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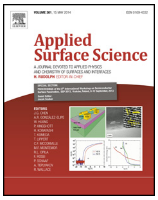

The effect of grain size on the oxidation of NiCoCrAlY

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ABSTRACT

Ultrafine NiCoCrAlY samples have been obtained through cryomilling of NiCoCrAlY feedstock powder and sintering via SPS, these samples have been subjected to isothermal oxidation tests at 950, 1000 and 1050 °C. Oxidation rates on the order of 10^{-13} $g^2/cm^4/s$ for samples oxidized at 950 °C, 10^{-11} $g^2/cm^4/s$ at 1000 °C and 10^{-12} $g^2/cm^4/s$ at 1050 °C have been found. In all cases cryomilled samples demonstrate lower overall oxidation rates than their conventional counterparts. Lower overall oxidation rates found in the cryomilled samples are ascribed to an earlier transition trough the metastable alumina phases, resulting in a stable slow growing α-Al_2O_3. Characterization by XRD and SEM corresponds well with this assessment. Lower oxidation rates seen at 1050 than at 1000 °C in both conventional and cryomilled samples is the result of a change from oxidation dominated by θ-alumina to oxidation dominated by α-alumina, as the θ–α transition speeds up with increasing temperature. This change in oxidation regime reduces, but does not eliminate, the beneficial impact of smaller grain size on oxidation rate.

1. Introduction

The ongoing campaign to increase efficiency in many industrial processes requires materials able to withstand extremely high temperatures and harsh environments. Industries including power generation, petrochemical refining, aero- and land-based turbines use numerous components that can be exposed to oxidative or corrosive gases at temperatures sometimes exceeding 1000 °C [1]. Among the most common methods to protect against high temperatures is the thermal barrier coating (TBC). A typical TBC consists of an yttria-partially-stabilized zirconia (YPSZ) top coat and nickel superalloy bond coat, normally of the MCrAlY class of alloys where M=Ni, Co or a combination of both. These alloys have the ability to grow oxide scales that result in good thermal matchup between other coating layers [2]. These same oxide scales also produce substantial high temperature corrosion resistance [3].

MCrAlY coatings have a two-phase structure consisting of the γ-phase, a solid solution of Ni, Co and Cr and the β-phase, an intermetallic of Ni and Al at 50 at% each. At some compositions γ'-Ni_3Al strengthening precipitates can also be found. The presence of the β-phase provides a source of aluminum that allows for the growth of Al_2O_3 on the surface of the coating when exposed to oxidative conditions [4]. The presence of Co in many of these alloys provides the advantage of increasing the stability of the β-NiAl phase at high temperature [1]. The long-term degradation of these coatings is normally caused by faster growing spinel oxides that occur over the thermally grown alumina layer. As a result, there have been a number of publications focusing on improving the oxidation behavior of MCrAlY alloys [5,6] including several that have focused on reducing grain size of the base alloy in order to lower overall oxidation rate [7–9].

The growth of alumina has been identified as passing through several metastable transition structures: γ-Al_2O_3, δ-Al_2O_3, and θ-Al_2O_3 before eventually transform to the stable corundum α-Al_2O_3 phase [10]. The importance of these transformations on oxidation behavior and coating stability is notable as the transformation from cubic γ to monoclinic β to rhombohedral α each result in an increase in density of over 10% [10]. The metastable alumina phases are responsible for an initial transient stage in oxidation while the final corundum structure dictates overall kinetics [11]. As a result α-Al_2O_3 is preferred because the slow diffusion of cations through its lattice limits oxygen diffusion and results in a slow growing oxide [12,13].

Several studies have focused on grain size modification to improve oxidation performance in MCrAlY alloys. Lou et al. have shown that an as-cast K38G superalloy forms a chromia oxide scale when oxidized in air at 1000 °C, while the same alloy, when nanostructured, forms an alumina scale under similar conditions [14]. The work of Zhang et al., Ajdelsztajn et al., Liu et al., and Tang et al. have all shown nanostructured MCrAlY coatings show improved oxidation behavior [7,15–17]. More recently, Todde et al.

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Table 1
Chemical composition of the NiCoCrAlY powder.

Alloy composition (mass %)				
Ni	Co	Cr	Al	Y
46.55	23	17	13	0.45

demonstrated in a study of cryomilling in CoNiCrAlY samples consolidated by spark plasma sintering, that the exclusive formation of an α-alumina oxide scale is promoted by cryomilling [18]. Citing several of the above-listed studies, Mercier et al. have shown that cryomilling can improve the distribution of aluminum throughout the MCrAlY sample while also reducing the distance required for lattice diffusion and increasing the number of pathways for grain boundary diffusion to the surface [8]. In so doing, the effective competition between Al-containing β-NiAl grains that will form alumina in the initial stages, and the γ-grains that require lattice diffusion of Al to oxidize, is reduced. This results in uniform and rapid transport of aluminum to the surface. A recent study by Kaplin and Brochu has also indicated the possibility that grain size reduction promotes an earlier transition through the metastable alumina phases, and this in turn results in improved oxidation performance [9].

The purpose of this study is to investigate the oxidation behavior of conventional and cryomilled NiCoCrAlY samples consolidated via Spark Plasma Sintering (SPS) in order to better understand the effect of grain size on the oxidation of this system. Cryomilling has been chosen as the method for grain size reduction in the NiCoCrAlY precursor powder, while SPS has been selected for sintering, as it is a promising technique for the consolidation of bulk nanostructured samples [19,20]. Particular emphasis will be placed on transition aluminum oxides through the study of oxidation kinetics via thermogravimetric analysis, and of morphology via scanning electron microscopy and X-ray diffraction.

2. Experimental procedures

NiCoCrAlY samples were produced from commercially available gas atomized Ni-130/Ni-191 powder from Praxair Surface Technologies. Chemical composition of the powder is presented in Table 1. Part of this powder was cryomilled for 16 h in a Union Process 1-D attrition mill at 180 rpm with stainless steel grinding media, with a ball to powder ratio of 32:1 and 0.2% stearic acid added as a surfactant to prevent coating the balls and interior of the milling vessel. Liquid nitrogen was continuously added to the vessel.

Spark-Plasma Sintering was used to consolidate the conventional and cryomilled powder using a Thermal Technologies 10-3 sintering press. In the case of conventional samples, sintering was conducted under vacuum using a 200 °C/min ramp to 1100 °C, held for 7 min and cooled to ambient temperature. Cryomilled samples were heated at 250 °C/min to 1100 °C, held for 10 s and finally cooled to ambient temperature. Density was measured using the Archimedes principle and grain size was direct measured via SEM using the intersecting line method averaging at least 100 grains as well as via X-ray diffraction using the Scherrer equation [21].

Isothermal Oxidation testing was conducted in a Netsch STA 449 F3 Jupiter DT-TGA with coincident Thermogravimetric Analysis (TGA) and Dynamic Scanning Calorimetry (DSC). Samples were cut to cubes of approximately 3 mm × 3 mm × 3 mm and ground to 1200 grit on all surfaces prior to oxidation testing. These samples were heated in the TGA at 10 °C/min in synthetic air up to 950, 1000 and 1050 °C, held at said temperature for 24 h and cooled to ambient temperature. Parabolic rate constants were calculated using the method developed by Pierragi [11]. X-ray diffraction (XRD) patterns were acquired using a Bruker D8 Discover XRD. Standard XRD and glancing-angle X-ray diffraction (GAXRD) patterns were obtained using a Cu source and Vantec-5000 2D detector. The GAXRD scans were conducted with a 2° incident angle. In all cases phase identification was completed using X'Pert HighScore software. Scanning electron microscope (SEM) observations were carried out on a Philips XL-30 FE-SEM with EDAX EDS.

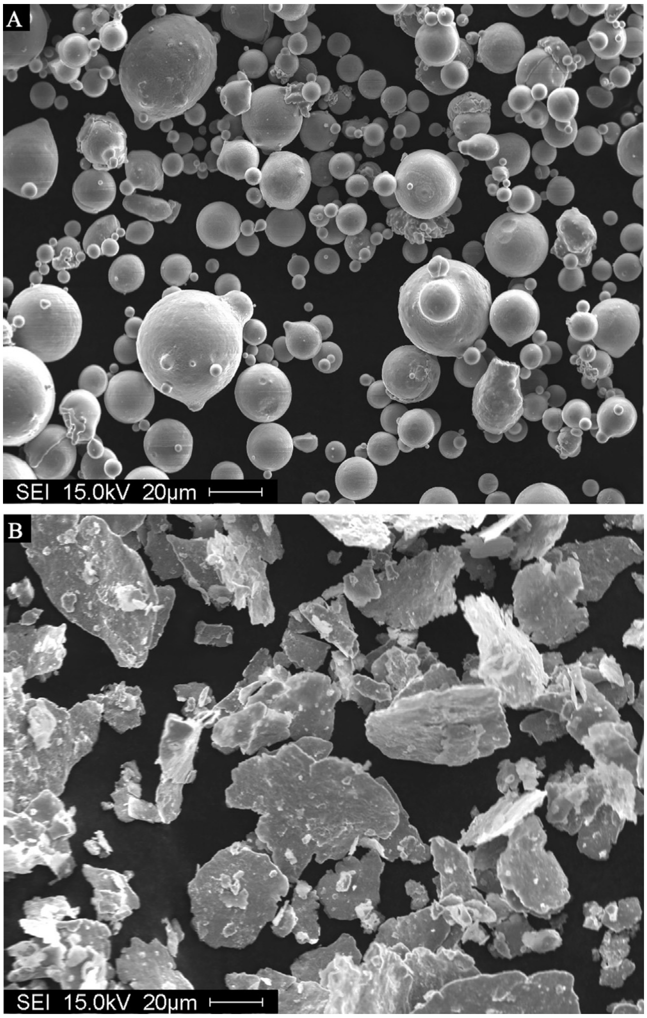

Fig. 1. SEM images of as-received NiCoCrAlY powder (A) and cryomilled powder (A).

3. Results and discussion

3.1. Cryomilling and consolidation

SEM images of the NiCoCrAlY powder before and after cryomilling can be found in Fig. 1. The flattened, flaky morphology of the cryomilled powder is typical of milled powders and typically indicates a reduction in grain size. The same milling parameters have been previously used to successfully nanostructure NiCoCrAlY powder [22]. Fig. 2 presents XRD patters of both powders. The conventional powder has the expected γ and β peaks, JCPDS no.'s 03-065-2865 and 03-065-4197, respectively, while the milled powder has only a single broad peak indicating that the β-NiAl phase has dissolved into γ and that grain size had been notably reduced.

Cross-sectional images obtained by SEM of SPS-consolidated conventional and cryomilled samples are presented in Fig. 3 and clearly show the difference in grain size of the consolidated