

## Spark Plasma Sintering of Cryomilled CoNiCrAlY Powders

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The influence of a cryomilling treatment in liquid N<sub>2</sub> on the characteristics of Co-32Ni-21Cr-8Al-0.5Y powders is first investigated in this work. The cryogenic process is then followed by a consolidation step performed using Spark Plasma Sintering. Different morphology, particle size increase, crystallite size decrease down to nanometric level and higher sinterability are the most important changes observed in CoNiCrAlY powders after cryomilling. Correspondingly, a relatively finer microstructure is obtained in SPSed samples. Moreover, if samples obtained starting from cryomilled powders are exposed to an oxidizing environment at high temperature, a protective  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> layer is produced on their external surface, while the formation of undesired unstable oxides is hindered. This result seems promising with the final aim of increasing high-temperature oxidation resistance in TBC of gas turbine engines.

### 1. Introduction

Due to their good oxidation and corrosion resistance properties, MCrAlY (where M=Ni, Co) alloys are currently used as bond-coats for thermal barrier coatings (TBC) for the protection of gas turbine blades against high-temperature oxidation (Sahoo et al., 1998). In this regard, recent studies have shown that the decreasing grain size in bond coat metal matrix as well as the presence of nano-sized dispersions of hard phases (oxides, nitrides, etc.) positively affect the oxidation resistance of TBC. Specifically, both these features seem to favour the formation of a protective layer of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> while hindering the formation of other, undesired, oxides (Tang et al., 2004). Nanostructured metallic powders and nanometric ceramic dispersions in metal matrices can be obtained by cryomilling, consisting in ball or attrition milling conventional raw powders in a cryogenic medium, typically nitrogen (Witkin and Lavernia, 2006). Ball to powder mass ratio, milling time and rotational speed are the most important parameters of milling processes (Suryanarayana, 2001).

In principle, the efficacy of such treatment can be assessed only after spraying the cryomilled powders to produce the bond coat. Nevertheless, long processing times and large amount of powders are required to optimise the procedure. In this context, the Spark Plasma Sintering (SPS), where the starting powders to be consolidated are

crossed by an electric pulsed current thus producing high local heating rates due to Joule effect (Orrù et al., 2009), could provide a powerful tool for the fast and relatively simple production of samples to be tested. This aspect is particularly true when evaluating the oxidation resistance, since the obtainment of the coating through spraying will not be required.

In this work, the influence of ball to powder mass ratio and milling times on the characteristics of cryomilled Co-32Ni-21Cr-8Al-0.5Y (wt.%) powders is first investigated. The cryogenic treatment is then followed by a consolidation step using an SPS apparatus at various sintering temperatures to identify the optimal conditions sufficient to reach the complete densification of the material. The bulk optimal products are then characterized and the results compared with those related to unmilled powders.

## 2. Experimental

Commercially available CoNiCrAlY powders (Sulzer Metco, Europe GmbH) prepared by gas atomization with nominal composition Co-32Ni-21Cr-8Al-0.5Y (wt.%) and particle size in the range of 15-45  $\mu\text{m}$  were used in the present investigation as starting material. Cryomilling experiments were conducted in a liquid  $\text{N}_2$  environment using an attritor mill (Union Process model 01-HD) and stainless-steel balls (2 mm diameter). The range of cryomilling time,  $t_{\text{CR}}$  investigated was 0-12 h, while the charge ratio, CR (ball to powder mass ratio) was changed from 4 to 30 and the rotation speed of the attritor, R, was maintained the same (1000 rpm) during all experiments.

The experimental procedure and set-up used in this work for consolidation by SPS are described elsewhere for the sake of brevity (Licheri et al., 2008). Briefly, an SPS 515 apparatus (Sumitomo Coal Mining Co. Ltd, Japan) was used under vacuum (10 Pa) for consolidating either the as received or cryomilled powders under temperature controlled mode. The SPS equipment combines an uniaxial press (50 kN) with a DC pulsed current generator (10 V, 1500 A, 300 Hz) to simultaneously provide a pulsed electric current through the sample and the graphite die (inside diameter 15 mm) containing it, together with a mechanical load through the die plungers. It should be noted that, in order to avoid graphite contamination from the plungers to the sample undergoing sintering, two tantalum disks were placed between them as diffusion barriers for C. The effect of the sintering temperature,  $T_{\text{D}}$  was investigated in the range 800-1000  $^{\circ}\text{C}$  by performing all SPS experiments at constant values of the heating rate, 100  $^{\circ}\text{C}/\text{min}$ , mechanical pressure,  $P=20$  MPa, and the dwell time,  $t_{\text{D}}=10$  min, i.e. the time for which the system temperature is held to the  $T_{\text{D}}$  value.

Fully dense SPSed samples were then subjected to oxidation treatment in air at 1100  $^{\circ}\text{C}$  for 20 h using a laboratory furnace (Naber-Labotherm, mod. N 50, Germany).

X-ray analysis performed by a Philips PW 1830 X-rays diffractometer using a Ni filtered  $\text{Cu K}_{\alpha}$  radiation ( $\lambda=1.5405$   $\text{\AA}$ ) was used for phase identification. In addition, crystallite size evolution during cryomilling was estimated from the line broadening of X-ray diffraction peaks using the Scherrer formula (Langford and Wilson, 1978), i.e.

$$B = \frac{k\lambda}{L\cos\theta}$$

where B is peak width, that is inversely proportional to crystallite size (L),

$\theta$  is the Bragg angle,  $k$  is the Scherrer constant which has been set equal to one, and  $\lambda$  is the x-ray wavelength. SEM (Hitachi, mod. S4000, Japan) and EDS (Kevex Sigma 32 Probe, Noran Instruments, USA) analysis were utilized to investigate powders morphology evolution during cryomilling as well as bulk products microstructure and local phase composition.

### 3. Results and discussion

Figure 1 shows the variation of the XRD patterns with cryomilling time for CoNiCrAlY powder when CR=4. The expected  $\gamma$  (CoNiCrAl, rich in Co, Ni, Cr),  $\gamma'$  ( $\text{Ni}_3\text{Al}$ ) and  $\beta$  ((Co, Ni)Al) phases are detected in the starting powders. Moreover, the initially sharp diffraction peaks broaden and their intensity decreases as the cryomilling process continues. This feature is even more evident when the CR ratio was increased to 30. Crystallite size refinement and internal strain increase induced by the milling treatment are responsible for such behaviour. When  $t_{\text{CR}}=12\text{h}$  and CR=30, the average crystallite size decreased down to 15-20 nm, as indicated by the Scherrer formula. This result is on the same order of the values reported in the literature for analogous systems (Tang et al., 2004).

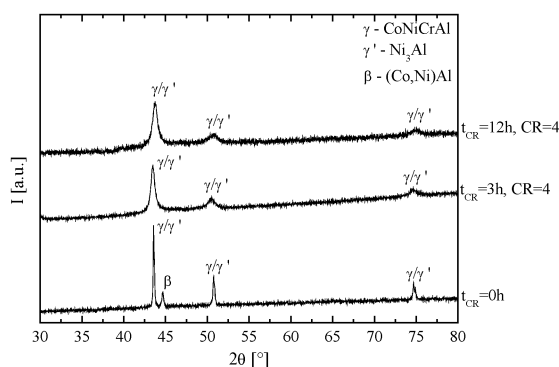


Figure 1: XRD patterns of CoNiCrAlY powders as a function of cryomilling time (CR=4).

As shown in Figure 2 for the case of CR=4, cryomilling strongly affects also morphology and particle size of CoNiCrAlY powders. This fact holds also true when the CR value was increased to 30. It is generally seen that, as a consequence of the mechanical treatment, the initially smooth and spherical particles become rough, irregular and flake-like-shaped. Moreover, particle size increases with cryomilling progress. For instance, it is observed that CoNiCrAlY flakes obtained at  $t_{\text{CR}}=12\text{h}$  and CR=30 are larger than 100  $\mu\text{m}$ . This outcome indicates that, as far as the system and the experimental conditions considered in this work are concerned, cold-welding phenomena among particles prevail on particle breakage during cryomilling.

As mentioned in the Experimental section, both the original and cryomilled CoNiCrAlY powders were consolidated using the SPS apparatus. Figure 3 reports the effect of sintering temperature and cryomilling time (CR=4) on the relative density ( $\rho_{\text{REL}}$ ) of final SPSed products.

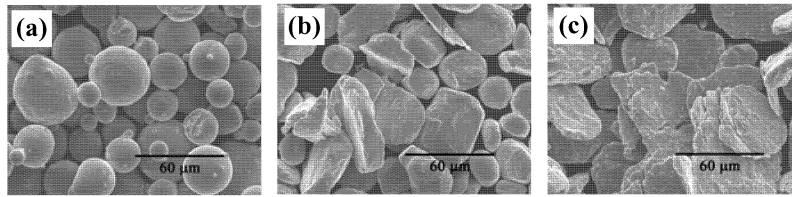


Figure 2: SEM images of as received (a), 3h (b) and 12h (c) cryomilled CoNiCrAlY powders (CR=4).

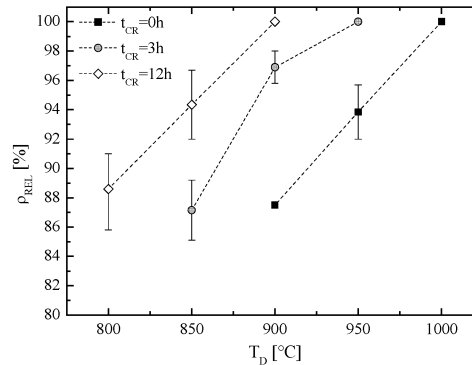


Figure 3: Influence of sintering temperature and cryomilling time on the relative density (theoretical value =  $7.24 \text{ g/cm}^3$ ) of the SPSed CoNiCrAlY samples (CR=4).

As expected, sample densification is gradually improved as the sintering temperature is augmented. In particular, the optimal sintering temperature to obtain fully dense specimens when starting from as received CoNiCrAlY powders is 1000 °C. Less obviously, the cryogenic milling treatment significantly favours powder consolidation, at least within the experimental conditions considered in this work. In fact, while particle size increases as the milling time is augmented, the optimal sintering temperature for obtaining completely dense samples correspondingly decreases from 1000 °C ( $t_{CR}=0h$ ) to 900 °C ( $t_{CR}=12h$ ). Similar considerations can be made when increasing the CR value. Grain size refinement and the formation of high defect concentration on processing powders, both induced by the mechanical treatment, are likely the main features responsible for facilitating sintering phenomena.

The microstructures of SPSed samples obtained when starting from unmilled and cryomilled powders are compared in Figure 4(a)-(d). Firstly, it is observed that some residual porosity is still present in the bulk material sintered at 900 °C using powders cryomilled for 12 h and CR=4 (cf. Figure 4(b)). This porosity is completely eliminated when increasing the  $T_D$  value to 1000 °C (cf. Figure 4(c)).

Two main regions can be generally identified in all samples. Based on EDS microanalysis, XRD diffraction results, and previous investigations reported in the literature (Tang *et al.*, 2004), it is possible to assess that the lighter continuous region contains  $\gamma/\gamma'$  phases while the dark ones correspond to the Al-rich  $\beta$  phase. It is apparent that the relatively coarser microstructure obtained from as-received powders (cf. Figure 4(a)) becomes finer when using cryomilled powders (cf. Figure 4(b)-4(d)) and this

effect is even more significant when the CR value is augmented. This outcome can be only partially justified on the basis of the retained grain growth caused by the lower sintering temperature required to consolidate the cryomilled- instead of the original gas-atomized- powders. This fact is clear when comparing Figure 4(a) and Figure 4(c) showing the cross-sections of samples both sintered at 1000 °C but using as-received or cryomilled powders. Thus, microstructure refinement in bulk material is directly related to the corresponding effect induced by the milling treatment on the processing powders.

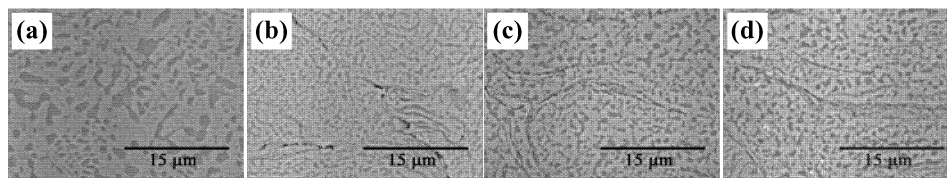


Figure 4: SEM micrographs of CoNiCrAlY SPSed dense samples starting from powders (a) unmilled ( $T_D=1000$  °C), cryomilled at (b)  $t_{CR}=12$ h,  $CR=4$  ( $T_D=900$  °C), (c)  $t_{CR}=12$ h,  $CR=4$  ( $T_D=1000$  °C), and (d)  $t_{CR}=12$ h,  $CR=30$  ( $T_D=900$  °C).

To establish if the cryogenic treatment of CoNiCrAlY powders also influences oxidation behaviour of SPSed products other than affecting their microstructure, selected dense specimens were exposed for 20 h to an oxidizing environment (air) at 1100 °C. It should be noted that, although such condition does not correspond to the actual situation (i.e. prolonged times, different type of gas and flow rates) encountered in turbine engines, this test certainly provides a preliminar indication of possible benefits deriving from the cryomilling treatment. As observed in Figure 5(a)-(c), an oxide layer is formed on the surface of samples obtained either from unmilled or milled powders. From XRD analysis, not reported here for the sake of brevity, these layers mainly consist of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. However other oxides, specifically Cr<sub>2</sub>O<sub>3</sub> and spinels, are also detected when starting from original powders. These undesired oxides tend to disappear for cryomilled samples and no traces of them are found by XRD when considering products obtained at  $CR=30$  and  $t_{CR}=12$  h.

#### 4. Conclusions

A cryomilling treatment performed on commercially available Co-32Ni-21Cr-8Al-0.5Y powders was found to affect significantly the characteristics of both the resulting powders and the properties of bulk products obtained after consolidation by Spark Plasma Sintering. Morphology changes, particles size increase, crystallite size decrease and higher sinterability are the most important consequences observed in CoNiCrAlY powders after such treatment. Specifically, with the cryogenic treatment, crystallite size was decreased down to the nanometric level and the optimal sintering temperature sufficient to reach the complete densification of the material was lowered from 1000 °C (unmilled powders) to 900 °C ( $t_{CR}=12$  h). A relatively finer microstructure in the bulk samples is correspondingly observed. Moreover, the results of oxidation tests evidenced that cryomilling promotes the selective formation of a more protective  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> layer

while other unstable and undesired oxides are also produced when using as-received gas-atomized powders. Although further studies are required on this subject, the results obtained in this and other investigations reported in the literature for similar systems, indicate that a cryomilling treatment of MCrAlY powders, before spraying deposition to obtain bond coats in TBC of gas turbine blades, is likely beneficial against high-temperature oxidation.

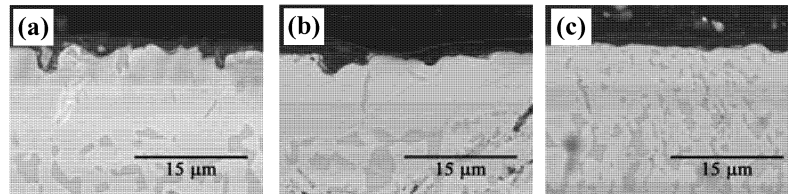


Figure 5: SEM images of the cross section of CoNiCrAlY SPSeD samples after oxidation for 20 h at 1100°C: (a) unmilled powders ( $T_D=1000$  °C), powders cryomilled at (b)  $t_{CR}=12h$ ,  $CR=4$  ( $T_D=900$  °C), and (c)  $t_{CR}=12h$ ,  $CR=30$  ( $T_D=900$  °C).

## 5. Acknowledgments

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