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Effect of ZrO_2 (9mol% Y_2O_3) coating thickness on the electronic conductivity of Mg-PSZ oxygen sensors

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Abstract: The ZrO_2 (9mol% Y_2O_3) coating was prepared evenly on the surface of MgO partially stabilized zirconia (Mg-PSZ) tube (oxygen sensor probe) by dipping the green Mg-PSZ tube in a ZrO_2 (9mol% Y_2O_3) slurry and then co-firing at 1750°C for 8 h. The double-cell method was employed to measure the electronic conductivity parameter and exam the reproducibility of the coated Mg-PSZ tube. The experimental results indicate that the good thermal shock resistance of the Mg-PSZ tube can be retained when the coating thickness is not more than 3.4 μm. The ZrO_2 (9mol% Y_2O_3) coating reduces the electronic conductivity parameter remarkably, probably due to the lower electronic conductivity of Y_2O_3-stabilized ZrO_2 than that of MgO-stabilized ZrO_2. Moreover, the ZrO_2 (9mol% Y_2O_3) coating can improve the reproducibility and accuracy of the Mg-PSZ tube significantly in the low oxygen measurement. The smooth surface feature and lower electronic conductivity of the coated Mg-PSZ tube should be responsible for this improvement.

Key words: oxygen sensor; stabilized ZrO_2; solid electrolyte; coating; electronic conductivity

1 Introduction

MgO partially stabilized zirconia (Mg-PSZ) as the main material of oxygen sensors is very important for steel-making processes in recent years, and it is estimated that the annual consumption of oxygen sensors is over six million pieces, and increasing every year. With the development of metallurgical technology, the harsh terms of processing necessitate an accurate data acquisition from the oxygen sensors. Many works have been done to improve the various properties of oxygen sensors [1-4], however the poor accuracy in low-oxygen measurement still limits the wide application of oxygen sensors in steel-making industries. For an oxygen sensor, it should have a stable and low electronic conductivity to obtain reliable results in the case of low-oxygen measurement. Unfortunately, zirconia electrolytes exhibit mixed ionic and electronic conduction when exposed to the surrounding of high temperature and low oxygen potential [1]. The electronic conduction of an electrolyte will cause a short circuit current inside the electrolyte, which will result in the polarization and EMF (electromotive force) decay problems. To improve the reliability of the oxygen sensor, an effective method is to decrease its electronic conduction, which is represented by the P_e value (the parameter P_e describes the relation between the ionic and n-type electronic conductivity of the solid electrolyte, and is defined as the oxygen partial pressure at which the ionic conductivity and n-type electronic conductivity of the electrolyte are equal). However, there was not always an accurate method to measure the P_e value until K. Huang, *et al.* [5] had proposed a new method to measure the parameter P_e of the ZrO_2-based electrolyte.

The previous study [1] proved that the ZrO_2 (Y_2O_3) coating on the surface of a Mg-PSZ tube could reduce the P_e value, whereas, to our best knowledge, there is no report so far concerning the effect of the coating thickness on the P_e value. In this study, different thicknesses of ZrO_2 (9mol% Y_2O_3) coatings were prepared on the surface of commercially used Mg-PSZ tubes (oxygen sensor probe), the corresponding P_e values were determined by using K. Huang's method. The improvement mechanism of the ZrO_2 (9mol% Y_2O_3) coating on the electronic conduction of Mg-PSZ tube was also discussed.

2 Basic theory

ZrO_2 oxygen sensors operate on the principle of solid oxide electrolysis [6]. MgO stabilized zirconia (Mg-PSZ) is usually used as the oxygen sensor electrolyte for the determination of oxygen concentration in molten steel, because of its excellent thermal shock resistance. The oxygen ion vacancies generated in the

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crystal structure of zirconia by the MgO dopant result in the selective oxygen ion conductivity, which is desired and required for the solid-state electrolyte. However, the ZrO_2-based electrolytes, especially Mg-PSZ, show a significant portion of electronic conduction at low oxygen potential and high temperature.

Under a low oxygen partial pressure, free electrons (n-type electrons) may be generated by the reaction:

$$2O_O=O_2(g)+V_O^{\cdot\cdot}+2e' \quad (1)$$

where O_o is an oxygen atom in a regular oxygen site, $V_O^{\cdot\cdot}$ is a doubly ionized oxygen vacancy, and e' is an excess electron. The presence of n-type electrons in solid electrolyte will influence undoubtedly the generation of an EMF signal in the electrochemical cell. The contribution of the electronic conduction to the measured EMF of an electrochemical cell in the presence of n-type electronic conduction can be expressed by

$$E=\frac{RT}{F}\ln\frac{P''_{O_2}{}^{1/4}+P_e^{1/4}}{P'_{O_2}{}^{1/4}+P_e^{1/4}} \quad (2)$$

where P'_{O_2} and P''_{O_2} are the oxygen partial pressures of reference and working (molten steel) electrodes, respectively. In order to convert the measured cell potentials to oxygen activities in the molten steel, the value of P_e is necessary. The previous method to determine P_e, coulo-metric titration technique [7-8], has a long response time at the measuring temperature, and the problem appeared that the results obtained by this method should be corrected. Then K. Huang, *et al.* [5] proposed a simple method to determine the parameter P_e of ZrO_2-based electrolytes. In their research, they developed the EMF method into a new style, a rapid immersion of double oxygen cells into a steel melt with a fixed oxygen activity, in which the measurement condition of P_e determination is very similar to the working condition of commercial oxygen sensors. By this method the direct P_e of solid oxide electrolyte can be easily obtained at steelmaking temperatures.

The electronic conduction parameter P_e of ZrO_2-based electrolytes should be a constant value at a constant temperature. If two kinds of reference electrodes are selected to assemble into the oxygen concentration cells for simultaneous EMF measurements, then, one can calculate out the P_e and P''_{O}, from the following dual equations by using the two measured EMF values and known oxygen partial pressures of two reference electrodes:

$$E_1=\frac{RT}{F}\ln\frac{P''_{O_2}{}^{1/4}+P_e^{1/4}}{P'_{O_2}{}^{1/4}(\mathrm{I})+P_e^{1/4}} \quad (3)$$

$$E_2=\frac{RT}{F}\ln\frac{P''_{O_2}{}^{1/4}+P_e^{1/4}}{P'_{O_2}{}^{1/4}(\mathrm{II})+P_e^{1/4}} \quad (4)$$

where $P'_{O_2}(\mathrm{I})$ and $P'_{O_2}(\mathrm{II})$ are the oxygen partial pressures of the two different reference electrodes.

In this experiment, Cr-Cr_2O_3 and Mo-MoO_2, which are widely accepted in commercial oxygen sensors, were selected as the reference electrode powders. The EMF of these two cells can be measured simultaneously in the same molten steel with low oxygen concentration in the form of "double-cells". The P_e value and oxygen potential in the steel melt can be calculated from equations (3) and (4). For these two different reference electrodes, their oxygen partial pressure can be represented by

$$\begin{cases}\ln P''_{O_2}(\mathrm{Mo-MoO_2})=\dfrac{-67210}{T}+18.69\\ \ln P''_{O_2}(\mathrm{Cr-Cr_2O_3})=\dfrac{-89545}{T}+20.21\end{cases} \quad (5)$$

3 Experimental

The ZrO_2 (2.25wt% MgO) solid electrolyte tubes used in this study were prepared in our laboratory. The preparation procedure included a mixture of $ZrOCl_2$ and MgO solution which was co-precipitated with NH_4OH and the powder was dried and then calcined at 700°C in order to decompose into ZrO_2 (MgO). With this powder the ZrO_2 tube was shaped by injection moulding and finally sintered at 1700°C for 8 h *via* an optimized heating schedule. The so-obtained Mg-PSZ tube had been testified to have an excellent thermal shock resistance in the steel-making process.

The dipping method was used in this study for preparing the ZrO_2 (9mol% Y_2O_3) coating on the surface of Mg-PSZ tube. The Y_2O_3 (9mol%) stabilized zirconia was dispersed in polyvinyl alcohol to form dipping slurry. Four kinds of slurries with mass fractions of 5%, 10%, 15% and 20% ZrO_2 (9mol% Y_2O_3) in polyvinyl alcohol were prepared respectively. Green ZrO_2 (MgO) tubes were immerged into different kinds of slurries for an adequate time to yield the ZrO_2 (9mol% Y_2O_3) coatings with different thicknesses. By adjusting the slurry concentration and the dipping speed, the coating thickness can be controlled. The coating thickness on the surface of the ZrO_2 (MgO) tube after sintered at 1700°C was measured *via* SEM observation on the cross section. Four different coating thicknesses were produced on the surface of ZrO_2 (MgO) tubes, as listed in **table *1.*** For *comparison, the* sample without coating is also listed here. After coated, **the** tubes were sintered by the identical heating schedule as mentioned for pristine Mg-PSZ tubes.

The phase composition of the coatings on the surface of the Mg-PSZ tubes was identified by using a D/MAX-RB X-ray diffractometer (XRD) with Ni-filtered Cu K_α radiation. The surface morphologies of the ZrO_2 tubes coated and uncoated with ZrO_2 (9mol% Y_2O_3) were observed by using a scanning electron microscope (SEM, S250-II).

Table 1 Coating thickness of different samples μm

Sample	A	B	C	D	E
Coating thickness	2.1	3.4	5.8	6.5	Without coating

With respect to the reference electrode, two kinds of powders were used here as the reference electrode powders, Cr/Cr_2O_3 and Mo/MoO_2. The mass ratios of Cr to Cr_2O_3 and Mo to MoO_2 were both set as 9:1. The Cr/Cr_2O_3 powders had been pretreated prior to use in the atmosphere of argon at 1600°C for 5 h and the Mo powders were also heated for 10 h in the atmosphere of hydrogen in order to remove the oxidation film on the surface of Mo powders. The reference electrode powders were tightly packed inside the ZrO_2 electrolyte tube, and a Mo wire was inserted into the reference electrode powder as the reference lead.

The double-cell test was conducted in the intermediate frequency furnace that contains 150 kg molten steel. The scheme of the double-cell test is presented in **figure 1.** The oxygen potential P''_{O_2} and the electronic conduction parameter P_e can be calculated *via* the EMF measurement of double-cells through equations (3) and (4).

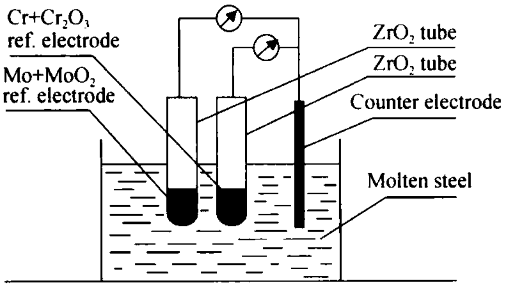

Figure 1 Scheme of the "double-cells" method to measure the electronic conduction parameter P_e.

4 Results and discussion

The XRD analysis indicated that the co-precipitated $Zr(OH)_4{\cdot}Mg(OH)_2$ powders decomposed into cubic ZrO_2 (MgO) completely after calcined at 700°C for 4 h, as indicated in **figure 2.** The 1700°C-sintered ZrO_2 (MgO) tubes showed the phase compositions of monoclinic ZrO_2 (m-ZrO_2), tetragonal ZrO_2 (t-ZrO_2) and cubic ZrO_2 (c-ZrO_2), as presented in **figure 3,** suggesting that the obtained pristine ZrO_2 (MgO) tube is Mg-PSZ material. For the coated ZrO_2 tube with ZrO_2(9mol% Y_2O_3) sintered at 1700°C, the XRD examination on the surface of the ZrO_2 tube indicated a pure cubic phase composition, as shown in **figure 4.**

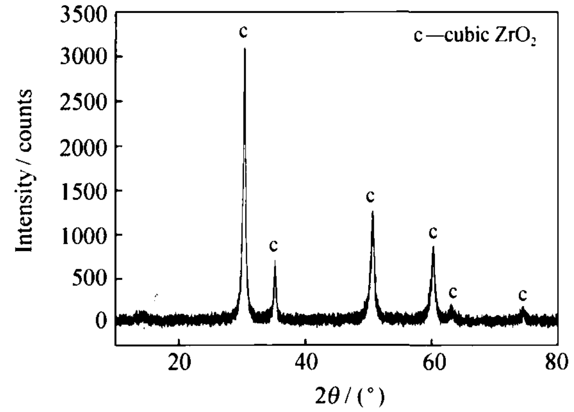

Figure 2 XRD pattern of the co-precipitated powders after calcined at 700°C for 4 h.

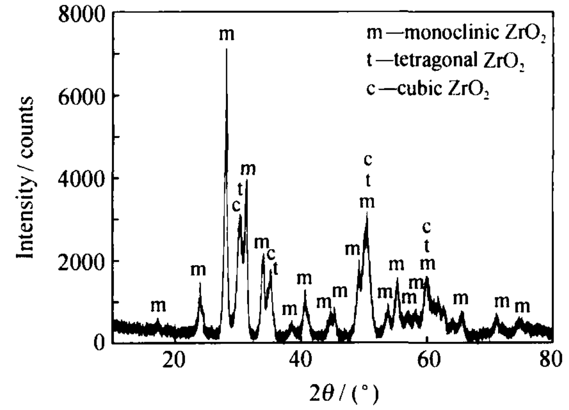

Figure 3 XRD pattern of the pristine ZrO_2 (MgO) tube after sintered at 1700°C for 8 h, suggesting the phase composition of partially stabilized ZrO_2.

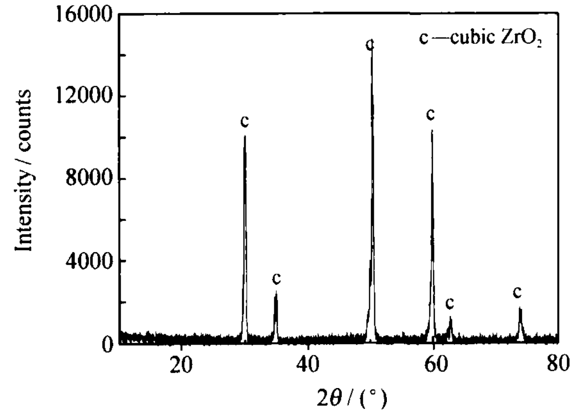

Figure 4 XRD pattern for the surface of the ZrO_2 tube coated with ZrO_2 (9mol% Y_2O_3) and sintered at 1700°C for 8h.

After sintered at 1700°C for 8 h, the Mg-PSZ tubes with and without ZrO_2 (9mol% Y_2O_3) coatings were assembled to a oxygen sensor just according to the scheme shown in figure 1. The measurement of the oxygen concentration in molten steel was carried out at three different temperatures respectively, in the sequence of 1590, 1610, and 1640°C. After recorded the output EMFs of the tested double-cells, the P_e values for different samples were calculated *via* equations (3) and (4) and the results are shown in **figure 5.** The average P_e value for an individual ZrO_2 tube was based on the repeated measurement of four identical samples. Because of the continual inserting of the ZrO_2 tube, the oxygen concentration will increase, so a certain amount of metal Al powder was added to keep the low oxygen concentration in the molten steel after several tests.

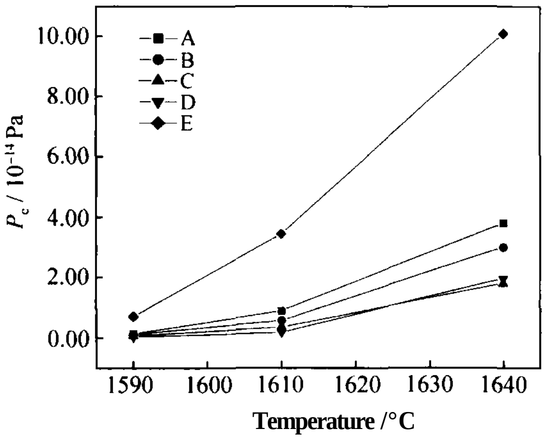

Figure 5 Effect of the coating thickness of ZrO_2 (9,mol% Y_2O_3) on the P_e value of ZrO_2 tubes.

During the measurement, samples C and D showed poor thermal shock resistance compared with samples A and B; about 20% and 40% of the tested tubes for samples C and D, respectively, have been broken, whilst almost all of the tubes of samples A and B can be tested successfully. This indicates that increasing the coating thickness of ZrO_2 (9mol% Y_2O_3) on the Mg-PSZ tube surface is unfavorable to the thermal shock resistance of the ZrO_2 tube, most probably due to the lower thermal conductivity and higher thermal expansion coefficient of Y_2O_3-stabilized ZrO_2 (YSZ) compared with MgO-stabilized ZrO_2 (the thermal expansion coefficients are 10.6×10^{-6} and 8.3×10^{-6}/°C, and the thermal conductivities are 0.4 and 2.1 W/(mK) for YSZ and Mg-PSZ, respectively) [9]. The thin coating (<3.4 μm) of ZrO_2 (9mol% Y_2O_3) on the Mg-ZrO_2 tube surface appears to have no obvious effect on the thermal shock resistance of the Mg-PSZ tube.

The coating with ZrO_2 (9mol% Y_2O_3) on the Mg-PSZ tube surface can decrease the P_e value of the Mg-PSZ tube effectively, as indicated in figure 5. With the increase of coating thickness, the P_e value decreases. The relatively low electronic conductivity of Y_2O_3-stabilized ZrO_2, compared with the CaO-stabilized ZrO_2 and MgO-stabilized ZrO_2, should be responsible for this decrease in P_e value.

According to equation (1), the electronic conductivity of the ZrO_2 solid electrolyte is mainly dependent on the atomic binding energy between cations and anions (oxygen ions) in the ZrO_2 electrolyte. Based on the thermodynamic data [10], we can calculate out the enthalpy of reactions (6)-(8) under the standard condition to be $\Delta H^0_{1600℃}=1582.1$, 1457.6 and 2701.5 kJ, respectively, indicating that the binding energy between Y and O atoms is much stronger than those between Ca and O and between Mg and O atoms. Therefore, it is reasonable to deduce that the incorporating of Y_2O_3 into ZrO_2 should increase the atomic binding energy between cations and oxygen ions and thus stabilize the structure of the ZrO_2 electrolyte, comparing with the incorporation of CaO and MgO into the ZrO_2 electrolyte. As a result, oxygen atoms are difficult to be detached to form molecular O_2 and free electrons from YSZ than from Mg-PSZ. Consequently, YSZ should have a lower electronic conductivity in comparison with Mg-PSZ. That is the reason why YSZ is usually employed in the low-temperature oxygen sensor [11-12] where a lower electronic conductivity of the sensor is much desired rather than good thermal shock resistance.

$$2CaO(s)=2Ca(g)+O_2(g) \qquad (6)$$

$$2MgO(s)=2Mg(g)+O_2(g) \qquad (7)$$

$$Y_2O_3(s)=2Y(g)+1.5O_2(g) \qquad (8)$$

A decrease of 70% in P_e value was achieved at 1640°C by sample B with the 3.4 μm ZrO_2 (9mol% Y_2O_3) coating, while a decrease of 82% was reached by sample C with the 5.8 μm ZrO_2 (9mol% Y_2O_3) coating. Unfortunately, sample C exhibits a poor thermal shock resistance, which will limit its wide application in steel making industries.

The P_e values for all investigated samples tend to be higher as the temperature increases. This is attributable to reaction (1), which will be facilitated at a higher temperature. Therefore, the electronic conductivity then becomes more obvious than that at a lower temperature.

The SEM observation indicated that a more smooth surface morphology has been formed on the ZrO_2 (9mol% Y_2O_3)-coated Mg-PSZ tube, as shown in **figure** 6(a), comparing with the pristine Mg-PSZ tube in which a coarse-grained surface was observed, as illustrated in figure 6(b). Undoubtedly, a fine and smooth surface condition for the ZrO_2 tube is of importance and will be favorable for the accurate determination of oxygen content in molten steel. When coated with more ZrO_2 (9mol% Y_2O_3), the Mg-PSZ tube tends to be cracked at its surface, as evidenced in figure 6(c), mainly owing to the mismatch of thermal expansion coefficient between ZrO_2 (Y_2O_3) and ZrO_2 (MgO). These cracks are apparently unfavorable for the successful measurement of the Mg-PSZ tube.

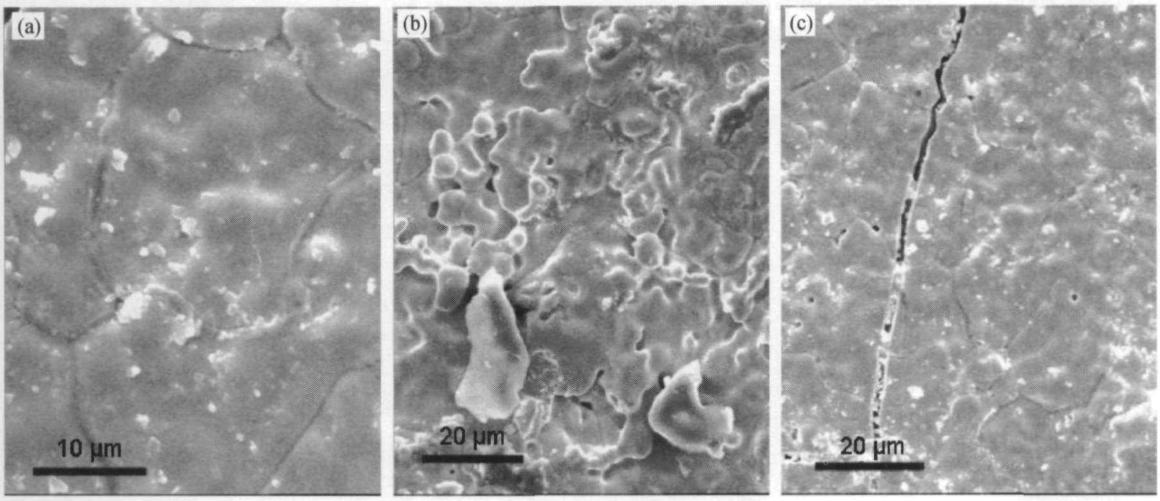

Figure 6 SEM images of the ZrO_2-tube surface coated and uncoated with ZrO_2 (9mol% Y_2O_3): (a) coated with 3.4 μm ZrO_2 (9mol% Y_2O_3); (b) Mg-PSZ tube without coating; (c) coated with 5.8 μm ZrO_2 (9mol% Y_2O_3).

In order to exam the stability and measurement accuracy of the ZrO_2 (9mol% Y_2O_3)-coated Mg-PSZ tube, double-cell tests, similar to figure 1 but both reference electrodes are set as Cr-Cr_2O_3, were carried out in the intermediate frequency furnace for samples A, B and E, respectively. Hereaus samples were also tested at the same time for comparison. Two ZrO_2 tubes from the same sample in the double-cell test were inserted into molten steel simultaneously at the same depth and the two tubes were set much close to each other comparing with the capacity of molten steel, therefore the gradient in oxygen concentration for these two tubes is neglectable. **Table 2** lists the experimental results. A1-A2, A3-A4 and A5-A6 represent the tested pair of tubes from sample A, respectively, likewise for samples B and E. Due to their poor thermal shock resistance, samples C and D were not tested here.

Table 2 EMFs **and calculated** oxygen **activities obtained by double-cells with different samples**

No.	Label for pair of tested cells	E/mV		$a_o/10_{-6}$	
		First cell	Second cell	First cell	Second cell
1	A1-A2	-195	-190	3.20	3.40
2	A3-A4	-190	-190	3.40	3.40
3	A5-A6	-190	-190	3.40	3.40
4	H1*	-195	—	3.20	—
5	B1-B2	-190	-185	3.40	3.60
6	B3-B4	-165	-173	4.80	4.30
7	B5-B6	-170	-180	4.50	3.90
8	E1-E2	-110	-150	10.40	5.97
9	E3-E4	-130	-155	7.90	5.57
10	E5-E6	-150	-170	5.97	4.50
11	H2*	-160	—	5.20	—

Note: (1) H1, H2, comparison probe from Hereaus, it is a commercial oxygen probe, single cell. (2) The fluctuation of the measured EMF between different pairs of tested cells is mainly due to the change of oxygen content in molten steel originated from the continual inserting of the ZrO_2 tube during the testing process, thus some aluminum was added to reduce the oxygen content in the process of measurement.

Table 2 shows that the two EMFs outputted by a pair of tested cells are very similar for samples A and B, however much different for sample E, indicating that coating with ZrO_2 (9mol% Y_2O_3) on the Mg-PSZ tube surface can improve the measurement stability and accuracy of Mg-ZrO_2 oxygen sensors significantly. The ZrO_2 (9mol% Y_2O_3)-coated Mg-ZrO_2 tube gives a good EMF reproducibility. This should be ascribed to the smooth surface and the decrease in P_e value of the coated Mg-PSZ tube, as presented in figures 4 and 5.

The general standard for judging whether an oxygen sensor probe (Mg-PSZ tube) is workable in the oxygen activity measurement for molten steel is mainly dependent on its EMF reproducibility, measurement accuracy and thermal shock resistance. When [O] is under 10×10^{-6}, it is allowed that the error for EMF value is in the range of ±10 mV, corresponding to the error in [O] is in the range of $\pm1.5\times10^{-6}$. The prepared Mg-PSZ tubes (oxygen sensor probe) with the ZrO_2 (9mol% Y_2O_3) coating have, when the coating thickness is less than 3.4 μm (samples A and B), only ±5 mV differences, and exhibit good measurement accuracy and excellent thermal shock resistance. Hence, it can be demonstrated that the coated Mg-PSZ tube should be an excellent kind of oxygen sensor probe for the measurement of oxygen activity in low oxygen concentration molten steel.

5 Conclusions

The ZrO_2 (9mol% Y_2O_3) coating was prepared evenly on the surface of a Mg-PSZ tube (oxygen sensor probe) by dipping the green Mg-PSZ tube in a ZrO_2 (9mol% Y_2O_3) slurry and then co-firing at 1750°C for 8 h. The coated-ZrO_2 tube shows a good thermal shock resistance when the coating thickness is not more than 3.4 μm. After coated with ZrO_2 (9mol% Y_2O_3), a dramatic decrease in the electronic conduction parameter P_e of the Mg-PSZ tube was observed, which is possibly ascribed to the lower electronic conductivity of Y_2O_3 stabilized-ZrO_2 compared with that of MgO stabilized-ZrO_2. Furthermore, the ZrO_2 (9mol% Y_2O_3) coated Mg-ZrO_2 tube exhibits a good reproducibility and an accurate EMF value output with an error of ±5 mV in the lower oxygen concentration measurement, which is considered to be related to its lower P_e value and its smooth surface morphology after coated. The excellent performance of ZrO_2 (9mol% Y_2O_3) coated Mg-PSZ tube indicates that it should be a promising kind of oxygen sensor probe for low oxygen measurement in molten steel.

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