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The synthesis of nanostructured NiCrAlY powders for plasma sprayed thermal barrier coatings

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Abstract
Thermal barrier coatings (TBCs) are used to protect hot sections of industrial gas turbine blades against high temperature corrosion and oxidation. They usually consist of a thermally insulating ceramic top layer (Yittria Stabilized Zirconia or YSZ) and an oxidation resistant metallic bond coat (MCrAlY) thermally sprayed onto the nickel-based superalloy substrate surfaces. Currently MCrAlY powders, up to 100μm in diameter are used in the production of thermal barrier coatings by the industrial gas turbine component manufacturers. It has been found that the nanocrystalline MCrAlY layer provide better oxidation behavior than the currently used microstructured MCrAlY layer at elevated temperatures. In this research work, nanocrystalline NiCrAlY powders were manufactured using a conventional Ni22Cr10Al1.0Y powder as the base material using a planetary ball mill device. The microstructural characterization of NiCrAlY powders before and after milling were explored using X-ray diffraction, scanning electron microscope equipped with energy dispersive spectrometer. The results indicated that the synthesized NiCrAlY powders mainly consists of two phases: γ (Ni,Cr-rich) and γ' (Ni_3Al) .
Key words: MCrAlY powders, High temperature oxidation, Ball milling, Air-plasma sprayed coatings.

1. Introduction

Applications of normal TBCs at elevated temperatures cause the transfer of oxygen through the top coat (YSZ) towards the bond coat-MCrAlY (Fox and Clyne, 2004). This phenomenon would cause two problems: (a) an oxidized scale can be formed onto the bond coat which is termed the thermally grown oxide (TGO) layer [Straussa et al 2002; Toscano et al 2008). Although this oxidized scale on the surface of the superalloy would protect the substrate against more oxidation, however, the growth of the TGO layer during high temperature oxidation can lead to the separation of the YSZ layer from the bond coat [Choi et al, 2002), (b) Formation of detrimental mixed oxides such as $NiCr_2O_4$, $NiCrO_3$, $NiCrO_4$ within the bond coat (NiCrAlY) during high temperature oxidation and are known to be accompanied with rapid volume increases and generate localized stresses and finally leads to the cracking or spallation of the ceramic layer from the bond coat [Quadakkers et al 2005]. The above mentioned problems were reduced using nanostructured NiCrAlY as bond coat in a TBC system. As nanostructured NiCrAlY layer creates a continuous and dense Al_2O_3 layer on the bond coat at elevated temperatures [Zhang et al, 2008; Kim et al, 2010]. Also, this oxide scale would be able to resist the penetration of oxygen within the NiCrAlY layer and itself. So this layer would delay the growth of the TGO (Al_2O_3) layer during subsequent thermal cycling [Zhang et al 2009].

Mechanical milling process is one of the main production methods used to create nanostructured materials for plasma spray applications. This mechanical milling process is a high-energy ball milling technique that can aid in the production of nanostructured materials when appropriate equipment and programs are used [Kim et al 2010].

Hussain found that the particle sizes of the MCrAlY powders currently used in the manufacturing of thermal barrier coatings on the industrial gas turbine components can be up to 100µm in diameter (Hussain and Ababtain 2009). TBCs with nanostructured bond coat have shown better oxidation behavior at higher temperatures compared to their conventionally microstructured counterparts (Zhang et al 2009).

Mechanical alloying was developed in the 1970's at International Nickel co (INCO) as a technique for dispersing nano-sized oxide inclusions into Nickel – based alloys [Hussain and Ababtain 2009]. This mechanical alloying (MA) process can be defined as a method of producing composite metal powders with a controlled microstructure. On a commercial scale, this process is carried out in vertical attrited or horizontal ball mills. Hussain reports that amorphization can occur immediately after the mechanical alloying process and the milled powders have grain size which could be as fine as 10nm [10]. Since these earlier works, the mechanical alloying/ball milling process has been successfully used to prepare a variety of alloy powders exhibiting supersaturated solid solutions, quasi-crystals, amorphous phases and nano intermetallic compounds. The fundamental principle size reduction in mechanical attrition devices lies in the energy parted to the sample during impacts between the milling media [Hussain and Ababtain 2009].

When a single ball–powder–ball collision is analyzed two characteristics are prevalent: (1) cold welding, (2) fracture (Ajdelsztajn et al 2009). The extent of welding and fracturing is determined by two factors, the material deformation behavior and the milling temperature (Kim et al 2010; Ajdelsztajn et al 2007). For face-centered cubic elements such as aluminum, copper and nickel, the tendency to weld together and with other surfaces during MA has been found to be quite high. For this reason the use of low temperatures has become popular for these types of materials (Picas et al 2004). The aims of this paper are to synthesis the nanocrystalline NiCrAlY powders and investigate the morphology of NiCrAlY powders before and after milling.

2. Experimental Procedures

The as-received powders used in this work were a conventional NiCrAlY (AMDRY 962) powder with an average grain size less than 100µm (Table 1). These powders were milled using a planetary ball mill (Retsch PM 400, Germany) device at a rotation speed of 180 rpm. Provided appropriate materials are used in the manufacture of the jar/grinding medium and by maintaining optimum geometry and developing a program -planetary ball mills are able to produce nanostructured NiCrAlY powders with an average grain size about 20-50 nm after 36h of milling. In this project, stainless steel balls with 0.635-0.7 cm diameter were used as the grinding media. The mass ratio of the stainless steel mill balls to the powder was 10:1, which means for each charge, 1 kg of normal NiCrAlY powders was milled with 10 kg of 0.635-0.7 cm diameter balls.

A commercially available particle size analyzer (Coulter LS) was used to determine the agglomerated size distribution of the milled powders. The morphology of NiCrAlY powders was characterized using a Philips XL.50, Holland-MV 2500 scanning electron microscope equipped with energy dispersive spectrometer before and after milling process. The X-ray diffraction measurement was carried out using a Philips, Xpert 1300 diffractometer equipped with a graphite monochromator using Cu kα (λ=0.13209 nm) radiation for phase identification. A Hitachi S-4160 field emission scanning electron microscopy was employed to determine the microstructure and grain size of NiCrAlY powders after milling.

3. Results and discussion

Fig.1 shows the morphological differences between the NiCrAlY powders before and after milling process, respectively. As received powders shows spherical structures which resemble an orange peel structured surface, smaller structures are observed stuck to the larger surfaces. Attrition milling of as-received spherical NiCrAlY powders (Fig.1a) shows morphology somewhat akin to dough (a soft elastic mixture of flour and water). Orange peel surface is no more visible after the milling process. These irregular shaped agglomerates of NiCrAlY powders are shown in Fig.1b. This morphology is attributed to the continuous welding and fracturing of the powder particles

during the milling process [Ajdelsztajn et al 2007].

It can be said that the processes of mechanical attrition are based on imparting a severe plastic deformation using high-energy ball milling technique. Chang et-al observed that by using this method high level of strain is imparted on the material hence structural refinement occurs by shear and fracture of phase mixtures and by recrystallization processes (Cheng et al 2000). Fig.2 shows a plot of average size of the agglomerated MCrAl powders before and after milling. Average size of as-received and milled powders has been found to be 12.5 and 126.2µm, respectively. This behavior depends on the powder material characteristic (whether ductile or brittle) and the milling atmosphere (such as liquid nitrogen, methanol, argon or oxygen) and is attributed to the fracturing and welding of the particles during the process. The formation of the nanocrystalline structure during milling is considered to be a consequence of plastic deformation at high strain rates and can be divided in three stages: First, the deformation is located in shear bands consisting of high density dislocations; second, at a certain strain level, these dislocations annihilate and recombine as small angle grain boundaries; finally, the small angle boundaries change their orientation under further deformation and randomly oriented small grains are formed (Huang et al 1995). In this research, the cold-welding seems to have overcome the fracture process with milling time, resulted in an increase in the agglomerate size (Ajdelsztajn et al 2007), as shown in Fig.1b.

Fig.3 shows the results of EDS analysis carried out on NiCrAlY powders after milling. The plot shows quite convincingly that the concentration of oxygen has increased from 0.2% to 6%. The concentration of Al went up from 10% to 19% whereas the concentration of Y, Cr and Ni showed no significant increase i.e. concentration remained almost the same. Fig. 4 shows FESEM image of NiCrAlY powders after milling along with the EDS plot for Al and oxygen. Various researchers have stated that the presence of fine grained Al_2O_3 around the NiCrAlY grains can significantly accelerate the formation of a continuous, uniform and dense Al_2O_3 (TGO) layer (Quadakkers et al 2005; Lee et al 2009; Ajdelsztajn et al 2007, Huang et al 2000). The difference in oxidation behavior of TBCs is a direct result of differences in microstructure and phase composition. One or both of the following mechanisms influences the oxidation kinetics: First, the nanocrystalline grain structure results in an increased grain-boundary area that could enhance aluminum diffusion. Secondly, the mechanical milling process introduces finely-dispersed oxides during milling e.g. Al_2O_3 and Ni_2O. This could promote the preferential nucleation of alumina on the nanocrystalline NiCrAlY layer at higher temperature (Kim et al 2010). It can be stated from the results obtained that substantial reduction of internal oxidation of NiCrAlY layer at elevated temperature would be due to the formation of dispersed Al_2O_3 oxides on the NiCrAlY grains during the milling process (planetary ball mill).

During high-energy milling the powder particles are repeatedly flattened, cold welded, fractured and re-welded. During the milling process whenever two balls collide, some amount of powder would get trapped in between them (Suryanarayana 2001). The force of the impact plastically deforms the powder particles leading to work hardening and fracture. The new surfaces created enable the particles to weld together and this leads to an increase in particle size. Since in the early stages of milling, the particles are soft (if we are using either ductile-ductile or ductile-brittle material combination), their tendency to weld together and form large particles is high. A broad range of particle sizes develops, with some as large as three times bigger than the starting particles (Hussain 2009). The composite particles at this stage have a characteristic layered structure consisting of various combinations of the starting constituents (Suryanarayana 2001).

With continued deformation, the particles get work hardened and fracture by a fatigue failure mechanism and/or by the fragmentation of fragile flakes. Fragments generated by this mechanism may continue to reduce in size in the absence of strong agglomerating forces. At this stage, the tendency to fracture predominates over cold welding. Due to the continued impact of grinding balls, the structure of the particles is steadily refined, but the particle size continues to be the same. Consequently, the inter-layer spacing decreases and the number of layers in a particle increase (Suryanarayana 2001).

Fig.5 shows the X-ray diffraction patterns of milled and as-received NiCrAlY powders. The Ni, Cr-rich (γ phase) and Ni_3Al (γ' phase) peaks and some traces of AlNi phase ($Al_{0.32}$ $Ni_{0.68}$) are observed. After 36h of milling, the broadening of characteristic Ni, Cr-rich (γ phase) and Ni_3Al (γ' phase) peaks are observed. The physical

occurrences of XRD peaks broadening are due to the formation of small grain size structure of the powder and micro-strain introduced into the material during processing (Klug and Alexander 1974). This is an indication that very fine grain structure can result due to milling the NiCrAlY powders. The accuracy of the grain size measurement by XRD in nano-crystalline materials has been demonstrated in previous works (Lee et al 2001). Furthermore, various empirical relationships have been developed in an effort to correlate the extent of grain size refinement with XRD peak broadening (Suryanarayana and Norton 1998).

According to the observations made by previous authors (Suryanarayana 2001; Klug and Alexander 1974; Lee et al 2001; Suryanarayana and Norton 1998), the peaks of different phases (γ/γ′) overlap, as has been observed in Fig.5b in the present study. This phenomenon may lead to an inaccuracy in the grain size of individual phase measurement using the Scherrer equation. Hence, in this research, field emission scanning electron microscopy (FESEM) was employed to study the morphology and measure the grain size of NiCrAlY powders after milling process. This microscope (FESEM) operates by scanning a focused beam of electrons over a surface and sensing secondary electrons ejected by the surface. The beam size determines the resolution. The secondary electrons are detected by a detector and magnified onto a CTR image. Also, the FESEM images confirmed that the average grain size of milled NiCrAlY powders is less than 65.1±15.7 nm after 36h of milling in a planetary ball mill device, as shown in Fig.6.

In this research work, nanocrystalline NiCrAlY powders have been manufactured by milling commercially available Ni22Cr10Al1.0Y alloy powder using a planetary ball mill. Microstructural characterizations of NiCrAlY powders have been carried out before and after milling using XRD and FESEM. FESEM was used to establish the particle size of the milled powders as sometimes XRD particle size measurement can cause confusion. FESEM results indicated that the synthesized NiCrAlY powders have particle size which was in the range of 65.1±15.7 nm after 36h of milling and consists mainly of two phases: γ (Ni,Cr-rich) and γ' (Ni_3Al).

4. Conclusions

4.1. Mechanical milling of as-received spherical NiCrAlY powders leads to the formation of irregular and flake-shaped agglomerates of powders.

4.2. The XRD test showed that the NiCrAlY powders are mainly constituted by two phases: γ (Ni,Cr-rich) and γ' (Ni_3Al). Also, after 36h of milling, the broadening of characteristic Ni,Cr-rich (γ phase) and Ni_3Al (γ' phase) peaks were observed.

4.3. In this research, the cold-welding seems to overcome the fracture process with milling time, resulting in an increase in the agglomerated average size.

4.4. The FESEM images confirmed that the average grain size of milled NiCrAlY powders is less than 65.1±15.7 nm after 36h of milling.

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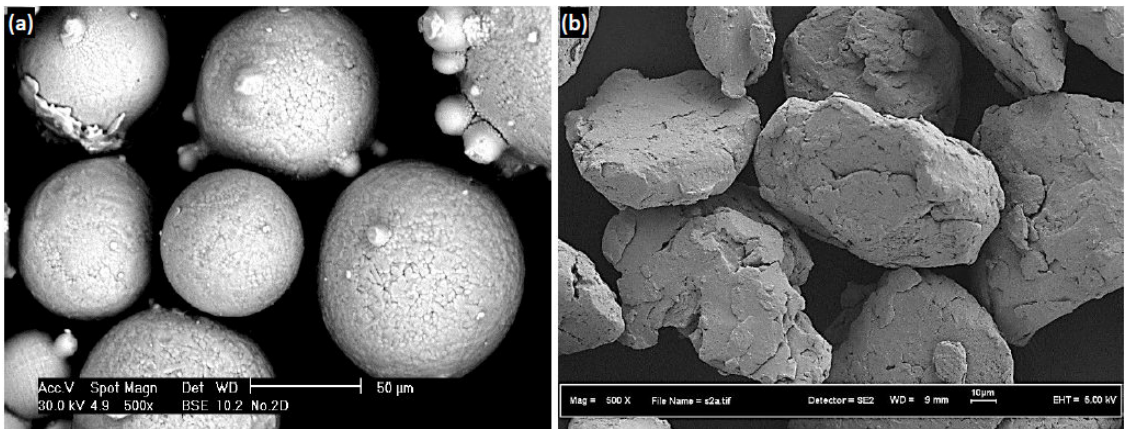

Fig. 1. Morphological characteristics of NiCrAlY powders, (a) before milling (powders in as-received conditions), and (b) after 36h of milling process.

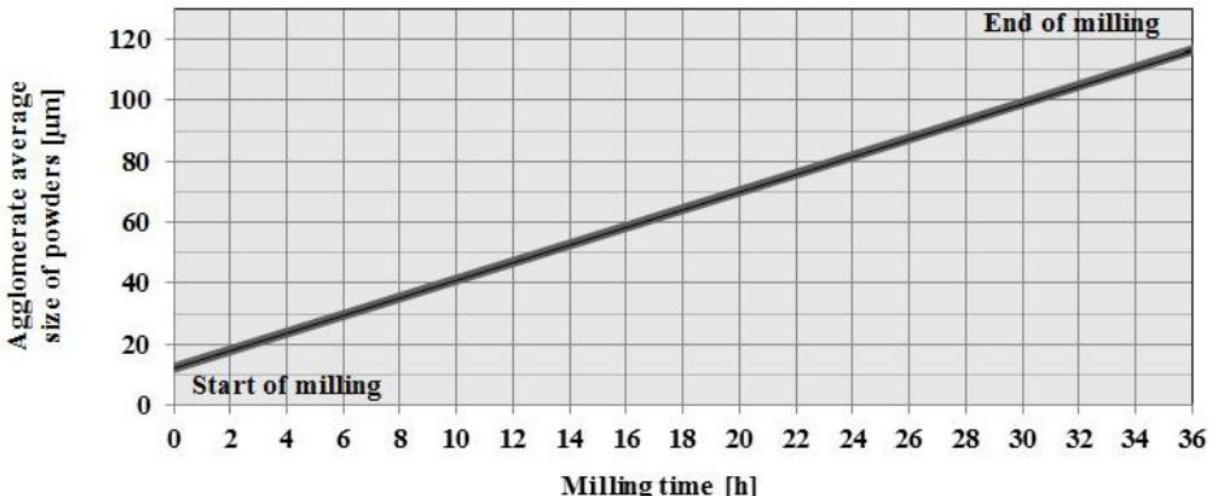

Fig.2. Plot shows agglomeration against time of milling

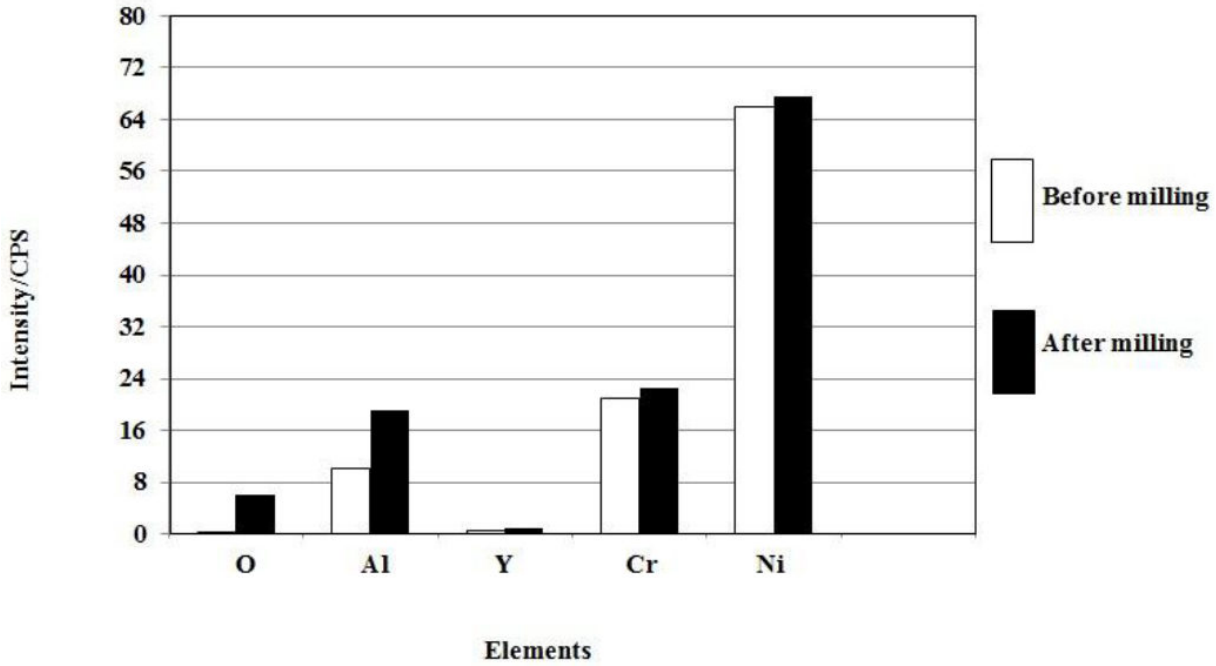

Fig.3. Plot shows that the concentration of O and Al has been substantially increased after milling for 36 hour of milling.

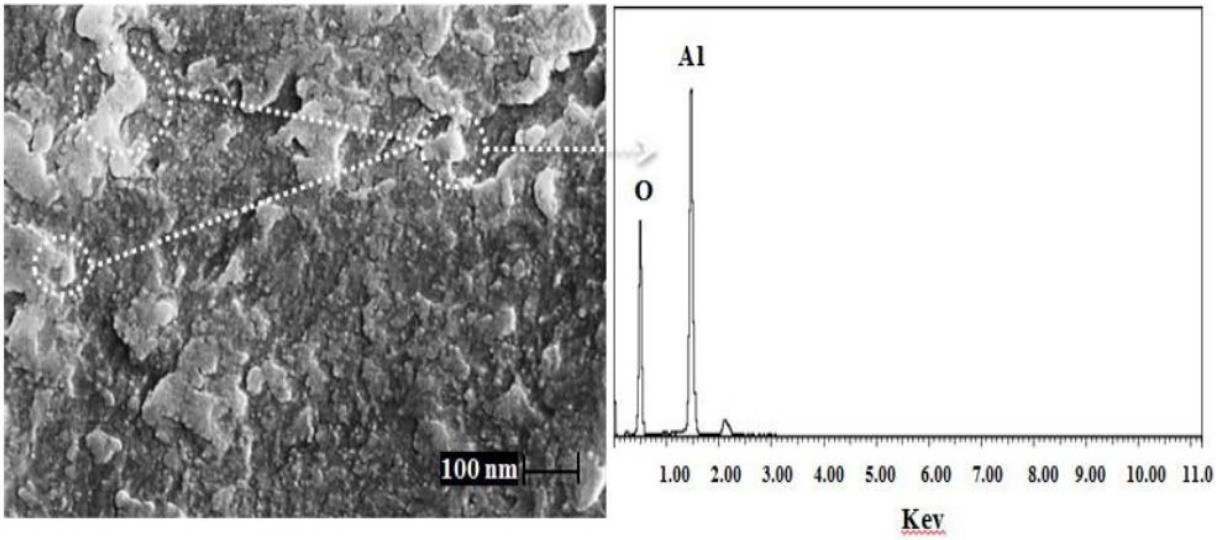

Fig.4. SEM image and EDS plots showing the formation of Al_2O_3 oxide on the NiCrAlY grains during milling process.

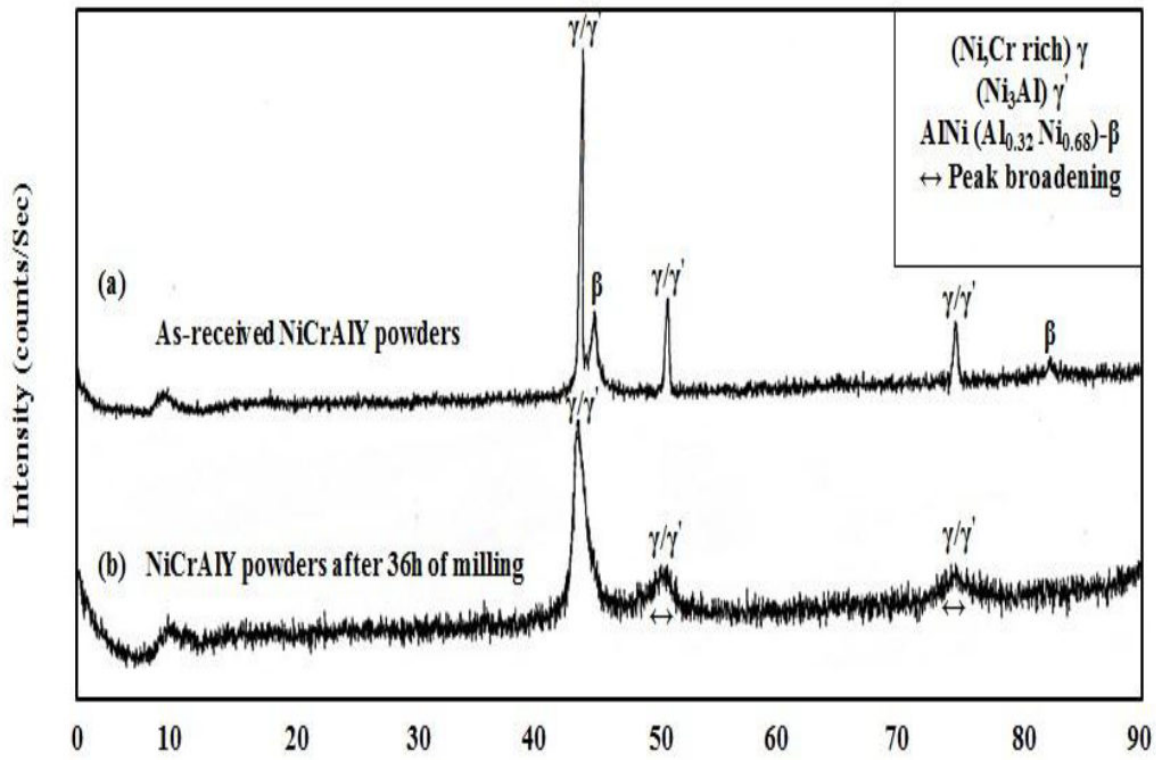

Fig.5 .X-ray diffraction analysis for (a) as-received NiCrAlY powders, (b) milled NiCrAlY powders.

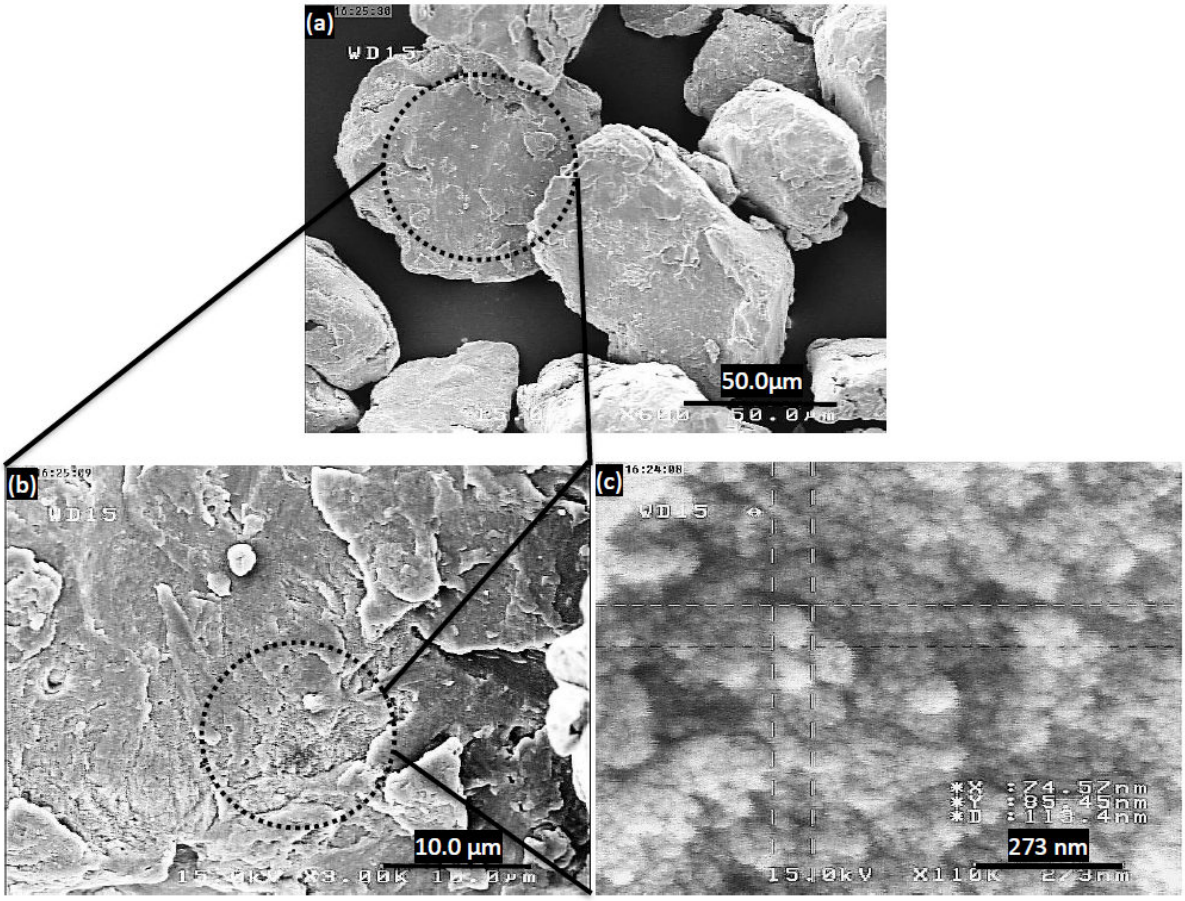

Fig.6. FESEM images of milled NiCrAlY powders with different magnifications;
(a) X 600, (b) X 3.00 K, and (c) X 110 K.