



Hot corrosion of nanostructured CoNiCrAlYSi coatings deposited by high velocity oxy fuel process



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ABSTRACT

This paper focuses on the structure and cyclic hot corrosion behavior of nanostructured MCrAlY coatings used in thermal barrier coatings of gas turbines as the bond coat. Cryomilling in a liquid nitrogen environment was used to prepare nanostructured CoNiCrAlYSi powders, as characterized by scanning electron microscopy and X-ray diffraction. Also, the long-term hot corrosion resistance of the coating deposited by high velocity oxy fuel thermal spraying of the cryomilled powders was studied in a molten salt medium of $\text{Na}_2\text{SO}_4\text{--Na}_2\text{VO}_3$ at 880 °C up to 640 h. According to the results, the cryomilling process improved the corrosion resistance of the nanostructured coating, as compared with coarse-grained CoNiCrAlYSi coatings. This improvement was attributed to some $\alpha\text{-Al}_2\text{O}_3$ particles dispersed in the structure, created by cryomilling, and high-diffusivity paths, created by nanocrystallization, which favors the formation of a continuous $\alpha\text{-Al}_2\text{O}_3$ barrier layer on the top of the coating.

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1. Introduction

Hot parts of gas turbines, normally being made of Ni-based superalloys, operate in highly harsh environments and are exposed to high temperature and corrosive media, which reduces their lifetime. One of the effective approaches to increasing their durability and efficiency is applying protective coatings, typically thermal barrier coatings (TBCs), on them [1,2]. TBCs generally consist of a MCrAlY (where M stands for either Co, Ni, or Fe) bond coat and an yttria partially stabilized zirconia top coat. Due to oxidation of the MCrAlY coating during the engine operation, a thermally grown oxide (TGO) is formed at the bond/top coat interface [3,4]. The characteristic of the TGO layer, including its composition, homogeneity, growth rate, and thickness [5–11], significantly affects the coating performance and thereby the engine efficiency and lifetime. The grain size of the deposited bond coat plays a key role in the TGO feature. Typically, it has been previously shown that nanocrystallization of the bond coat improves the TGO nature and consequently the oxidation and hot corrosion resistance of the component [12–16].

Among various methods used to deposit MCrAlY bond coats, high velocity oxy fuel (HVOF) spraying process has attracted much attention, due to its low operation cost and high-quality coatings obtained. Typically, HVOF deposited coatings present a high density and a good adhesion to the substrate, and also for nanostructured sprayed powders the nanostructure is maintained even

after spraying [15]. Recently, Mohammadi et al. [17] have investigated the hot corrosion behavior of HVOF-MCrAlY coatings in a molten salt film of $\text{Na}_2\text{SO}_4\text{--Na}_2\text{VO}_3$ at 880 °C. On the other hand, the oxidation behavior of coarse-grained and nanostructured HVOF-MCrAlY coatings has widely been studied [3,5,15,16]. However, to the best of our knowledge, little systematic work has been reported on the cyclic hot corrosion behavior of nanostructured HVOF-MCrAlY coatings.

In this work, the cryomilling process, mechanical milling in a liquid nitrogen medium, was used to produce nanostructured CoNiCrAlYSi powders. The obtained powder was HVOF-thermally sprayed on a Ni-based IN-738LC superalloy substrate used widely in turbine engines. Afterwards, the structure and cyclic hot corrosion behavior of the deposited coating were studied.

2. Experimental procedure

2.1. Cryomilling and structural characterization of the CoNiCrAlYSi powder

CoNiCrAlYSi powder (Sicoat 2231), with the chemical composition of Co–29%Ni–26%Cr–8%Al–0.6%Si–0.8%Y (in wt.%), was used as the initial material. The powder was mechanical cryomilled in liquid nitrogen at a rate of 180 rpm for 12 h. Stainless steel balls of 6.35 mm in diameter at a ball-to-powder weight ratio of 25:1 were employed as the grinding media. The as-received and milled powders were structurally characterized by a field emission scanning electron microscope (FE-SEM, Mira Tiscan) and X-ray diffraction (XRD, Shimadzu Lab X-6000 with Cu K α radiation). The XRD experiments were done at a step size of 0.03° and a step time of 3 s from the diffraction angle of 25° to 90°. The XRD qualitative and quantitative analyses were conducted by X'pert HighScore and MAUD programs, respectively. The MAUD software employs the Rietveld refinement, so that this is able to analyze overlapping XRD reflections [18].

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2.2. HVOF deposition and structural characterization of the CoNiCrAlYSi coating

The cryomilled CoNiCrAlYSi powder was HVOF sprayed on a Ni-based IN-738LC superalloy substrate by a Met-Jet 4L system with a Kerosene fuel. The thermal spraying parameters are listed in Table 1. The coated samples were heat-treated at 1100 °C for 4 h and then at 850 °C for 20 h in a vacuum furnace. The structure of the samples was studied by XRD and SEM, where the latter was performed in both top and cross section views.

2.3. Hot corrosion of the CoNiCrAlYSi coating

To evaluate the cyclic hot corrosion behavior of the coated samples, a Na₂SO₄-20 wt.% Na₂VO₃ solution was sprayed on the sample preheated to 200 °C to get a salt thin layer of 0.5–1 mg/cm². Then, the sample was placed at the temperature of 880 °C, and the weight change was recorded every 20 h up to the total exposure time of 640 h, where the same salt-spraying process was done after every weighing. Also, to determine corrosion mechanisms, XRD and SEM analyses were performed on the sample exposed to hot corrosion for selective durations.

3. Results and discussion

3.1. Cryomilled powder

Fig. 1 indicates the SEM micrograph of the as-received and cryomilled CoNiCrAlYSi powders. As can be seen, the as-received powder particles are spherical in shape with an average diameter of 20 μm. But after cryomilling, the powder morphology tends to be irregular and flake-shaped, due to a compromise among continuous deformation, welding, and fracture during milling. Additionally, an increase in the powder particle size to about 50 μm is observed after cryomilling, which is attributed to the fact that cold-welding dominates fracture in the used milling process.

The XRD profiles of the as-received and cryomilled powders are presented in Fig. 2. Characteristic peaks of a Ni–Cr-rich FCC-structured solid solution (γ), a Ni₃Al BCC-structured intermetallic phase (γ'), and an Al_{0.42}Ni_{0.58} (β) phase are detectable in the XRD data, as previously reported in other work [15,17]. The increase in the XRD peak broadening for the milled sample, compared with the as-received powder, is indicative of a crystallite size reduction and strain introduced during mechanical milling. As measured by the XRD Rietveld method which allows reliably analyzing overlapping XRD reflections, the mean crystallite size of the milled material is estimated to be 20 nm, due to severe plastic deformation at high strain rates [19].

3.2. As-coated sample

Fig. 3 shows the SEM micrograph of the coated sample before the hot corrosion test. The top view image indicates a relatively dense, uniform and crack-free coating deposited on the substrate. The cross sectional SEM picture also demonstrates that the film has uniformly covered the substrate and a good adhesion to the substrate has been obtained. In addition, the coating thickness is estimated to be 200 μm, based on the cross sectional observation. The light and dark regions in the micrograph are attributed to the γ and γ' phases, respectively [3], as confirmed by the XRD analysis (Fig. 4). As well as these phases, the XRD analysis shows an amount of the β phases, as also observed in the cryomilled powder, and a small amount of α-Al₂O₃. Compared to the cryomilled powder

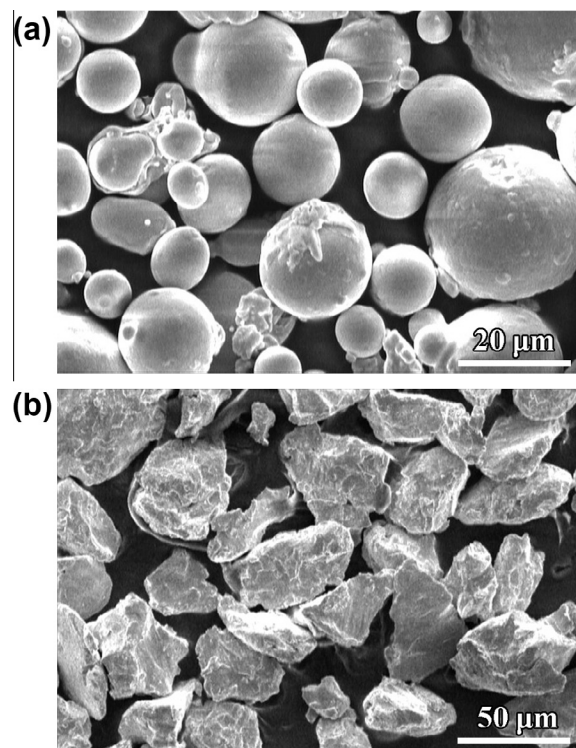


Fig. 1. SEM micrograph of (a) the as-received CoNiCrAlYSi powder and (b) the CoNiCrAlYSi powder cryomilled for 12 h.

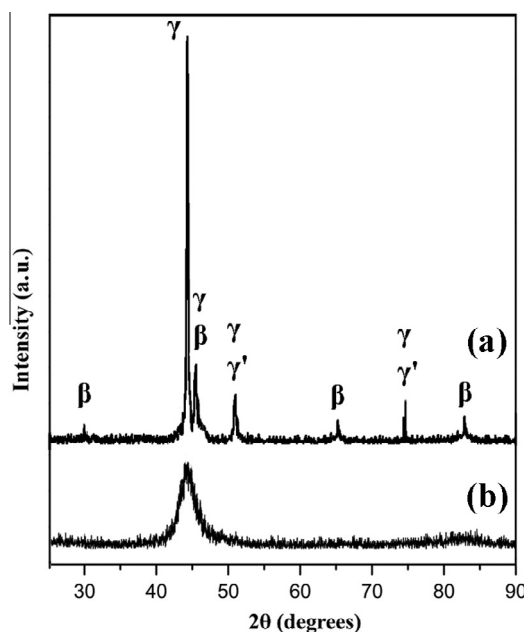


Fig. 2. XRD pattern of (a) the as-received powder and (b) the powder cryomilled for 12 h.

Table 1
Thermal spray parameters used to deposit the CoNiCrAlYSi coating.

Parameter	Amount
Fuel flow	280 ml/min
Oxygen flow	835 l/min
Oxygen pressure	2 MPa
Powder feed rate	70 gr/min
Spray distance	50.8 cm

characterized above, the alumina formation in the coating is due to the fact that oxygen exists in the entrained air and combustion products during the thermal spraying process; accordingly, the sprayed particles in flight are subjected to oxidation [15]. On the other hand, the presence of alumina in this coating, compared to coarse-grained HVOF CoNiCrAlYSi coatings for example in Ref. [17], is due to the fact that the CoNiCrAlYSi powder in this work has experienced the cryomilling process before spraying, where

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