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The effect of cryomilling on the morphology and particle size distribution of the NiCoCrAlYSi powders with and without nano-sized alumina

Zahra Khodsiani [a,*], Hojatoallah Mansuri [a], Traneh Mirian [b]

[a] *Department of Materials Engineering, Malek-Ashtar University of Technology, Shahinshahr, Isfahan, Iran*
[b] *Fatemeh Zahra Campus, Farhangian Universitya, Isfahan, Iran*

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ABSTRACT

Particle size is a crucial parameter in the High Velocity Oxy-Fuel thermal spray processing that directly affects coating microstructure and porosity, and eventually, coating strength, and hardness. In this work, commercially available NiCoCrAlYSi powder with and without 2 wt.% nano alumina powder particles were cryomilled for 8, 12 and 16 h. The microstructure and morphology of these powders were characterized by X-ray diffraction, scanning electron microscope and energy dispersive spectroscopy and particle size distribution obtained with Image Analyzer and Particle Size Analyzer. The average agglomerate size increased with milling time for NiCoCrAlYSi powder, but adding Al_2O_3 particles caused a reduction in average particle size after cryomilling. After 12 h cryomilling, the Al_2O_3 particles were distributed homogeneously inside NiCoCrAlYSi particles. Cryomilling of NiCoCrAlYSi powder led to the formation of flake-shaped agglomerates, but cryomilling of NiCoCrAlYSi powder mixed with nano-sized alumina after 12 h led to the formation of highly irregular agglomerates and particle size distribution. The broadening of characteristic Ni,Cr-rich (γ phase) and Ni_3Al (γ' phase) peaks with milling time and the absence of the β peak on the milled powder were observed.

1. Introduction

During their service, blades and vanes of stationary gas turbines are subjected to high temperature and corrosive media. Coatings are generally applied to provide oxidation, corrosion or thermal protection depending on the nature of the operating environment [1]. MCrAlY (M = Ni, Co, or a combination) coatings have been widely studied due to their good mechanical properties and excellent high temperature oxidation resistance [2]. Alumina scales, which are formed on the MCrAlY's, can offer excellent protection due to their slow growth rate and thermodynamic stability [1,3].

Using nanostructured feedstock powders, thermal spraying has allowed researchers to generate coatings having higher hardness, strength and corrosion resistance than the conventional counterparts [4]. In recent years, many studies have proven that nanocrystallization of the coating has improved the oxidation resistance of MCrAlY [5]. Mercier et al. have found that nanostructuring speeds up the transition from θ-Al_2O_3 to α-Al_2O_3 and results in a denser and slow-growing α-alumina layer [6]. Preparation of nanostructured feedstock powders is the first step for the synthesis of nanostructured coatings [4]. For thermal spray applications, especially for High Velocity Oxy-Fuel (HVOF) processes, one of the leading production methods is mechanical attrition (MA). MA process is characterized by repeating powder welding and fracturing. The extent of welding and fracturing is determined by two factors, the material deformation behavior and the milling temperature [7].

For face-centered cubic elements such as aluminium, copper and nickel, the tendency to weld together and to other surfaces during MA has been found to be quite high. For this reason, the use of low temperatures or cryogenic MA has become popular for these types of materials [7]. Cryomilling, the MA of powders within a cryogenic medium (liquid N or Ar), is a method of strengthening materials through grain size refinement and the dispersion of fine nanometer-scale particles. Compared to conventional mechanical milling techniques, the main benefits of cryomilling include high tonnage potential, decreased milling times, ability to limit contamination and enhanced thermal stability [8]. The cryomilling technique has been utilized to modify the NiCrAlY bond coat material and has demonstrated that TBCs with cryomilled bond coats exhibit improved thermal cycle lifetime [9].

The presence of hard particles can affect the fracturing process (e.g., facilitate fracture) and thus the process of grain refinement in the metal matrix. As a consequence, a shorter milling time may be required to attain steady-state conditions during milling [10]. The presence of alumina in the cryomilled powder could lead to the formation of the stable α-Al_2O_3 phase in the thermally grown oxide [6,11].

Temperature and velocity of particles at the point of impact on the substrate are two crucial parameters in the HVOF thermal spray processing that directly affect coating microstructure and porosity, and eventually, coating strength, and hardness [12]. Particle velocity and

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* Corresponding author. Tel.: +98 3112302415; fax: +98 3125228530.
E-mail address: z_khodsiani@yahoo.com (Z. Khodsiani).

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temperature at the point of impact depend strongly on particle size [13]. Therefore, the objective of this study is to investigate the effect of cryomilling time on morphology and particle size of NiCoCrAlYSi powder and the role of nano-sized alumina particles on morphology and particle size of NiCoCrAlYSi powder during cryomilling. This work aims to analyze the microscopic morphologies and size distribution of particles and distribution of nano-Al_2O_3 particles in the NiCoCrAlYSi matrix with cryomilling time and also we have determined the suitable times for cryomilling of NiCoCrAlYSi powders with and without nano-sized Al_2O_3 for HVOF thermal spray processing.

2. Material and methods

The feed stock powder used in this work was a commercially available NiCoCrAlYSi powder with an average particle size of 12.6 μm. The original powder chemistry, in wt.%, is presented in Table 1. This powder is mixed with 2 wt.% alumina powder with an average particle size of 150 nm and grain size of 40 nm. NiCoCrAlYSi powder with and without nano-sized alumina was mechanically cryomilled at a rate of 224 rpm in a modified attritor mill for 8, 12 and 16 h in a liquid nitrogen environment. Stearic acid was added as a process control agent at 0.2% by weight, in order to prevent agglomeration of the powder and to facilitate the breakage of the particles. During cryomilling, Liquid nitrogen was constantly added to compensate for evaporation. Stainless steel balls, 0.635 cm in diameter, were used as the grinding media, and the powder to ball mass ratio was 1:30.

The morphology of the powders, before and after cryomilling, was examined using a scanning electron microscope (SEM). Backscattered electron images were obtained, and energy dispersive spectroscopy (EDS) analysis was conducted. Also agglomerate size distribution was obtained with Image Analyzer and Particle Size Analyzer. The X-ray diffraction characterization was performed on a Philips PW1877 X-Ray Diffractometer between 30° and 100° 2θ with a step scan of 2 and a time per step of 1 min.

3. Results and discussion

The morphology of the as-received NiCoCrAlYSi powder and cryomilled NiCoCrAlYSi particles after 8, 12 and 16 h are presented in Fig. 1, respectively. Mechanical cryomilling of the as-received spherical NiCoCrAlYSi led to the formation of irregular agglomerates, as shown in the SEM images (Fig. 1b, c and d). The rough oval shape of this powder after 8 h of milling is characteristic of high levels of deformation [14]. However, the flakiness of the particles after 12 h of milling, indicates the beginning of the fracturing stage and leads to the formation of irregular and flake-shaped agglomerates [14]. These morphologies are attributed to the continuous welding and fracturing of the powder particles during the mechanical milling process [7,11].

Fig. 2 shows the particle size distribution of the as-received NiCoCrAlYSi powder and cryomilled NiCoCrAlYSi powders. The average agglomerate sizes for as-received and cryomilled powders after 8, 12 and 16 h were 12.65, 25.7, 34.2 and 40.5 μm, respectively. The fact that the average particle size changes as milling time increases and approaches a constant value is an indication of fracture and cold welding occurring during milling [4]. Therefore, the cold-welding seems to overcome the fracture process with milling time, resulting in an increase in agglomerate size. The increase in agglomerate size with milling time was also observed in related studies with the cryomilling of NiCrAlY powder [7].

Table 1
Chemical composition (wt.%) of NiCoCrAlYSi powder.

Element	Ni	Co	Cr	Al	Y	Si
Composition	33.1	32	28	6	0.5	0.4

Particles coarsening observed in the present work after the cryomilling treatment is consistent with the results obtained in a similar study involving a Ni-based superalloy (INCONEL 625) milled under liquid N2 for 8 h, where the average particles size increased from 40 to 80 μm [15] and CoNiCrAlY powders cryomilled under liquid N_2 for 3 and 12 h [16]. In contrast, the opposite behavior was exhibited by Mg-based cryomilled alloys, as recently reported in the literatures [17,18]. These discrepancies could be readily associated to the different systems taken into account and cryomilling conditions adopted (attrition devices, powder to ball mass ratio, milling time, etc.). In this regard, Zheng et al. [17] evidenced that during the cryogenic treatment under liquid Ar, the original spherical particles of the Mg AZ80 alloy (55 μm average size) were first converted to disks-like shape and, subsequently, to spherical shaped powders with smaller size (17.8 μm average size). This is followed by a period of cold welding and fracturing of Mg particles. As the particles work hardens, they fracture more readily; hence the average particle size tends to decrease with increasing milling time. The decrease in the average particle size indicates a stage of fracture dominance [17].

The milling environment also affects the relationship between average particle size and milling times of milled Ni powder. As milling time increases, the Ni powder particle size decreases when milled in methanol but increases when milled in liquid nitrogen [4].

Also, to ascertain the continuous flow of feedstock powder in the powder feed system, the thermal spray process typically requires a powder particle size within the range of 10–50 μm [4]. The particle size of NiCoCrAlYSi powder specially after 16 h cryomilling is not in this range because many particles have sizes larger than 50 μm. Therefore, we suggest that 16 h cryomilled powders are less suitable for thermal spraying.

Fig. 3 shows the morphology of the NiCoCrAlYSi powder mixed with 2 wt.% alumina powder after the cryomilling process. Mechanical cryomilling of this powder after 8 h led to the formation of flake-shaped agglomerates, as shown in the SEM image (Fig. 3a) but after 12 and 16 h cryomilling of this powder, it led to the formation of highly irregular agglomerates, as shown in the SEM image (Fig. 3b and c). These morphologies are also attributed to the continuous welding and fracturing of the powder particles during the mechanical milling process [7,11].

The particle size distribution of the NiCoCrAlYSi powder mixed with 2 wt.% alumina powder after cryomilling is shown in Fig. 4. The average agglomerate sizes for these powders after 8, 12 and 16 h cryomilling were 19, 10.8 and 7.4 μm, respectively. The increase in agglomerate size after 8 h cryomilling for this powder was observed in this study. But after 12 h cryomilling, the decrease in agglomerate size with milling time was observed. The nano-sized alumina particles attach onto the particle surfaces of NiCoCrAlYSi powder, making the cold-welding of the NiCoCrAlYSi particles more difficult during the cryomilling process [19]. After enough time, the average particle size decreases by adding Al_2O_3 particles, and this behavior suggests that the fracture and/or welding phenomena changed by adding Al_2O_3 particles [20].

Particles of very small size have small mass inertias and are easily accelerated when the gas velocity is larger than the particle velocity. However, small particles are also easily decelerated when the particle velocity is larger than the gas velocity. Particles with even smaller size fully track the motion of the exhaust gases and may not stick to the substrate. Similar behavior is also observed for the particle temperature [12]. The behavior of particles with very small sizes in the gas stream explains why NiCoCrAlYSi powder mixed with 2 wt.% alumina powder after 12 h cryomilling is less suitable for thermal spraying.

Fig. 5a and b shows Backscattered SEM micrographs of a particle of cryomilled powder after cryomilling for 8 and 12 h, respectively. The tiny black spots observed in these figures are the nano-sized alumina particles that were dispersed inside the NiCoCrAlYSi particles. These spots can act as markers to indicate the extent of milling of the