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Preliminary Results of the Isothermal Oxidation Study of Pt-Al-NiCoCrAlYTa multi-layered coatings prepared by Sparks Plasma Sintering (SPS)

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Abstract. MCrAlY coatings (where M = Co, Ni or Co/Ni) are widely used on turbine blades and vanes as oxidation and corrosion resistant overlays or as a bond-coating in thermal barrier coatings systems. MCrAlY are usually fabricated by Plasma Spraying, Physical Vapour Deposition, High Velocity Oxy-Fuel spraying or electrolytic techniques. The use of emergent Spark Plasma Sintering technique as a preparation method for NiCoCrAlYTa coatings has been presented previously [1]. SPS technique allows fast development of new coatings with a one-step fabrication of multilayered coatings. This work presents first results of the long term isothermal oxidation behaviour of Pt-Ni aluminide/NiCoCrAlYTa multi layered coatings. The obtained coating is dense and homogeneous. Isothermal oxidation up to 500 h at 1100°C leads to the formation of an adherent alumina scale with Y-rich precipitates and deep intergranular oxidation.

Introduction

Spark Plasma Sintering (SPS) revealed very convenient potentiality for quick preparation of new design of composite metallic materials such as multilayered or composition graded materials. Recently, we demonstrated the feasibility of MCrAlY coating preparation, with successful enrichment of the coating surface with aluminium and platinum [2]. Al and/or Pt alloying of the external part of a MCrAlY coating improves its oxidation and corrosion resistance [3,4]. This work presents the first results on the oxidation behaviour of SPS-fabricated samples, for different oxidation durations up to 500 h at 1100°C. Microstructural examinations of the samples are reported here. Oxide thickness, platinum diffusion deepness, Y segregation and intergranular oxidation are also considered.

Experimental procedures

All samples were prepared using a Dr Sinter 2080 SPS apparatus. The details of this apparatus have been described previously [1]. The materials were loaded onto 15-mm inner diameter cylindrical graphite dies. A heating rate of 100°C/min was used to reach the final temperature of 1000°C. Then, the sample was cooled down without high temperature dwell. The applied pressure was 15 MPa in the first minute of the sintering cycle.

The substrates used for this study were 8 mm diameter discs prepared from a single crystal nickel-base superalloy AM3® rod. The substrate surface was mechanically polished down to 0.25 μm diamond grit and cleaned with acetone and alcohol. NiCoCrAlYTa powder used for this study was from AMDRY® 997 (NiCo23Cr20Al8Y0.5Ta4.5). XRD analysis of this powder reveals a γ/β microstructure. Powder quantity was selected to form a thick NiCoCrAlYTa coating (about 1 mm) in order to study independently the substrate/NiCoCrAlYTa interdiffusion and the Pt-modified aluminide/NiCoCrAlYTa interdiffusion and oxidation. Sintering conditions were established for the MCrAlY powder on the AM3 substrate. Al and Pt were added as 10 μm thick pure Al and pure Pt foils over the NiCoCrAlYTa powder before sintering. It was shown in previous work that SPS-sintered NiCoCrAlYTa led to the usual γ/β microstructure with small TaC precipitates dispersed in the bulk of the coating. In addition, it was also shown that other carbides, such as chromium carbides, developed in a superficial zone of the coating because of the processing in graphite die [1]. It was shown that an Al foil placed on the surface of NiCoCrAlYTa reduces this additional carbide formation [1] and that a Pt foil completely suppress it [2].

Isothermal high temperature oxidation was carried out in an open furnace during 24, 192 and 500 h at 1100°C. Samples were introduced in the pre-heated furnace and removed from the hot furnace for a fast cooling in ambient air. After that, samples were characterized by SEM and EDX, using a LEO 435VP microscope equipped with an IMIX-PC EDX system from PGT. Some X-ray maps were done using an IDFixe EDX system. Quantitative EDX analyses were performed using real standards and a $\phi\rho z$ model.

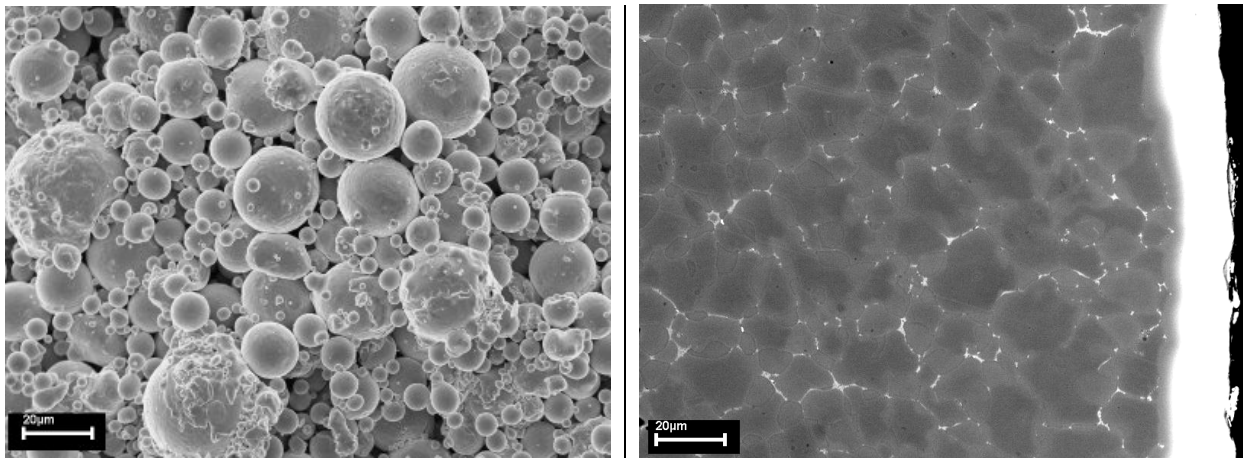


Fig. 1. a) slightly sintered NiCoCrAlYTa powder morphology after SPS at 600°C, b) Cross section of the Pt-Ni-Al/NiCoCrAlYTa multi-layered coating as prepared by SPS at 950°C.

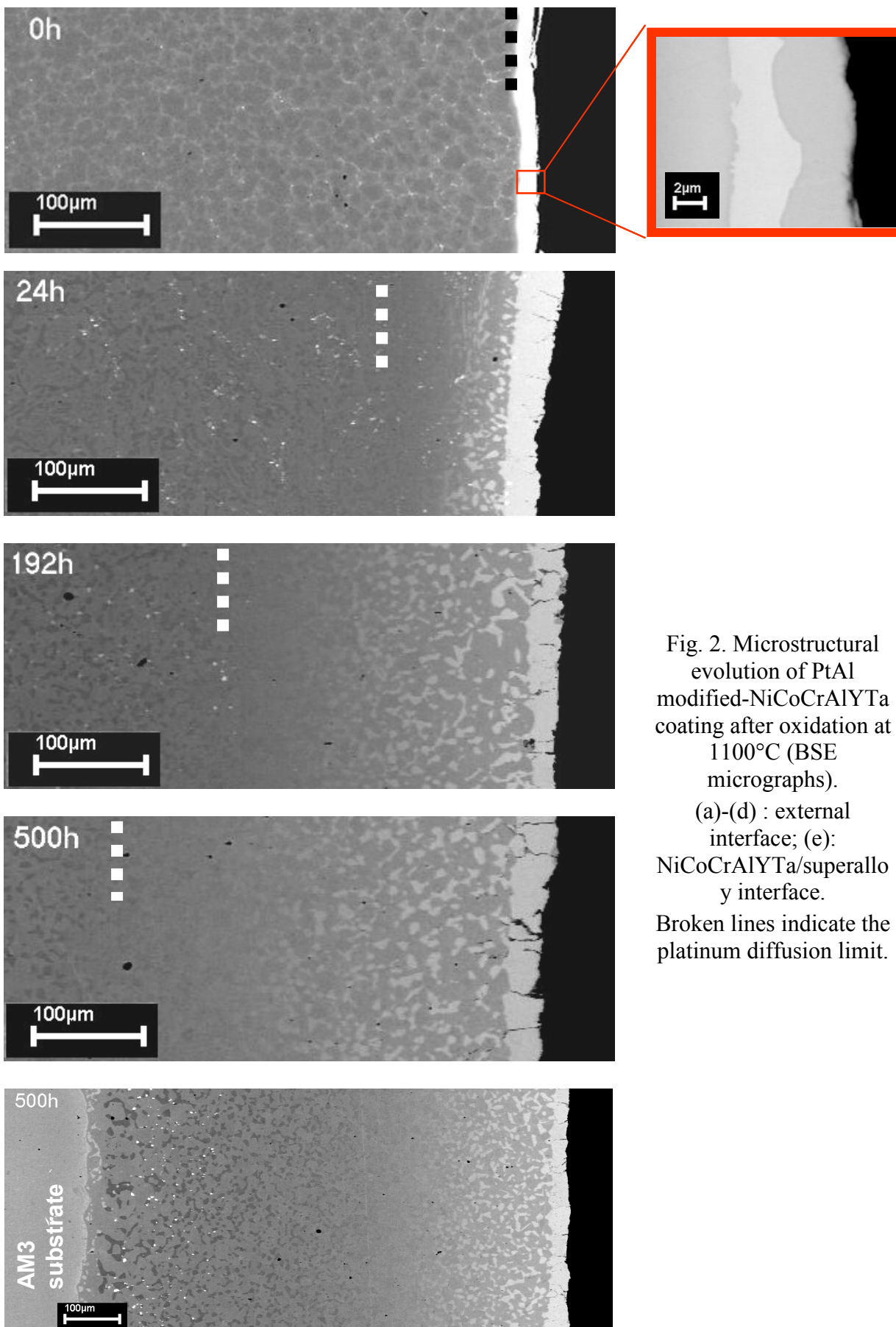


Fig. 2. Microstructural evolution of PtAl modified-NiCoCrAlYTa coating after oxidation at 1100°C (BSE micrographs).

(a)-(d) : external interface; (e): NiCoCrAlYTa/superalloy interface.

Broken lines indicate the platinum diffusion limit.

Results and Discussion

Coating microstructure after SPS fabrication. Fig.1 shows the starting NiCoCrAlYTa powder slightly sintered (Fig.1a) and the microstructure of the SPS made coating (Fig.1b). The as made SPS sample is composed of a top Pt-rich Ni-Al intermetallic layer (right side of Fig. 1b) over a NiCoCrAlYTa layer with equiaxed grains. Intergranular regions are enriched in heavy elements (e.g. Ta and Y). Higher magnification BSE (Back Scattered Electrons) images (Fig.2 top right) and EDX analyses of the Pt-rich external layer leads to the conclusion that it is composed of 3 sub layers: an external ξ -PtAl₂, followed by ε -PtAl and an internal Pt-rich β -NiAl. This is in agreement with the published Ni-Pt-Al phase diagram determined at 1100°C [5].

The NiCoCrAlYTa close to the surface, below the Pt-rich intermetallic layer, has a dendritic-like microstructure. This is certainly due to the exothermic character of the platinum aluminide formation, locally rising the temperature over the measured 1000°C on the SPS machine die. Grains size is in the range of 20 μ m, which is the average size of the NiCoCrAlYTa powder grains, i.e. a fully dense coating was fabricated without noticeable grain growth.

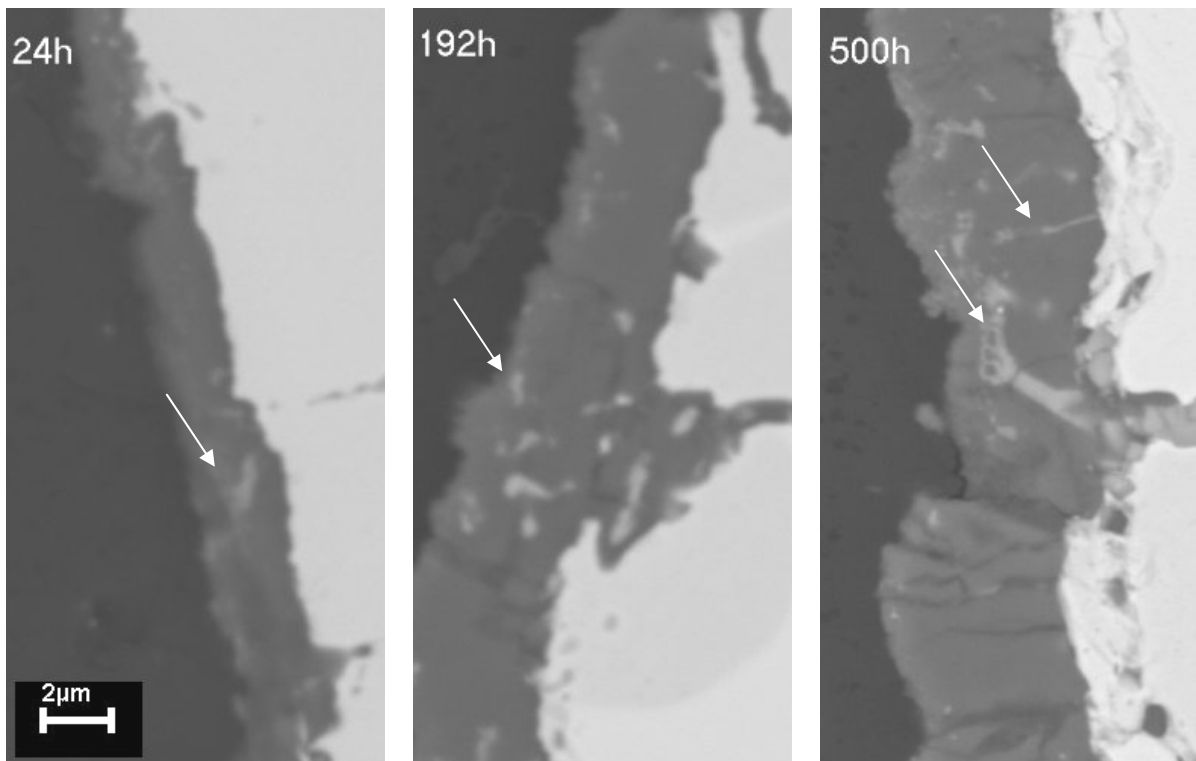


Fig. 3. Cross section micrographs of samples oxidized at 1100°C, showing the presence of yttria (white arrows) inside the alumina layer (BSE images).

Microstructure evolution during heat treatment and isothermal oxidation. After 24, 192 and 500 h at 1100°C, samples were retrieved from the furnace and cooled down. Even for the longest test duration, samples showed only very little oxide spallation after cooling. The cross sections were analysed by SEM and EDX. Fig. 2 shows comparative micrographs of unoxidized and oxidized samples. The BSE contrast was settled to show metallic parts of the samples with a composition contrast. The oxide layer which is not visible on these pictures is shown in Fig. 3. During long term oxidation at 1100°C, changes are induced in the sample microstructure. First of all, during the first 24 h, the Pt-rich surface intermetallic layer is transformed to β -(Ni,Pt)Al by the outward diffusion of

Ni from the underlying NiCoCrAlYTa. The distribution of the elements is reported in Fig.4 for the sample after 192 h oxidation, which is similar to the sample oxidized during 24 h.

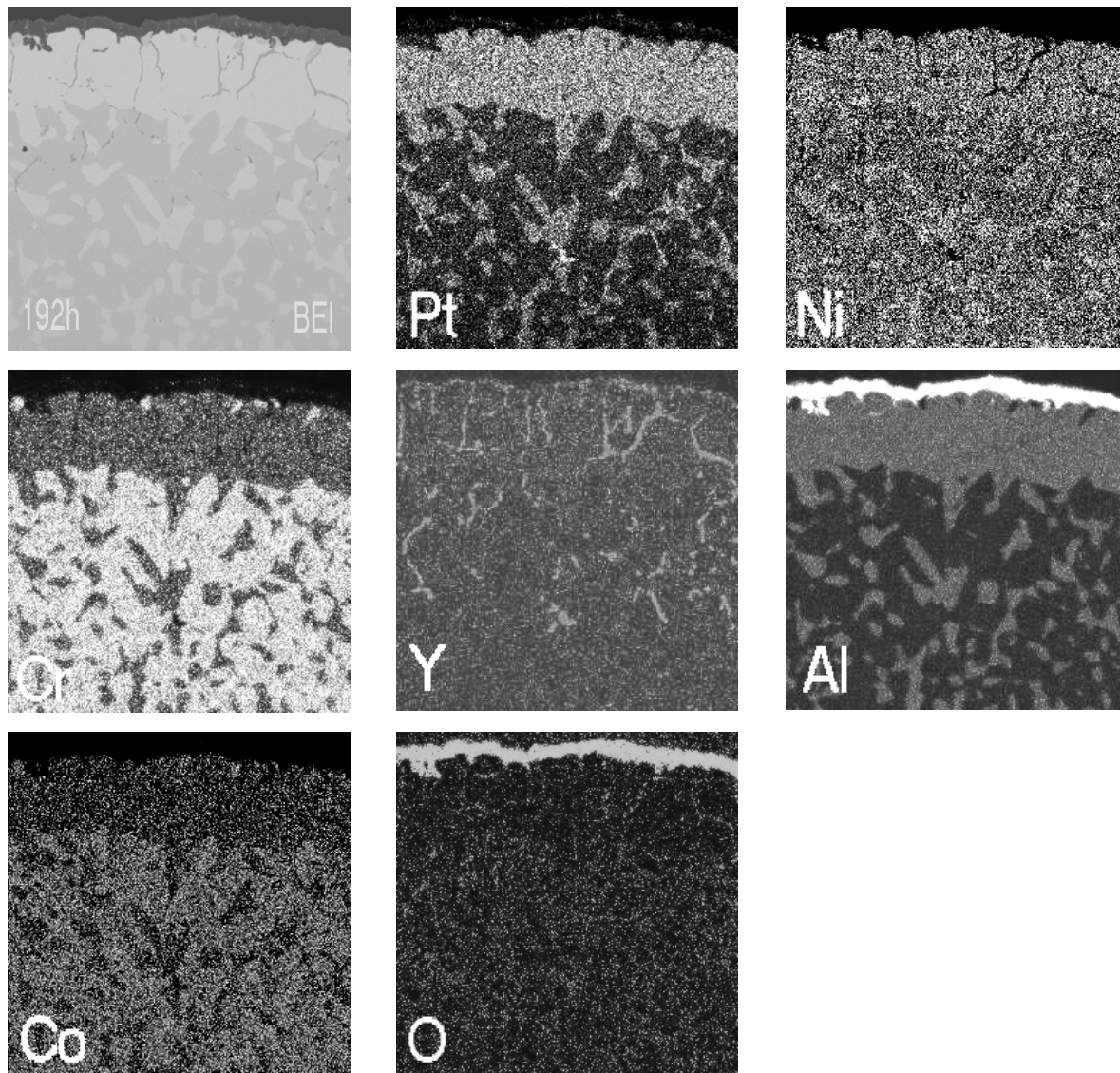


Fig. 4. X-ray map of the cross section of a sample oxidized 192 h at 1100°C.

Beneath that external β -(Ni,Pt)Al layer, microstructural transformations can be observed deep in the NiCoCrAlYTa, leading to a mainly γ -Ni / β -(Ni,Pt)Al microstructure. On these BSE images, Pt containing β -phase appears in bright (e.g. Fig.2d), whereas the same β -phase in NiCoCrAlYTa without Pt appears in dark (e.g. Fig.2a). Platinum inward diffusion can be followed using the image contrast.

Kinetics of the inward Pt diffusion front (dotted line on Fig.2) is reported on Fig.5. These kinetics are slightly sub-parabolic, with a diffusion parameter which can be roughly estimated using the expression $D = x^2/t$ (where x is the thickness of the Pt-rich β/γ layer and t the time). D is decreasing slowly from 10^{-9} cm²/s after 24 h to $4 \cdot 10^{-10}$ cm²/s after 500 h. This diffusion parameter is slightly higher than Al or Ni diffusion coefficients in γ and β phases [6,7] and Pt in β [8]. Fig. 2e shows the microstructure of the entire coating after 500 h at 1100°C. It can be seen that interdiffusion affects the microstructure on a few hundreds micrometers at both external surface and substrate/coating interface.

The thermally grown oxide (Fig. 3) is composed of Y-rich phase and alumina. Some pure yttrium oxide is also detected (white arrows in Fig. 3). The exact nature of the Y containing phase remains to be determined using appropriate techniques (e.g. TEM). A measurement of the oxide thickness on the cross sections, as a function of the oxidation duration is presented in Fig. 6. The evolution of oxide scale thickness as a function of time is subparabolic.

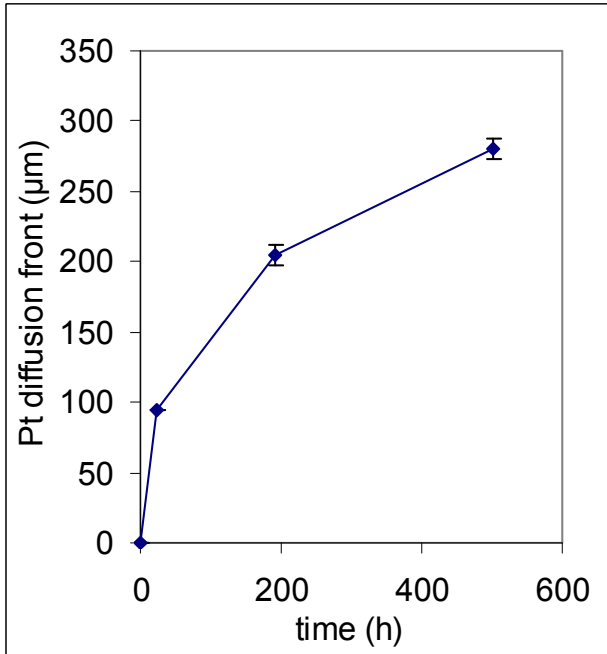


Fig. 5. Pt diffusion front estimated from the change in the microstructure as shown in Fig. 2

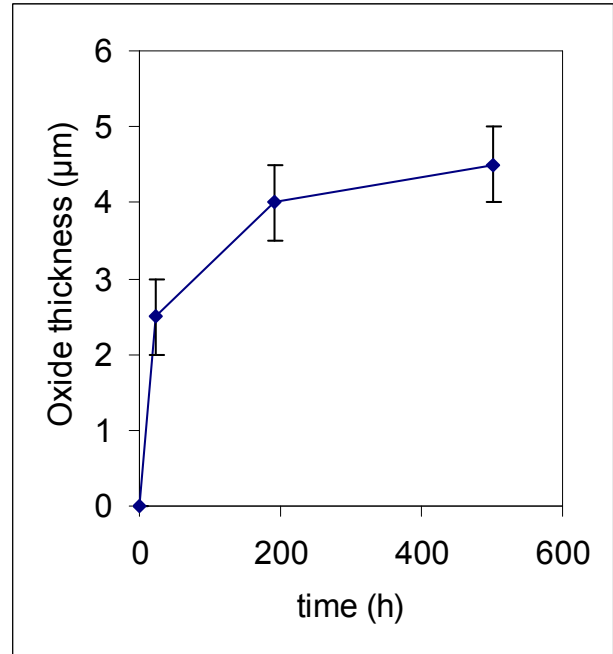


Fig. 6. Alumina layer thickness vs oxidation time, measured on SEM micrographs of samples cross sections.

Assuming that the oxide scale is alumina and protective, the evolution of the parabolic constant “ k_p ” can be calculated using the following equation:

$$k_p = \left(\frac{e_f^2 - e_i^2}{t_f - t_i} \right) \left(\frac{\rho \cdot 3M_o}{2M_{Al} + 3M_o} \right)^2$$

Where “ e ” is the oxide scale thickness at time “ t ”, subscripts “ i ” and “ f ” represent two successive durations, ρ is the oxide density, M_o and M_{Al} are the molar weight of O and Al. This calculation leads to a parabolic constant decreasing with time from $1 \cdot 10^{-6}$ down to $9 \cdot 10^{-8}$ and $2 \cdot 10^{-8}$ $\text{mg}^2/\text{cm}^4/\text{s}$ after resp. 24 h, 192 h and 500 h. The last two values are characteristic of a slow growing alpha alumina layer doped with reactive elements.

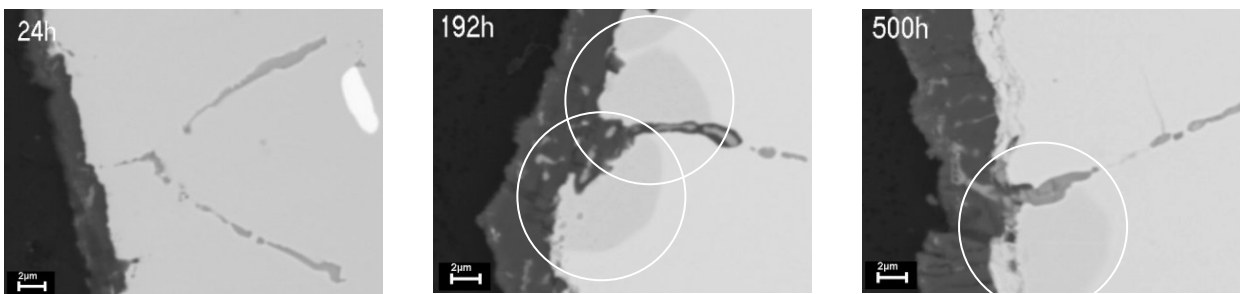


Fig. 7. Intergranular oxidation (alumina around yttrium rich oxide) induced by Y-rich segregated phase in the grain boundaries. Circles indicate Cr rich γ phase below the oxide layer.

For long-term oxidation, Cr outward migration in addition to Al depletion due to oxide growth, leads to a Cr rich γ -Ni phase formation under the oxide layer (white circles on Fig. 7). γ -Ni phase is especially visible close to intergranular oxidation region. Intergranular oxide is composed of alumina around Y-rich core oxide. This observation can be linked to the observation of Y segregation at grain boundaries during sintering. Indeed, X-ray mapping shows Y enrichment at grain boundaries, both inside the β -(Ni,Pt)Al layer and in the γ -Ni/ β -(Ni,Pt)Al region (Fig.8). This Y enrichment increases with heat treatment time. As a consequence, a deep intergranular oxidation due to rapid diffusion of oxygen in the Y-rich oxide occurs. Rapid inward growth of Y-rich oxide pegs was already reported in the literature for MCrAlY coatings elaborated by conventional methods [9], but this phenomenon seems to be enhanced in the present case because of large Y segregation during SPS.

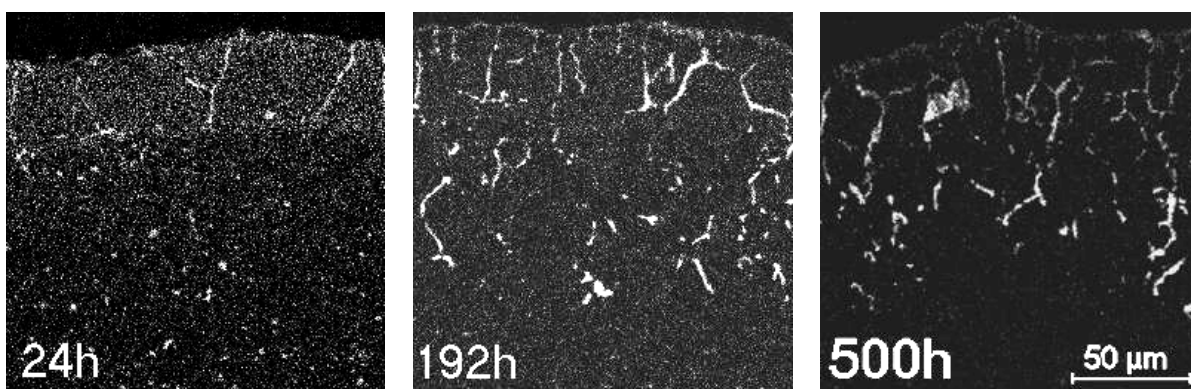


Fig. 8. X-ray map showing segregation of Y during oxidation heat treatment for 24, 192 and 500h at 1100°C.

Conclusions

This work shows first of all, the interesting ability of the Spark Plasma Sintering technique to design fast preparations of new materials, including multi-layered coatings realized in a one-step process. Both powder and foils can be used to prepare coatings. SPS sintered Pt and Al foils on NiCoCrAlYTaNi powder lead to a compact and uniform coating, without porosity or cracks. The external Pt foil prevents the formation of any new carbide during the sintering in the graphite die. During the oxidation treatment at 1100°C, the Pt-rich layer (ξ -PtAl₂ + ϵ -PtAl + β -(Ni,Pt)Al) located at the surface is quickly transformed to β -(Ni,Pt)Al phase by the outward diffusion of Ni from NiCoCrAlYTaNi. Then, Pt diffuses inward following almost parabolic kinetics. Inward Pt diffusion and NiCoCrAlYTaNi/superalloy interdiffusion kinetics are of the same order of magnitude. The isothermal oxidation of the Pt and Al surface-enriched NiCoCrAlYTaNi leads to a compact and adherent oxide scale formed of alumina but also of Y-rich oxide precipitates. Nevertheless, after a transient stage, the oxidation kinetics appears to be controlled by alumina growth with a low parabolic constant of $1.6 \cdot 10^{-8} \text{ mg}^2/\text{cm}^4/\text{s}$ after 500 h at 1100°C. A serious drawback of the fabrication method is the enhanced segregation of Y in the surface layer and in the coating grain boundaries which leads to deep intergranular oxidation. As a consequence, MCrAlY with much lower Y concentration should be tested.

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