# THE CORROSION OF 30% Mo-$ZrO_2$ CERMET IN MOLTEN SLAG OF CaO-MgO-$Al_2O_3$

Xiaopeng Li, Ziming Wang,Yang Yang, Yanling Guo*, Jieyu Zhang, Wende Dan
(State Key Laboratory of Advanced Special Steel, School of Materials Science and Engineering, Shanghai University, Shanghai 200072, China)

Keyword: Mo-$ZrO_2$ cermet, corrosion, molten slag

## Abstract

Mo-$ZrO_2$ cermet is a potential material for application as electrode in steel purifying process with addition of electrical field because of its high electrical conductivity and good corrosion resistance to molten slag and steel at high temperature. This paper describes the static corrosion test of Mo-$ZrO_2$ cermet sample with Mo content 30 vol.% in CaO-MgO-$Al_2O_3$ molten at 1550℃. The results showed that a dense $CaZrO_3$ layer was formed during test and it will prevent the further corrosion of cermet by slag.

## Introduction

Cermet with some of the advantages of both metals and ceramics is widely discussied by international scholars' [1][2]. With the development of metallurgical technology and the requirement of environmental protection, scholars raised a new clean deoxidizing method "controlled oxygen flow metallurgy"[3], namely in the slag-metal interface. A certain direction of the electric field is applied in the slag-metal interface, by controlling the oxygen ion transport in the slag to achieve pollution-deoxy metal melt[4] [5]. Deng [6] found that adding 10% alumina zirconia ceramic thermal shock resistance is the best. Lei Tang [7] studied its resistivity, thermal shock resistance, and found that the electric conductivity is good. Yanling Guo[8] found that Mo-$ZrO_2$ cermet in molten steel and slag corrosion is associated with the composition of the ceramic substrate .The cermet without adding stabilizer of pure monoclinic zirconia matrix m-$ZrO_2$/Mo cermet anti-corrosion steel is best, while adding 3Y-PSZ/Mo of 3% (mol) $Y_2O_3$ cermet slag corrosion resistance is best. Chang [9] studied the influence of the Mo content on the Mo-$ZrO_2$ cermet liquid steel and slag corrosion resistance. The influence showed that with the increase of Mo content, cermet corrosion resistance to molten steel weaken and slag corrosion resistance increased.

In this paper,we use powder metallurgy method to prepare the Mo-$ZrO_2$ cermet which Mo volume fraction was 30% and the relative density is greater than 95% . The corrosion medium was the slag CaO-MgO-$Al_2O_3$ which the CaO, MgO, $Al_2O_3$ mixed uniformly by melting.

## The experiment

### materials

Experimental material are Mo powder (99.00% purity), ZrO2 powder (99.00% analysis purity), polyvinyl alcohol (99.00% purity), alcohol (national medicine group chemical reagent co.LTD.) and argon (the Shanghai five steel gas company). The composition of slag as follows.

Table 1. Synthetic slag composition

| ingredient | CaO | $Al_2O_3$ | MgO |
|---|---|---|---|
| Content | 44.16% | 51.14% | 4.7% |

The preparation of metal ceramic

In this experiment ,we weighed powder Mo with 36.1% and $ZrO_2$ with 63.9% according to the stoichiometric ratio and put the mix into the ball mill tank of PTFE material with the ball material ratio approximately 6:1[10].Wet grinding ball mill tank was put a certain amount of alcohol. Raw material was mixed in the planetary ball mill with speed 500 r/min for 12 h. The slurry was put into the oven till the paste is completely dry. The dried block material was put into the mortar with adding PVA binder of about 5% then grinded. The particle size was selected about in the range of 60~100 mesh [11]. The mold diameter is 20mm and forming pressure is 12 Mpa. Then the green bodies were sintered in horizontal furnace at 1600℃ in argon for 2 h [12] .

Corrosion experiment

In this experiment, we used static corrosion method. We put the pre-melting alkaline slag $CaO\text{-}MgO\text{-}Al_2O_3$ into the bottom of corundum crucible and then put cermet sample into the tubular furnace heating to 1550 ℃ at a speed of about 3 ℃ /min. Choosing temperature 1550 ℃ was that the alkaline slag melting point is at about 1500 ℃. The sample was heated for 1h and 2h then cooled.

## Results and Discussion

Metal ceramic sample morphology corrosion before

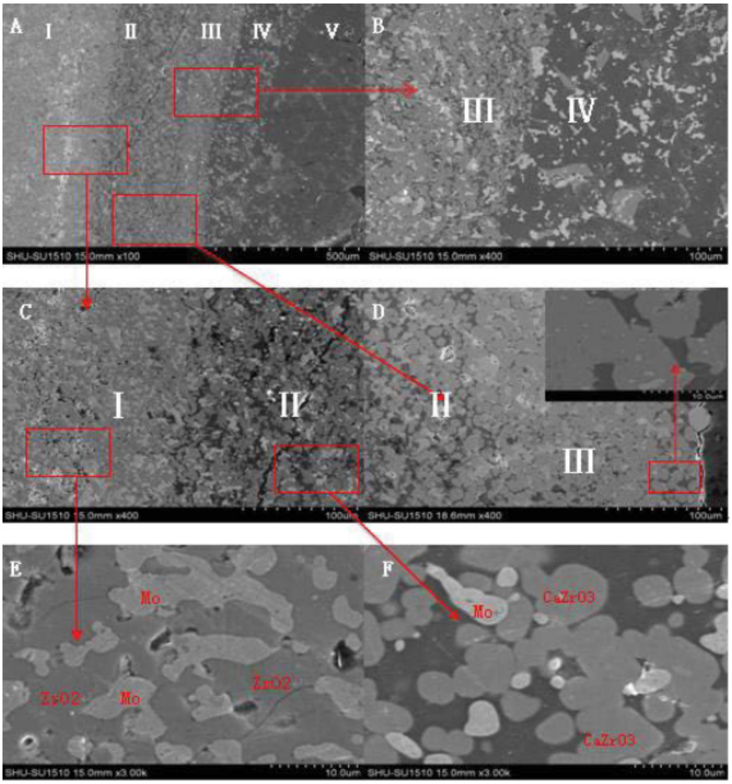

Fig 1.SEM of sample after corrosion in CaO-MgO-$Al_2O_3$ slag at 1550℃ for 1h

Figure 1 shows the details of cermet sample after corrosion. There are five distinct layers formd in the sample after corrosion and they are marked as layer I to layer V from the side of ceramic to slag. Layer I is uncorroded cermet and Layer II and III are corrosion layer at cermet side. The thickness of layerⅡand Ⅲare 0.45 mm. Its internal slag is much more than of Ⅲ layer from the morphology of Ⅱwith corrosion which is far from slag. Layer Ⅲ with the thickness of 0.16 mm is densed corrosion layer, which is identified by EDS and XRD as $CaZrO_3$.Ⅳwas the excessive layer of slag corrosion diffusing into cermets, Ⅴis the layer of slag without corrosion. Fig. 1B is the border morphology of the layerⅡ and Ⅲ. C is the border morphology of the layerⅠand Ⅱ . D is the border morphology of the layer Ⅱ and Ⅲ, The Mo and $ZrO_2$ of Ⅲ disappeared entirely and was replaced by a new generation of

$CaZrO_3$ and slag which diffused. E is the amplification of layer and the layer is the cermet raw ingredients without corrosion. Light grey part is the metal Mo and dark gray parts is $ZrO_2$. F is the cermet sample Ⅱ with corrosion. Former $ZrO_2$ disappeared and a new phase of $CaZrO_3$ appeared.$CaZrO_3$ of this layer is smaller than of Ⅲ because layer Ⅲ is near the slag and more fully contacted with the $ZrO_2$ and continuously generated $CaZrO_3$ which generated by the CaO of invasion in the sample. so the slag with diffusion was constantly digested and $CaZrO_3$ grain grew gradually.

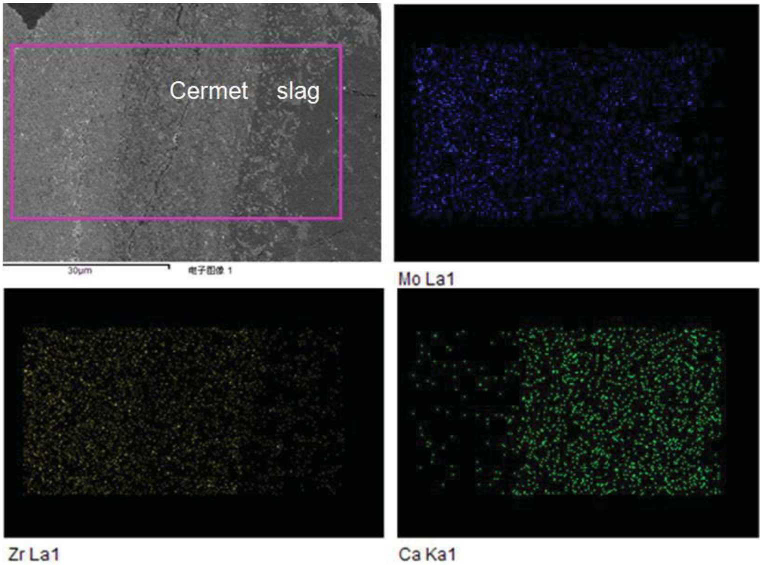

Fig 2. SEM - DES of sample after corrosion in CaO-MgO-$Al_2O_3$ slag at 1550℃ for 1h

Figure 2 shows that after corrosion of cermet samples the depth of cermet sample corrosion about Ca was overlapped with the depth of $CaZrO_3$ which generated. From the picture, the amount of Zr element in the cermet in the boundary of the cermet and slag began to significantly reduce also proving the point of view. The Mo would significantly reduce when Ca appeared in the corresponding area in the sample.

### The corrosion mechanism

From the cermet XRD analysis after corrosion, the boundary layer of sample after corrosion appeared a new phase $CaZrO_3$.

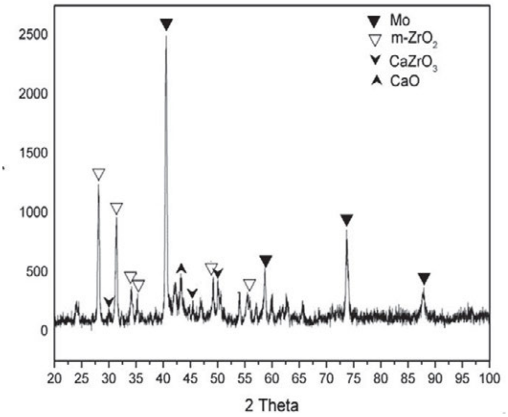

Fig 3 XRD of sample after corrosion in $CaO$-$MgO$-$Al_2O_3$ slag at 1550℃ for 1h

From the corrosion of cermet sample, the Ca element diffusing into the cermet sample from slag, it is not a gradient distribution. But it gathered in the excessive layer corrosion in the ceramic sample. This fully proves the existence of the $CaZrO_3$ in layers of excessive corrosion and the block of slag composition further diffusing into cermet sample. The stratification from Zr of the edge of sample and slag in the sample is obvious. There is the same reason because the $ZrO_2$ in the cermet and CaO in slag generated $CaZrO_3$ to prevent the loss of $ZrO_2$. Metal element Mo gradually reduced in the sample from the cermet to the slag. The loss of Mo in the sample prepared the blank for CaO which diffused from slag to sample.

The experiment gets enough data to obtain the result that corrosion process can be summed up in three steps from the XRD spectrum, SEM and SEM EDS. First, cermet sample was surrounded by alkaline molten slag. Second, the elements diffused each other, which are in slag and cermet. The invasion compound in this paper is Mo, $ZrO_2$ in the cermet and CaO in the slag. The Mo in the cermet gradually diffused into slag and the CaO of slag gradually diffused into cermet to form excessive layer. Finally, when temperature rose to 1180 ℃,CaO and $ZrO_2$ generated $CaZrO_3$ which CaO diffused into the cermet to generate $CaZrO_3$ with $ZrO_2$.

### The relationship between degree of corrosion and corrosion time

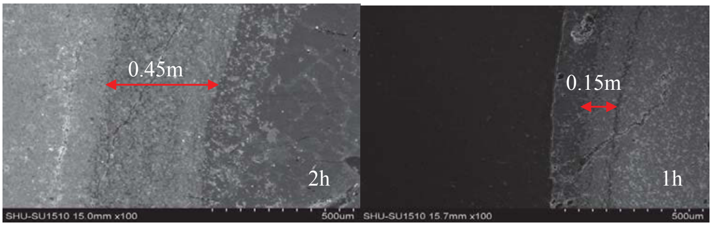

Fig 4 SEM of sample after corrosion in CaO-MgO-$Al_2O_3$ slag at 1550℃ for 2h and 1h

Figure 4 shows that the thickness under 2h is deeped than that under 1h. The degree of erosion increases with time becomes dark.

## Conclusion

The static corrosion test of Mo-$ZrO_2$ cermet was conducted in CaO-MgO-$Al_2O_3$ at 1550 ℃ for 1 h and 2 h, respectively and the conclusions are obtained as follows.

The corrosion resistance of Mo-$ZrO_2$ cermet in CaO-MgO-$Al_2O_3$ slag is mainly due to that the outflow of Mo in the cermet provided CaO with space reacting with $ZrO_2$ to generate $CaZrO_3$ dense layer to prevent further corrosion

The more time of corrosion is, the worse corrosion resistance is, the more slag diffusing into the cermet is, the deeper thickness of corrosion is.

## Acknowledgement

The authors gratefully acknowledge the support from the National Natural Science Foundation of China (51304131), and the Innovative Foundation of Shanghai University, China (sdcx2012003).

## References

1. Rongjiu Li， “Ceramic-metal composite materials,” Beijing: Metallurgical industry press, 23 (2004), 105-109.

2. Kuihan Wang and Chuanmeng Cui, “Molybdenum fund of ceramic thermocouple protection tube study,” Journal of northeast institute of technology, 13 (4) (1992), 348-352.

3. Chou K C. et al., “Metallurgy with Controlled Oxygen Flow,” The Iron and Steel Institute of Japan, 14 (2004), 162−167.

4. kuo-chih Chou. et al., “The exploration of new directions - metallurgical process controlled oxygen flow metallurgy,” Beijing: science press, 16 (2006).

5. Xionggang Lu and kuo-chih Chou, “medium. Charged particles control technology application and prospect in metallurgical process,”. Journal of college of iron and steel research journal, 15 (5) (2003), 10.

6. Xuemeng Deng. et al., “equality additives on the influence of zirconia ceramics reting resistance,” Rare metal materials and engineering 12(2007).8

7. Lei Tang. et al., “Mo-$ZrO_2$ ceramic preparation and conductive performance study,”. Shanghai: shanghai University, 2013.

8. Yanling Guo. et al., “Zirconia - molybdenum metal ceramic molten steel and slag corrosion resistance”. Journal of process engineering of 2014.06.

9. Chang Jie. et al., “Mo-$ZrO_2$ ceramic metal corrosion resistant performance and the relationship between composition,”. Journal of process engineering of 2014.06,1206-1211.

10. Panxin Wang. “Powder metallurgy,”. Beijing: metallurgical industry press, 19 (1997).145-162

11. Peiyun Huang. et al. “Powder metallurgy principle,”. Metallurgical industry press, (1982).

12. Jifang Xu. “Plus oxygen transfer mechanism in the process of slag deoxidation dc field research,” Shanghai University, (2012). 25.