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## OXIDATION BEHAVIOUR OF CONVENTIONAL AND NANOCRYSTALLINE CONICRALY BOND COATS MANUFACTURED BY COLD SPRAY

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## ABSTRACT

The purpose of the present study is to investigate and compare the oxidation behaviour of conventional and nanocrystalline CoNiCrAlY bond coats. The nanocrystalline feedstock powder is produced from the conventional feedstock powder using the cryogenic milling process. Conventional and nanocrystalline bond coats are produced using the Cold Spray (CS) process in order to avoid the onset of thermally induced grain growth and minimize the inclusion of oxides in the bond coat microstructure. The oxidation behaviour of free-standing CoNiCrAlY coating samples is determined by means of isothermal oxidation experiments consisting of heat treatments in air at 1000°C for various periods of time. Characterization of the feedstock powders and resulting CS coatings, as well as investigation of the oxide scale growth dynamics, is achieved by means of SEM, XRD and TEM analyses. Mass gain measurements were also carried out throughout the oxidation tests to evaluate oxide growth rates.

## INTRODUCTION

The application of thermal barrier coatings (TBC) on hot components of gas turbine engines for improved performance and durability has been the focus of numerous studies. TBC systems typically consist of an underlying MCrAlY bond coat (M = Co, Ni or both) having good oxidation and corrosion resistant properties over which a thermally insulating zirconiabased ceramic top coat is applied. To this date, the development of a "prime-reliant" TBC system, where life expectancy of the coating system does not govern that of the turbine blade, has yet to be achieved due to premature cracking and delaminating of the ceramic top coat. It is generally accepted that the primary mechanism responsible for TBC failure is growth of the thermally grown oxide (TGO) which forms at the top coat / bond coat interface during thermal cycling [1]. A dense, uniform and continuous TGO scale composed of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is desirable [2] as it has a slow growth rate and inhibits further oxidation due to its low diffusivity [3]. Other oxides such as NiO and mixed spinel-type oxides can also form in the TGO and are considered detrimental due to their fast growth rates. These oxides have been shown to form protrusions in the TGO that initiate the failure mechanisms leading to premature TBC failure [1]. The bond coat oxidation behaviour is thus of much interest for those seeking to improve the longevity of TBC systems.

Thermal spray techniques such as plasma spraying and HVOF have been successfully used to deposit MCrAlY coatings [4-7]. A potential issue with these spraying techniques is their inherently elevated processing temperatures which can cause changes in the coating microstructure and may also introduce significant amounts of oxide inclusions within the coatings due to in-process surface oxidation of the sprayed particles. Such microstructural changes necessarily alter the intended oxidation behaviour of the material. For instance, high oxide contents within the bond coat microstructure have been shown to promote the formation of undesirable fast-growing non-alumina oxides [7, 8]. Although thermal spraying is a convenient and popular method for the deposition of MCrAlY alloys, it may not be the ideal solution for such chemically sensitive materials.

Developed in the mid 1980s as an alternative to traditional thermal spraying, Cold Spray (CS) is a high rate material deposition process that uses a supersonic gas flow to accelerate powder particles above a critical velocity [9]. Upon impact, the particles plastically deform and adhere to the substrate to produce a coating [9-11]. CS has been successfully used to deposit coatings with numerous types of materials as well as various microstructures including nanocrystalline, amorphous and metastable structures [11-19]. Studies have also demonstrated that the low processing temperatures inherent to CS inhibit grain growth and thus allow for conservation of the feedstock's microstructure throughout deposition [12, 19]. In addition to the lower process temperatures, the use of inert gases allows for the deposition of dense coatings with low oxide content [7, 11, 13].

In a previous study, nanocrystalline MCrAlY coatings had been successfully deposited by means of HVOF spraying [20]. Although some thermally induced grain growth was observed, the grain structure was shown to remain nanocrystalline. This work showed that upon oxidation testing, the coating's nanocrystalline grain structure promoted the formation of a continuous  $\alpha$ -alumina oxide scale and contributed in reducing the coating's overall oxide growth rate. This suggests that improved oxidation behaviour could potentially be achieved by developing bond coats with nanocrystalline microstructures. In addition, previous work has shown that CS MCrAlY coatings with a conventional microstructure exhibit favourable oxidation behaviour when compared to HVOF and plasma sprayed coatings manufactured from the same feedstock powder as a result of their lower oxide content [7]. The purpose of the present study is thus to investigate and compare the microstructure and oxidation behaviour of conventional and nanocrystalline CS CoNiCrAlY coatings. Given that CS has the ability to preserve the feedstock microstructure and has been previously used to produce nanocrystalline coatings with low oxide content, it has been selected as the preferred coating technology for this study.

## EXPERIMENTAL APPROACH

## **Feedstock Material**

The original feedstock powder considered in this study is a commercially available CoNiCrAlY alloy with a conventional microstructure and a nominal composition of Co-32Ni-21Cr-8AI-0.5Y (wt. %) (Sulzer Metco). This powder was manufactured by gas atomization and has a spherical morphology with a particle size distribution ranging from 5 to 37 µm. This powder was used to manufacture CS coatings having a conventional microstructure. In order to obtain powder particles with a nanocrystalline microstructure, some of

the conventional feedstock was subjected to cryomilling, a technique that has been shown to be one of many successful processes used to produce materials with nanocrystalline microstructures [21]. The conventional feedstock was thus mechanically milled for 8 hours at 200 rpm under a constant supply of liquid nitrogen in an Attritor Union Process 01-HD Szegvari mill. Stainless steel 440 balls (4.8 mm in diameter) were used as the grinding media with a ball-to-powder weight ratio of 24:1. Prior to deposition, both the conventional and nanocrystalline feedstock powders were sieved below  $25\mu$ m for aerodynamic considerations [10].

## **Cold Spray Facility**

The conventional and nanocrystalline CoNiCrAlY coating samples were produced using the CS system developed at the University of Ottawa Cold Spray Laboratory facility. Details of this system are available elsewhere [22]. For the present study, a nozzle with an exit diameter of 7.3mm was used with a nozzle inlet temperature and pressure of 550C° and 2.0 MPa respectively. Helium was used as both the main propellant and carrier gases. Coatings were manufactured onto aluminum 6061 substrates and were then removed from the substrates prior to analysis and oxidation testing, as detailed in a subsequent section. The nature of the substrate material thus had no impact on the experimental findings presented in this paper.

## **Powder and Coating Evaluation**

The conventional and nanocrystalline feedstock powders were characterized by various analytical techniques. Powder morphologies and size distribution were determined by means of SEM using a Zeiss, model Evo10 microscope. Both powders were also investigated by X-Ray Diffraction (XRD) to assess and compare their phase composition. This analysis was performed using a Philips X-Pert model PW 1830 generator diffractometer with CuKa radiation. Detailed scans with step size of  $0.01^{\circ}$  and step time of 2 seconds were conducted with 20 values ranging from 20° to 85°. TEM investigation of the powders was also carried out using a FEI Tecnai-G2 F20 microscope operated at 200kV. Prior to TEM observation, the powder samples were cold mounted in epoxy followed by grinding, polishing, and ion milling. Selected area electron diffraction (SAED) patterns and bright field (BF) images were taken to determine grain structures within the powders. The cross-sections of the CS coatings produced from these two powders were then prepared according to standard metallographic techniques and examined by SEM for porosity and interlamellar crack content. TEM images of the coatings were also obtained to investigate their grain structure and compare them with those of the original feedstock powders. TEM coating samples were initially removed from the substrate by sanding and then prepared by dimpling and ion-milling. The coating samples used for the oxidation experiments were subjected to XRD analysis after their respective heat-treatments in order to determine the composition of the oxide scale and the phases present in the bond coats. Following each oxidation test, the coating samples were also sectioned, polished, and investigated by SEM to qualitatively examine the growth of the oxide scale and  $\beta$ -phase depletion zone. SEM images of the oxidized coating surfaces were also taken to show the oxide scale morphologies.

#### **Oxidation Experiments**

The samples used for the oxidation experiments were produced from both CoNiCrAlY feedstock powders as 15mm x 15mm coatings with a thickness of approximately 500µm. The coatings were then sectioned from the substrates and polished using 320-grit SiC paper in order to remove any remaining substrate material on the coating sample, thus resulting in freestanding conventional and nanocrystalline CoNiCrAlY coating flakes. The outer surface of the flakes was also polished using the same SiC paper in order to eliminate surface irregularities and minimize errors when evaluating the sample surface area. The samples were then subjected to isothermal heat treatments at 1000°C in static atmospheric air. The samples were positioned in the furnace once the set point temperature was reached and then allowed to soak for durations of 5, 25, 50 and 100 hours respectively. Following the heat treatments, the samples were removed from the furnace and allowed to cool to room temperature. Each sample was weighed before and after the oxidation experiments using a digital weighing scale with 100µg resolution (Sartorius Extend - model ED124S). Mass gains from the oxidation reaction were recorded and normalized with respect to each sample surface area in order to investigate the overall oxide growth rates.

## **RESULTS AND DISCUSSION**

#### **Powder Characterization**

The morphologies and cross-sections of the as-received (conventional) and as-cryomilled (nanocrystalline) CoNiCrAlY powders are shown in Fig. 1. As seen in this figure, the ascryomilled CoNiCrAlY powder no longer has the spherical morphology observed in the as-received powder, but rather has an irregular flake-like morphology resulting from the severe plastic deformation and crushing of the particles throughout the milling process. The as-cryomilled feedstock was measured to have a particle size distribution ranging from 1 to 70 µm with an average equivalent particle diameter of 20µm. Examination of the particles cross-sections also reveals that the as-received powder exhibits the expected two-phase  $\gamma/\beta$  microstructure whereas the as-cryomilled powder does not. This is further evidenced in Fig. 2 which shows the XRD spectra of both the as-received and as-cryomilled CoNiCrAlY powders. The absence of  $\beta$ -precipitates in the as-cryomilled feedstock had been previously observed and was attributed to a  $\beta$ -phase dissolution mechanism resulting from the cryomilling process [22]: extensive plastic deformation of the powder particles during cryomilling produces a high density of point and line defects in the material which extend the solubility of Al in the  $\gamma$ - matrix, thereby dissolving the Al-rich  $\beta$ -phase. Peak broadening for the  $\gamma$ -phase peaks of the as-cryomilled powder is also observed, thus suggesting a refinement of the material's grain structure.



Figure 1. SEM IMAGES OF AS-RECEIVED (A, B) AND AS-CRYOMILLED (C, D) CONICRALY POWDERS SHOWING THE FEEDSTOCK MORPHOLOGIES AND PARTICLE CROSS-SECTIONS.



Figure 2. XRD SPECTRA OF AS-RECEIVED AND AS-CRYOMILLED CONICRALY POWDERS.

In order to verify the nanocrystalline microstructure of the as-cryomilled powder and compare it to that of the as-received powder, TEM investigation of both powders was carried out. Fig. 3 shows the SAED pattern and corresponding BF TEM images of these two powders. The diffraction pattern for the as-received powder (Fig. 3a) reveals strong diffraction spots that were identified to correspond to the  $(2\ 0\ 0)$  and  $(4\ 0\ 0)\ \gamma$ -phase. This suggests that this powder is likely polycrystalline and

composed of microsized  $\gamma$ -phase grains. Ring-shaped diffraction patterns are also observed and reveal the presence of the  $\beta$ -phase. These rings are identified to be (2 0 0), (2 1 1) and  $(2 \ 2 \ 0) \beta$ -NiAl. The ring-like shape of this diffraction pattern indicates a fine grain size, therefore suggesting the presence of fine precipitates of the  $\beta$ -NiAl phase within the  $\gamma$ -matrix. The BF image for the as-received powder (Fig. 3b) confirms the presence of very fine grained precipitates (β-NiAl) embedded in the  $\gamma$ -matrix. The diffraction pattern for the as-cryomilled powder (Fig. 3c) is significantly different as it clearly reveals multiple diffraction rings associated to the y-phase Co-Ni-Cr solid solution. The presence of these diffraction rings as opposed to diffraction spots demonstrates that the grains in the  $\gamma$ -matrix have undergone considerable refinement. Diffractions associated to the  $\beta$ -phase appear as very faint ring fragments, thus suggesting a much lower  $\beta$ -phase content. The BF image for the as-cryomilled powder (Fig. 3d) reveals that the material has a nanocrystalline microstructure with an average grain size below 25nm. Findings from the TEM investigation are in accordance with results from the XRD analysis and confirm that nanocrystalline powder particles were successfully synthesized from conventional particles by means of cryomilling.



Figure 3. TEM IMAGES (SAED PATTERNS AND BF IMAGES) SHOWING THE MICROSTRUCTURES OF THE (A-B) AS-RECEIVED AND (C-D) AS-CRYOMILLED CONICRALY POWDERS.

## As-Deposited CS Coating Characterization

Fig. 4 shows SEM images of both the as-sprayed conventional and nanocrystalline CoNiCrAlY coatings manufactured by the CS process. Both coatings exhibit a large

build-up thickness achieved in a single pass and feature limited visible defects such as porosity and interlamellar cracks. Porosity measurements were carried out on the conventional and nanocrystalline coatings and revealed average porosities of  $1.1 \pm 0.4\%$  and  $2.9 \pm 0.9\%$  respectively. The difference in porosity is likely attributed to the inherent higher hardness and mechanical strength of the nanocrystalline feedstock particles, thereby increasing its critical velocity and leading to more particles undergoing incomplete plastic deformation. The difference in porosity may also be partly explained by the different particle morphology of both feedstocks. The flakelike nanocrystalline particles have a higher drag coefficient than the spherical conventional particles, and are therefore more susceptible to natural disturbances in the flow such as bow shocks ahead of the substrate. Similarly to the influence of shock waves on the acceleration of very small particles [23], such disturbances may hinder the actual impact velocity of the nanocrystalline particles upon deposition, thus causing fewer of these particles to have the required velocity to achieve adequate plastic deformation.





TEM investigation of both the as-sprayed conventional and nanocrystalline coatings was carried out in order to investigate their microstructures, and more specifically to confirm that the CS deposition process preserved the nanocrystalline microstructure throughout the deposition process. Fig. 5a and Fig. 5b show TEM images of different regions within the conventional CoNiCrAIY CS coating. The images reveal that the coating is characterized as having a bi-modal grain-size distribution with some areas clearly depicting a nanocrystalline microstructure with grain sizes below 50nm (Fig. 5a) as well as other areas exhibiting a microstructure more similar to the original feedstock with micron-sized grains (Fig. 5b). Such microstructural features are significantly different to those of

the original as-received powder (Fig. 3a-b). Analysis of the indexed diffraction pattern from Fig. 5a demonstrated that the  $\gamma$ matrix had undergone grain refinement down to the nanocrystalline range during the deposition process, whereas the  $\beta$ -phase precipitates had been observed to experience partial dissolution. These microstructural transformations are nearly identical to those observed in the powders during cryomilling and therefore the mechanisms responsible for such microstructural transformations are believed to be the same. This suggests that the severe plastic deformation induced in the particles during the CS process is similar to that during cryomilling. The bimodal grain size distribution has been attributed to localized varying extents of plastic deformation within the coating, thereby leading to different extents of grain refinement. A more detailed analysis of the microstructural changes observed in the conventional coating can be found elsewhere [22]. Fig. 5c shows the microstructure of the assprayed CoNiCrAlY coating produced from the nanocrystalline feedstock. This TEM image shows the nanocrystalline nature of this coating. Contrarily to the conventional coating, there appears to be no significant difference when compared to the microstructure of the original nanocrystalline powder (see Fig. The apparent absence of microstructural changes 3c-d). induced throughout the CS deposition process for this coating is attributed to the fact that such transformations have already occurred in the material during the cryomilling process, as discussed in section 3.1. The extent of grain refinement that can be achieved in a material by means of induced severe plastic deformation has been investigated in mechanical milling and has been shown to be limited [24]. Given that substantial grain refinement had already occurred in the material during the cryomilling process, further grain refinement by means of additional plastic deformation is not likely to occur. This explains why the additional plastic deformation resulting from the CS deposition process did not cause further grain refinement in the cryomilled powder. Finally, Fig. 5d shows a highresolution TEM image of a single grain in the nanocrystalline coating microstructure. This grain features an equiaxed morphology and has an equivalent diameter of approximately 10-15nm, thus demonstrating the nanocrystalline grain structure of the coating. This figure also demonstrates that the grains in the nanocrystalline CS coating exhibit a high density of planar defects (twins), which indicates that twinning is an important deformation mechanism during particle impact. Twinning typically dominates over dislocation-based plasticity under the following conditions: very small grain sizes and high strain rates, both of which are known to be present during CS deposition of the nanocrystalline powder. It is thus believed that although the nanocrystalline coating does not exhibit further grain refinement or the formation of dislocation structures during CS deposition, it does show evidence of deformation in the form of twinning.



Figure 5: BF AND SAED TEM IMAGES OF AS-SPRAYED (A-B) CONVENTIONAL AND (C) NANOCRYSTALLINE CONICRALY COATINGS. (D) HRTEM OF A SINGLE GRAIN IN THE AS-SPRAYED NANOCRYSTALLINE COATING.

## **Oxidation Experiments**

#### Oxide Growth Rates

Following each heat treatment, the overall oxide growth rate for both the conventional and nanocrystalline coating samples was investigated by means of mass gain measurements. Given that oxidation is a surface phenomenon, results of this analysis are presented as the mass gain for each sample normalized per unit surface area. These results are presented in Fig. 6 as the average mass gain obtained from five coating samples for both the conventional and nanocrystalline coatings. Error bars have also been included to illustrate the mass gain standard deviation obtained from this analysis.

Results from the mass gain analysis demonstrate that the nanocrystalline coatings generally experience a slower overall oxide growth rate when compared to the conventional coatings. Looking at the trends of both curves however, it appears that the nanocrystalline coatings experience a slightly increased mass gain in the early stages of oxidation (less than 5 hours). It is believed that the nanocrystalline microstructure promotes the formation of a protective oxide scale in the early stages of oxidation which in turn helps inhibit additional oxidation of the coating upon further exposure. This is in accordance with findings reported by Ajdelsztajn et al. [20] who observed the oxidation behaviour of conventional and nanocrystalline NiCrAIY coatings manufactured by HVOF spraying. This study demonstrated that slower overall oxide growth rates were

achieved with the nanocrystalline coatings as a result of their ability to rapidly form of a protective oxide layer in the early stages of oxidation. It was explained that enhanced diffusion of aluminum at the grain boundaries, which are present in greater proportion in nanocrystalline microstructures, promotes the rapid formation of a dense, continuous and homogeneous alumina oxide layer in the early stages of oxidation. This stable alumina scale was then said to act as a diffusion barrier, thereby reducing the oxide growth rate upon prolonged exposure when compared to the conventional coating. This explanation of the oxidation behaviour of nanocrystalline coatings appears to agree with the overall oxide growth rate trends observed in this study. A more detailed investigation of the oxidation behaviour in the early stages of oxidation would however be required to further validate this hypothesis.



Figure 6. NORMALIZED MASS GAIN MEASUREMENTS OF CONVENTIONAL AND NANOCRYSTALLINE COATING SAMPLES AS A FUNCTION OF OXIDATION TIME AT 1000°C.

Another important consideration is the influence of coating porosity on the recorded mass gain measurements. It has been demonstrated that increased porosity in a coating sample resulted in higher measured mass gains during isothermal oxidation testing [7]. For example, it was shown that increasing the porosity of a conventional CoNiCrAlY coating from 1.0% to 4.1% approximately doubled the observed mass gain during oxidation testing. This was explained by the fact that pores within a coating microstructure effectively increase the available surface area for the oxidation reaction to take place, thereby resulting also in an apparent increase in the measured mass gain. As such, direct comparison of the mass gains for the conventional and nanocrystalline coatings considered in the present study may not be entirely accurate given their different porosity levels. Based on previous findings [7], it is believed that nanocrystalline CoNiCrAlY coatings with a lower porosity level would lead to further reduction of the oxide growth rate, thereby revealing an even greater improvement of the oxidation behaviour when compared to the conventional coatings. The

fact that the nanocrystalline coatings considered in this study exhibit a slower oxide growth rate than the conventional coatings despite having a porosity level nearly three times larger is a clear indication of the potential benefits that nanocrystalline bond coats could offer.



Figure 7. SEM IMAGES OF CONVENTIONAL AND NANOCRYSTALLINE COATING CROSS-SECTIONS SHOWING THE EVOLUTION OF THE OXIDE SCALE AND  $\beta$ -PHASE DEPLETION ZONE WITH INCREASING OXIDATION TIME.

Fig. 7 shows the evolution of the oxide scale and depletion zone in the conventional and nanocrystalline CoNiCrAIY coatings as a function of oxidation time. After 5 hours of oxidation, both coatings exhibit a thin continuous oxide scale with a similar average thickness ( $0.8\mu$ m and  $1.2\mu$ m for the conventional and nanocrystalline coatings respectively). The slightly thicker oxide scale observed on the nanocrystalline coating is consistent with results from the mass gain measurements and supports the theory of the rapid initial growth of the alumina scale. Also, the typical two-phase  $\gamma/\beta$ microstructure is now visible in both coatings. The  $\beta$ -phase precipitates in the conventional coating are observed to have an equiaxed morphology whereas those in the nanocrystalline coating appear in the form of thin elongated strips. The reappearance of the  $\beta$ -phase is attributed to the fact that the oxidation test acts as a heat treatment and manifests itself as a decrease in the density of point and line defects, thereby decreasing the solubility of Al in the  $\gamma$ -matrix and causing the  $\beta$ -phase to once again become visible in the form of precipitates. Depletion of the  $\beta$ -phase near the coating surface is also observed in both coatings. As oxidation time increases, both coatings experience similar oxide scale growth rates. The rate of change in thickness of the oxide scales for these two coatings appears to be parabolic and correlates well with the mass gain measurements reported in Fig. 6. An interesting distinction between both coating appears to be generally more uniform in thickness when compared to that on the conventional coating. This is most obvious after 100 hours of oxidation and is typically desirable for improved TBC performance [2].

#### Oxide Scale Composition

XRD analysis was carried out after each different oxidation period in order to identify the composition of the oxide scale that formed on the coatings surface. The XRD spectra obtained from this analysis for the conventional and nanocrystalline coatings after the various oxidation times are presented in Fig. 8. It can be seen from this figure that both coatings exhibit very similar oxide compositions after each oxidation period. The spectra for both coatings in the as-sprayed condition reveal that only the  $\gamma$ -phase is present, further confirming that the  $\beta$ -phase has dissolved. As discussed previously, this deformation driven dissolution process was demonstrated to have occurred during CS deposition for the conventional coatings and during cryomilling for the nanocrystalline coatings. The  $\gamma$ -matrix peaks also show evidence of peak broadening, thus further demonstrating the fine grain structure of the  $\gamma$ -matrix as a result of severe plastic deformation [22]. No detectable amounts of oxides are seen in the as-sprayed coating, which was to be expected given that typical CS coatings commonly feature low oxide contents [7, 10, 11]. After 5 hours of oxidation, both coatings are observed to form an oxide scale composed of a- $Al_2O_3$  as well as other metastable alumina phases such as  $\gamma$ - $Al_2O_3$  and  $\theta$ - $Al_2O_3$ . The appearance of such metastable alumina phases upon oxidation of CoNiCrAlY alloys is not uncommon [2, 4, 25] and is believed to be attributed to rapid heating rates of the coating samples at the beginning of the oxidation tests. At this stage of the oxidation process, small  $\beta$ -phase peaks also become visible, thus further confirming that the oxidation test has acted as a heat treatment allowing the  $\beta$ -phase to precipitate out. After 25 hours of oxidation however, the  $\beta$ -phase peaks are no longer discernable by XRD as the  $\beta$ -phase depletion zone has now reached a thickness that is greater than the penetration depth of the incoming X-rays. Increasing the oxidation time to 100 hours shows the emergence of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as the dominant oxide for both coatings, with lesser amounts of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\theta$ - $Al_2O_3$ .



Figure 8. XRD SPECTRA OF A CS CONVENTIONAL AND NANOCRYSTALLINE CONICRALY COATING AFTER VARIOUS OXIDATION TIMES AT 1000°C.

Most importantly, the XRD analysis shows that even after 100 hours of oxidation at 1000°C, both coatings exhibit no detectable peaks to suggest the presence of significant amounts of detrimental NiO or spinel-type mixed oxides. This is considerably different to results reported in other publications having studied the oxidation behaviour of CoNiCrAlY coatings manufactured by thermal spray techniques such as HVOF and plasma spraying [4, 7, 25]. Tang et al. [25] observed the onset of mixed spinel-type oxides on the surface of HVOF-sprayed conventional CoNiCrAlY coatings after only 24 hours of oxidation at 1000°C. Conversely, their HVOF-sprayed nanocrystalline coatings did not exhibit these mixed oxides following the same heat treatment. The difference between these results and the ones obtained in the present study may be explained by various factors. Firstly, the use of thermal spray techniques results in significantly larger coating oxide contents when compared to lower temperature deposition processes such as CS. Numerous studies have demonstrated that the increasing presence of oxide inclusions within a coating resulting from inspray oxidation of the deposited particles promotes the onset of detrimental fast-growing oxides [7, 8]. The inherently lower oxide contents of the CS coatings considered in this study can thus partly explain why they do not contain any detectable amount of mixed spinel-type oxides even after 100 hours of Secondly, conventional coatings manufactured by oxidation. thermal spray processes typically feature coarse grain structures due to recrystallization resulting from the total/partial melting and re-solidifying of the particles. Inversely, the CS conventional coatings considered in this study were shown to have a microstructure with some regions featuring a very fine grain structure resulting from a plastic deformation induced grain refinement mechanism. Much like the nanocrystalline coatings, it is believed that the regions in the conventional coatings having a fine grain structure improve the oxidation behaviour by promoting the rapid formation of a protective alumina scale in the early stages of oxidation. The grain refinement mechanism may thus also explain the discrepancies in oxidation behaviour observed for the conventional coatings considered in this study and those reported by Tang et al [25]. Finally, it is interesting to point out that Tang et al [25] observed significant improvements in the oxidation behaviour of their nanocrystalline coatings despite manufacturing these coatings by means of thermal spraying (HVOF): even though some coarsening of the grain structure is likely to have occurred due to the elevated processing temperatures, the resulting microstructure featured sufficiently fine grain sizes to promote the rapid formation of a protective layer of alumina in comparison to the conventional coatings. This is further evidence of the relative importance of the bond coat's grain structure and its influence on the coating oxidation behaviour.

In summary, these findings demonstrate that the conventional and nanocrystalline CS coatings considered in this study successfully formed an alumina layer in preference to other detrimental mixed oxides upon oxidation testing.

Furthermore, the ability of the CS process to minimize in-spray oxidation as well as to induce grain refinement in the conventional CoNiCrAlY material or to fully preserve the microstructure of the nanocrystalline feedstock throughout deposition significantly improves the coatings oxidation behaviour.

## CONCLUSION

Nanocrystalline CoNiCrAlY feedstock particles were successfully synthesized from commercially available gas atomized conventional powder by cryomilling. TEM analysis of the powders showed grain refinement of the cryomilled powder into the nanocrystalline range as well as dissolution of the  $\beta$ -phase precipitates as a result of severe plastic deformation. Both the as-received conventional and cryomilled powders were then successfully deposited using the CS coating process. TEM investigation of the coatings showed that the plastic deformation from the CS deposition process caused grain refinement and  $\beta$ -phase dissolution in certain regions of the conventional coating, but such changes were not observed in the nanocrystalline coatings as they had already taken place during the cryomilling process. The nanocrystalline coating did however show evidence of a twinning deformation mechanism which was observed to be the main microstructural transformation to occur during CS deposition of the cryomilled powder.

Oxidation experiments revealed that the nanocrystalline coatings exhibited a slower overall oxide growth rate when compared to the conventional coatings despite the larger porosity level of the nanocrystalline coatings. This is believed to be attributed to the nanocrystalline coating's ability to rapidly form a protective alumina scale in the early stages of oxidation as a result of enhanced diffusion of Al at the grain boundaries. XRD analysis revealed that both coatings exhibited very similar oxide compositions throughout oxidation testing. No detectable amounts of detrimental NiO or mixed spinel-type oxides were observed on either coating after 100 hours of oxidation. Findings from this study thus suggest that significant improvements to TBC performance could be achieved by manufacturing nanocrystalline bond coats using the CS deposition technique.

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