

As shown in Fig. 4, the zirconia grains in the sample treated at 1540°C were larger than the grains of the samples treated at 1300 and 1410°C; in addition, abnormal growth of grains occurred after heat treatment at 1540°C, especially in sample A. These observations indicate that the zirconia grains in samples A and B enlarged with increasing heat-treatment temperature in a simulated casting environment. Because the temperatures of the original, transition, and affected layers during continuous casting were 1300, 1410, and 1540°C, respectively, the grain sizes in these three layers would vary during continuous casting because of the existence of a temperature gradient.

3.3. Damage mechanism of zirconia metering nozzles

The main factors that lead to the damage of zirconia metering nozzles during continuous casting are identified in Fig. 5.

(1) Mechanical factors.

During continuous casting, the constant scouring of molten steel will break the bonds among grains, leading to diameter extension and peeling.

(2) Chemical factors.

Part of the stabilizing agent MgO is enriched in the areas of SiO_2 impurities, forming a low-melting phase; thus, the stability of the sample cannot reach its equilibrium state [15].

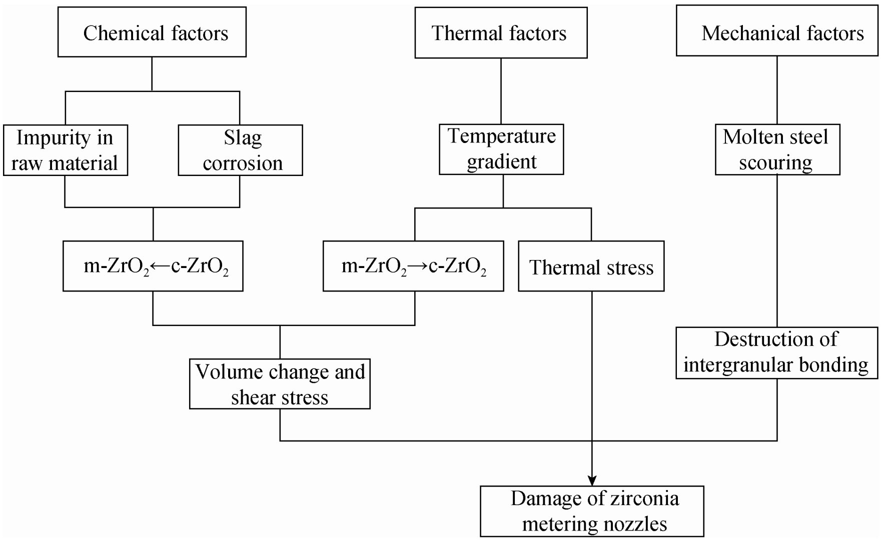

Fig. 5. Main factors that interact and lead to nozzle damage.

The infiltration of steel slag components such as SiO_2, MnO_2, and Al_2O_3 leads to the extraction of a part of the CaO and MgO from PSZ grains, accompanied by grain fracturing [14].

(3) Thermal factors.

The metering nozzle is at a low temperature (approximately 900°C) before casting and suddenly contacts the high-temperature molten steel (approximately 1540°C). These conditions will cause a significant temperature difference inside the nozzle, thereby producing great thermal stress and a possible nozzle burst.

The temperature gradient generated during the casting process causes the mineral phase of the zirconia metering nozzle to change from m-ZrO_2 to c-ZrO_2 with increasing temperature; the c-ZrO_2 content in the affected layer (1540°C) is the highest, whereas the c-ZrO_2 content in the original layer (1310°C) is the lowest. Meanwhile, grains of PSZ increased in size from the original to the affected layer.

Fig. 6 shows that the ceaseless m-ZrO_2 $\rightleftarrows$ c-ZrO_2 phase transition during the continuous casting process is caused by the comprehensive effects of slag corrosion and temperature gradient; thus, the change of the mineral phase varies from the affected to the original layer, as mentioned in the introduction. The m-ZrO_2 and c-ZrO_2 phases have different thermal expansion coefficients; thus, the continuous grain expansion and shrinkage caused by phase transition will reduce the intergranular binding and accelerate grain breakage. In addition, the simultaneous grain growth caused by temperature gradient and grain fracture induced by slag corrosion also accelerates the structural collapse of zirconia metering nozzles.

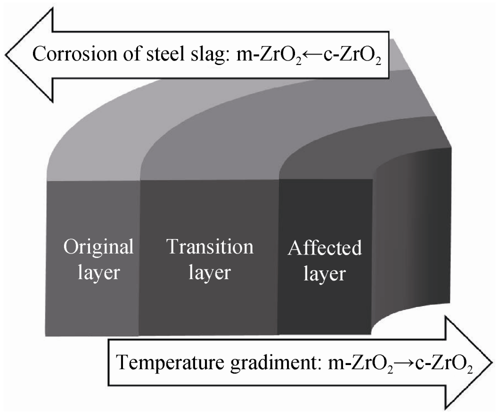

Fig. 6. Schematic of the comprehensive effect.

4. Conclusions

With increasing heat-treatment temperature, the monoclinic phase was gradually stabilized and a transformation into the cubic phase occurred from the original to the affected layer, accompanied by grain growth. The mineral phase and microstructure of nozzles were strongly affected by temperature gradient, which accelerated nozzle damage, aside from the corrosion induced by steel slag, impurities in starting materials, and steel scouring.

Acknowledgements

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