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Degradation Studies of Micro and Nanocrystalline NiCrAlY coatings for High Temperature Corrosion Protection.

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Abstract

NiCrAlY coatings are widely used in gas turbines for the protection against the high temperature oxidation and corrosion. Micro and Nanocrystalline NiCrAlY coatings on Superalloy were fabricated by Sputtering and High Velocity Oxide Fuel Spray (HVOF), respectively, in the present work. The coatings were subjected to high temperature cyclic oxidation at 900°C in presence of air to investigate its oxidation kinetics. The weight change of the microcrystalline (mc) and nanocrystalline (nc) coatings was monitored after each cycle to establish its degradation rate in the corrosive environment. The parabolic rate constant was evaluated using the weight change data obtained for both mc and nc coatings by least square fitting method. It was observed that the nanocrystalline coatings showed lower value of parabolic rate constant as compared to that of its bulk coatings. The protective oxide scales were identified by the characterisation techniques such as XRD, FESEM, EDS and X-ray Mapping. The nanocrystalline NiCrAlY coatings exhibit superior high temperature corrosion resistance in air due to the formation of adherent, non-porous, and uniform protective scales such as NiCr₂O₄, Cr₂O₃ etc when compared to mc coatings. On the other hand, the protective scales formed over the mc coatings are non-uniform, discontinuous which provides relatively less protection in the corrosive environment. The mechanisms of nanosize effect on the rapid formation of protective scale, through high diffusivity of alloying elements, in nc coatings are proposed.

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Keywords: Nanocrystalline coatings, Oxidation, Sputtering, HVOF

Nomenclature

HVOF high velocity oxide fuel
K_p parabolic rate constant

1. Introduction

NiCrAlY coatings are widely used in gas turbines for the protection against the high temperature oxidation and corrosion. The performance of these coatings depends upon its micro structural features and other properties. The thermal spray technique has been widely used for the deposition of these coatings [1-3].

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It can produce bulk coatings with lesser time and is cost-effective. However, density and oxide contents are the major concern which limits the use of thermal spray coatings.

Sputtering deposition is a physical vapour deposition technique (PVD), which can produce dense and pure coatings along with excellent bonding strength. The beneficial features of PVD are high coating density, high adhesion strength, formation of multi-component layers, and low substrate temperature [4]. The other major difference between these two techniques is the ability to form nanocrystalline grains in the coatings. The sputtering techniques can produce nanocrystalline coatings with grain size upto 10 nm. However, the production of nanocoatings with the help of thermal spray techniques is still a challenge. The effect of the nanosize on the oxidation behaviour of the coatings has been studied by Chen *et al.* [5]. They observed that the nanocrystallization of the Ni based coatings leads to the formation of the uniform and adherent Al_2O_3 oxide layer, which provide desired protection. On the other hand, the corresponding mc coatings exhibit non uniform Al_2O_3 oxides layer. The other advantage of the nc coatings has been explained by Chen & Lau *et al.* [6] in which they have showed that the minimum amount of the Al required to produce the protective oxide layer get lowered in nc coatings.

The nature of thermal spray coatings and the Sputtered coatings are different and therefore their performances also vary. The present manuscript deals with the comparison of the two types of the coatings such as mc and nc deposited by HVOF process and sputtering technique (nc), respectively. The microstructural features and their high temperature oxidation resistance have been also compared.

2. Experimental

2.1. Coating Deposition by HVOF

The NiCrAlY coatings were deposited on superni76 substrate by using commercially available NiCrAlY coatings. The detailed parameters of the deposition have been already described in earlier work [7].

2.2. Sputtered deposition

The sputtered coating has been also deposited on the superni 76 substrate by using DC-sputtering technique. The target (spherical with 2 inch dia) which was used in this process for the deposition was prepared by using following steps

1. The conventional available NiCrAlY powder was milled for 6 hrs to get some deviation from the complete spherical particle size.
2. The powder was then mixed with binder (PVA) uniformly.
3. This powder was compacted at 35 ton load in a die of desired dimension.
4. The green compact was sintered at 1100°C in Ar atmosphere for 3hrs.

This sintered target was used in DC sputtering unit for the deposition of the NiCrAlY coatings

Table1: parameters used during the DC sputtering process of depositing NiCrAlY coatings.

| Pressure | Temperature | Voltage | Current | Time |
|----------------|---------------------|---------|---------|------------|
| 10^{-4} Torr | 250°C | 300V | 200mA | 30 minutes |

2.3 Cyclic Oxidation Tests

Cyclic oxidation studies were performed in air environment at 900°C for 50 Cycles (1 h heating followed by 20 min cooling). The specimens were subjected to weight change measurements at the end of each cycle with the help of electronic balance Model CB-120 (Contech, India) having a sensitivity of 0.01 mg. The spalled scale if any was also included during the weight change measurements. The Kp value for the oxidation process was then calculated by using least square fit method.

2.4 Characterisation Techniques

The oxidation products of the coated samples were analysed by using the X-ray Diffraction (Bruker AXS D-8Advance Diffractometer with Cu K α radiation), FESEM with attachment of EDS (FEI company, Quanta 200F). The BSEI was used to analyse the cross-sections of the corroded samples.

3. Result and Discussion

3.1 Characterisation of as received coatings

The surface morphologies of the nc and mc coatings differs significantly due to the differences in the methods of deposition. The HVOF sprayed coatings showed the presence of unmelted and semimelted particles on the surface (Fig.2 (a)). However, the sputtered deposited coatings showed very smooth surface as shown in Fig.1 (a). Due to presence of the nanograins, the morphology of the sputtered coatings was visible only at very high magnification by using AFM as shown in Fig.3. The average grain size calculated by AFM analysis comes out to be 40 nm. The cross section images of the both coatings shows that the nc coatings are denser and free of any types of inclusion or oxide formation as compared to the mc coatings (Fig. 1(b) & 2(b)). The presence of some amount of oxygen in case of nc coatings was due to the oxides formed on the surface of the target during sintering process.

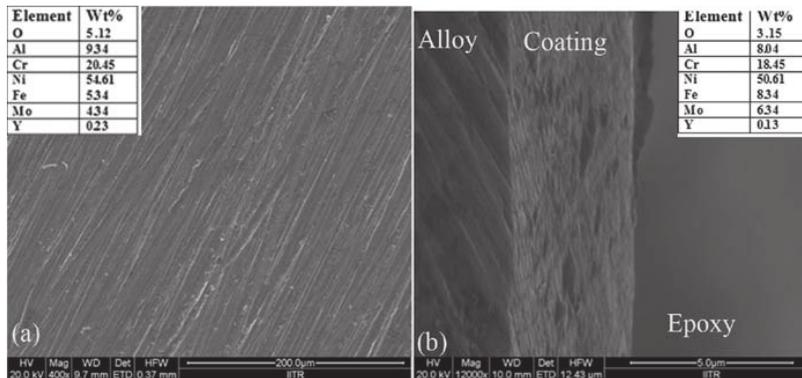


Fig. 1: FESEM images of the (a) Surface (b) Cross section of the Sputtered nc NiCrAlY coatings.

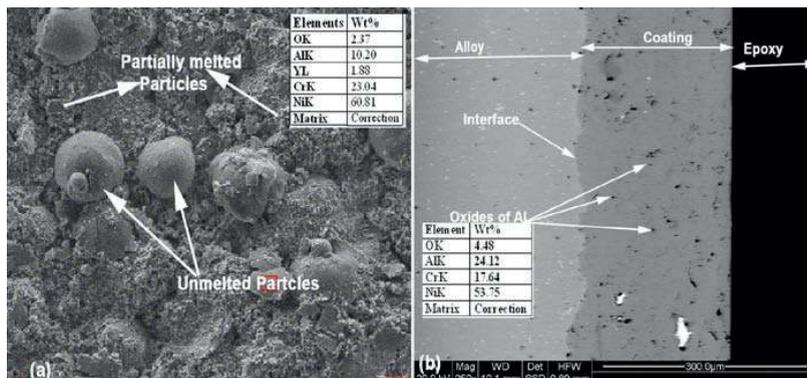


Fig. 2: FESEM images of the (a) Surface (b) Cross section of the HVOF sprayed mc NiCrAlY coatings.

The XRD pattern of the nc and mc coatings showed that the mc coatings exhibited the two phase structure (γ/γ' & β) of the starting powder. However, the nc coatings showed the presence of the only γ/γ' phase. The absence of the β phase may be

attribute to the transformation of the β -NiAl phase to γ' -Ni₃Al and γ - Ni phase because of the diffusion and the formation of Al₂O₃ during sintering process. Such type of transformation has been also observed by Li et al. in their study [8].

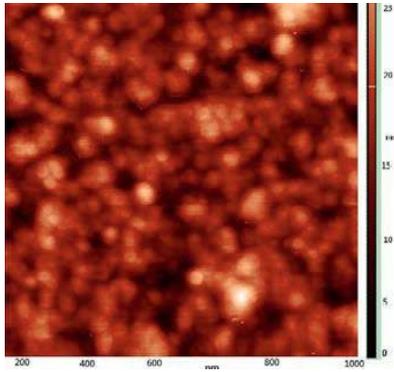


Figure 3: AFM image of the Sputtered nc NiCrAlY coating.

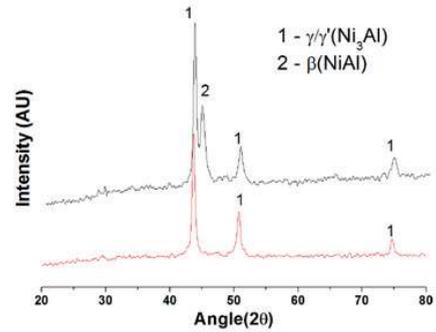


Figure 4: XRD pattern of the nc and mc coatings.

3.2 Analysis of the oxidized samples

3.2.1 Weight Change Analysis

The weight change of the mc and nc coatings is shown in Fig.5. It is clear from the figure that nc exhibited lesser weight change as compared to mc coatings. The K_p values of both coatings are shown in Fig.3. The K_p value of mc coatings was found to be ~4 times of the nc coatings. However, both coatings followed the parabolic rate law of oxidation, after initial fast gain in the weight.

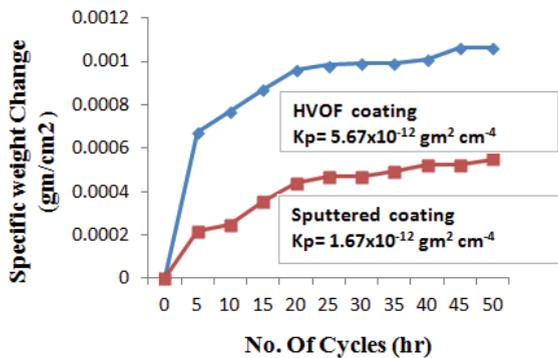


Figure 5: Weight change behaviour of the nc and mc coatings up to 50 cycles in air.

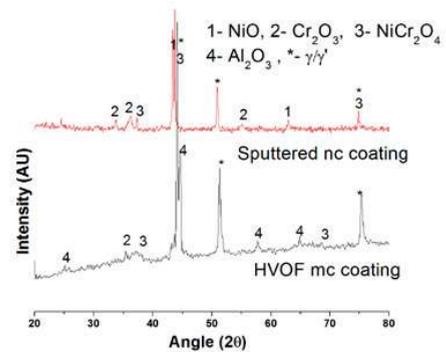


Figure 6: XRD pattern of the nc and mc coatings after 50 cycles of oxidation in air at 900°C.

3.2.2 Phase identification

XRD pattern of the oxidized coatings is shown in Fig.6. The oxides formed on the mc coatings are Al₂O₃, NiCr₂O₄ and very small amount of Cr₂O₃. On the other hand, the oxides formed on the nc coatings are mainly NiO, Cr₂O₃, and spinels. The absence of the Al₂O₃ in case of nc coatings may be attributed to the absence of the β phase in the nc coating. The β phase is considered as Al-reservoir of the NiCrAlY coating. The absence of β phase led to the absence of the Al₂O₃ in the

oxidized surface.

3.2.3 Surface morphology and composition of oxidized surfaces

The surface morphology of the oxidized surfaces is shown in Fig.7. The scale formed on the nc coatings showed the presence of very fine oxides nodules and crystals. The nanocrystalline nature of these coatings resulted in the formation of very fine oxides on the surface. On the other hand, the mc showed the formation of larger oxide nodules. Despite absence of the Al_2O_3 , the nc coatings showed more resistance to the oxidation at 900°C . This fact can be explained on the basis of the formation of the very fine and uniform oxides nodules on the nc coatings. The fine grained structure of the nc coatings leads to the formation of very uniform and compact morphology of the oxides. The role of nanocrystallisation on the improved oxidation behaviour of the sputtered coatings has been studied by Chen and Lou *et al.* [6]. They have reported that the fine grained structure favours the early formation of the protective oxide scale on the surface due to high diffusivities of the elements through the nano grains. The formation of protective oxides in early stages reduces the further migration of the oxygen inside the coating. In the present case, the nc showed the sharp weight gain up to 5 cycles after which, the weight gain was very less. Hence, the coating elements diffuse fast up to 5 cycles and form a uniform and adherent oxide layer.

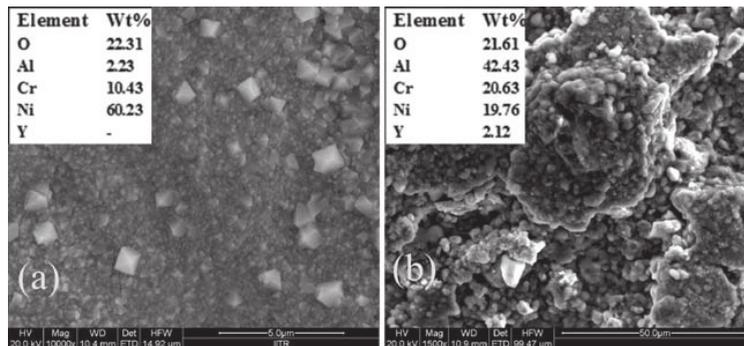


Figure 7: Surface morphology and composition of (a) Sputtered nc coatings and (b) HVOF deposited mc coatings.

4. Conclusions

The sintered target of the NiCrAlY powder was used as sputtering target to develop the nc coatings on the superalloy substrate. The oxidation resistance of the sputtered deposited nc coatings was found to be superior to the HVOF sprayed mc coatings. The fine grained microstructure of the nc coatings lead to the formation of the continuous and compact oxides on the surface, which provided the desired protection against oxidation.

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