



Comparative Study of Plasma Sprayed Yttria and Ceria Stabilized Zirconia Properties

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ABSTRACT

Thermal Barrier Coatings are subjected to spalling and destabilization due to hot corrosion. Recently, Ceria Stabilized Zirconia (CSZ)-based TBCs have been intensively investigated for the YSZ replacement because CSZ has a much lower thermal conductivity and a higher expected thermal expansion coefficient than those of YSZ. In this research, Yttria stabilized zirconia (YSZ) and ceria stabilized zirconia (ZrO_2 25CeO₂ 2.5Y₂O₃) TBCs were fabricated, followed by hot corrosion tests with a Na₂SO₄+V₂O₅ salt at 1050°C. The treated samples were characterized using XRD and SEM equipped with EDS. From studies on microscopic failure behavior, the formation of YVO₄ crystals and the amount of phase transformations of tetragonal ZrO₂ to monoclinic lead to degradation of coatings. Results revealed that CSZ TBCs had better resistant to hot corrosion than YSZ TBCs. The amount of YVO₄ crystals and monoclinic ZrO₂ in YSZ are much more than CSZ which leads to faster degradation of YSZ than CSZ. The strength of the Adhesive coatings of the substrate was also measured in this study.

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1. INTRODUCTION

Thermal barrier coatings (TBCs) are frequently used on the blades and vanes of gas turbines to provide thermal insulation, thus lowering the metal temperature and consequently improving component durability and increasing engine efficiency [1]. A common two layer structured TBCs system consists of yttria stabilized zirconia (YSZ) top coat for reducing the temperature of the substrate, with high temperature stability and low thermal conductivity and an oxidation-resistant MCrAlY (M=Ni and/or Co) bond coat on the superalloy to efficiently prevent its oxidation and hot corrosion by molten salts and corrosive gases [2,3]. For applications in more severe environments, such as higher temperature, strains and corrosion, the properties of YSZ-based TBC systems need to be improved further, which has become the focus in TBC field [4,5].

Various attempts have been made to improve hot corrosion resistance of TBCs. The most promising approach is to substitute Y₂O₃ with more acidic stabilizer elements for tetragonal zirconia such as CeO₂,

In₂O₃ and Sc₂O₃ [4]. Some investigators have reported that the ceria stabilized zirconia (CSZ) coatings do not only have higher temperature stability, good corrosion resistance and high fracture toughness, but also lower thermal conductivity and higher thermal expansion coefficient than YSZ coatings [6,7]. Lower thermal conductivity of CSZ in comparison to YSZ is due to much heavier atomic weight and a bigger ion radius of cerium than yttrium [8].

Although it is expected that by replacing Y₂O₃ with CeO₂, TBC will be more chemically stable, it is not clear about its corrosion resistance in a working temperatures above 1000°C when low quality fuels were used [9]. In previous studies, hot corrosion behavior of CSZ and YSZ with vanadium compounds such as V₂O₅ and NaVO₃ in temperatures below 1000 °C has been investigated. However, gas turbine fuel or air intake steam may contain impurities such as Na, S and V, a mixed Na₂SO₄-V₂O₅ compound tends to form and deposit onto turbine blades [10-13].

In this work, hot corrosion (at temperature higher than 1000°C) and adhesive strength tests were carried out on YSZ and CSZ TBCs. Consequently, the effect of yttria stabilizer substitution with ceria on hot corrosion

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behavior at very high temperatures and adhesive strength of TBCs has been investigated in microscopic respects.

2. EXPERIMENTAL PROCEEDURE

Nickel-Based superalloy (Inconel738) and 1020 steel with dimensions of $\text{Ø}25 \times 10$ mm was used as the substrate. Duplex TBCs composed of ceramic top coating (350 μm) and NiCrAlY bond coating were deposited on the superalloy substrate by atmospheric plasma spray (APS) process. The powders consisting of micro sized ceramic particles (ZrO_2 -4.5 wt. % Y_2O_3 -25 wt. % CeO_2) and (ZrO_2 -8 wt. % Y_2O_3) were used for CSZ and conventional YSZ top coatings, respectively. The plasma spraying was carried out using a Metco type 3M plasma spraying system. The spraying parameters are given in Table 1. The morphology and microstructure of coatings were examined using scanning electron microscopy (SEM, Oxford cam scan MV2300) equipped with EDS. X-ray diffraction (XRD, Cu $K\alpha$, Philips) was used to establish the phase composition of the coatings. For hot corrosion test, a eutectic mixture of 55 wt. % V_2O_5 and 45 wt. % Na_2SO_4 powders was selected as corrosive salt. The physical specifications of each salt are presented in Table 2. The corrosive salt was spread over the surface of the coatings in a concentration of 30 mg/cm^2 leaving 2 millimeters distance from the uncoated edge to avoid edge effect. The specimens were set in an electric furnace with air atmosphere at 1050 $^\circ\text{C}$ for 40h and then cooled inside the furnace. The coatings were inspected every 4 hours.

For tinseling bond strength measurement, specimens were prepared and tested according to the ASTM-C633-79 standard. A high performance epoxy adhesive, Scotch weld-2214 (3M, USA), was used to join the two specimens. The surface of uncoated specimens was grit blasted to enhance the adhesion strength. The tensile bond strength was the maximum tensile strength measured with a Zwick/Z050 at crosshead speed of 1 mm/min. The coated bond strength value is an average of three measurements.

3. RESULTS AND DISCUSSIONS

3. 1. Microstructure of the Coatings Before Hot Corrosion Figure 1 shows the as-sprayed cross-sectional microstructure of both conventional YSZ and CSZ TBCs consisting of ceramic top coating and NiCrAlY bond coating deposited on the Inconel 738 substrate. Both the conventional YSZ and CSZ upper layers of the as-sprayed samples exhibited similar microstructures with no visible cracks under the optical

microscope which shows the integrity of coatings.

From X-ray diffraction analysis shown in Figure 2, the CSZ top coating contains tetragonal phase of zirconia ($t\text{-ZrO}_2$), $t\text{-Zr}_{0.82}\text{Ce}_{0.18}\text{O}_2$ and cubic CeO_2 phase in the as sprayed state, while the conventional YSZ coatings consists mainly of $t\text{-ZrO}_2$ phases. It is obvious that the tetragonal zirconia should be the predominant phase in the as sprayed conventional YSZ and CSZ coatings.

TABLE 1. Plasma spraying parameters

Voltage (V)	Current (A)	Argon (l/min)	Hydrogen (l/min)	Powder Feed Rate (g/min)	Spray distance(cm)
70	500	80	15	35	7.5

TABLE 2. Some physical properties of the used salts

Type of salt	Melting point ($^\circ\text{C}$)	Density (g/cm^3)
Na_2SO_4	884	2.7
V_2O_5	690	3.3

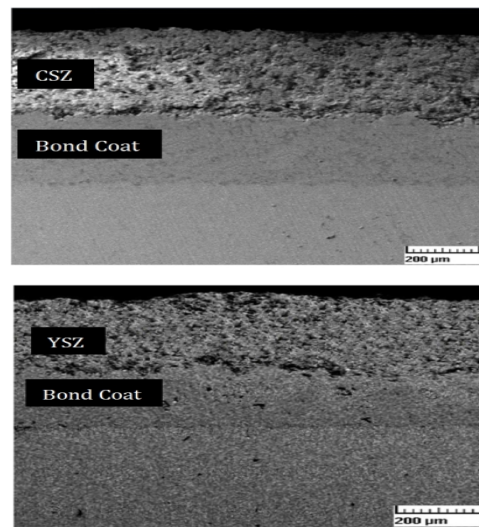


Figure 1. As-sprayed cross-sectional microstructure of both conventional YSZ and CSZ TBCs

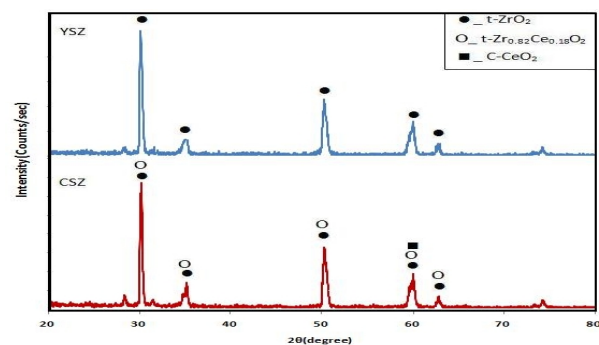


Figure 2. XRD patterns of As-Sprayed YSZ and CSZ TBCs

3. 2. Surface Morphology and Crystalline Structure After Hot Corrosion

Visual examination of the conventional YSZ coating revealed that the color of the surface changed from yellow to brown after exposure to the molten salt. SEM surface morphologies of both conventional YSZ and CSZ coatings are presented in Figures 3 and 4. Further, SEM examination showed many rod-like crystals on the surface of the conventional YSZ coatings (see Figure 3). EDS analysis (see Figure 3) exhibited that the crystals were composed of yttrium, vanadium and oxygen. These crystals were identified to be YVO_4 by the XRD pattern after hot corrosion testing.

Visual examination of the surface of CSZ coating showed that the surface was white at first and it became yellow after hot corrosion testing. In Figure 4, from the SEM surface image of CSZ TBC after hot corrosion, it can be seen that some types of different crystals were emerged. According to EDS analysis (see Figure 4) and XRD patterns, these crystals are YVO_4 and CeO_2 . The YVO_4 crystals on the surface of CSZ are much smaller in number and size as compared to that of conventional YSZ.

The XRD analysis was performed on the surface of the coatings after hot corrosion. Figure 5 illustrates the XRD patterns of coatings after hot corrosion tests. Monoclinic ZrO_2 and YVO_4 were formed on both conventional YSZ and CSZ after exposing to molten salt at $1050^\circ C$ for 40 hours, but the intensity of their peaks were different. On the surface of CSZ, the formation of $CeVO_4$ crystals and free CeO_2 were detected after 40 hours of tests as shown in Figure 5.

The cross-sectional micrographs of coatings after hot corrosion are exhibited in Figure 6. The wide crack in conventional YSZ coating (see Figure 6a, b) and spalling of YSZ top coating are the results of formation of monoclinic ZrO_2 and YVO_4 crystals in thermal cycling, while in Figure 6c there is not a wide crack in the thickness of CSZ coating. The molten salts penetrated through thickness of Conventional YSZ and reached the YSZ/NiCrAlY interface. YVO_4 crystals formed at this area too (see Figure 6b).

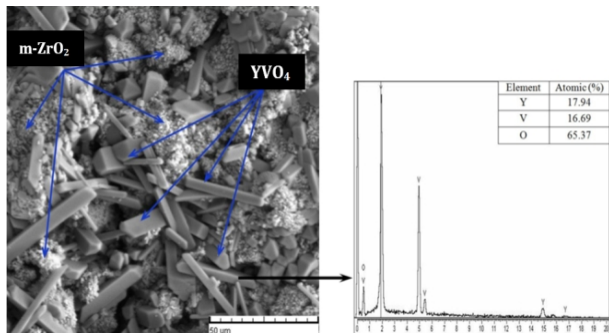


Figure 3. SEM surface Image of conventional YSZ TBC after hot corrosion test.

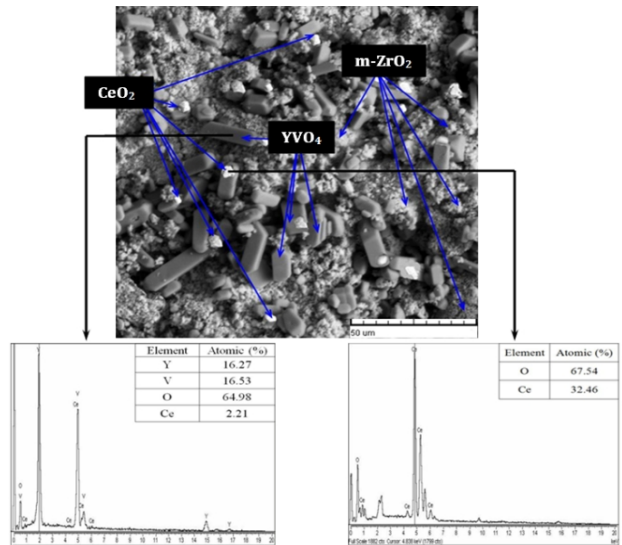


Figure 4. SEM surface Image of CSZ TBC after hot corrosion test.

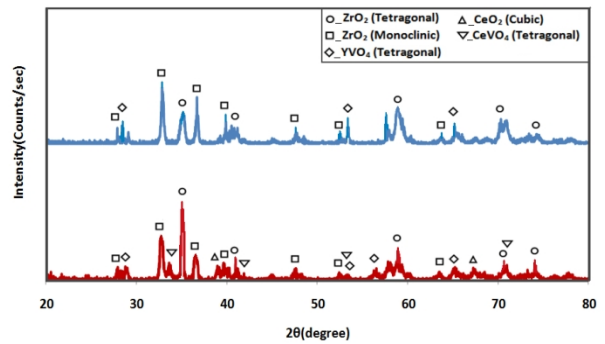


Figure 5. XRD patterns of conventional YSZ and CSZ TBCs After hot corrosion test.

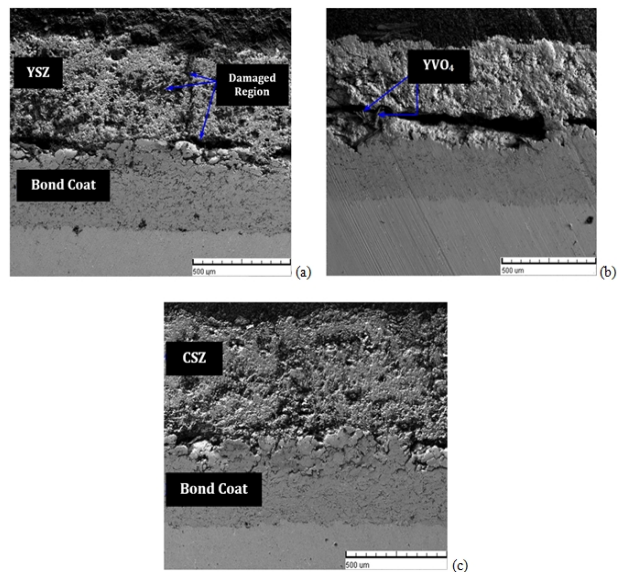
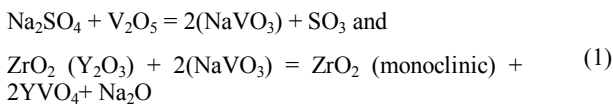
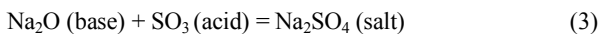


Figure 6. SEM cross-sectional image of (a),(b)conventional YSZ, (c) CSZ TBCs

3. 3. Hot Corrosion Test Results of YSZ and CSZ TBCs The mechanism of degradation of conventional YSZ TBC during hot corrosion in the presence of corrosive salts such as Na_2SO_4 and V_2O_5 can be explained by the following reactions:



The first stage of the reaction involves the formation of NaVO_3 from the initial salts; then NaVO_3 penetrates through the entire coating and the defects and initiates the reaction with Y_2O_3 to form YVO_4 . Due to the depletion of Y_2O_3 , monoclinic ZrO_2 is formed in the cooling stage of the test. V_2O_5 may also react with Y_2O_3 directly, Equation (2), and the same corrosion products can be produced [12-14]. Also, free SO_3 and Na_2O can react and form Na_2SO_4 as side reactions; moreover, Na_2O can react with V_2O_5 directly and form NaVO_3 [9,12]



After hot corrosion test, very porous areas, damaged by molten salts, were observed throughout the entire zirconia top layer shown in Figure 6a. In addition, the YVO_4 crystals were detected at the YSZ/NiCrAlY interface (Figure 6b). Due to salt attack, the damaged areas of the YSZ sample include the entire coating thickness from the YSZ top surface to the YSZ/NiCrAlY interface after the 40h hot corrosion test using $\text{Na}_2\text{SO}_4 + \text{V}_2\text{O}_5$. As shown in Figure 6c, the damage to the CSZ TBC sample is less severe than that of conventional YSZ TBCs.

It is well known that the phase transformation of zirconia from tetragonal to monoclinic due to depletion of Y_2O_3 , is accompanied by 3-5% volume expansion of the coating leads to crack initiation. Then, the entire thickness of coating would be under tensile stress. Therefore, cracks can easily initiate in the ceramic material and damage the coating. It is believed that the damaged areas were formed during the cooling stage after the hot corrosion tests. The molten salt can deeply penetrate in coating through porosities in entire coating. Wherever molten salt is in close contact with Y_2O_3 in entire coating, YVO_4 can form. The formation of YVO_4 rod shaped crystals throughout the coating may cause additional stresses in the coating. Thus, under thermal cycling and mechanical shock, these damaged areas can break into small pieces easily, and at last, the conventional YSZ coating will gradually degrade.

In the case of CSZ TBCs, the porous thickness of coating shows that the salts also penetrated through the CSZ coating (Figure 6c) and the YVO_4 crystals formed

and the phase transformation of tetragonal to monoclinic happened (see Figure 5). In contrast to those of YSZ, the YVO_4 crystals on the surface of CSZ are much smaller in number and size (see Figure 4). The amount of monoclinic zirconia, consequently, is much less than that of conventional YSZ coating (see Figure 3). It can be obviously seen that the YVO_4 formation and monoclinic transformation of zirconia were greatly retarded and consequently the damaged areas through the thickness of coating are much less compared to conventional YSZ coatings; also no visible wide crack were formed in the thickness of coating.

It is stated that CeO_2 , presumably because of its greater Lewis acidity is more resistant to chemical reaction with SO_3 - Na_2SO_4 , V_2O_5 and NaVO_3 than Y_2O_3 . This resistance to chemical reaction of CeO_2 leads to high stability of zirconia tetragonal phase in CSZ coatings either.

On the other hand, the destabilization process of zirconia in CSZ TBCs differs from that of conventional YSZ due to different chemical behavior of their contents [12]. As shown in Figure 3, the chemical reaction between Y_2O_3 and molten salt (NaVO_3 and V_2O_5) and formation of YVO_4 resulted in destabilization of conventional YSZ, while the CSZ TBCs destabilized through mineralization process. Mineralization is a type of phase reaction involving a non-reactive liquid that tends to move a stresses or non-equilibrium phase towards equilibrium [14, 15]. As shown in Figure 4, in case of CSZ TBCs, free CeO_2 is formed and precipitated during the hot corrosion process instead of having chemical reaction with molten salts.

XRD pattern of CSZ TBC after hot corrosion (Figure 5) reveals the CeVO_4 crystals on the surface of CSZ TBC. In contrary to the mineralization effect, CSZ TBCs can also be destabilized by chemical reaction between V_2O_5 or NaVO_3 - V_2O_5 mixture and CeO_2 as stabilizer and the product is CeVO_4 . It is thought that these two CSZ TBC destabilization processes can occur during the hot corrosion process. According to S.Y. Park et al. [7], the depletion of CeO_2 stabilizer in CSZ occurs in two steps: mineralization to form pure CeO_2 inside the zirconia coating matrix and chemical reaction with the salt to produce CeVO_4 crystals.

As previously discussed, the main mechanism of degradation of zirconia-based TBCs is formation of YVO_4 crystals accompanied with tetragonal to monoclinic transformation of zirconia which leads to deterioration of TBCs [16]. In case of CSZ TBCs, due to stronger acidity and higher stability of CeO_2 than Y_2O_3 as stabilizer in CSZ, CSZ destabilization is retarded much more than conventional YSZ. Additionally, with the formation of CeVO_4 crystals, the formation of YVO_4 crystals have been retarded in an effective manner. Consequently, less zirconia changed to monoclinic phase. CSZ TBCs can have strong stability in tetragonal phase and less additional stress is

endured by the coating. These results clearly indicate that the resistance of CSZ TBCs to hot corrosion is much higher compared to conventional YSZ TBCs.

3. 4. Bond Strength Figure 7 shows the bond strength of YSZ and CSZ coatings and the topographic structure of fractured samples. The mean strength for YSZ coating was measured to be about 34 MPa, while that for CSZ coating was about 37 MPa. As it is indicated, there is no large difference between YSZ and CSZ bond strengths because of the same fracture mechanism. As a matter of fact, the mode of fracture in both samples is a complex adhesive/cohesive [17]. It means that in this type of coatings, adhesive fracture is occurred at the NiCrAlY/zirconia interface, whereas cohesive fracture occurred within zirconia layer. It is interesting to know that in none of the cases the fracture occurred at the NiCrAlY/substrate interface. This is certainly the high adhesion strength of NiCrAlY layer applied by APS method (Figure7).

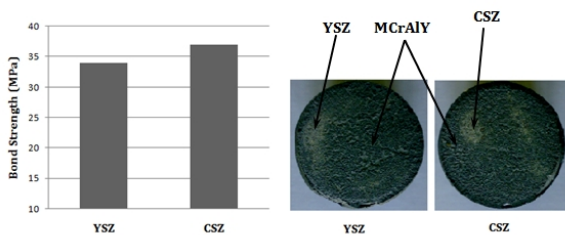


Figure 7. Comparison of bond strength and Fracture topography of YSZ and CSZ.

4. CONCLUSION

In this investigation the microstructure, bond strength and hot corrosion behavior of plasma-sprayed CSZ and conventional YSZ coatings under $\text{Na}_2\text{SO}_4 + \text{V}_2\text{O}_5$ environment at 1050°C were compared. Hot corrosion of YSZ and CSZ coatings was mainly due to the reaction of NaVO_3 or salt containing V_2O_5 with zirconia stabilizer (Y_2O_3 and CeO_2) which was accompanied by the formation of monoclinic ZrO_2 and $\text{YVO}_4/\text{CeVO}_4$ crystals. The formation rate of $\text{YVO}_4/\text{CeVO}_4$ crystals is an important parameter to evaluate the TBC hot corrosion behavior. Depletion of CeO_2 stabilizer in zirconia can occur either through mineralization and forming free CeO_2 or chemical reaction and forming CeVO_4 . Based on the experimental results, it is concluded that CSZ TBCs have better hot corrosion resistance than the YSZ TBCs. In addition, experimental results indicated that the bond strength of as-sprayed duplex YSZ and CSZ coatings were 34 and 37 MPa respectively, and the mode of their fractures were adhesive/cohesive. It was found that having ceria

as a stabilizer in addition to yttria is quite promising to improve hot corrosion behavior of zirconia, but there is no remarkable difference for adhesion resistance.

5. REFERENCES

- Mohan, P., Patterson, T., Desai, V.H. and Sohn, Y.H., "Degradation of free-standing air plasma sprayed CoNiCrAlY coatings by vanadium and phosphorus pentoxides", *Surface and Coating Technology*, Vol. 203, (2008), 427-431.
- Pint, B.A., Haynes, J.A. and Zhang, Y., "Effect of superalloy substrate and bond coating on TBC lifetime", *Surface and Coating Technology*, Vol. 205, (2010), 1236-1240.
- Chen, Z., Wu, N.Q., Singh, J. and Mao, S.X., "Effect of Al_2O_3 overlay on hot-corrosion behavior of yttria-stabilized zirconia coating in molten sulfate-vanadate", *Thin Solid Films*, Vol. 443 (2003), 46-52.
- Wei, S., Xu, B., Wang, H., Jin, G. and Lv, H., "High-temperature corrosion-resistance performance of electro-thermal explosion plasma spraying FeAl-base coatings", *Surface and Coating Technology*, Vol. 201, (2007), 6768-6771.
- Tsipas, S.A., "Effect of dopants on the phase stability of zirconia-based plasma sprayed thermal barrier coatings", *Journal of the European Ceramic Society*, Vol. 30, (2010), 61-72.
- Gong, W.B., Sha, C.K., Sun, D.Q. and Wang, W.Q., "Microstructures and thermal insulation capability of plasma-sprayed nanostructured ceria stabilized zirconia coatings", *Surface and Coating Technology*, Vol. 201, (2006), 3109-3115.
- Park, S.Y., Kim, J.H., Kim, M.C., Song, H.S. and Park, C.G., "Microscopic observation of degradation behavior in yttria and ceria stabilized zirconia thermal barrier coatings under hot corrosion", *Surface and Coating Technology*, Vol. 190, (2005), 357-365.
- Jones, R.L., "Some aspects of the hot corrosion of thermal barrier coatings", *Journal of Thermal Spray Technology*, Vol. 6, (1997), 77-84.
- Chen, Z., Mabon, J., Wen, J. and Trice, R., "Degradation of plasma-sprayed yttria-stabilized zirconia coatings via ingress of vanadium oxide", *Journal of the European Ceramic Society*, Vol. 29, (2009), 1647-1656.
- Tolpygo, V. K. and Clarke, D. R., "Morphological evolution of thermal barrier coatings induced by cyclic oxidation", *Surface and Coating Technology*, Vol. 163, (2003), 67-74.
- Ueno, K., Sodeoka, S. and Tsutsumi, M., "Thermal and mechanical properties of CeO_2 -4mol% Y_2O_3 partially stabilized ZrO_2 ceramics", *Journal of Thermal Spray Technology*, Vol. 32, (1995), 221-226.
- Sodeoka, S., Suzuki, M., Ueno, K., Sakuramoto, H., Shibata, T. and Ando, M., "Thermal and Mechanical Properties of ZrO_2 - CeO_2 Plasma-Sprayed Coatings", *Journal of Thermal Spray Technology*, Vol. 6, (1997) 361-367.
- Jafari, A.H. and Karaminezhad, M., "Hot corrosion behavior of magnesite - chromite refractories used in reverberatory furnaces at sarcheshmeh copper complex", *International Journal of Engineering*, Vol. 16, (2003).
- Keyvani, A., Saremi, M. and Heydarzadeh Sohi, M., "Microstructural stability of zirconia-alumina composite coatings during hot corrosion test at 1050°C ", *Journal of Alloys and Compounds*, Vol. 506, (2010), 103-108.
- Han, Z., Xu, B., Wang, H. and Zhou, S., "A comparison of thermal shock behavior between currently plasma spray and

supersonic plasma spray $\text{CeO}_2\text{-Y}_2\text{O}_3\text{-ZrO}_2$ graded thermal barrier coatings”, *Surface and Coating Technology*, Vol. 201, (2007), 5253–5256.

16. Lee, J., Tsai, P. and Chang, C., “Microstructure and thermal cyclic performance of laser-glazed plasma-sprayed ceria–yttria-

stabilized zirconia thermal barrier coatings”, *Surface and Coating Technology*, Vol. 202, (2008), 5607-5612.

17. Khoddami, A.M., Sabour, A. and Hadavi, S.M.M., “Microstructure formation in thermally-sprayed duplex and functionally graded NiCrAlY/Yttria-Stabilized Zirconia coatings”, *Surface and Coating Technology*, Vol. 201, (2007), 6019–6024.

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به دلیل خواص حرارتی مطلوب تر پوشش های زیرکونیای پایدار شده با سریا (CSZ) در مقایسه با زیرکونیای پایدار شده با ایتریا (YSZ)، رایج ترین پوشش سد حرارتی، تحقیقات فراوانی به منظور بررسی امکان استفاده گسترده این ماده به عنوان پوشش سد حرارتی انجام می شود. یکی از دلایل تخریب پوشش های سد حرارتی، خوردگی داغ می باشد که در این پژوهش برای پوشش های YSZ و CSZ بررسی شده است. ابتدا این پوشش ها با روش پاشش پلاسمایی بر روی زیرلایه هایی از جنس سوپر آلیاژ پایه نیکل ایجاد شدند. برای بررسی مقاومت به خوردگی داغ نمونه ها، آزمون های خوردگی داغ روی سطح این پوشش ها در نمک مذاب (۵۵٪ وزنی V_2O_5 و ۴۵٪ وزنی Na_2SO_4) در دمای 1050°C انجام شد. بر اساس مطالعه میکروسکوپی فرآیند خوردگی داغ و بررسی میزان تشکیل YVO_4 به عنوان محصول خوردگی داغ در نمونه ها، پوشش های سد حرارتی CSZ مقاومت به خوردگی داغ بالاتری از خود نشان دادند. در واقع کریستال های YVO_4 کوچک تر، و به تبع آن زیرکونیای مونوکلینیکی کمتری در نمونه های با پوشش CSZ دیده شد که نشان دهنده مقاومت بیشتر و عمر طولانی تر این پوشش ها می باشد. استحکام چسبندگی پوشش ها نیز مورد بررسی قرار گرفته است.

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