

# Modification Effect of $\text{Al}_2\text{O}_3\text{-ZrO}_2$ composite powder on fine-particle and ceramic type zirconia metering nozzles

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**ABSTRACT:**  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  composite powder by sol-gel method was added into fine-particle and ceramic type zirconia metering nozzle to prepare modified metering nozzle. The differences in performance of nozzles were studied through XRD, SEM analysis and physical property test. The results are as follows: After modified, density and strength of two type nozzles increase, porosity and stability degree decreases. The thermal shock resistance of fine-particle type nozzle improves significantly for the formation of spinel reinforcing phase, however that of ceramic type nozzle don't enhance because microstructure isn't optimized.

**KEYWORD:** Continuous casting; Metering nozzle;  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  composite powder; Modification effect

## 1 INTRODUCTION

Metering nozzle is the key function device of controlling molten steel flow and adjusting the continuous casting speed during steelmaking process. However, the service life of metering nozzle is far shorter than that of tundish lining, which is the bottleneck of overall tundish. At present, the requirements for the service life of tundish only can be met by the coordination of quick-change institutions, which will make the process of continuous casting process complex and production cost rise. Therefore, research and development on new type and long-life metering nozzle matching with the service life of tundish can not only save the production cost, but also improve working environment, reduce labor intensity and simplify the process greatly.

With excellent properties, such as high refractoriness, chemical erosion resistance, high strength, good toughness, good volume stability, partially stabilized zirconia is widely used in high-performance structural ceramics, which is the main raw material of metering nozzle currently. Metering nozzle can be divided into ceramic and particle type from the particle size of zirconia raw material. Common zirconia stabilizers are  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Y}_2\text{O}_3$ . The main reason for the

failure and offline of metering nozzle are fracture, diameter extension and blocking caused by stabilizer precipitation, continuous molten steel erosion and scouring in continuous casting process. Therefore, good erosion, scouring, and thermal shock resistance, excellent microstructure play a crucial role in improving the performance and service life of metering nozzle.

The  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  composite powder was added to modify the ceramic and fine-particle type zirconia metering nozzle for improving the performance and service life. After modified, the physical properties, thermal shock resistance, mineral phase and microstructure of metering nozzles were researched respectively, which can provide a basis for improvement of performance and service life of metering nozzles.

## 2 EXPERIMENTS

The modification effect of ceramic and fine-particle type zirconia metering nozzles was studied in this paper. The raw materials for experiment are  $\text{Mg-PSZ}$  particles, monoclinic zirconia powder and  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  composite powder prepared by sol-gel method. The chemical composition is shown in Table 1.

Table 1 The composition of the raw material (wt%)

Composition	$\text{ZrO}_2$	$\text{Y}_2\text{O}_3$	$\text{MgO}$	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{TiO}_2$	$\text{Na}_2\text{O}$
Zirconia particle	96.50	-	2.61	-	0.11	-	0.01	-	0.36
Zirconia powder	94.90	0.18	2.77	0.35	0.28	0.02	0.21	0.05	0.37
Composite powder	52.96	2.68	-	-	43.65	-	-	-	-

Table 2 The formula of various samples (wt%)

Sample	Zirconia particle	Zirconia powder	Compo-site powder	Polyving akohol
A	-	100	-	8
B	-	96.35	3.65	8
C	35	65	-	8
D	35	61.35	3.65	8

According to the formulation in Table 2, ceramic type zirconia metering nozzle A, modified ceramic type zirconia metering nozzle B, fine-particle type zirconia metering nozzle C and modified fine-particle type zirconia metering nozzle D were prepared with diameter of  $\Phi 20$  mm, height of 75 mm after firing at 1710°C for 2 h. The apparent porosity and volume density of metering nozzle were measured by XLMY-360107 apparent porosity volume density determinator. Compressive strength was measured by TYE-300B pressure tester. The thermal shock resistance at 1100°C was measured by KRZ-S01A automatic thermal shock resistance tester. The mineral phase composition had been determined by D/MAX 220 X-ray diffraction. The microstructure was observed by Quanta 200 scanning electron microscope.

### 3 TEST RESULTS AND ANALYSIS

The apparent porosity, bulk density, compressive strength and thermal shock resistance of four type metering nozzle samples are showed in Table 3.

Table 3 Physical properties of various samples

Sample	Porosity /%	Density /g.cm-3	Compressive strength /MPa	Thermal shock /Time
A	4.3	5.48	778	35
B	3.1	5.52	981	28
C	5.4	5.36	529	41
D	4.8	5.45	765	>60

From Table 3, ceramic type metering nozzle(A, B) had lower apparent porosity, larger bulk density, higher compressive strength, and poorer thermal shock resistance, compared with fine-particle type metering nozzle(C, D). This is because the ceramic type metering nozzle compression was prepared by moulding method with pure fine powder. The high reactivity of powder has a promoting effect for sintering and makes the nozzles more compact. But high density can lead to very few pores and micro cracks existing. The large thermal stress can't be absorbed by the appropriate pores which can prevent crack propagation. Therefore, the high density material is not advantage for thermal shock resistance.

After adding  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  composite powder modified, the apparent porosity of ceramic type nozzle decreased by 27.9%, bulk density increased by 0.7%, compressive strength increased by 26.1%, but the

number of thermal shock decreased; The apparent porosity of fine-particle type nozzle decreased by 11.1%, bulk density increased by 1.7%, compressive strength increased by 44.6%, especially thermal shock resistance had a great improvement, the number of thermal shock exceeded more than 60 times. The number of thermal shock was about 1.5 times higher than the unmodified.

The factors which influence the thermal shock resistance of metering nozzle are divided into material properties and the ceramic structure.

Material properties, such as thermal expansion coefficient, heat conduction coefficient, modulus of elasticity, the inherent strength, fracture toughness, etc. The second thermal stress resistance fracture factor  $R'$  is always used to evaluate thermal shock resistance of compact metering nozzle:

$$R' = \lambda \cdot \sigma_f \frac{(1 - \mu)}{\alpha E} \quad (1)$$

where  $\lambda$  = thermal conductivity;  $\sigma_f$  = strength;  $\mu$  = a poisson ratio;  $\alpha$  = thermal expansion coefficient;  $E$  = elastic modulus.

In general, the larger elastic modulus and thermal conductivity, the better thermal shock resistance; The smaller thermal expansion coefficient, the better thermal shock resistance; The higher inherent strength of sample, the greater ability to resist thermal stress and better thermal shock resistance.

The inherent strength of the material is shown in Equation 2:

$$\sigma_f = (\sigma_0 + K_I \cdot d^{-\frac{1}{2}}) e^{-nP} \quad (2)$$

where  $d$  = grain size;  $P$  = porosity;  $\sigma_0$  and  $K_I$  is a constant related to the material.

From the formula 2, the lower porosity and the smaller the grain size, the greater strength of the samples. Therefore, low porosity and small grain size are the key to obtain high strength ceramic material.

Ceramic structure, such as the structure of internal organization and geometric shape of samples. In general, relatively loose material organization, proper porosity and micro cracks existing can improve the fracture energy, make internal crack length of product short, the times of thermal shock increases, mesh degree of cracks increase, which have inhibition of fracture generating and improve thermal shock resistance of the product effectively. In addition, the samples with relatively simple shape and homogeneous component have better thermal shock resistance than the samples with complex shape and structure. Therefore, in order to obtain the best thermal shock resistance, the porosity of metering nozzle should be kept in a certain range, meanwhile try to improve thermal conductivity and fracture toughness, reduce the thermal expansion coefficient and elastic modulus and control grain size.

Figure 1 is the XRD analysis results of the A, B, C, D four metering nozzle groups.

It can be seen from Figure 1, after adding  $\text{Al}_2\text{O}_3\text{--ZrO}_2$  composite powder, the content of high temperature phase c- $\text{ZrO}_2$  decreased and that of low temperature phase m- $\text{ZrO}_2$  increased in the samples. It suggests that after being modified, c- $\text{ZrO}_2$  phase transferred to m- $\text{ZrO}_2$  phase because the introduction of  $\text{Al}_2\text{O}_3$  in composite powder consumed stabilizer  $\text{MgO}$  in Mg-PSZ materials. This martensitic transformation will cause a volume expansion of about 3% and an amount of shear deformation. With appropriate expansion, micro cracks generating in the samples have toughening effect which can improve the thermal shock resistance of material. However if content of phase transformation is too much, namely excessive introduction of  $\text{Al}_2\text{O}_3\text{--ZrO}_2$  composite powder, the volume expansion will exceed the limit. This volume expansion will destroy the structure of the samples and are not conducive to improve the thermal shock resistance.

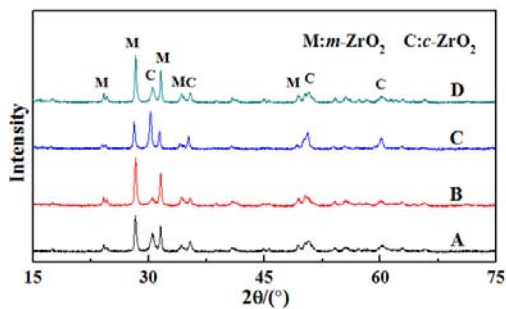


Figure 1. XRD pattern of the samples

Figure 2 shows the microstructure image of sample A, B, C and D.

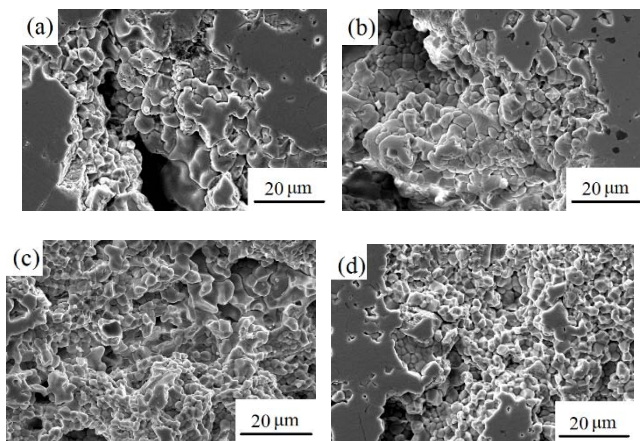


Figure 2. SEM photographs of different samples

Based on Figure 2, grains of sample A and B were flat and accumulated closely, and grains of sample C and D had relatively distinct edges. The contact area between the flat zirconia grains was larger and closer. So from the morphology and combination condition of zirconia grain, the grains of ceramic type nozzles were significantly closer than the fine-particle type nozzles. The detection results of physical properties

also proved that ceramic type nozzles indeed had lower apparent porosity and greater compressive strength, namely the ability of ceramic nozzles to resist erosion and scouring of molten steel should be better.

After the addition of  $\text{Al}_2\text{O}_3\text{--ZrO}_2$  composite powder,  $\text{Al}_2\text{O}_3$  reacted with  $\text{MgO}$  stabilizer precipitating from zirconia raw material to form magnesia-alumina spinel ( $\text{MgAl}_2\text{O}_4$ ). Figure 3 is the distribution and binding of  $\text{MgAl}_2\text{O}_4$  spinel in the sample B. It can be seen that the distribution of deep color material was relative uniform, and its constituent was magnesia-alumina spinel through EDS. Complete magnesia-alumina spinel crystal embedded in the zirconia particles tightly. With the volume expansion (5%~8%) of magnesia-alumina spinel generation, pores were filled partly, and it could prevent the abnormal growth of zirconia particles during high temperature sintering process by pinning effect, thereby reducing porosity of metering nozzle and increasing its strength. From the microstructure of samples B and D, it can be found that the crystal form of zirconia particles were relatively complete, with less of abnormal growth of particles, which is conducive to the properties of metering nozzle. Whereas, part of zirconia grains grows abnormally in unmodified samples A and C.  $\text{MgAl}_2\text{O}_4$  spinel has high strength and chemical stability, the thermal conductivity of  $\text{MgAl}_2\text{O}_4$  spinel is higher than that of zirconia, thermal expansion coefficient is lower than that of zirconia, which can effectively reduce the thermal stress, buffer and resist thermal stress, thereby improving thermal shock resistance and erosion resistance of zirconia metering nozzle.

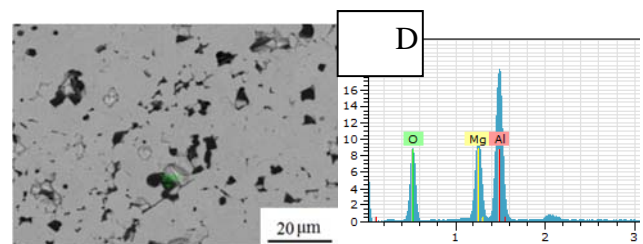


Figure 3. The distribution of the  $\text{MgAl}_2\text{O}_4$  in sample B

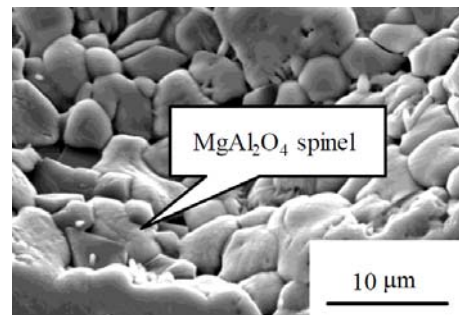


Figure 4. The microstructure of sample B

The ceramic metering nozzle had high density and a little amount of pores so that cracks instantaneous diffusion could not be prevented and the thermal expansion could not be absorbed effectively. Thermal stress generating in continuous casting process exceeded the fracture strength of material, so that fracture occurred. The molten steel permeated into the nozzles through cracks, which would cause erosion. The high density and strong erosion resistance weren't reflected. After being modified, nozzle porosity reduced further, thermal shock resistance didn't improve. The thermal shock and erosion resistance are closely related. The poor thermal shock resistance is the main reason for ceramic metering nozzle expanding and flaking.

#### 4 CONCLUSIONS

1. Ceramic type metering nozzles had lower apparent porosity, larger volume density, higher compressive strength, and poorer thermal shock resistance compared with fine-particle type metering nozzles.

2. After  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  composite powder modified, apparent porosity of ceramic type nozzle decreased by 27.9%, bulk density increased by 0.7%, compressive strength increased by 26.1%, apparent porosity of fine-particle type nozzle decreased by 11.1%, bulk density increased by 1.7%, compressive strength increased by 44.6%, especially thermal shock resistance improved greatly and exceed more than 60 times.

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