Abrasive wear behavior of nano-ceria modified NiCoCrAlY coatings deposited by the high-velocity oxy-fuel process

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Abstract
In this study, the as-received and nano-ceria modified NiCoCrAlY coatings were deposited by the high-velocity oxy-fuel spraying (HVOF) process. The various mixture ratios of ceria nanoparticles (0.5, 1.0 and 2.0 wt%) were chosen for the development of modified coatings. Microstructural investigations for the conventional and modified coatings were carried out using a field-emission scanning electron microscope (FESEM) and x-ray diffraction (XRD) analysis. Moreover, the adhesive strength, the fracture toughness, and the abrasive wear behavior of nano-ceria modified NiCoCrAlY coatings were examined and compared to the original NiCoCrAlY coating. The obtained results demonstrated that, the modified NiCoCrAlY-1.0 wt% nano-ceria coating represented a relatively denser structure owing to lower amounts of porosity and oxide compared to other types of as-received and modified NiCoCrAlY coatings. Results also indicated that the indentation fracture toughness of nano-ceria modified coatings up to 1.0 wt% accordingly increased. The modified NiCoCrAlY-1.0 wt% coating had a higher bond strength compared to other types of as-received and modified coatings. In addition, the modified NiCoCrAlY-1.0 wt% nano-ceria coating also had better abrasive wear resistance due to its higher microhardness and desirable dispersion of nano-ceria reinforcement in the layer of coating.

1. Introduction
Recently, the development of advanced novel materials and coatings to resist in wear, corrosion and high-temperature environments has been one of the most challenging issues for researchers [1–10]. Among from them, thermally-sprayed MCrAlY coatings (M = Ni, Co or both of them) have come out as a robust to cover a broad range of high-temperature applications with a significant improvement in the service life for hot section components [11–14]. The MCrAlY coatings could form such stable α-Al2O3 oxide scale and other mixed oxides like NiO, CoO, NiAl2O4 and/or CoAl2O4 spinels. This oxide scales can enhance the performance of the coating against high-temperature wear, corrosion, and oxidation [15–18]. Abrasive wear rate and friction coefficient could be considered as essential factors in the performance of the MCrAlY coated components such as gas turbines and related parts, that are subject to be in service at high and low temperatures [19–24].

Recently, several investigations have been carried out on the improvement of MCrAlY coatings by adding metallic, carbide or oxide reinforcements [25–29]. The micro- and nano-scaled particulate oxide reinforcements for MCrAlY coatings not only improve the physical properties and oxidation resistance [30, 31] but also enhance the mechanical properties and wear resistance in erosive or abrasive environments [19, 20, 32–34]. In this case, with the widespread use of the modified/nanocomposite coatings in the hot sections of turbine components, modification of MCrAlY coatings with hard oxide particles are the main subjects for many researchers in the recent years [19, 27, 28, 35]. Whereas, the modified MCrAlY coatings have also been investigated by many researchers in the field of abrasive and erosive wear applications under low and high temperatures [20, 36]. Some of the above-mentioned investigations have found that rare earth oxides such as
The microstructures of the as-received and the modified NiCoCrAlY coatings were investigated by Cao et al.\cite{39}. They found that NiCoCrAlY containing Al₂O₃–B₄C showed better room- and high-temperature wear resistance compared to un-strengthened NiCoCrAlY coating. Li et al.\cite{38} showed that nano-ceria dispersion strengthened NiCrBSiFe coating applied by laser cladding had a higher wear resistance at room temperature compared with un-strengthened NiCrBSiFe coating.

The erosive wear resistance and thermal shock behavior of the modified NiAl depositions with and without micro-scaled CeO₂ particles (as a rare earth oxide modifier) were investigated by Wang et al.\cite{40,41}. They reported that, NiAl-2 wt% CeO₂ coating had a higher mechanical properties as well as good erosion resistance due to its higher amounts of hardness and fracture toughness. A similar study has been carried out on the synergistic effects of CeO₂ and WC reinforcements on the tribological properties of NiAl coatings using laser surface alloying process\cite{42}. Results indicated that better tribological properties could be obtained by the synergistic effect of CeO₂ and WC on the case of microstructure refinement and improvement of hardness and mechanical properties of the modified NiAl coating.

The mechanical properties and abrasive wear resistance of nano-ceria modified NiCoCrAlY coatings applied by HVOF spraying process have not been previously investigated. According to the literature mentioned above, in the current study, ceria nanoparticles were utilized as a modifier for HVOF-sprayed NiCoCrAlY coatings. The fracture toughness and abrasive wear resistance of the conventional and nano-ceria modified NiCoCrAlY coatings were also investigated. In addition, the abrasive wear behavior of the nano-ceria modified NiCoCrAlY coatings were also analyzed using FESEM, and the obtained results compared with the conventional NiCoCrAlY coating.

### 2. Experimental

#### 2.1. Materials and coating process

The commercial gas atomized NiCoCrAlY powder with the chemical composition of Ni-20Co-14Cr-12Al-0.5Y (wt%) attained from Amdry 365-1 (Oerlikon-Metco, Westbury, US) was used as a feedstock. The commercial ceria (CeO₂) nanoparticle with the purity of 99.99% (Sigma-Aldrich, USA) was used as a rare-earth oxide modifier. The main features of using powders are listed in table 1. Besides, Inconel 738 superalloy (Ni: 61.8 wt%, Cr: 15.7 wt%, Co: 8.5 wt%, Al: 3.4 wt%, Ti: 3.20 wt%, W: 2.7 wt%, Ta: 1.8 wt%, Mo: 1.7 wt%, Nb: 0.8 wt%) was used as a substrate with 25 mm diameter and 4 mm thickness. Nano-ceria modified NiCoCrAlY powders (0.5, 1.0 and 2.0 wt%) were prepared using dry ball milling process. The preparation process and ball milling parameters were described in detail elsewhere\cite{16}.

A commercial HVOF spraying system with propane/oxygen was used to deposit both as-received and nano-ceria modified NiCoCrAlY coatings. In order to achieve the highest quality of the coating, all processed powders were carefully sieved to attain ~45 + 15 μm particle size distribution which appropriated for HVOF deposition process. The main HVOF parameters used for the deposition of as-received and nano-ceria modified NiCoCrAlY coatings are listed in table 2. The twin air jet was used in the back of the substrate surface for preventing thermal effects during and after HVOF spraying. Before spraying, Inconel 738 substrate was cleaned using an ultrasonic bath with ethanol, then the surface of substrates has been sandblasted with alumina under 4.0 bar working pressure. Table 3 summarizes the composition and thickness of as-received and nano-ceria modified NiCoCrAlY coatings deposited by HVOF spraying process.

#### 2.2. Characterization of the coatings

The microstructures of the as-received and the modified coatings were analyzed by field-emission scanning electron microscopy (FESEM, MIRA3-TESCAN, Czech Republic) equipped with energy dispersive x-ray...
Table 2. HVOF spraying parameters for the as-received and the nano-ceria modified NiCoCrAlY coatings.

| Parameters                        | Conventional coatings | Nano-ceria modified coatings |
|-----------------------------------|-----------------------|-----------------------------|
| Fuel type                         | Propane               | Propane                     |
| Fuel flow rate (l/min)            | 35                    | 35                          |
| Oxygen flow rate (l/min)          | 210                   | 200                         |
| Powder feeder rotation (rpm)      | 430                   | 400                         |
| Powder feed rate (g/min)          | 38                    | 35                          |
| Carrier gas type                  | N₂                    | N₂                          |
| Carrier gas flow rate (l/min)     | 20                    | 20                          |
| Stand-off distance (mm)           | 280                   | 250                         |

Table 3. Composition, thickness and feedstock particle size of the as-received and the nano-ceria modified NiCoCrAlY coatings deposited by HVOF spraying process.

| Type                    | Composition               | Feedstock particle size (μm) | Coating thickness (μm) |
|-------------------------|---------------------------|-----------------------------|------------------------|
| Conventional NiCoCrAlY | NiCoCrAlY                 | 45 ± 15                     | 250 ± 50               |
| Nanocomposite NiCoCrAlY | NiCoCrAlY + 0.5 wt% nano-CeO₂ | 25 ± 15                     | 250 ± 50               |
| Nanocomposite NiCoCrAlY | NiCoCrAlY + 1.0 wt% nano-CeO₂ | 25 ± 15                     | 250 ± 50               |
| Nanocomposite NiCoCrAlY | NiCoCrAlY + 2.0 wt% nano-CeO₂ | 25 ± 15                     | 250 ± 50               |

spectroscopy (EDXS). In this case, Image J software (NIMH, USA, ver. 1.2) were utilized for measurements of the porosity and oxide content of the as-received and the modified coatings. Microhardness evaluations in the cross-section surface of the coatings were done using a Vickers microhardness tester with a 300 g load for 15 s. At least five porosity and microhardness measurements were carried out on each type of as-received and nano-ceria modified NiCoCrAlY coatings. The structural phases of both conventional and nano-ceria modified NiCoCrAlY coatings were analyzed using x-ray diffraction testing method (XRD) with an x’pert Phillips diffractometer equipped with Cu-Kα (1.5406 Å) source at 40 kV and 40 mA.

2.3. Fracture toughness of the coatings
Fracture toughness of as-received and nano-ceria modified NiCoCrAlY coatings were estimated using the Vickers indentation testing method with 1 kg load and 15 s dwell time. To eliminate the edge- and interfacial-effects, the Vickers indenter applied on the center-line of the cross-section of the coating layers. Because of the lamellar structure of HVOF-sprayed coating, two horizontal cracks appeared and propagated from the opposed corners of the indent after indentation under considered load. It was also found that the direction of the crack propagations was approximately parallel to the coating/substrate interface. The calculation of the indentation fracture toughness of the coatings were carried out in accordance with equation proposed by Evans et al \[43\] which also used in other investigations \[4, 5, 44\]:

\[
K_I = 0.16 \left( \frac{c}{a} \right)^{1/2} (H V a^2)
\]

Where \(K_I\) is the indentation fracture toughness (MPa.m\(^{1/2}\)), \(c\) is half-length of the end-to-end crack tips length (m), \(a\) is the average half-length of indentation diagonal (m) and HV is the Vickers hardness of the coating layer (MPa).

In this case, the measurements of fracture toughness of as-received and nano-ceria modified NiCoCrAlY coating layers were calculated using the cross-sectional FESEM micrographs and Image-J analyzer. Whereas, the measurements of the indent size as well as the horizontal diagonal crack length were also carried out by FESEM and Image-J analyzer. The values of standard deviation for indentation fracture toughness were based on the average of at least 10 random measurements made on each coating specimens.

2.4. The bonding strength of the coatings
Adhesive bond strength of as-received and nano-ceria modified NiCoCrAlY coatings were evaluated according to ASTM C633–13 standard testing method. For this reason, cylindrical steel specimens were coated using HVOF deposition with the same corresponding spray parameters. Subsequently, the cylindrical coated specimen was adhered to another un-coated and grit-blasted cylindrical steel specimen using a 3M ScotchWeld™ SW-2214 (Fort Worth, TX, USA) adhesive. To provide pure tension during the tensile test, two adhered specimens were pulled-off to fracture/detachment using a tensile testing machine equipped with a
universal joint apparatus. For calculating the average bond strength with higher precision, five measurements for each as-received and nano-ceria modified NiCoCrAIY coatings were calculated.

2.5. Abrasive wear test

Abrasive wear investigations on the as-received and nano-ceria modified NiCoCrAIY coatings were accomplished using standard rotational pin-on-disk testing equipment. For this purpose, all of the coatings applied on the Inconel-718 disk-shaped substrate with 30 mm in diameter and 4 mm in thickness. For this case, the abrasive wear investigations were carried out under perpendicular sliding load of 10 N and sliding distance were chosen up to 250 m. Besides, sliding speed was selected 0.5 m s\(^{-1}\) and the diameter of the sliding track was set 15 mm for all types of as-received and nano-ceria modified NiCoCrAlY coatings. It was also mentioned that Si\(_3\)N\(_4\) pin (hardness HV = 18 GPa) was considered as a pin in contact with the coated disks. Before wear testing, all pin and disk specimens were cleaned in an ultrasonic bath containing ethanol and dried subsequently. The variation of wear track width and abrasive wear rate were determined after sliding wear test. For investigation of wear mechanisms of the coatings, FESEM investigations of the worn surface of the coatings (both backscatter and secondary electron modes) were also employed.

3. Results and discussions

2.6. 3.1. Characterization of the coatings

Backscattered electron micrographs of the cross-section of the as-received NiCoCrAlY and the modified NiCoCrAlY-1.0 wt% nano-ceria coatings are shown in figure 1. As can be seen, both types of the original and the modified coatings represent a typical lamellar structure of thermally-sprayed coating including Ni- and Co-rich solid solution phase (\(\gamma\)) FCC austenitic structured (light contrast) and (Ni,Co)Al (\(\beta\)) phase BCC structured (grey contrast). In addition, oxide stringers, macro- and micro-porosities and partially- or un-melted zones can be observed. In accordance with figure 1(a), less amount of oxide streaks and micro-porosities recognize in the cross-sectional microstructure of the as-received NiCoCrAlY coating compared with those modified coatings. In contrast, interlamellar pores and considerable amounts of the oxide phases were detected in the modified NiCoCrAlY-1.0 wt% nano-ceria coating (see figure 1(b)). It is worth mentioning that, no considerable structural difference were observed for various types of the nano-ceria modified coatings (0.5 to 2.0 wt%), according to the previous studies \([16, 45]\).

The cross-sectional image of a conventional NiCoCrAlY coating at higher magnification is shown in figure 2. According to this figure, two types of \(\beta\) phases can be detected in the conventional coating microstructure. The primary \(\beta\) phase with finer size (dendrites) was maintained from the \(\beta\) phase of the feedstock powder structure. On the other hand, the secondary \(\beta\) phase with a coarser size nucleated and grew after HVOF spraying in the coating structure. Some of the un-melted powder particles maintained their dual \(\gamma/\beta\) phases after HVOF spraying and preserved their primary microstructure in the coating. In contrast, the main part of the powder particles was completely melted and formed in a typical lamellar structure after spreading on the surface. Therefore, the secondary \(\beta\) phases may create from the supersaturated solid solution phase during the coating build-up.

Comparative investigations of the XRD patterns for the as-received NiCoCrAlY and the nano-ceria modified NiCoCrAlY coatings are shown in figure 3. Accordingly, both types of the as-received and the nano-ceria modified coatings showed the diffraction peaks related to the formation of Ni- and Co-rich solid solution (\(\gamma\))
and NiAl/CoAl (\(\beta\)) phases. In fact, the presence of Co and Cr in NiCoCrAlY coating may cause to increase the phase stability of the \(\beta\)-NiAl at higher temperatures [46]. When the coating expose to a high-temperature oxidative state, the existence of the \(\beta\)-phase provides Al source to permit the formation of Al\(_2\)O\(_3\) on the surface when exposed to high-temperature oxidative states [17, 46]. Moreover, the formation of nanostructured/ nanocrystalline phases in the nano-ceria modified NiCoCrAlY coating might be predictable (a broad hump between 12 \(\sim\) 18° and 45 \(\sim\) 49° that indexed by ‘N’ in figure 3) due to the finer microstructure of the ball-milled nano-ceria modified NiCoCrAlY powder. By this, the nano-scaled microstructure of the processed powder can maintain in the coating owing to its higher traveling speed and shorter time-of-flight of powder particles [15, 17, 47]. Based on the XRD results of the modified coatings, it may be concluded that no traces of CeO\(_2\) were detected because of its nano-scaled particle size and its lower amount (wt\%) in the nano-ceria modified coating [16].

Figure 4 represents the amounts of porosity and oxides of the as-received and the nano-ceria modified NiCoCrAlY coatings as a function of nano-ceria weight percentage. As can be observed, the average porosity percentage for the as-received NiCoCrAlY coating was about 1.4%. Except for the high-ceria coating (NiCoCrAlY-2.0 wt\% nano-ceria), the same behavior can be obtained for the porosity content for the modified coating.
coatings. From the obtained results of the oxide values of the coatings, it can be concluded that with increasing the nano-ceria content in the coating, the percentage of oxide streaks were accordingly increased (3.2% for the as-received NiCoCrAlY to 4.7% for the modified NiCoCrAlY-1.0 wt% nano-ceria coating). Conversely, by adding a higher amount of nano-ceria (e.g., 2.0 wt%), the structural characteristics of the coating can be deteriorated owing to increase of porosity percentage and insufficient melting of the powder during HVOF spraying process. Subsequently decreasing the inter-splat cohesion within the coating layer led to increase of porosity of the coatings [11, 16].

Figure 5 shows the microhardness profiles of the as-received NiCoCrAlY and the nano-ceria modified NiCoCrAlY coatings. As can be observed, the nano-ceria modified coatings had a higher microhardness in comparison with the as-received NiCoCrAlY coating (450 ± 12 HV300). In the case of the modified coatings, the microhardness of the NiCoCrAlY-2.0 wt% nano-ceria coating is about 535 ± 15 HV300, and it is higher than that of both NiCoCrAlY-0.5 wt% nano-ceria coating (475 ± 18 HV300) and NiCoCrAlY-1.0 wt% nano-ceria coating (490 ± 14 HV300).

As a consequence, by increasing the weight percentage of nano-ceria, the microhardness of the modified coatings was subsequently improved. Generally, the microhardness of the modified coatings is directly proportional to the amount of hard nano-ceria oxide phases in the modified coatings. Whereas, the microhardness of the as-received NiCoCrAlY coating mostly depends on structural factors, e.g., pores, grain boundary residual stress, and oxide streaks [48]. Kamal et al [37] reported that by adding oxide nanoparticles into the detonation gun sprayed NiCrAlY coatings, the grain size of the coating was reduced and the lamellar grain boundaries were accordingly purified. On the other hand, by increasing the weight percentage of nano-ceria, the value of hard reinforcement in the coating was increased and the grain size of the coating was
Table 4. The average values of fracture toughness for the as-received and the nano-ceria modified NiCoCrAlY coatings.

| Coating type                  | Indentation fracture toughness (MPa m$^{1/2}$) | Standard deviation |
|-------------------------------|-----------------------------------------------|--------------------|
| NiCoCrAlY                     | 1.37                                          | 0.058              |
| NiCoCrAlY + 0.5 wt% nano-CeO$_2$ | 2.05                                          | 0.061              |
| NiCoCrAlY + 1.0 wt% nano-CeO$_2$ | 2.25                                          | 0.049              |
| NiCoCrAlY + 2.0 wt% nano-CeO$_2$ | 1.41                                          | 0.075              |

Accordingly decreased. This phenomenon causes to improve microhardness of the nano-ceria modified NiCoCrAlY coatings.

2.7. Fracture toughness of the coatings

The average value of the fracture toughness ($K_{IC}$) for the as-received NiCoCrAlY and the nano-ceria modified NiCoCrAlY coatings are presented in Table 4. The calculated fracture toughness of the as-received and the nano-ceria NiCoCrAlY modified coatings were in accordance with other fracture toughness estimations based on NiCoCrAlY coatings [49, 50]. Compared with the modified coatings, the conventional NiCoCrAlY coating has a minimum amount of the average fracture toughness (1.37 MPa m$^{1/2}$). Moreover, the modified NiCoCrAlY-1.0 wt% nano-ceria coating has a maximum fracture toughness due to its higher hardness as well as better resistance to crack propagation during the indentation process (2.25 MPa m$^{1/2}$). Nonetheless, decreasing of the fracture toughness for NiCoCrAlY-2.0 wt% nano-ceria coating (1.41 MPa m$^{1/2}$) may be related to its higher brittleness due to the addition of a higher amount of the ceria nanoparticles in the coating composition. In addition, for NiCoCrAlY 2.0 wt% nano-ceria coating, the considerable amount of structural porosity may increase the tendency of crack propagation during the indentation process. The above-mentioned results are in accordance with other related investigations on the basis of the fracture toughness properties of thermally-sprayed coatings [44, 49, 50]. For the case of modified NiCoCrAlY-1.0 wt% nano-ceria coating, the dispersion of nano-scaled CeO$_2$ reinforcements in the NiCoCrAlY (matrix), is the main reason for the improvement of hardness and fracture toughness. Particularly, each oxide nanoparticle can play important role as a barrier to crack tip growth. The nanocomposite structure of the modified NiCoCrAlY-1.0 wt% nano-ceria coating including Ni- and Co-rich matrix phase and nano-ceria reinforcement can deflect the spreading path of the horizontal microcracks during indentation testing. This deflection offers resistance to the formation of through cracks in the horizontal direction from diagonal tips. Thus, well distribute ceria nanoparticles can absorb the energy of the crack during crack propagation through NiCoCrAlY coating and lead to increasing the fracture toughness of the modified coating [20].

Secondary electron micrographs of the Palmqvist-type cracks propagated for the as-received NiCoCrAlY and the modified NiCoCrAlY-1.0 wt% nano-ceria coatings after indentation testing are indicated in Figure 6. As depicted, the Palmqvist-type cracks horizontally propagated and approximately parallel to the lamellar-structured direction for both types of the as-received and the nano-ceria modified coatings. FESEM micrographs for the as-received NiCoCrAlY coating (Figure 6(a)) showed a relatively long Palmqvist cracks which propagated through the weaker boundaries between splats. It should be noted that, the longer cracks are the main reason to decrease the fracture toughness of the as-received NiCoCrAlY coating ($K_{IC} = 1.37$ MPa m$^{1/2}$). Conversely, the modified NiCoCrAlY-1.0 wt% nano-ceria coating (Figure 6(b)) showed a shorter crack length and greater fracture toughness ($K_{IC} = 2.25$ MPa m$^{1/2}$) because of the homogenous distribution of ceria nanoparticles along with the relatively adhered NiCoCrAlY splats [51]. Similar investigation has been carried out on the basis of the calculation of indentation fracture toughness of CoNiCrAlY bond-coat by Qi et al [52]. They reported that the fracture toughness of the coating decreased about close to 30% because of the Al depletion process when exposed to high-temperature oxidative condition. Besides, Mao et al [49] concluded that, the fracture toughness of MCrAlY bond-coat varied from 0.9 to 1.5 MPa m$^{1/2}$. As can be observed, the amounts of fracture toughness for the modified NiCoCrAlY coating in this investigation were more than those values reported in other related investigations. These increments were extensively related to the improvement of indentation fracture toughness of the NiCoCrAlY coating by the addition of nano-ceria as a reinforcement.

2.8. Bond strength of the coatings

Figure 7 shows the bond strength of the as-received and the nano-ceria modified coatings as a function of the weight percentage of nano-ceria content. Results indicated that except for the high ceria coating (NiCoCrAlY-2.0 wt% nano-ceria coating), the addition of nano-ceria into the NiCoCrAlY coatings increased their adhesive strength. In this context, the modified NiCoCrAlY-1.0 wt% nano-ceria coating had a higher adhesive strength compared to the as-received NiCoCrAlY coating. These results may be established by the formation of...
condensed splats as well as the presence of a relatively good distribution of ceria nanoparticles along with the lamellar structure of the NiCoCrAlY coating.

It is worth mentioning that, for the case of the as-received NiCoCrAlY coatings, micro-cracks may be scattered on the line of interface between coating and substrate. It is evident that during the tensile bond strength test, the above-mentioned micro-cracks may gradually propagate and connect to create a macron-sized crack during tensile adhesion test which causes to reduce the adhesive strength of the as-received NiCoCrAlY coating compared with the nano-ceria modified coatings [8]. Besides, during HVOF spraying, the agglomerated nanocomposite NiCoCrAlY/nano-ceria powders melt more easily than the conventional NiCoCrAlY powders.
This matter may cause the better spreading of fully melted NiCoCrAlY/nano-ceria agglomerates to the substrate surface and therefore may lead to improve the bond strength of the coating/substrate in the interface zone [8, 37]. As a consequence, according to Nithin et al [51], ceria nanoparticles may act as a surface-active element which refine the lamellar structure of the modified NiCoCrAlY/nano-ceria coating and causes to improve the cohesive strength between splats.

2.9.3.4 Abrasive wear behavior of the coatings
Figure 8 indicates comparative wear rates for the as-received and the nano-ceria modified coatings. As can be observed, the as-received NiCoCrAlY coating showed a higher wear rate compared with the nano-ceria modified coatings. These behaviors are mostly attributed to the higher amounts of microhardness of the nano-ceria modified NiCoCrAlY coatings. Wear track width versus sliding distance for the as-received and the nano-ceria modified NiCoCrAlY coatings were also presented in figure 9. Comparative values showed that the conventional NiCoCrAlY coating is wider wear track compared with the nano-ceria modified NiCoCrAlY coating. Furthermore, the wear track width of NiCoCrAlY–2.0 wt% nano-ceria is higher than that of 0.5 and 1.0 wt%, due to its higher wear rate and its brittle nature.

For a better comparison, figure 10 indicates the examined friction coefficient of the as-received and the modified coatings. For all types of the coated specimens under abrasion wear test, a steady-state condition of abrasive wear behavior was recognized after passing from a short period of comparatively intensive wear.
In accordance with the results obtained, except for the NiCoCrAlY-2.0 wt% nano-ceria coating, the wear rates of the rest nano-ceria modified coatings were lower than the wear rate value for the as-received NiCoCrAlY coating. In this case, the optimum wear resistance was acquired for the modified NiCoCrAlY-1.0 wt% nano-ceria coating. Despite its maximum hardness value, the wear rate of the NiCoCrAlY-2.0 wt% nano-ceria coating was slightly higher than that of other NiCo coatings containing nano-ceria (0.5 and 1.0 wt%). The deterioration of wear behavior might be related to a higher brittleness and higher amounts of porosity and structural defects for NiCoCrAlY-2.0 wt% nano-ceria coating.

The most used abrasive wear model is Archard’s wear law equation (2) which describes the wear volume as directly proportional to the product of the applied load with the contacting and sliding distance and as inversely proportional to the surface hardness of the wearing material [53]:

\[ V_s = K \frac{PL}{H} \]  

(2)

where, \( V_s \) is wear volumetric loss (mm\(^3\)), \( K \) is the dimensionless wear coefficient, \( P \) is applied normal load (N), \( L \) is sliding distance (mm) and \( H \) is the hardness of the observed surface (MPa).

According to Archard’s wear law [53], there is an inverse relationship between hardness value and abrasive wear rate of the coatings. As a consequent, except for modified NiCoCrAlY-2.0 wt% coating because of its higher amounts of oxide and porosity content, when the wear resistance of the coating decreases, its surface hardness accordingly increases. The mentioned findings justifies the comparative outcomes of the hardness and abrasive wear rate results for the as-received and the nano-ceria modified NiCoCrAlY coatings.

FESEM images (secondary electron mode) of the worn surfaces of the as-received NiCoCrAlY and the nano-ceria modified coatings are presented in figure 11. It can be observed that, even when sliding takes place against Si\(_3\)N\(_4\) ball, the NiCoCrAlY coating without nano-ceria undergoes severe plastic deformation (figure 11(a)), might be related to its lower amount of microhardness. Also, partially detached flakes and/or particles from the substrate can be seen in the worn surface of the conventional NiCoCrAlY coating because of its lower cohesive strength [19, 51].

Among them, both modified NiCoCrAlY-0.5 wt% nano-ceria and NiCoCrAlY-1.0 wt% nano-ceria coatings tolerate a relatively slight plastic deformation under room temperature wear test (see figures 11(b) and (c)). It could be closely related to the improvement of its mechanical characteristics by the addition of dispersed nano-ceria up to 1.0 wt%. Besides, a few irregular craters were also observed in NiCoCrAlY-1.0 wt% nano-ceria modified coating, which may be related to its finer and denser microstructure. Nevertheless, for NiCoCrAlY-2.0
wt% nano-ceria coating, owing to its lower bond strength and higher porosity content, it is predicted that the hard nano-ceria oxides are gradually uncovered until they become susceptible to removal by fracture. Consequently, the worn materials were completely detached in various shapes of flakes, crushed pieces or fine particles from the worn surface.

As can be observed from figure 11, the worn surfaces for all type of the as-received and nano-ceria modified NiCoCrAlY coatings indicate a typical abrasive wear mode and the grooves are detected along wear direction (figure 11(a)). Besides, surface microcracks and subsequent coating detachments are rarely detected beneath the worn surface for the modified NiCoCrAlY-0.5 wt% and NiCoCrAlY-1.0 wt% nano-ceria coatings (figures 11(b) and (c)). Specially, for NiCoCrAlY-2.0 wt% nano-ceria coatings, the grooves are deep (figure 11(d)) because of its cohesive strength whereas the mentioned grooves are relatively shallow for the NiCoCrAlY-1.0 wt% nano-ceria modified coating (figure 11(b)).

Figure 12 shows the backscattered micrographs of the worn surfaces of the as-received NiCoCrAlY and modified NiCoCrAlY-1.0 wt% nano-ceria coatings. For the case of the conventional NiCoCrAlY (figure 12(a)), the light contrasts in the remained coating in the substrate, and the backscatter images are cerium- and yttrium-rich zones (see zone A in figure 12(a)), whereas the darker regions are the substrate and the coating materials.

Figure 11. FESEM images (secondary electron) of the worn surfaces of (a) as-received NiCoCrAlY coating, (b) NiCoCrAlY-0.5 wt% nano-ceria, (c) NiCoCrAlY-1.0 wt% nano-ceria and (d) NiCoCrAlY-2.0 wt% nano-ceria coatings after 250 m. Counterpart: Si₃N₄ ball (R = 6 mm), load: 10 N, distance: 250 m.

Figure 12. Backscatter electron micrograph of the worn surface of the modified NiCoCrAlY-1.0 wt% nano-ceria coating under 10 N load and 250 m distance.
were completely detached from the surface (see zone B in figure 12(a)). Comparatively, the higher portion of the worn surface of the modified NiCoCrAlY–1.0 wt% nano-ceria coating (figure 12(b)) showed the coating remained on the surface because of fretting wear mechanism (see zone A in figure 12(b)). On the other hand, a limited scattered dark regions were observed for the worn surface of the modified NiCoCrAlY–1.0 wt% nano-ceria coating (see zone B in figure 12(b)). The mentioned results indicated that less coating material had been removed from the surface of the modified NiCoCrAlY–1.0 wt% nano-ceria coating after 250 m of sliding compared to NiCoCrAlY coating without nano-ceria.

The wear mechanism was found from abrasive/adhesive wear to fretting wear with 1.0 wt% nano-ceria addition. This findings are in accordance with other investigation on the effect nano-ceria modified Co-based coating presented by Li et al [38]. For NiCoCrAlY–1.0 wt% nano-ceria coating, the worn trace was the lowest and the weight loss was the least. But when the content of nano-ceria increased to 2.0 wt%, deeper worn trace and higher weight loss appeared.

According to investigations by Koga et al [34], delamination of coating material and surface oxides during abrasive wear was the main wear mechanism for the as-received NiCoCrAlY coating. In addition, the considerable coating removal was also attributed to the presence of porosity and oxide in the coating. In addition, according to Li et al [38] the presence of CeO2 into the Co-based coatings applied by laser processing can improve its wear performance at room temperature by decreasing the structural defect of the modified coating.

Indeed, because of the presence of surface-active element (CeO2), the microstructure of the nano-ceria modified coatings is much finer than the conventional NiCoCrAlY [37, 55]. As a result, the concentration of grain boundaries in the modified coating increased accordingly [16, 37]. The microstructural characteristic has a significant effect on preventing material removal throughout sliding abrasion.

For the case of the conventional NiCoCrAlY coating, the material removal due to the delamination of the coating, micro-cutting and micro-fracturing significantly increases with increasing sliding distance. Whereas, for the case of the nano-ceria modified coatings, the presence of oxide nanoparticle phases were enhanced the hardness and wear characteristics of the modified NiCoCrAlY coatings only when there is a good dispersion of oxide phases in Ni-rich metallic matrix. However, the increasing the nano-ceria content more than 1.0 wt% may cause to agglomeration of oxide phases. In NiCoCrAlY–2.0 wt% coating, the agglomeration of ceria nanoparticles also decreases the cohesion between the lamellar grains in the coating structure and increases the material removal during wear test. The agglomerated oxide nanoparticles in the layers adjacent to the surface were easily pulled out from the coating during the friction process of abrasive wear testing and as a consequent decreased its wear resistance.

Thus, there shall always be an optimum level of nano-ceria addition to HVOF-sprayed NiCoCrAlY coating (1.0 wt%) in order to provide a good dispersion of nano-ceria oxide reinforcement through the Ni-rich matrix, thereby leading to improve the mechanical characteristics and wear behavior. For the case of modified NiCoCrAlY–1.0 wt% nano-ceria coating, which has a uniform nanocomposite structure, can not only absorb crack growth energy during abrasion but also inhibit or delay crack generation and propagation, resulting in enhanced fracture toughness and abrasive wear resistance.

Regarding discussion as mentioned above, it could be concluded that the modified NiCoCrAlY–1.0 wt% nano-ceria coating would be a remarkable competitive protective coating to Ni-based superalloy in terms of abrasive wear at room temperatures. The main reason could be regarded as a relatively denser structure, higher microhardness and fracture toughness in correlation with the strengthening effect of the dispersed ceria nanoparticles for the modified NiCoCrAlY–1.0 wt% nano-ceria coating.

4. Conclusions

In this study, the fracture toughness and wear property of the as-received NiCoCrAlY and the nano-ceria modified NiCoCrAlY coatings were investigated. Based on the experimental examination, the following conclusions were drawn:

- Nano-ceria modified NiCoCrAlY feedstock powders (up to 2.0 wt%) were successfully applied using the HVOF process on Inconel 738 substrate. All types of the as-received and the modified coatings had a lamellar structure including major Ni- Co-rich solid solution (γ) and (Ni,Co)Al (β) phases along with partially melted splats, interlamellar oxides, structural pores, and microporosities.

- By increasing the amount of dispersed nano-ceria, the hardness of the modified coatings increased accordingly. Furthermore, NiCoCrAlY–1.0 wt% nano-ceria coating demonstrated minimum amount of porosity and higher hardness compared with all other types of coatings.
• Adhesive bond strength of the modified NiCoCrAlY-1.0 wt% coating improved up to 65 MPa owing to better melting of the agglomerated powder during spraying and the subsequent spreading to form splats, which may cause to increase the adhesive and cohesive bond strengths of the modified coating. Conversely, the coating with a higher amount of nano-ceria (NiCoCrAlY-2.0 wt%) had a lowest adhesive strength due to the incomplete melting and spreading of the particles during spraying and subsequent weakening of coating/substrate interface.

• Nano-ceria modified NiCoCrAlY coatings had better fracture toughness compared with as-received coating. In addition, the value of indentation fracture toughness of modified coatings improved by increasing nano-ceria content up to 1.0 wt%.

• The abrasive wear rate of the modified NiCoCrAlY-1.0 wt% nano-ceria coating was relatively higher than that of other types of the as-received and the nano-ceria modified coatings which could be related to the increment of its hardness, adhesive bond strength and fracture toughness. This improvements may be related to the incorporation of fully dispersed 1.0 wt% ceria nanoparticles into the NiCoCrAlY coating.

• The wear mechanism was found from abrasive/adhesive wear to fretting wear for the modified NiCoCrAlY-1.0 wt% nano-ceria coating. Furthermore, when the content of nano-ceria increased to 2.0 wt%, deeper worn trace and higher weight loss were appeared.

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