

# AN INVESTIGATION ON EFFECT OF BOND COAT REPLACEMENT ON HOT CORROSION PROPERTIES OF THERMAL BARRIER COATINGS

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Received: January 2013

Accepted: May 2013

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**Abstract:** In the present study NiCrAlY bond coating layer was produced by electroplating against common atmospheric plasma spraying (APS). Both types of the bond coats were applied on IN738LC base metal then, the YSZ ( $ZrO_2$ -8%  $Y_2O_3$ ) thermal barrier top layer was coated by atmospheric plasma spray technique. Hot corrosion is one of the main destructive factors in thermal barrier coatings (TBCs) which come as a result of molten salt effect on the coating-gas interface. In this investigation the hot corrosion behavior of coatings was tested in the furnace which was contain  $Na_2SO_4$ -55%  $V_2O_5$  and mixed salts environment at 900°C up to 15 hr. dwell time. Optical microscopy, scanning electron microscopy (SEM / EDS) and X-ray diffraction analysis (XRD) was used to determine the crystallographic structure and phase transformation of the coatings before and after the hot corrosion tests. The transformation of tetragonal Zirconia to monoclinic  $ZrO_2$  and formation of  $YVO_4$  crystals as hot corrosion products caused the degradation of mentioned TBCs. The results showed NiCrAlY coated by economical electroplating method a viable alternative for common thermals sprayed bond coats in hot corrosive environments with same corrosion behavior.

**Keywords:** Electroplating, Atmospheric Plasma Spraying, NiCrAlY bond coat, Thermal barrier coatings, YSZ, Hot corrosion.

## 1. INTRODUCTION

Thermal barrier ceramic coatings have been applied to sheet metal combustor components and they have been used in the turbine section for about 25 years [1, 2].

Thermal barrier coatings (TBCs) are widely used in gas turbines to prevent thermal effect and increase turbine efficiency. The TBCs are usually composed of a partially stabilized Zirconia by Ytria (YSZ) as a top coat which is provides thermal insulation toward metallic substrate and an oxidation resistant layer like MCrAlY as a bond coat [3- 5].

MCrAlY (M = Ni, Co) alloys are most generally multiphase materials. The micro structure of MCrAlY alloys may depend on cooling rates during the thermal spray process. It is to be noted that in the Ni-Cr-Al ternary system a phase transformation can occur at about 1000 °C where by  $\gamma+\beta$  stable at high temperature, transforms into  $\gamma'$ -Ni<sub>3</sub>Al +  $\alpha$ -Cr. Based on the phase diagrams established by Taylor and Floyd, This reaction is accompanied by a significant volume variation, which may be deleterious for

the mechanical integrity of a coating substrate system. It is therefore recommended that an composition outside this field is selected, limiting the aluminium content, or that cobalt is added to destabilize  $\gamma'$  formation [1].

Low quality fuels usually contain impurities such as Na and V which can form  $Na_2SO_4$  and  $V_2O_5$  salt on the surface of turbine blades. Such fused salts can react with Ytria (the stabilizer component of YSZ) and cause transformation of tetragonal or cubic Zirconia to monoclinic phase during cooling [6]. This transformation is accompanied by 3–5% volume expansion, leading to cracking and delaminating of TBCs [6].

In recent researches, development activities have been concentration on the following points:

- Degradation mechanisms in high-temperature corrosion of metallic coatings.
- Alternative techniques for depositing MCrAlY coatings like, electrolytic co deposition and electrophoresis.
- Improve the thermal barrier coatings reliability and in the case of stationary gas turbines their hot corrosion resistance. Both

structural and mechanical approaches are required to determine, in particular, the role of microstructure, micro cracking, porosity, residual stresses oxidation of the bond layer in the degradation mechanisms of these coatings [1].

In this research, the effect of two types of bond coats (plasma sprayed and electrolytic co deposition) on hot corrosion were compared. For this reason usual TBC (NiCrAlY plasma spray + YSZ plasma spray) and (electrolytic co deposited NiCrAlY +YSZ plasma spray) samples were tested. The protective effects and changes in NiCrAlY and the mechanism of destabilization of coatings during hot corrosion were investigated.

**2. EXPERIMENTAL**

Nickel based super alloy (Inconel 738LC) disks of (Ø25×5 mm), which grit blasted with alumina particles were used as substrates. Two types of commercial powders were selected: Amdry 962 (Ni–22Cr–10Al–1Y, –106+52µm) as bond coat, Amdry 142F (ZrO<sub>2</sub>–8%Y<sub>2</sub>O<sub>3</sub>, –125+45µm) as TBC.

Two types of coatings bond layer were produced by air plasma spray (APS) and

**Table 1.** Types and thickness of TBCs samples (µm)

samples	1	2
Type of bond coat processing	Thermal spray	Electroplating
NiCrAlY thickness (µm)	100	80-100
YSZ thickness (µm)	200	200

electrochemical methods, YSZ as a topcoat on the surface. Table I indicates the characteristics of the samples. The parameters of plasma spraying were listed in Table II.

Before electro co-deposition in sample 2, IN738LC substrate was roughened with various numbers of SiC (150-800) sandpaper then it was soaked in alkali solution of 10% NaOH to remove surface contamination materials. Sample according to ASTM standard numbers B558 [7] and B343 [8], was prepared as follow:

- a. Sample put in a solution of concentrated sulfuric acid 65-70% for a minute with Current density 20A/dm<sup>2</sup> as anodic.
- b. The sample was coated with a thin layer of nickel from acid nickel chloride bath containing 240g/l NiCl<sub>2</sub>.6H<sub>2</sub>O and 31ml/l

**Table 2.** Parameters of plasma spraying

	Bond Coat	Top Coat
Types of guns and spraying systems	SULZER-METCO F4	
Current(A)	600	
Voltage(V)	53	58
Primary gas rate, Ar (l/min)	55	35
Secondary gas rate, H <sub>2</sub> (l/min)	12	
Powder carrier gas rate, Ar (l/min)	2.5	3
Powder feed rate(g/min)	30	20
Spraying distance(Cm)	12	
Gun velocity (Cm/min)	20	

**Table 3.** Physical specifications of salts

Type of salt	T <sup>m</sup> (°C)	%wt	Density (g/cm <sup>3</sup> )
Na <sub>2</sub> SO <sub>4</sub>	884	45	2.7
V <sub>2</sub> O <sub>5</sub>	670	55	3.3

hydrochloric acid (37% with 1.16 g/ml density).

In electrochemical co-deposition method for bond coat, a Watt's bath containing 250 g/l NiSO<sub>4</sub>. 6H<sub>2</sub>O, 45 g/l NiCl<sub>2</sub>. 6H<sub>2</sub>O and 40 g/l H<sub>3</sub>BO<sub>4</sub>, Nickel bath additives 25 g/l, Current density 5-7 A /dm<sup>2</sup> and temperature 50±1 was used. The pH level was regulated between 3.6 to 4.0 by adding 10% dilute sulfuric acid because the pH level increases with the generation of hydrogen gas on cathode. 5 g/l Al and 25 g/l Cr particles with an average particle size of 20 μm and 40 μm respectively were added in to the bath and these particles were co-deposited with Ni.

A pure nickel plate and a super alloy disk were used as anode and cathode, respectively. Stirring rate was 350 rpm.

Yttrium (Y) was hot doped to the coating by a methods which is presented as follows:

- The 10% solution of yttrium nitrate was prepared.
- Then the sample was heated in the oven with a temperature of 500 °C for 5 minutes.
- Heated sample immediately immersed in the 10% yttrium nitrate solution at room temperature.
- Samples rapidly out of solution and put in the oven with a temperature of 500 °C for 5 minutes.

After hot doping, sample was heat treated for diffusion of alloying elements and homogenization full coverage at 1000 °C for 2 hours under Argon gas inert atmosphere. Coating thickness was calibrated at about 80-100 micrometers.

Then this sample coated by YSZ as top coat same as first sample which its plasma spray conditions were presented in Table II.

For hot corrosion testing, mixture of 55wt. % V<sub>2</sub>O<sub>5</sub> and 45wt. % Na<sub>2</sub>SO<sub>4</sub> powders was selected

as corrosive salt. Some physical specifications of each salt are presented in Table III.

The mixture spread over the surface of the coatings in a concentration of 30 mg/cm<sup>2</sup>, leaving 3 mm distance from the uncoated edge to avoid edge effect. The specimen was set in an electric furnace with air atmosphere at 900°C for 15 hr. The coating was inspected periodically after each of 3 hr.

The microstructure, morphology and chemical composition of the surface and the cross-section of the coatings before and after hot corrosion tests were examined by scanning electron microscopy (SEM) equipped with energy dispersive spectrometer (EDS) and X-ray diffraction (XRD).

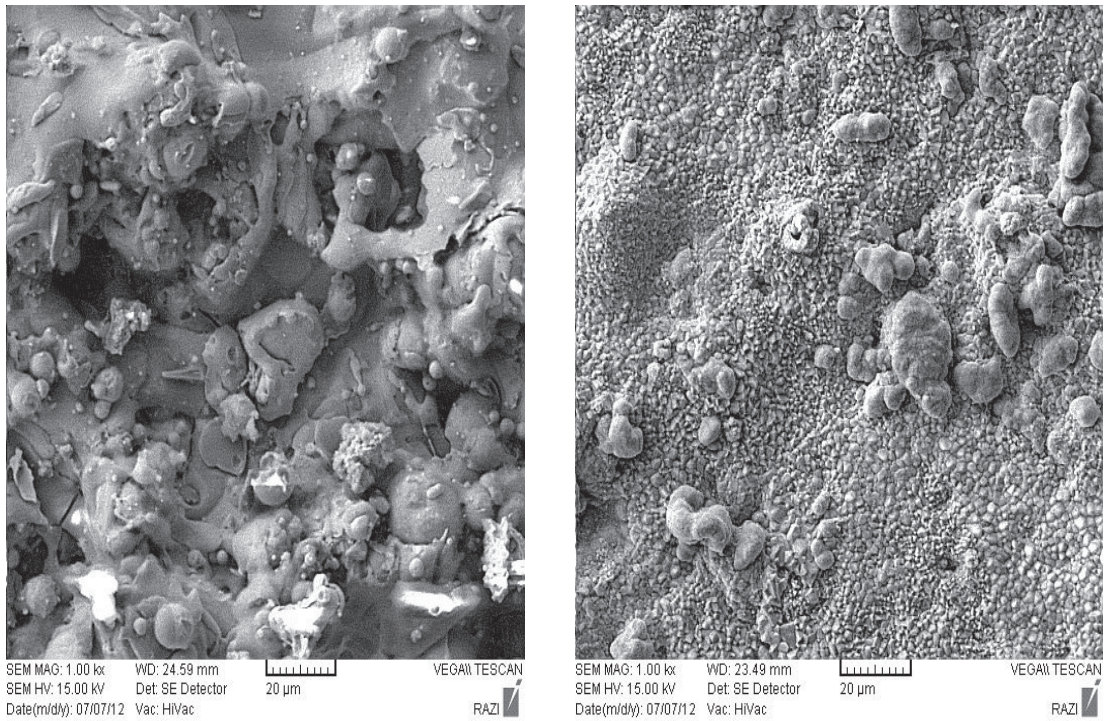
### 3. RESULTS AND DISCUSSION

Microstructures of the coatings were investigated by observation of the microstructure and chemical analysis with using SEM, EDS and XRD.

Fig.1 shows surface topography and morphology of bond coats before thermal spraying of top coat. Fig 1a is related to atmospheric plasma sprayed NiCrAlY. As it can be seen, the plasma spray process makes flattened splats of metallic material which is rapidly solidified from molten powder during the spray process.

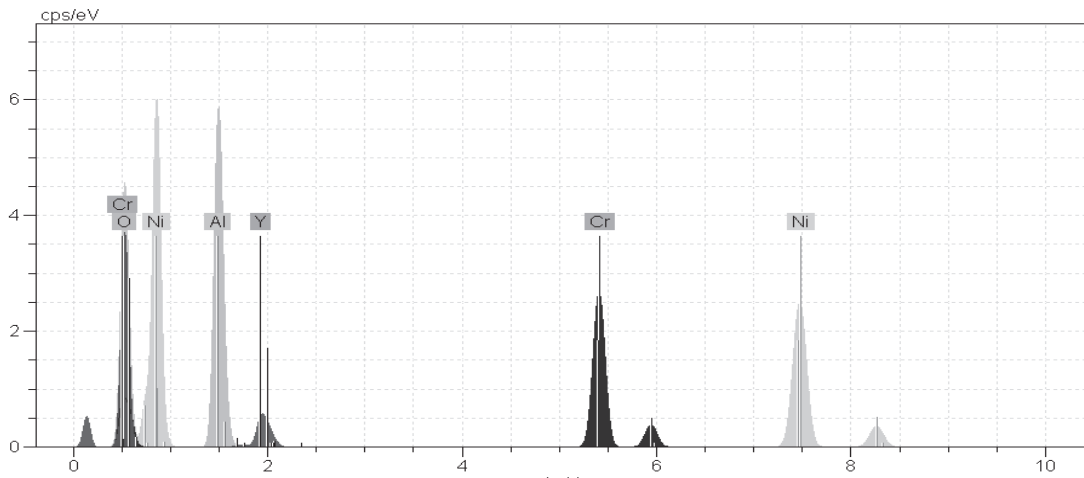
Figure 1b shows the surface morphology of the electrochemically co-deposited NiCrAlY. This coating has a large number of very small nodules which were nucleated and growth during the electroplating and Al and Cr powder particles which were merged and coated with electroplated Ni base metal. Energy dispersive analysis (EDS) of this coating (Fig. 1c) shows the successfully doping of yttrium which was diffuse in to the electro co deposited band coat layer.

Figure 2 Optical microscope images from surface of the electroplated NiCrAlY before and after heat treatment. Energy dispersive X-ray



a.

b.



c.

**Fig. 1.** Scanning electron microscope image (a) of the surface bond coat by plasma spraying, (b) electrochemical method is applied to the bond coat, (c) EDS spectrum from the surface of the bond coatings

map from scanning electron microscopy of electro co-deposited and heat treated bond coat surface were presented in Figure 3. It can be seen uniform distribution of Ni, Cr, Al and Y in the

bond coat. Therefore, Heat treatment makes a completely homogenization and diffusion of the coated elements to gather because of reducing the holes, surface roughness and uniform distribution



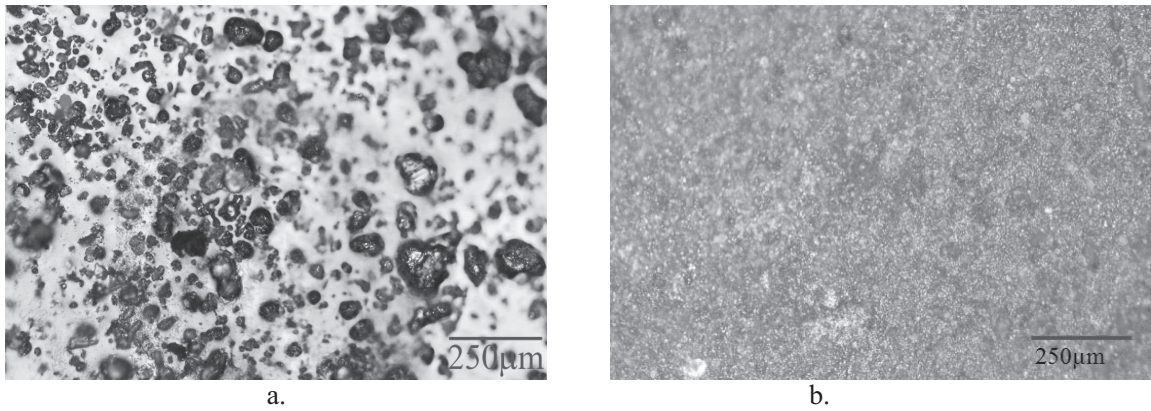


Fig. 2. Optical microscope image of NiCrAlY coating surface, (a) Before heat thermal, (b) After heat thermal

of elements after the heat treatment cycle. So the heat treatment makes a good uniformity in the structure and alloying of the coating.

X-ray diffractions of bond coats were presented in Figure 4. It can be seen, the main phases in the both of coatings is Ni, NiO and  $\beta$ -NiAl. Electro plated bond coat also contain many small amount of  $\text{NiCr}_2\text{O}_4$  and metallic yttrium

phases. Presence of oxides like NiO and  $\text{NiCr}_2\text{O}_4$  in the electro co-deposited NiCrAlY may due to low levels of oxygen, which exist in the heat treatment and Yttrium doping process atmospheres.

The microstructure of electroplated MCrAlY alloys may depend on and previous heat treatments. If the aluminum content is

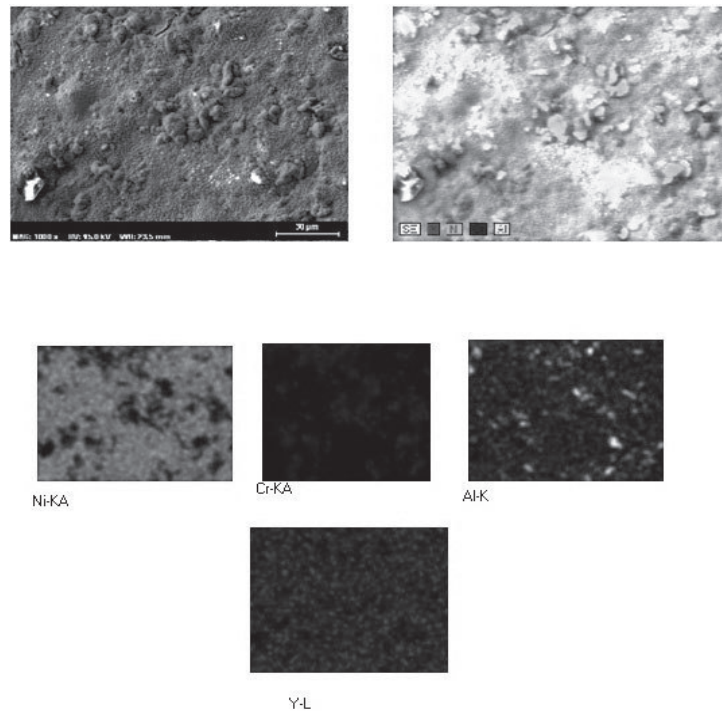


Fig. 3. Image of X-Ray Map of nickel, chromium, yttrium and aluminum NiCrAlY coating after heat treatment at  $1000\text{ }^\circ\text{C}$  for 2 hours

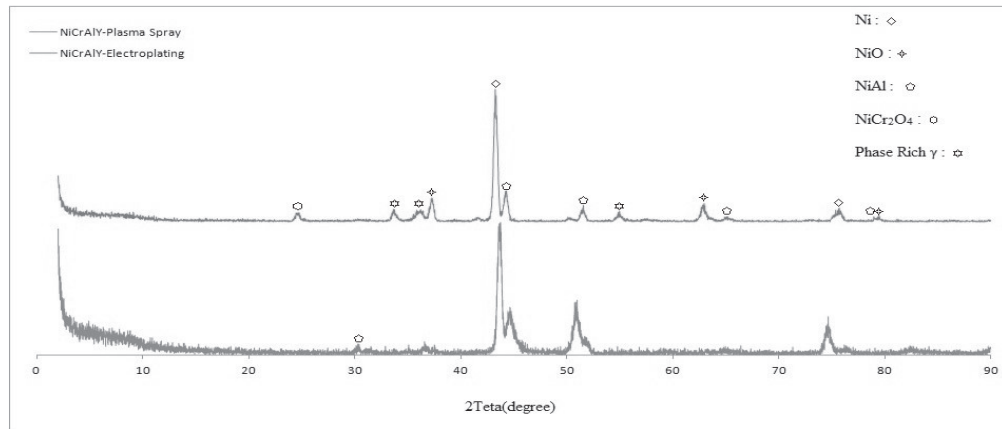


Fig. 4. X-ray diffraction analysis of the coverage of the bond coat after 2 h of heat & of the coating by plasma spraying

sufficiently high, the  $\beta$  phase percolates and contains a dispersion of  $\gamma$ -Ni particles. Such a structure is certainly less favorable in terms of ductility. If the aluminum content is not too high, nickel and cobalt base alloys consist basically of a ductile  $\gamma$  solid solution (face centered cubic) containing a dispersion of  $\beta$ -NiAl or  $\beta$ -CoAl phase [1]. For avoid of presence of brittle mortal  $\gamma$ -Ni and  $\gamma'$ -Ni<sub>3</sub>Al phases, balance level of Al powders with optimum heat treatment parameters was selected. Absence of these phases were proofed by X-ray diffraction pattern (Fig.4)

After completing researches on bond coat layers, both of samples coated by air plasma spray YSZ as top coat of TBCs. Fig. 5 shows the cross-sections of the two types of TBCs. In Fig. 5a, usual thermally sprayed TBC is observed which includes NiCrAlY bond coat and YSZ layers. In Fig. 5b, changes TBC are observed which includes electroplated NiCrAlY bond coat and thermally sprayed YSZ layers. Both of the coatings showed the lamellar structure on the top coat which is a characteristic of plasma sprayed coatings.

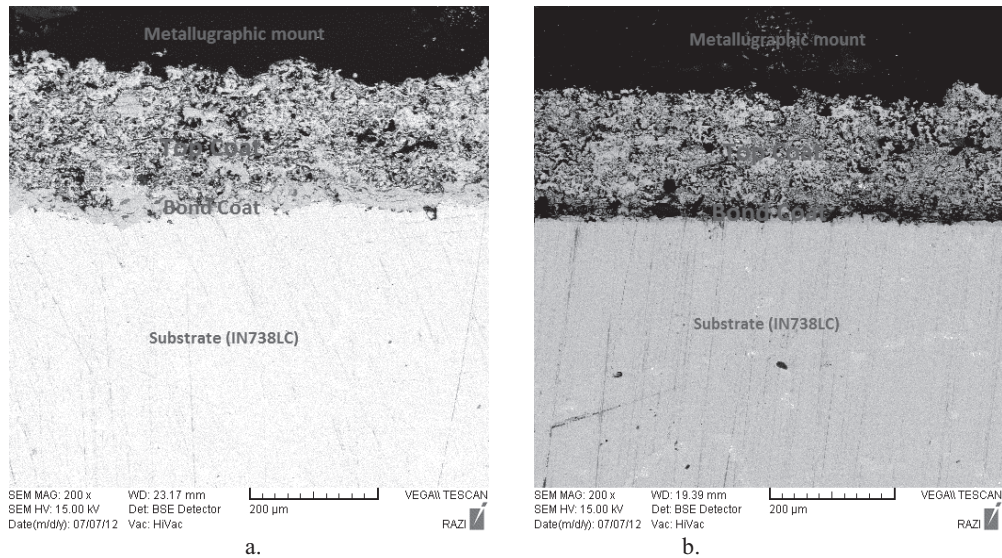


Fig. 5. Scanning electron microscope image, (a) Cross section of the bond coat of the plasma spray coated, (b) Cross section of the bond coat is coated with electrochemical method.

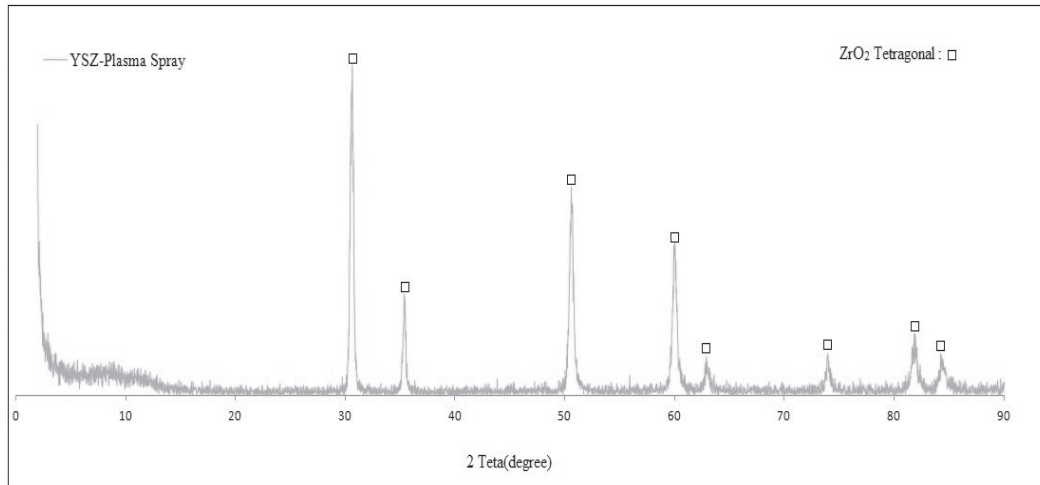


Fig. 6. XRD patterns from the surface of the Top coat before hot corrosion test.

Surface morphology and X-ray diffraction pattern of final coats were presented in Figure 6. These figures shows a Lamellar as spray ceramic structure which flattened splats without melting because of high temperature melting point of YSZ. Completely crystalline tetragonal Zirconia was produced during the thermal spray without any phase transformation to amorphous phases.

Surface morphology and crystalline structure

after hot corrosion also were investigated by SEM- EDX and XRD.

Fig. 7 shows the SEM surface morphology of the coatings and corrosion products after 6 h of corrosion testing. Usual TBC (NiCrAlY plasma spray +YSZ plasma spray) and (NiCrAlY electroplating +YSZ plasma spray) coatings revealed a porous surface having some cracks and many dendrite  $YVO_4$  crystals grown on the

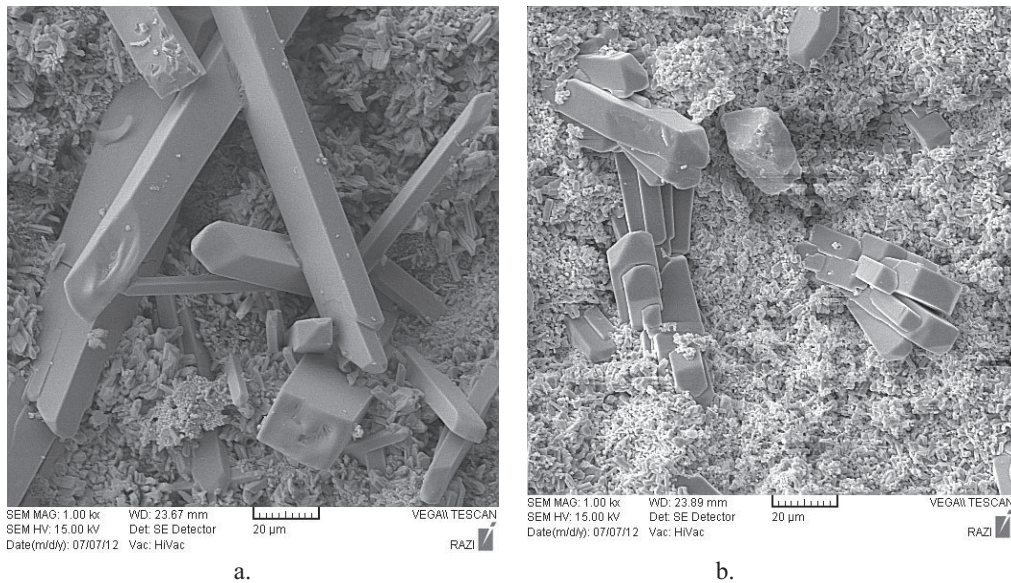


Fig. 7. SEM micrographs of  $YVO_4$  crystals on the surface of coatings: (a) NiCrAlY-YSZ; (b) Ni-Cr-Al-Y-YSZ.



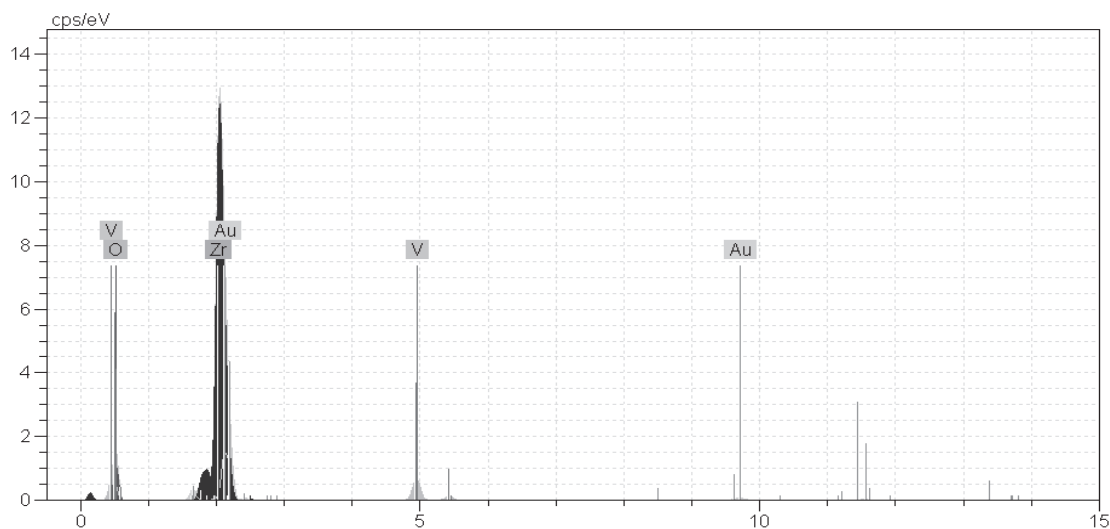


Fig. 8. EDS spectrum from the surface of the hot corroded coatings.

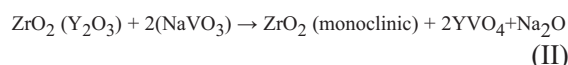
surface (Fig. 7 a and b).

EDS analysis from the surface of the hot corroded coatings (Fig. 8) demonstrated that the crystals were composed of yttrium, vanadium and oxygen, then they were identified by XRD analysis to be  $YVO_4$ .

Fig. 9 exhibits the XRD patterns of the coatings after hot corrosion tests. Monoclinic  $ZrO_2$  and  $YVO_4$  were formed on all of the coatings after exposing to molten salt at 900 °C for 6 hr, but the intensity of their peaks was different.

The mechanism of degradation during hot corrosion can be explained by the following

reactions [6, 9- 10].



At first  $NaVO_3$  was formed after the reaction of initial salts (45 wt. %  $V_2O_5$  + 55 wt. %  $Na_2SO_4$ ), then  $NaVO_3$  reacted with  $Y_2O_3$  to produce monoclinic  $ZrO_2$ ,  $YVO_4$  and  $Na_2O$ .

The hot corrosion behavior and failure mechanism of TBCs in present study comprises the following steps that are in agreement with

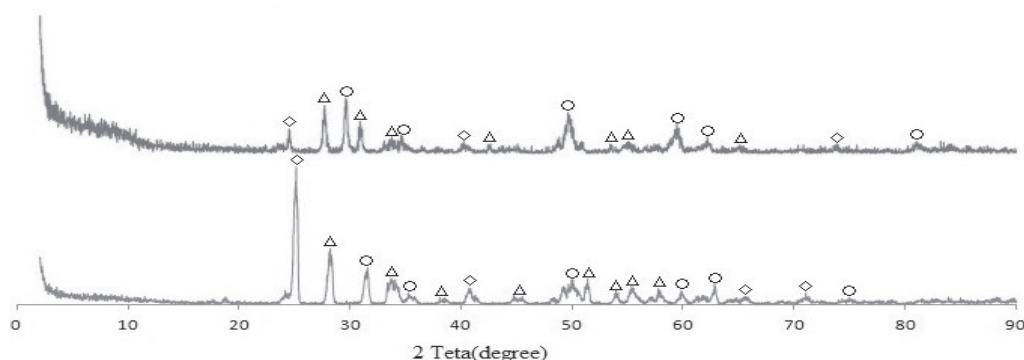


Fig. 9. XRD patterns from the surface of the coatings after hot corrosion test: pattern A (NiCrAlY&YSZ Plasma Spray) and pattern B (NiCrAlY&YSZ Electroplating & Plasma Spray).



previous investigations:

- Molten salt penetration through micro cracks and open porosities.
- Reaction of molten salt with the stabilizer of zirconia ( $Y_2O_3$ ).
- Phase transformation of zirconia from tetragonal to monoclinic, due to the depletion of stabilizer, which is accompanied by volume expansion of the coating.
- Formation of  $YVO_4$  crystals with rod shape and average length of 40  $\mu m$  usual YSZ coating that grow to outward of surface and cause additional stresses in the coating (Fig. 8) [6, 9- 10].

The volume fraction of monoclinic phase in TBCs (M %) was estimated by the following equation:

$$M (\%) = \frac{M (1) + M (2)}{T + M (1) + M (2)}$$

Where T is the intensity of tetragonal  $ZrO_2$  (1 0 1) peak, M (1) the intensity of monoclinic  $ZrO_2$  ( $\bar{1}$  1 1) peak and M (2) is the intensity of monoclinic  $ZrO_2$  (1 1 1) peak in XRD patterns after hot corrosion tests [6]. The quantities of destabilized Zirconia phase (M %) have been compared in Fig. 10 which shows the monoclinic  $ZrO_2$  fraction decreased from 71% in (NiCrAlY electroplating +YSZ plasma spray) to 78% in conventional TBC.

This means that transformation of Zirconia from tetragonal to monoclinic phase during cooling was much lower in (NiCrAlY electroplating +YSZ plasma spray). This is better

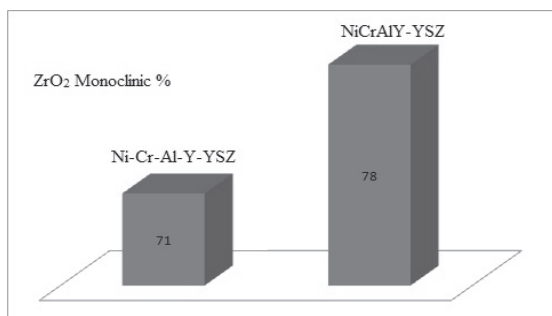


Fig. 10. Volume fraction of monoclinic zirconia in the coatings after hot corrosion test.

for hot corrosion and thermal shock resistance; because it can be decrease thermal expansion which was usual amount of volume expansion for commercial thermal barrier coatings is about 3–5% [6].

#### 4. CONCLUSIONS

- NiCrAlY coatings can be electroplated on IN738LC with a nickel bath containing metal particles of Al and Cr followed Yttrium doping with periodically immersion in salt solution of yttrium and heating at 500 °C for diffusion.
- Electro co-deposited NiCrAlY coating composition is very close to the composition of the conventional atmospheric plasma sprayed NiCrAlY.
- Hot corrosion of YSZ coating was mainly due to reaction of molten salt containing  $V_2O_5$  with  $Y_2O_3$  which was accompanied by formation of monoclinic  $ZrO_2$  and  $YVO_4$  crystals.
- Monoclinic  $ZrO_2$  and  $YVO_4$  crystals led to crack formation and failure of TBCs.
- Hot corrosion resistance patterns have been applied to the bond coat electrochemical methods are competitive with Samples atmospheric plasma spraying method which is applied to the bond coat.

#### REFERENCES

- Mervel, R., "State of Art on High-Temperature Corrosion Resistant Coating", Journal of the Material Science and Engineering, A.Vol.120, (1989), pp.13-24.
- Tamura, M., Takahashi, M., Ishii, J., Suzuki, K., Sato, M. And Shimomura, K., "Multilayered thermal barrier coating for landbased gas turbines", Journal of the Thermal Spray Technology, (1999), Vol.8 (1), pp.68–72.
- Khanna, A. S., "Introduction to High Temperature Oxidation and Corrosion", The material information society, April (2002), pp.20-260.
- Cao, X. Q., Vassen, R., Stoeber, D., " Ceramic Materials for Thermal Barrier Coatings", Journal of the European Ceramic Society, Vol

- 24, (2004), pp.1-10.
5. Lee, C. H., Kim, H. K., Choi, H. S., Ahn, H. S., "Phase Transformation and Bond Coat Oxidation Behavior Plasma-Sprayed Zirconia Thermal Barrier Coating", *Journal of the Surface & Coatings Technology*, Vol. 124, (2000), pp.1–12.
  6. Afrasiabi, A., Saremi, M., Kobayashi, A., "A Comparative Study on Hot Corrosion Resistance of Three Types of Thermal Barrier Coatings: YSZ, YSZ+Al<sub>2</sub>O<sub>3</sub> and YSZ/Al<sub>2</sub>O<sub>3</sub>", *Journal of the Materials Science and Engineering A*, Vol. 478, (2008), pp.264-269.
  7. ASTM B 558-79 R97, "Standard Practice for Preparation of Nickel Alloys for Electroplating", (2004).
  8. ASTM B 343-92a R98, "Standard Practice for Preparation of Nickel for Electroplating with Nickel", (2004).
  9. Chen, Zh., Wua, N. Q., Singh, J., Mao, S. X., "Effect of Al<sub>2</sub>O<sub>3</sub> overlay on hot-corrosion behavior of yttria-stabilized zirconia coating in molten sulfate-vanadate salt", *Journal of the Thin Solid Films*, Vol 443, (2003), pp 46-52.
  10. Gosipathala Sreedhar, MD. Masroor Alam, V. S. Raja, "Hot corrosion behaviour of plasma sprayed YSZ/Al<sub>2</sub>O<sub>3</sub> dispersed NiCrAlY coatings on Inconel-718 super alloy", *Journal of the Surface & Coatings Technology*, Vol 204, (2009), pp 291-299.