



HOT CORROSION OF CERIA-YTTRIA STABILIZED ZIRCONIA PLASMA SPRAYED THERMAL BARRIER COATING BY EUTECTIC VANDIUM PENTAOXIDE-SODIUM SULFATE

Mohammed Jasim Kadhim*, Mohammed Hliyil Hafiz⁺, Maryam Abduladeem Ali Bash*
* Department of Production Engineering and Metallurgy,
University of Technology Baghdad, Iraq / + College of Engineering, Al-Iraqi University
maryam_uot@yahoo.com

ABSTRACT

The high temperature corrosion behavior of thermal barrier coating (TBC) system consisting of IN-738 LC superalloy substrate, air plasma sprayed Ni_{24.5}Cr₆Al_{0.4}Y (wt%) bond coat and air plasma sprayed ZrO₂-20 wt% ceria-3.6 wt% yttria (CYSZ) ceramic coat were characterized. The upper surfaces of CYSZ covered with 30 mg/cm², mixed 45 wt% Na₂SO₄-55 wt% V₂O₅ salt were exposed at different temperatures from 800 to 1000 °C and interaction times from 1 up to 8 h. The upper surface plan view of the coatings were identified for topography, roughness, chemical composition, phases and reaction products using scanning electron microscopy, energy dispersive spectroscopy, talysurf, and X-ray diffraction. XRD analyses of the plasma sprayed coatings after hot corrosion confirmed the phase transformation of nontransformable tetragonal (t') into monoclinic phase, presence of YVO₄ and CeVO₄ products. Analysis of the hot corrosion CYSZ coating confirmed the formation of high volume fraction of YVO₄, with low volume fractions of CeVO₄ and CeO₂. The formation of these compounds were combined with formation of monoclinic phase (m) from transformation of nontransformable tetragonal phase (t').

Keywords: Ceria-yttria-stabilized zirconia; Plasma sprayed coating; Na₂SO₄-V₂O₅; High temperature corrosion; YVO₄; CeVO₄

التاكل الساخن لطبقات الرش بالبلازما للحواجز الحرارية للسيرييا-ياتريا المثبتة للزركونيا
بالاويتكتيك لخماسي اوكسيد-الفناديوم- كبريتات الصوديوم

محمد جاسم كاظم محمد هليل حافظ مريم عبد العظيم علي باش

أخلاصة

تم تقييم التاكل الكيميائي بدرجة الحرارة العالية لطلاءات الحواجز الحرارية المنتجة بالرش بالبلازما للزركونيا الحاوية على 20 wt% سيريا و 3.6 wt% ياتريا والمطلية على طبقة طلاء وسطية من Ni_{24.5}Cr₆Al_{0.4}Y (wt%). ان طبقات الطلاء السيراميكية والوسطية المنتجة بالرش بالبلازما تم طلاؤها على سبيكة فانقة من IN-738. LC طبقات الرش بالبلازما السيراميكية التي تم تغطيتها بمزيج ملحي من Na₂SO₄-55 wt% V₂O₅ 45 wt% وبمعدل تغطية 30 mg/cm² تم اختبارها بدرجة حرارة من 800 الى 1000 °C ولفترات زمنية 1 و 8 ساعات. طوبوغرافية الاسطح والخشونة والتركييب الكيميائي والاطوار ونواتج التاكل للاسطح العلوية لطبقات الرش تم تحديدها باستخدام المجهر الالكتروني الماسح ومطياف مفرق الطاقة و جهاز قياس الخشونة وحيود الاشعة السينية. اثبتت نتائج حيود الاشعة السينية لطبقات الرش بعد التاكل الكيميائي تحول الطور السداسي الغير متحول (t') الى الطور احادي الميل (m)

و الاطوار YVO_4 و $CeVO_4$. اوضح تحليل طبقات الرش بالبلازما بعد التاكل بان الطور السائد بكسر حجمي كبير هو YVO_4 وكمية قليلة من الاطوار $CeOV_4$ و CeO_2 . أن تركز هذه الاطوار مصاحب لتكوين الطور الاحادي الميل (m) الناتج من تحول الطور السداسي الغير متحول (t').

INTRODUCTION

The applications of any engineering system require the scientific and engineering approaches for selection of all elements to controlling the design efficiency. The performance of gas turbine advanced engines is mainly determined by the maximum temperature that can be sustained by the alloy components, e.g, the blades of the engine **Miller et al. (1981)**. The key factor for reliable and reproducible servicing for these advanced engines is the selections of successful thermal barrier coatings (TBCs) resist highly the high temperature corrosion resistance **Cao et al. (2004)**, **Stover et al. (2004)**. They require the selection of elements of materials, processing involve, design variables and principles govern all of these **Davis (2004)**. In TBCs, there is intimate interrelationship between the processing variables of thermal plasma spraying and the features of stabilized zirconia based ceramic **Bai et al. (2011)**, **Mohammed Jasim (2011)**.

Detail analysis of the state of the art of TBCs field explored many requirements should be present for successful advanced engines **Grunling and Schneider (1981)**, **Nicoil et al. (1985)**, **Clarke (2003)**, **Wang and Sayre (2009)**, **Fauchais et al. (2010)**. It is very crucial to understand what is meant by thermal barrier coating? It should be having many requirements, designed and selected carefully the successful processing to withstand thermal shock resistance and salt high temperature corrosion attack. These adversely requirements sometime does not easy monitor. It requires adequate combination of low thermal conductivity, high thermal expansion near the bulk substrate, phase stability, critical volume fraction of porosity and good hot corrosion resistance **Steven (1986)**.

Examination the open literatures of TBCs suggest clearly from balancing between advantages and disadvantage of plasma sprayed coatings, the only promising systems of TBCs are based on yttria partially stabilized zirconia (YPSZ), YPSZ + ceria stabilized zirconia (CSZ) and alumina yttria partially stabilized zirconia (AlYPSZ) **Strangman (1985)**, **Ma et al. (1988)**, **Mohammed Jasim et al. (1988)**, **Nejati et al. (2013)**, **Mohammed Jasim, (2015)**, YPSZ systems which are worldwide acceptable TBCs for many advanced turbine engines were widely investigated for high temperature corrosion resistance **Jones and Williams (1987)**, **Susnitzky et al. (1988)**, **Jones (1989)**, **Jones (1997)**, **Mohan et al. (2007)**. They were found that the performance of TBCs can improve considerably due to enhance the aerodynamically and melt part of the ceramic coating to close the undesirable porosity and cracks. However, there are extensive literatures highlight the behavior of YPSZ plasma sprayed coatings during high temperature corrosion. It still there is a dearth of detail information regarding the reaction between species in the fuel such as V_2O_5 and Na_2SO_4 . The proposed failure mechanisms of hot corrosion plasma sprayed TBCs have been documented by many investigators **DeMasi et al. (1990)**, **Clake et al. (1997)**, **Singh et al. (2001)**.

The failures of TBCs were taken place due to sever attacks of vanadium compounds such as $NaVO_3$ and V_2O_5 with yttria causing leaching of yttrium from YPSZ **Wu et al. (2005)**. These reactions are accompanied with severe transformation of nontransformable tetragonal (t') phase to mixtures of transformable tetragonal (t), cubic (c) and monoclinic (m) phases **Singh et al. (2001)**. The formation of m phase is the main destructive outcome causing severe stresses leading to spalling **Nagelberg (1985)**. The other failure mechanism is a purely oxidation mode **Lu et al. 2013**. It takes place by diffusion of oxygen during service which forms a

thermally growth oxide (TGO). The thickness of a thermally growth oxide (TGO) forms at the interface between bond layer and ceramic layer increases considerably during service. Severe thermal expansion mismatch will produce due to the difference between thermal expansion of bond coat and TGO layer. This will cause at a critical thickness of TGO to spallation **Nitin et al. (2002)**.

A considerable scientific works have attempted to improve the high temperature corrosion resistance of yttria partially stabilized zirconia and ceria stabilized zirconia thermal barrier coatings **Jones (1997)**, **Mohan et al. (2007)**, **Sreedhar and Raji, (2009)**, **Ghasemi et al. (2014)**, **Bajpai et al. (2015)**. It is appeared that developing of ceria-yttria-stabilized zirconia thermal barrier coatings require to be evaluated at high temperature corrosion resistance. This study investigates the performance of zirconia-20 wt% CeO₂- 3.6 wt% Y₂O₃ at high temperature corrosion through molten salt of mixed of V₂O₅ and Na₂SO₄.

MATERIALS AND EXPERIMENTA METHODOLOGY

Ni-based grit blasted with alumina Inconel 738 LC (Ni-15Cr-8.5Co, wt%) superalloy in the shape of discs, 25 mm diameter and 3 mm thickness were used as substrates for plasma spraying. Amdry 963 bond coat powder (Ni_{24.5}Cr₆Al_{0.4}Y, wt%) and premixed powder of zirconia-20 wt% ceria-3.6 yttria (obtained from mixing different weight percentages of standard Sulzer Metco 204NS-G and 205NS powders, ZrO₂-8 wt% Y₂O₃ and ZrO₂-25 wt% CeO₂-2.5 wt% Y₂O₃ respectively) were air plasma sprayed on the substrate respectively (Table 1). Plasma spraying was performed, using 3MB gun Metco INC, Westury, L.I.N.Y. The thicknesses of the bond and plasma sprayed coats are approximately 90 ± 15 and 400 ± 25 μm respectively. The angle of plasma sprayed gun was kept to be perpendicular to the substrate. The particle size distribution of both sprayed powders is -125 μm +11 μm.

Quarters of the plasma sprayed thermal barrier coating discs were tested for corrosion at high temperatures. The upper surfaces of the sprayed samples were covered with a mixture of 55 wt% V₂O₅-45wt% Na₂SO₄ salt. About 1 mm from the edges of the samples was kept uncovered to prevent the substrate attack by salt. The concentration of the salt was approximately 30 mg/cm². The high temperature corrosion tests were conducted at different temperatures of 800, 900 and 1000 °C for interval time of 1 and 8 hours. The heating rate was maintained at 10 °C/min. The detail procedures of corrosion test were mentioned previously **Maryam Ali Bash (2017)**. The tested samples were thoroughly inspected visually and with optical microscopy for possible crack imitation or degradation. The samples were allowed to cool down inside the furnace to prevent thermal shock failure. The phases and reaction products were evaluated using X-ray diffraction (XRD) and scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS) facilities for qualitative and quantitative chemical analysis. The detail procedures of corrosion test, topographical, roughness and phases analyses were mentioned elsewhere **Maryam Ali Bash (2017)**.

RESULTS AND DISCUSSION

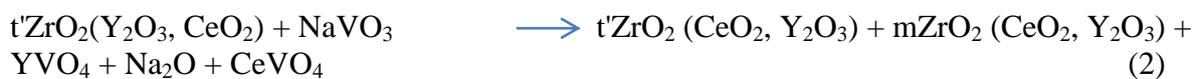
Fig.1 shows the typical upper surface plan view of the plasma sprayed CYSZ coating. It can be observed from Fig. 1 that the coating consists of typical topography of plasma sprayed ceramic coating having lamellar grains with some unmelted and semimelted particles of CYSZ. The coatings also present some defects of porosity, voids and cracks. SEM analysis of the plasma sprayed coatings at higher magnification showed the high quality of the coatings as suggest from the effective bonding between the splats (Fig. 1). The average of center line average (CLA) roughness of the coatings is approximately 6.2 μm. The amount of open porosity as determined from Image J is less than 15%. In order to postulate extra structural

data for the thermal barrier coating CYSZ system, numerous features from the transverse section were observed. Fig. 2 presents clearly the good bonding between the constituent of the system, substrate/bond coat, bond coat/thermally grown oxide and thermally grown oxide/CYSZ coat. Fig. 2 also shows the lower volume fraction of porosity and relatively larger voids and porosity observed from transverse section compares with those observed from upper surface plan view (closed porosity is relatively less than 12%). These defects are common nature of plasma sprayed ceramic coatings that play a vital role at high temperature corrosion of TBCs as active penetration paths of corrosive salts. The amount of porosity was found to be within the reasonable value satisfies the lower thermal conductivity and gives the mechanical cohesion between splats and bonding with TGO/bond coat. It should be emphasis that, it is very necessary before evaluate the response of thermal barrier coating to hot corrosion to investigate the features of plasma sprayed coating. This is because the hot corrosion mechanism is highly affected by the state of plasma sprayed coating.

Investigation of upper surface plan views of the hot corrosion plasma sprayed CYSZ showed the formation of agglomerated crystals with different shapes of semi-rods of yttrium vanadate (YVO₄), cerium vanadate (CeVO₄) and some semi-cubic ceria (CeO₂). EPMA analysis of the as-sprayed top coat showed at lower temperature of hot corrosion and shorter interaction timem, the main harmful phase formed is YVO₄ rather than CeOV₄ (Fig. 3). Increasing the hot corrosion temperature from 800 to 1000 °C and increasing the reaction time from 1 to 8 hr, the as-sprayed coats color changed remarkably from yellow to dark brown. With increasing the hot corrosion time, the mainly rod like structure of YVO₄ and small amount of CeVO₄ increased considerably (Fig. 4). This is formed due to the continuous reaction between plasma sprayed coat and the salt with increasing interaction time. This is taken pace via many steps. The dominant important step is the formation of the most harmful compound of NaVO₃ due the following reaction formula:



The formation of sodium metavanadate (NaVO₃) is the key factor as oxygen carrier for degradation of the plasma sprayed coating. It is due to severe interaction inside the pores rather than the splats. It was observed that, the formation of YVO₄ was related to leaching of yttrium form yttria which forms the YVO₄ compound and less amount of CeVO₄ and CeO₂ via the following reaction:



Careful examination of the hot corrosion products by SEM, EDS and EPMA showed that the formation of YVO₄ increased rapidly with increasing the temperature (Fig. 4). The size and the amount of the needles of YVO₄ increased considerably with increasing the temperature. The needles volume fraction of CeOV₄ was low for all reaction temperatures. This is related directly to increasing the acidity of the plasma sprayed coating due to the presence of high amount of ceria in the coating. Nevertheless, small amounts of CeOV₄ and CeO₂ were also observed. Strong evidence confirmed that the hot corrosion mechanism was obtained from XRD analysis. The XRD pattern of plasma sprayed coatings confirmed the presence of these phases (Figs. 5). The formation of harmful phases of YVO₄, CeOV₄ and CeO₂ resulted in reducing t' phase and increasing m phase. The growths of these harmful phases were on the surface rather than inside the porosity. They led to increase the roughness of the degradation coats (Figs. 6 and 7). The absence of detection any sodium element from EPMA may be related directly to the sublimit at high temperature of Na₂O Jones et al. 1986.

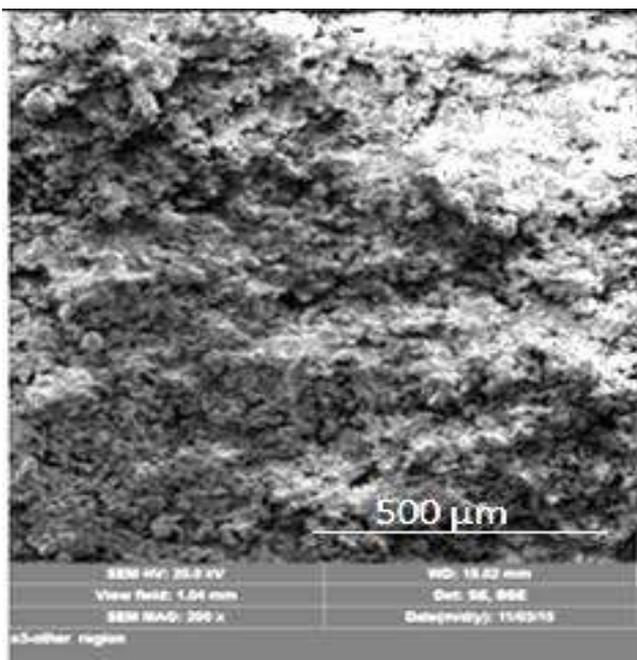
In this study, increasing the temperature of hot corrosion test to higher than 690 °C (melting temperature of V₂O₅) led to melt it and some reaction with ceramic coatings will take place. With increasing the temperature, the Na₂SO₄ melts producing Na₂O (highly basic oxide) which react with fused V₂O₅ (acidic oxide) forming the harmful phases of sodium metavanadate.

CONCLUSIONS

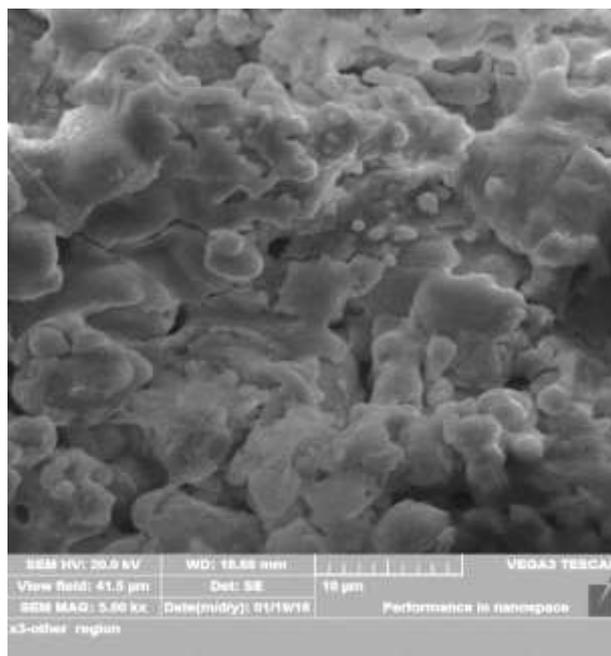
- 1- The base of the plasma sprayed thermal barrier coating, zirconia oxide is very stable to corrosive salts; there were no zirconia based phases formed.
- 2- The deleterious phases produced after hot corrosion are due to reaction of yttria rather than ceria with the mixed vanadium pentoxide-sodium sulfate salt to form the rod type phases of mainly yttrium vanadate (YVO₄), some amount of cerium vanadate (CeVO₄) and small amount of semi-cubic phase of ceria (CeO₂).
- 3- The transformation of t' phase to m phase with low yttria and ceria content was due to depletion of mostly yttrium and to less extent cerium from the plasma sprayed coatings to form the harmful phases.
- 4- The volume fraction and size of YVO₄, CeVO₄ and CeO₂ increased considerably at 1000 °C reaction temperature. The reaction rates at 800 and 900 °C were much lower.

Table 1. Processing sheet for bond coat and ceramic coat.

Parameter	Bond coat Ni24.5Cr6Al0.4Y	Plasma spray coat ZrO₂-20 wt% CeO₂-3.6 wt% Y₂O₃
Primary gas, Ar (SLPM)	39.95	53.25
Secondary gas, H ₂ (SLPM)	6.11	7.52
Current, A , Ampere	450	525
Voltage (V), Volt	50	55
Spray distance, mm	120	70
Powder feed rate, g/min	45	35



(a)



(b)

Fig. 1. SEM micrographs of upper surface plan view of the plasma sprayed CYSZ coating (a) low magnification and (b) high magnification.

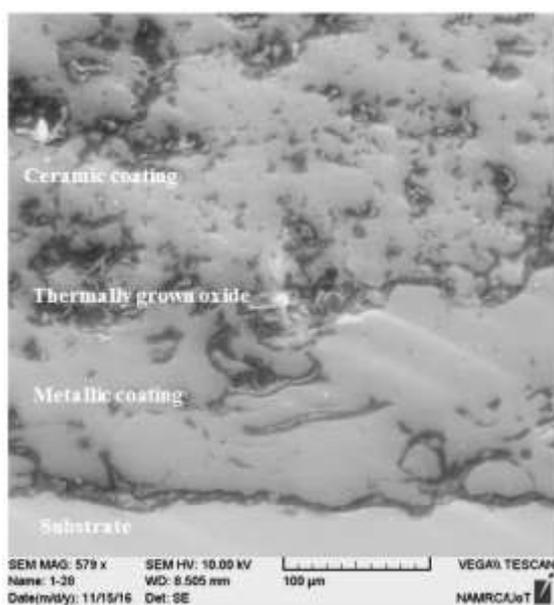


Fig. 2. SEM micrograph of polished transverse section of CYSZ plasma sprayed CYSZ TBC system showing the different coating (layer and substrate).

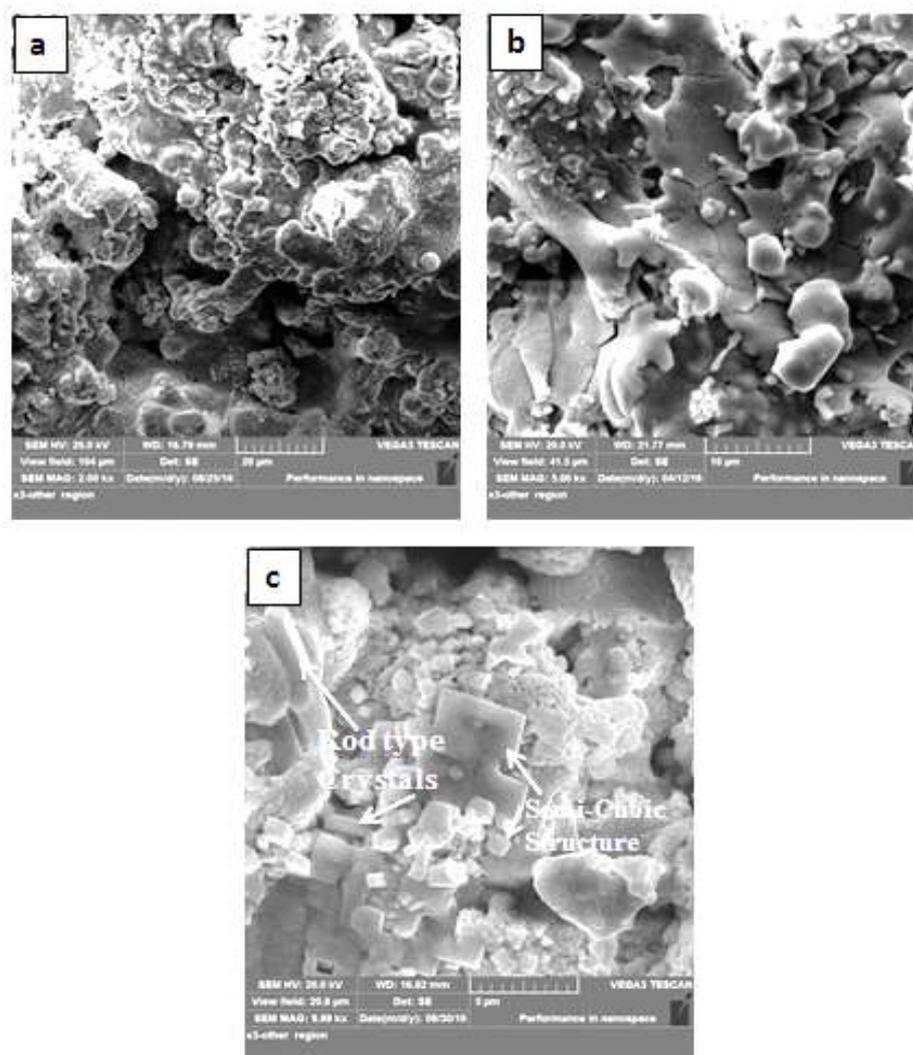


Fig. 3. SEM micrographs showing the effect of hot corrosion temperature at 8 hr reaction time (a) 800 °C, (b) 900 °C and (c) 1000 °C.

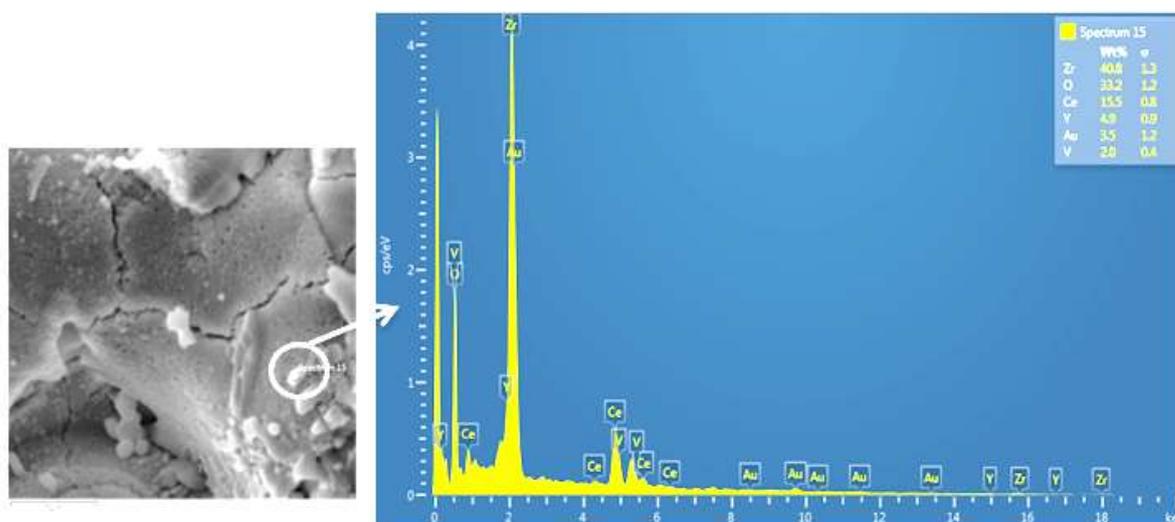
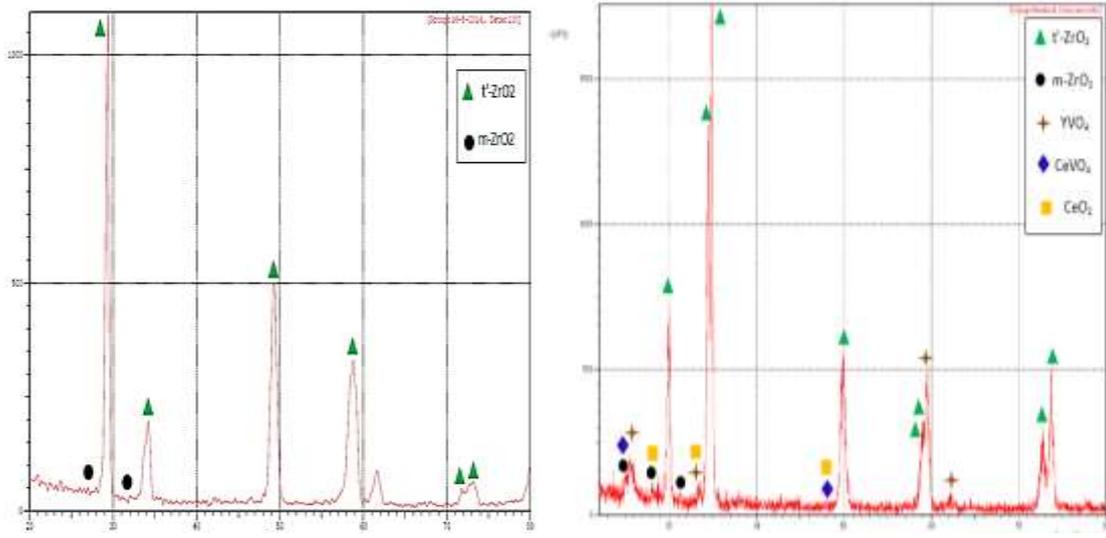


Fig. 4. EDS of rod type crystal on the CYSZ coating after hot corrosion at 900 °C for 8 hr.



(a)

(b)

Fig. 5. XRD patterns of (a) as-sprayed CYSZ coating and (b) as-sprayed CYSZ coating exposed to hot corrosion at 900 °C for 8 hr.

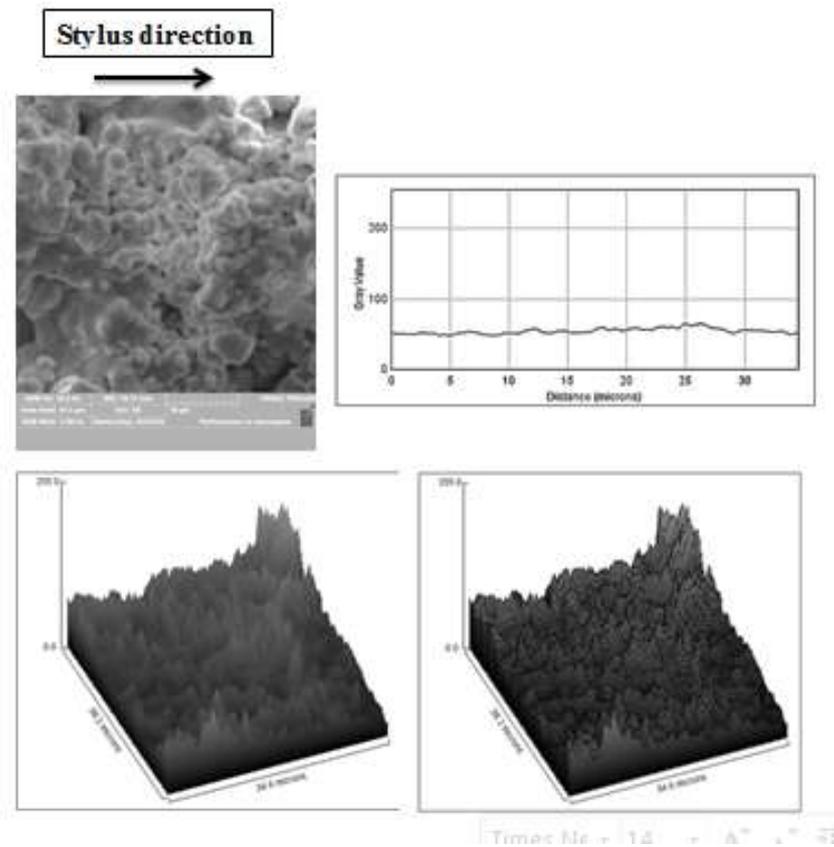


Fig. 6. Image J of as-sprayed CYSZ coating.

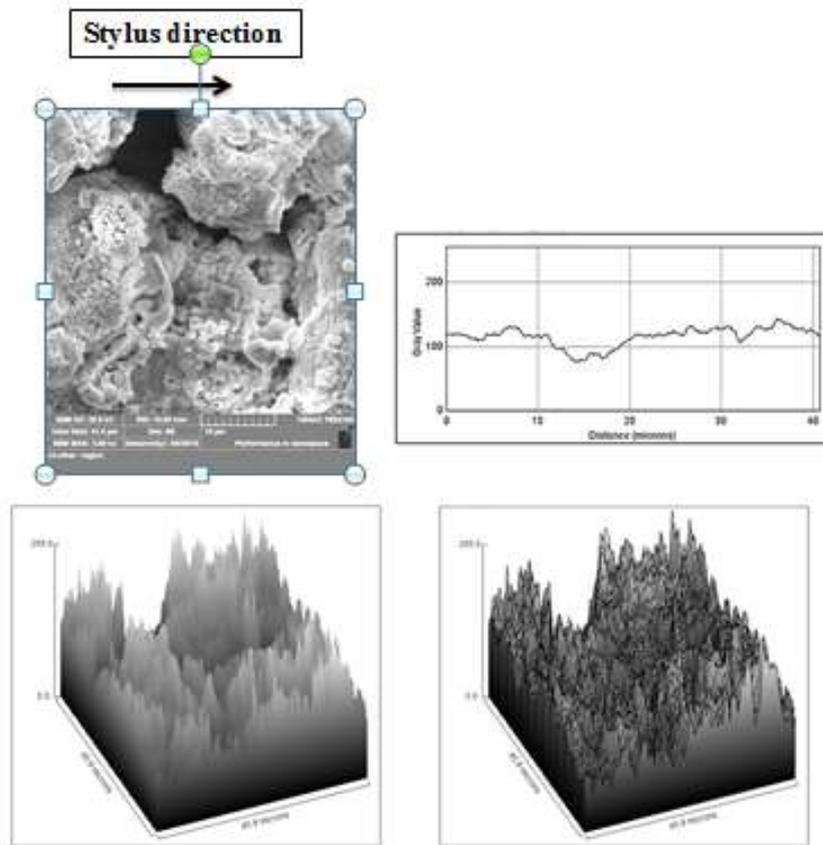


Fig. 7. Image J of as-sealed CYSZ after hot corrosion at 1000 oC for 8 hr showing the increasing of roughness due to formation of harmful compounds.

REFERENCES

- Bai Y, Han Z, Li H, Xu C, Xu Y, Wang Z, High performance nano-structured ZrO₂ based thermal barrier coatings deposited by high efficiency supersonic plasma spraying, *Applied Surface Science*, 257(2011)7210-7216.
- Bajpai P, Das A, Bhattacharya P, Madayi S, Kulkarni K, Omar S, Hot corrosion of stabilized zirconia thermal barrier coatings and the role of Mg inhibitor, *J. of the American Ceramic Society*, 98(2015)2655-2661.
- Cao XQ, Vassen R, Stoeber D, Ceramic materials for thermal barrier coatings, *Journal of the European Ceramic Society*, 24(2004)1-10.
- Clarke DR, Christensen RJ, Tolpygo V, The evolution of oxidation stresses in zirconia thermal barrier coated superalloy leading to oxidation Failure,” *Surface and Coating Technology*, 94-95(1997)89-93.

Clarke DR, Materials selection guidelines for low thermal conductivity thermal barrier coatings, *Surface and Coating Technology*, 163-164(2003)67-74.

Davis JR, *Handbook of Thermal Spray Technology*, ASM, ASM International, Materials Park, OH 44073-0002, USA, 2004.

DeMasi-Marcin JT, Sheffler KD, Bose S, Mechanisms of degradation and failure in a plasma deposited thermal barrier coating, *J. Engineering of Gas Turbine Power*, 112(1990)521-526.

Fauchais P, Montavon G, Bertrand G, From powders to thermally sprayed coatings, *J. of Thermal Spray Technology*, 19(2010)56-80.

Ghasemi R, Razavi RS, Mozafarinia R, Oghaz HM, Pidani RA, The influence of laser treatment on hot corrosion behavior of plasma sprayed nanostructured yttria stabilized zirconia thermal barrier coatings, *J. of European Ceramic Society*, 34(2014)2013-2021.

Grunling HW, Schneider K, Coatings in industrial gas turbines: Experience and further requirements, *Thin Solid Films*, 84(1981)1-15.

Jones RL, Williams CE, Jones SR, Reaction of vanadium compounds with ceramic oxides. *J. of Electrochemical Society: Advancing Solid-State Electrochemical Science and Technology*, 133(1986)227-230.

Jones RL, Williams CE, Hot corrosion studies of zirconia ceramics, *Surface and Coating Technology*, 32(1987)349-358.

Jones RL, High temperature vanadate corrosion of yttria-stabilized zirconia coatings on mild steel, *Surface Coatings and Technology*, 37(1989)271-284.

Jones RL, Some aspects of the hot corrosion of thermal barrier coating, *J. of Thermal Spray Technology*, 6(1997)77-84.

Lu Z, Myoung S, Jung Y, Balakrishnan G, Lee J, Paik U, Thermal fatigue behavior of air-plasma sprayed thermal barrier coating with bond coat species in cyclic thermal exposure, *Materials*, 6(2013)3387-3403.

Ma B, Li Y, Su K, Characterization of ceria–yttria stabilized zirconia plasma-sprayed coatings, *Applied Surface Science*, 255(2009)7234-7237

Jones RL, Some aspects of the hot corrosion of thermal barrier coatings, *J. of Thermal Spray Technology*, 6(1997)77-84.

Maryam Ali Bash, Optimizing, phase transformation and hot corrosion resistance of laser sealing plasma sprayed ceria stabilized zirconia thermal barrier coatings, PhD Thesis, Department of Production Engineering and Metallurgy, University of Technology, Baghdad, Iraq, 2017.

Miller RA, Smialek JL, Gurlick RG, in *Advances in Ceramics*, Vol. 3, *Science and Technology of Zirconia*, Eds. A.H. Heuer and H.W. Hobbs, Published by The American Ceramic Society (ACerS), USA, 1981, p. 241.

Mohammed Jasim K, West DRF, Steen WM, Laser sealing of plasma-sprayed calcia-stabilized zirconia, *J. of Materials Science Letters*, 7(1988)1307-1309.

Mohammed Jasim K, Characterization of laser sealed coatings of yttria partially stabilized zirconia, *Optics and Lasers in Engineering*, 49(2011)785-792.

Mohammed Jasim K, Laser sealing of zirconia-yttria-alumina plasma sprayed coating, *J. of King Saud University- Engineering Sciences*, 25(2013)11-20.

Mohan P, Yuan B, Patterson T, Desai VH, Sohnw YH, Degradation of yttria-stabilized zirconia thermal barrier coatings by vanadium pentoxide, phosphorous pentoxide, and sodium sulfate, *J. of The American Ceramic Society*, 90(2007)3601-3607.

Nagelberg AS, Destabilization of yttria-stabilized zirconia induced by molten sodium vanadate-sodium sulfate melts, *J. Electrochemical Society*, 132(1985)2502-2507.

Nejati M, Rahimipour MR, Mobasherpour I, Pakseresht AH, Microstructural analysis and thermal shock behavior of plasma sprayed ceria-stabilized zirconia thermal barrier coatings with micro and nano Al_2O_3 as a third layer, *Surface and Coatings Technology*, 282(2015)129-138.

Nicoil AR, Gruner H, Prince R, Wuest G, Thermal spray coatings for high temperature protections, *Surface Engineering*, 1(1985)59-71.

Nitin R, Padture P, Gell M, Jordan EH, Thermal barrier coatings for gas-turbine engine applications, *Science*, 296(2002)280-284.

Singh JP, Nair BG, Rensch DP, Sutaria MP, Grimsditch MH, , *J. of the American Ceramic Society*, 84(2001)2385-2393.

Sreedhar G, Raja VS, Hot corrosion of YSZ/ Al_2O_3 dispersed NiCrAlY plasma-sprayed coatings in Na_2SO_4 -10 wt% NaCl melt, *Corrosions Science*, 52(2009)2592-6002.

Stevens R, *Science and technology of zirconia*, Published by Magnesium Electron Ltd, 1986.

Strangman TE, Thermal barrier coatings for turbine airfoils, *Thin Solid Films*, 127(1985)95-105.

Stover D, Pracht G, Lehmann H, Dietrich M, Doring JE, Vaben R, New material concepts for the next generation of plasma sprayed thermal barrier coatings, *J. of Thermal Spray Technology*, 13(2004)76-83.

Susnitzky DW, Hertl W, Carter CB, Destabilization of zirconia thermal barriers in the presence of V_2O_5 , *J. of the American Ceramic. Society*, 71(1988) 992-1004.

Wang Y, Sayre G, Commercial thermal barrier coatings with a double-layer bond coat on turbine vanes and the process repeatability, *Surface and Coating Technology*, 203(2009) 2186-2192.

Wu N, Chen Z, Mao SX, Hot corrosion mechanism of composite alumina/yttria-stabilized zirconia coating in molten sulfate-vanadate salt, *J. of the American Ceramic Society*, 88(2005)675-682.