# A Mechanism of Slagline Wear of Graphite-Bonded Zirconia Submerged Nozzle during Continuous Casting of Steel

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## ABSTRACT

Polished and thin sections from used graphite-bonded CaO-stabilized zirconia submerged entry nozzles were observed under the optical microscopes and by means of the electron optics. A new mechanism for the excessive slagline attack is advanced as follows: Once graphite dissolves in the metal, the slag comes in contact with zirconia particles embedded in the graphite bond which have been receded in contour. The graphite bond reduces $SiO_2$, $Na_2O$, MgO and probably $B_2O_3$ in the mold flux to SiO, Na, Mg and B. The gaseous products diffuse into $ZrO_2$ particles through their pores and oxidize to form low-melting compounds, thus destabilizing the zirconia. In addition, the compounds etch grain boundaries, resulting in loose particles with well-defined roundness. Fresh slag penetrates the weakened particles and breaks them down into pieces, which are, in turn, dispersed into the slag. When the slag reaches the graphite-rich region, the metal replaces the slag. The process then repeats itself.

## 1. INTRODUCTION

Extensive studies[1,2,3,4,5)] were made on the slagline attack of graphite-bonded zirconia submerged entry nozzles (SEN) in contact with molten mold flux which invariably leads to a cyclic mechanism. This process is well-established: Refractories contact the slag, zirconia can dissolve in the slag, while if steel is in contact with refractories, graphite will dissolve, exposing zirconia. Since the zirconia cannot be wetted by the steel, the flux will wet the refractories and dissolve zirconia exposing graphite, and the process repeats itself.

It is also generally accepted that oxide dissolution is the rate-controlling step.[3,6)] There is a number of reports that the nozzle failure starts with the destabilization of the calcia stabilized zirconia[5,7)] from cubic-$ZrO_2$ to monoclinic-, rendered by complexing the CaO by components from mold flux, graphite ash and/or molten steel. In this study, used $ZrO_2$-graphite SENs were recovered from steel works and looked into, in order to discern whether or not the destabilization really takes place in an industrial setting and which source(s) serves as the destabilizer among those three.

## 2. Investigation of SENs after Service

Three typical SENs used to cast ultra low carbon (0.003wt%C), low carbon (0.040wt%C) and medium carbon steels (0.13wt%C) were recovered and cut into specimens. The specimens from slag/nozzle, slag/metal/nozzle and metal/nozzle interfaces were made into polished and thin sections. These polished and thin sections were observed by means of optical and electron microscopes, including XRD, SEM, EDS and TEM to investigate attack morphology, phase identification and phase transformation.

**Table I Chemical composition of mold powders**

| Powder | Basicity | CaO | $SiO_2$ | $Na_2O$ | MgO | $B_2O_3$ | F | $Al_2O_3$ | $Li_2O$ | $Fe_2O_3$ | $K_2O$ | C total | $\eta$ 1300℃ poise |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A[*] | 0.74 | 28.90 | 33.88 | 4.27 | 7.64 | 2.50 | 4.80 | 4.27 | 0.70 | 0.55 | 0.62 | 1.80 | 1.90 |
| B | 0.96 | 29.26 | 30.57 | 9.50 | 7.87 | 4.40 | 4.00 | 3.31 | 0.70 | 0.66 | 0.12 | 3.50 | 1.14 |
| C | 1.18 | 34.21 | 29.10 | 4.47 | 6.99 | 4.50 | 4.00 | 2.75 | 0.08 | 0.015 | 0.15 | 3.75 | 2.87 |

[*]Mold Powders used for A: Ultra Low Carbon Steel, B: Low Carbon Steel, C: Medium Carbon Steel

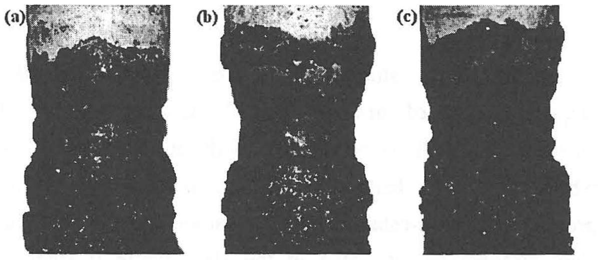


**Fig. 1** Three SENs used to cast (a) ultra low carbon (b) low carbon and (c)medium carbon steel

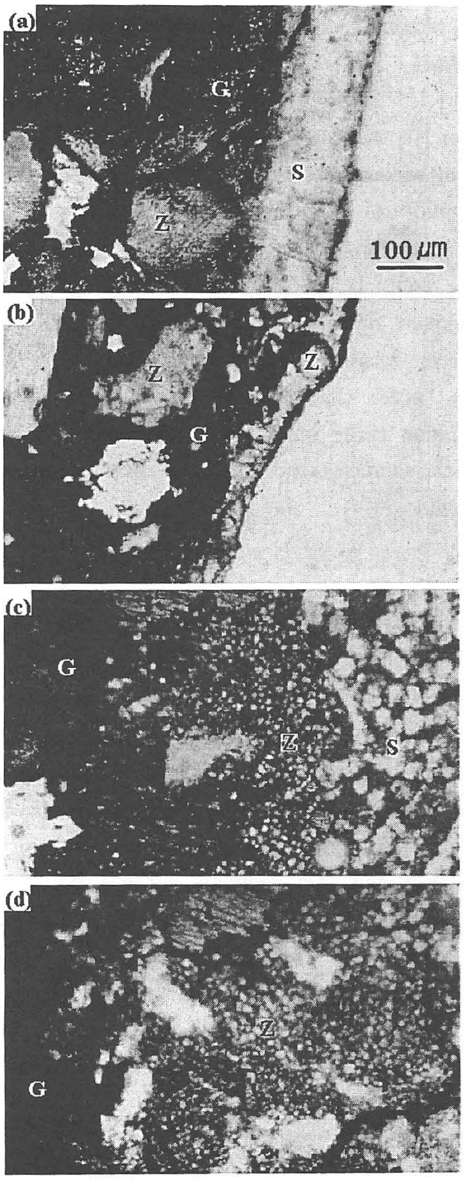


**Fig. 2** Microstructures of the slagline
(a) slag/nozzle (b) Slag/metal/nozzle
(c) metal/nozzle (upper) (d) metal/nozzle (lower)
( Z: zirconia G: graphite S: slag I: steel )

**Table Ⅱ Chemical composition of $ZrO_2$-C nozzle**

| Chemical Composition(wt%) | | | Physical Property | |
|---|---|---|---|---|
| $ZrO_2$ | CaO | C + SiC | Porosity | Density(g/㎤) |
| 71 | 3 | 25 | 15% | 3.50 |

The compositions of mold powders and zirconia/graphite SENs used to cast those steels are given in Tables Ⅰ and Ⅱ.

### 2.1 Observations of SENs under Optical Microscopes

Appearances of the three nozzles after service are given in Fig. 1. The SEN used to produce the low carbon steel was attacked more severely than others. However, the microstructures of the specimens recovered from the slaglines did not show significant dissimilarities among themselves. As an example, the specimens for the low carbon steel are given in Fig. 2.

### 2.1.1 Slag/Nozzle Interface

Slag/nozzle interface at which nozzle is always in contact with slag was covered with thick slag ranging in thickness from 40 to 100㎛, as shown in Fig. 2(a). The interface showed protruded graphite flakes and receding zirconia grains due to nonwetting nature of graphite by molten slag.[8,9]

Since the distance drew near from top slag to metal level, the temperature sets higher and the viscosity of slag gets lower, the thickness of slag cover tended to decrease. A few bubbles were observed in the slag which was adhered to the nozzle. These are thought to be the gaseous products of reaction between slag and graphite.[1,10]

### 2.1.2 Metal/Nozzle Interface

The metal/nozzle interface consists consecutively of three layers, i.e., original nozzle, zirconia and slag layers, as shown in Figs. 2(c) and (d). The most noticeable of the three was the "zirconia layer" which is completely devoid of graphite, forming an alignment of fine spherical subgrains of zirconia whose diameters range from a few to 40㎛. A large number of bubbles and small number of steel drops were also observed in these layers. Down along the surface of the nozzle from slag/metal/nozzle to metal/nozzle levels, the thicknesses of zirconia and slag layers also increased. Once graphite is dissolved in steel, zirconia grains would be exposed, allowing slag to wet and creep down over the zirconia subgrains. The graphite in receded configuration would be contacted with slag and reaction would take place, thus weakening the graphite bond.

The ferrostatic pressure and friction by molten steel current in the mold would make the zirconia subgrains a nice alignment over the surface of the nozzle. The slag which lost some of its components on reaction with graphite absorbs $Al_2O_3$,$^{11,12)}$ and dissolves zirconia whereby increased its viscosity. It is postulated here that the highly viscous slag may serve as a bond for the zirconia grains leading to a formation of "zirconia layer". This layer then retards disruption and collapse of zirconia subgrains. At some time later it is imagined that aggressive fresh slag would come down over the layer, thinning the slag bond and disrupting fine subgrains and washing away the zirconia layer. Subsequently, the viscosity of slag would increase and both zirconia and slag layers would thicken. Since the reduction reactions continue, the number of the bubbles in both layers would increase.

### 2.1.3 Slag/Metal/Nozzle Interface

The microstructures of slag/metal/nozzle interface are shown in Fig. 2(b). There was a slag layer covering the surface of the original zirconia-graphite refractories whose bond between slag and nozzle was less coherent than that of slag/nozzle bond described previously in Fig. 2(a). The slag holds both zirconia grains and subgrains in suspension. Once graphite is dissolved in metal, which is considered a fast step, zirconia grains are exposed and projected into aggressive fresh slag and are disrupted and collapsed. When zirconia grains are washed away, the metal come into play, dissolving graphite and so on. This cyclic process would accelerate the local corrosion of the slagline.

## 2.2 XRD Analysis

XRD analysis of the slag formed in the molds and slag films on nozzles were carried out after annealing at 800℃$^{13)}$ for 14 hours. In the case of the mold slags, crystal phases were identified as cuspidine ($3CaO \cdot 2SiO_2 \cdot CaF_2$), nepheline ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2$) and monticellite ($CaO \cdot MgO \cdot SiO_2$) which are low-melting. The patterns of the mold slags are similar to one another, however their relative intensities were different. It is considered that the phases existing in slags were identical but their concentrations were different. In addition, gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$) was identified for the case of the slag films on the nozzle surfaces.

Original zirconia grains have its stabilization ratio$^{7,14)}$ of 80%. However, XRD analysis of the zirconia grains which had not been contacted directly with slag showed that stabilization ratio had increased over the distance from slag/nozzle to metal/nozzle levels. This trend was in good agreement with that of concentrations of slag component which had rendered zirconia grains to destabilize.

## 2.3 SEM Investigation and EDS Analysis

The zirconia grains that were not in direct contact with slag remained intact as shown in Fig. 3(a). In Fig. 3(b), however, the zirconia grains exposed to slag have been subdivided into subgrains.

EDS quantitative analysis of slags which had been retained on the surface of the nozzle are given in Table Ⅲ. Concentrations of aluminum and zirconium increased over the distance from slag/nozzle to metal/nozzle interfaces. This was due to assimilation of $Al_2O_3$ and dissolution of zirconia particles into slag.

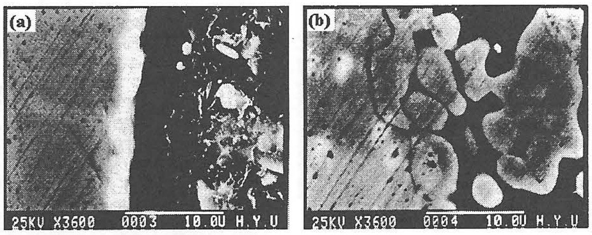


**Fig. 3** $ZrO_2$ contacting with (a) graphite (b) slag

**Table Ⅲ EDS Quantative analysis of slags on the surface of nozzle (wt%)**

| | Ultra Low Carbon Steel | | | Low Carbon Steel | | | Medium Carbon Steel | | |
|---|---|---|---|---|---|---|---|---|---|
| Element | S/N* | S/M/N | M/N | S/N | S/M/N | M/N | S/N | S/M/N | M/N |
| Ca | 30.6 | 41.0 | 40.0 | 42.6 | 38.7 | 40.8 | 48.0 | 36.4 | 36.7 |
| Al | 7.2 | 6.0 | 12.5 | 3.9 | 5.6 | 19.8 | 5.3 | 18.1 | 17.7 |
| Mg | 7.8 | 4.2 | 4.4 | 7.4 | 7.3 | 4.2 | 5.7 | 3.7 | 3.9 |
| Zr | 6.7 | 12.7 | 13.8 | 4.6 | 7.6 | 6.5 | 10.7 | 21.5 | 21.0 |
| Na | 5.3 | 4.9 | 4.7 | 12.9 | 13.9 | 6.7 | 5.7 | 3.4 | 3.9 |
| Si | 42.4 | 31.2 | 24.5 | 28.7 | 26.9 | 22.0 | 24.6 | 16.9 | 16.8 |

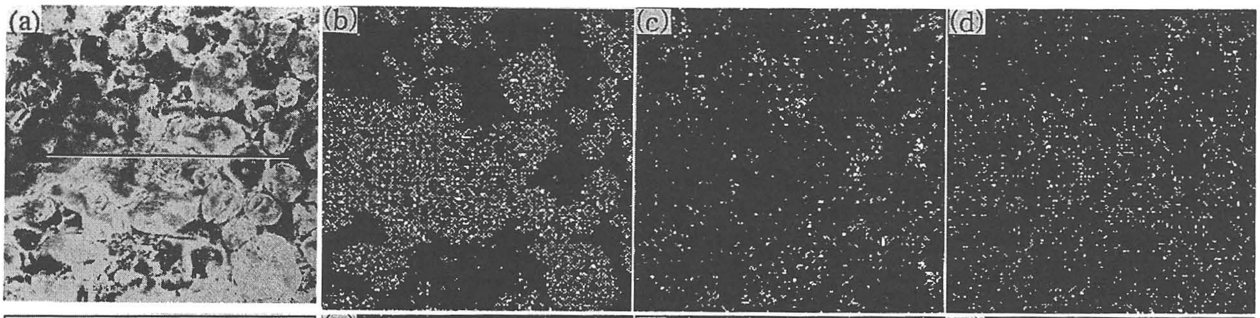
*S/N: slag/nozzle, S/M/N: slag/metal/nozzle, M/N: metal/nozzle interface

On the contrary, those of silicon, magnesium, and sodium decreased over the distance. This was a clear evidence that $SiO_2$, MgO, and $Na_2O$ in slag would have been reduced mainly by the following reactions:

$$SiO_2 + C = SiO + CO$$
$$MgO + C = Mg + CO$$
$$Na_2O + C = 2Na + CO$$

The reduction products of these reactions were detected in the zirconia grains which had not been penetrated by the slags, as shown in Fig. 4. It is remarkable to note that aluminum, one of the slag components, was detected in the slag-penetrated portion of the zirconia grains but not in portions which had not been penetrated with slag.

EDS line analysis on identical specimens are given in Fig. 5. The above-mentioned reduction products were detected in subgrain boundaries of zirconia grains. These components would react CaO and make c-$ZrO_2$ transform to m-$ZrO_2$ and simultaneously form low-melting compounds, thus etching the subgrain boundary surfaces. Once subgrain boundaries had been etched, slag would readily penetrate through boundaries and have liquidized the solid bond of zirconia subgrains. Finally, so called subdivision along zirconia subgrain boundaries would result.



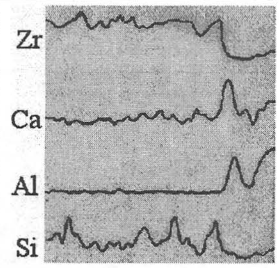


Fig. 5 EDS Line Analysis

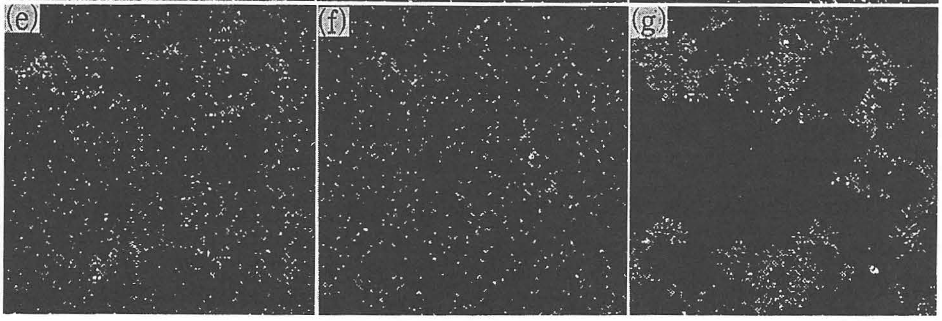


**Fig. 4** EDS dot map of $ZrO_2$ contacting with slag (a) image (b) Zr (c) Ca (d) Si (e) Mg (f) Na (g) Al

### 2.4 Investigation with TEM

The zirconia grains examined in this study are 4% CaO partially stabilized fused-cast zirconia. The average size of the zirconia grains was 130$\mu$m in diameter consisting of subgrains whose sizes range from a few to 40$\mu$m, as shown in Fig. 6(a). The stabilization ratio of the original zirconia was 80%. Each subgrain is a single crystal of cubic $ZrO_2$ in which very fine unstabilized monoclinic phases are dispersed,[15,16] as shown in Fig. 6(b). On the other hand, the stabilization ratio in the sample taken from slag/metal/nozzle interface of a used SEN reduced to 30%. Fig. 6(c) shows a phase transformation which had occurred in a sample after service in which cubic $ZrO_2$ has become dispersed phases in a matrix of monoclinic $ZrO_2$.

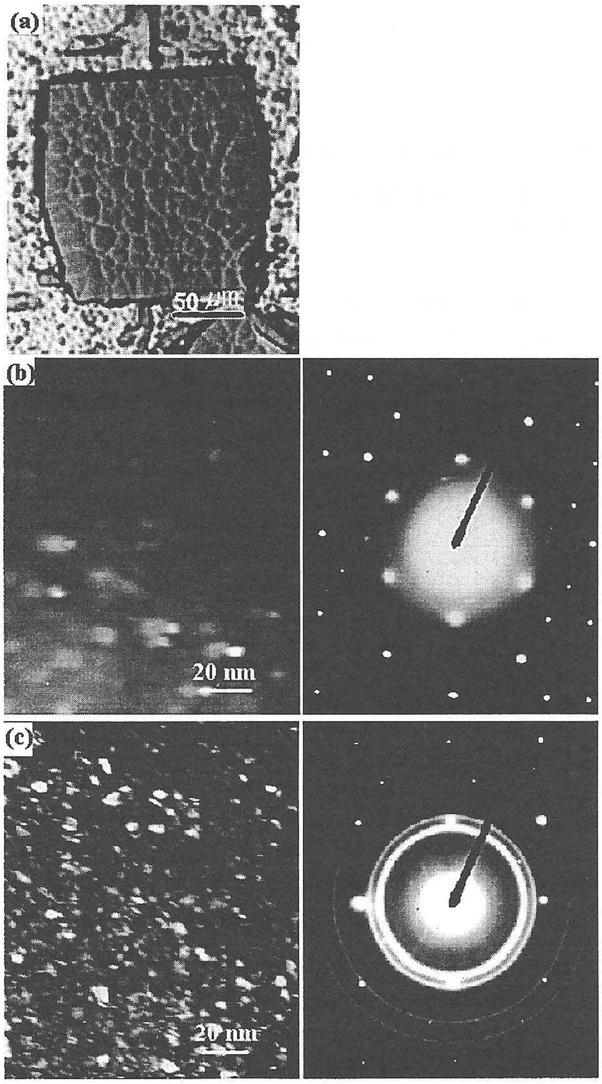


**Fig. 6** Optical and transmission electron micrographs (a) microstructure of zirconia (b) dark-field image of monoclinic zirconia in a cubic matrix (c) dark-field image of polycrystalline cubic zirconia (ring pattern) in a monoclinic zirconia matrix and its SAD pattern

## 3. CONCLUSIONS

(1) The slagline wear of the zirconia/graphite SENs was due to cessation of the mutual protections of graphite to slag and zirconia to steel. In other words, the absence in slag/metal/nozzle interface of graphite layer at slag/nozzle and of zirconia layer at metal/nozzle interfaces has resulted in the excessive wear of the nozzle.

(2) The mechanism by which zirconia grains had been subdivided into subgrains was that SiO, Mg and Na, the gaseous products of slag and graphite reactions, diffused through the subgrain boundaries and combined with CaO to destabilize the zirconia. The action of reaction products which is of low-melting causes etching of the subgrain boundaries.

(3) The wear of the zirconia/graphite SENs by mold slag in the presence of molten steel was due to breaking down of the subdivided zirconia grains, which were, in turn, disrupted, dispersed, and washed away by fluid slag rather than straight dissolution of zirconia as some have claimed. Hence, the viscosity of the mold flux is viewed as a dominating factor.

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