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Thermal Barrier Systems and Multi-Layered Coatings Fabricated by Spark Plasma Sintering for the Protection of Ni-Base Superalloys

Daniel Monceau$^{1,a}$, Djar Oquab$^{1,b}$, Claude Estournes$^{2,3,c}$, Mathieu Boidot$^{1,d}$, Serge Selezneff$^{1,e}$, Nicolas Ratel-Ramond$^{1,f}$

$^1$: Institut Carnot CIRIMAT; ENSIACET, 4, allée Emile Monso, BP-44362, 31432 Toulouse, France
$^2$: CNRS; Institut Carnot CIRIMAT; Université Paul-Sabatier, 118 route de Narbonne, 31062 Toulouse France
$^3$: Plateforme Nationale de Frittage Flash du CNRS (PNF2); MHT, Université Paul-Sabatier, 118 route de Narbonne, 31062 Toulouse France

$^a$daniel.monceau@ensiacet.fr, $^bdjar.oquab@ensiacet.fr, $^cestourne@chimie.ups-tlse.fr,
$^dmathieu.boidot@ensiacet.fr, $^eserge.selezneff@ensiacet.fr, $^fnicolas.ratel-ramond@cemes.fr

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Abstract. Aeronautical gas turbine blades, vanes and combustion chambers are protected against high temperature oxidation and corrosion by single or multilayered coatings. These include environmental coatings, generally based on Pt-modified Ni aluminides or MCrAlY overlays (where M = Ni and/or Co), thermal barrier coating (TBC) systems including a ceramic thermally insulating layer, and abradable seals. The present work shows the ability of the Spark Plasma Sintering technique to rapidly develop new coatings compositions and microstructures. This technique allows combining powders and metallic foils on a superalloy substrate in order to obtain multilayered coatings in a single short production step. Fabrication of MCrAlY overlays with local Pt and/or Al enrichments is shown, as well as fabrication of coatings made of $\zeta$-PtAl$_2$, $\epsilon$-PtAl, $\alpha$-AlNiPt$_2$, martensitic and $\beta$-(Ni,Pt)Al or Pt-rich $\gamma/\gamma'$ phases, including their doping with reactive elements. The fabrication of a complete TBC system with a porous and adherent Yttria Stabilized Zirconia (YSZ) layer on a bond-coating is also demonstrated, as well as the fabrication of a CoNiCrAlY-based cermet coating for abradable seal application. Difficulties of fabrication are reviewed, such as Y segregation, risks of carburization, local over-heating, or difficulty to coat complex shaped parts. Solutions are given to overcome these difficulties.

Introduction

Powders which are difficult to sinter by other techniques, such as SiC or WC, have been densified by Spark Plasma Sintering (SPS) without any additives [1]. The reasons for this success are not clearly identified [2]. It was thought initially that plasma was created between grains by the pulse current, but this was not proven. When comparing the technique with other sintering processes, one can notice that 1/ the electric current causes the fast heating of a graphite die by Joule effect and the apparatus arrangement allows a fast cooling [3]; 2/ the sintering is performed in a vacuum chamber with graphite die and punch which impose a very low oxygen partial pressure [2] and 3/ an uniaxial load is applied by the graphite punch.

To the authors’ knowledge, the possibility to coat structural alloys using SPS has never been reported in review papers on coatings fabrication [4], nor in reviews on the SPS technique [3] including a recent review on patents [5]. Only the extensive paper by Orru et al. [1] reports few works on ceramic coatings for structural metallic alloys. Indeed, questions arise about the possibility to industrialise such SPS coating process. Nevertheless, uncoated parts of complex shape as large as 500 mm, are currently in production [5]. In addition, pseudo-isostatic pressure can be obtained by embedding the part to sinter in a not sintering powder [5]. Then, it is reasonable to think that SPS coatings could be produced in a close future as it has been demonstrated for Functionally Graded Materials (FGM) [6]. If so, this process has several advantages including no pollution by chemicals, no dangerous gases, a minimum waste of materials, and a very fast processing.
Moreover, it was shown recently that SPS allows rapid development of new coatings compositions and microstructures, not with the direct objective to industrialize the SPS process but with the goal of fabricating laboratory samples on which properties, such as the resistance to high temperature oxidation, can be studied. It was demonstrated that a fully dense and unoxidized MCrAlY and Al-Pt surface modified NiCoCrAlYTa coating could be prepared in less than 1 h using this process [7-8]. These results were completed by the development of several kinds of Ni aluminides diffusion coatings, including reactive elements (RE) doped Pt-rich ε-Ni/γ'-Ni3Al bond coatings, and the possibility to process a full TBC system in a one step process [2].

The development of such coatings is driven by the objectives of increasing the operating temperature and the durability of gas turbines. Multi-layered coatings are developed to protect single crystal Ni-base superalloy blades against several types of attacks. An ideal coating should be a thermal barrier reducing the operating temperature of the superalloy blade, it should be resistant to erosion and to CMAS corrosion, and should prevent high temperature oxidation and hot corrosion of the superalloy, and finally it should not degrade the mechanical properties of the superalloy [2]. Development of such multi-layered coatings requires numerous fabrication techniques [4] and the cost, complexity and delay to obtain test coupons certainly slow down and limit research works. Then, any shortcut in the development process should allow to test innovative solutions or to optimize existing compositions.

Materials and Processing

The substrates used for this study were 8, 9 or 24.5 mm diameters discs prepared from single crystal rods made of first generation Ni-base superalloys AM1® or AM3® [9]. Before use, the substrate surface was mechanically polished down to 0.25 µm diamond grit for MCrAlY-base coatings or ground to #600 SiC grit for Ni aluminide-base coatings. NiCrAlY, CoNiCrAlY and NiCoCrAlYTa commercial powders (resp. Sultzer-Metco AMDRY® 962, 995 and 997, grain size of 35 µm), pure Pt and Al foils (GoodFellow) with thickness between 2 and 10 µm, Yttria Stabilized Zirconia powder (Tosoh Corporation, with either 8 or 10 mol%Y2O3, grain size of 50 to 200 nm) were used for the fabrication of the systems. For the making of CoNiCrAlY-talc –base cermet, the CoNiCrAlY powder was mixed with 1:20 weight ratio of natural talc particles with an average size around 1.8µm. All samples presented in this study were prepared by SPS (Dr Sinter 2080, SPS Syntex Inc., Japan). This SPS equipment, consists of a pulsed direct current (3.3 ms of duration) generator, a hydraulic press system, a vacuum and water cooled chamber, two upper and lower punch electrodes graphite spacers and finally a control system for the temperature (thermocouples and optical pyrometer), for the environment pressure inside the chamber and for the positioning of the lower electrode on z-axis which allows to follow the shrinkage of the sample. The materials were loaded onto 8, 15 or 24.5 mm inner diameter cylindrical graphite dies. The pulse pattern 12-2 (i.e. 12 pulses followed by 2 rest intervals) recommended by the system manufacturer was used. The temperature was monitored by a thermocouple placed in a small hole located at the surface of the die. A heating rate of 100°C/min was used to reach the final temperature of 950, 1000°C or 1150°C depending of the samples. Dwell time at the desired temperature was between 0 and 30 min. Loads of several kN depending on the systems and corresponding to uniaxial stresses between 16 and 100 MPa were applied during the cycle [2,7,8,10,11]. In order to add controlled quantities of reactive elements in their metallic form (Y, Hf, Si) in Ni aluminide coatings, some of the AM1® superalloy substrates were PVD coated by RF-sputtering before the SPS process [2]. Some of the samples where annealed in secondary vacuum in order to obtain the desired microstructure. For example, it was shown that the combination of Pt and Al foils can be used to obtain ζ-PtAl2, ε-PtAl, α-AlNiPt2, martensitic and β−(Ni,Pt)Al or Pt-rich γ/γ' phases, depending of the thickness of the foils, the temperature and duration of the SPS processing, and the temperature and duration of a post-SPS annealing at 1100°C [2].

Most of the coatings were tested under a cyclic oxidation test. An automatic rig was used. One cycle consists in 4 min heating and 56 min dwell at 1100°C under laboratory air followed by a 15 min cooling to room temperature under a high pressure and filtered air flow. Samples surfaces and
polished cross sections were characterized by metallography, SEM and TEM when necessary, after 0, 300 and sometimes 1000 cycles. Thermogravimetric experiments were also run at 1050°C under synthetic air to determine the oxidation kinetics of bulk CoNiCrAlY-talc mixture after SPS sintering.

Results and Discussion

Fig. 1 shows some architectures which have been fabricated using the SPS process. The process consists in stacking up several layers in the die: the superalloy substrate with or without PVD thin films is covered with metallic foils (Al or Pt) or MCrAlY powder or a mixture of CoNiCrAlY and talc powders and finally a ceramic YSZ powder to realize a TBC system. Several difficulties were encountered during the development of SPS coatings. They were reviewed in [2] and include the measurement of the temperature during the SPS process, the carburization and the Y segregation. Satisfactory solutions were found concerning the measurement of temperature and the carburization [2]. Using this “know how”, the SPS processing of these assemblies at high temperature under vacuum and mechanical load, results in smooth and homogeneous metallic bond coatings without pores or internal oxidation [2,7,8] with a porous YSZ top coat of desired porosity (between 15 and 35 vol%) in order to ensure a low thermal conductivity [11]. It is noticeable that fully dense metallic coatings can be obtained even in the presence of a hole in the substrate when using a powder [7] and without Kirkendall pores when combining pure Al and Pt foils [2]. This is certainly a beneficial effect of the combination of the uniaxial load in a confined die which leads to a pseudo-isostatic stress state, and to the very low oxygen partial pressure in the apparatus which limits the oxidation of the foils and powders and then facilitates their sintering.

Figure 1: Schematic of several stacking used to fabricated coated superalloy systems before introduction in the spark plasma sintering (SPS) apparatus.
Figs. 2-4 present three examples of SPS-processed coatings. In Fig. 2, the coating consists of an overlay NiCoCrAlYTa dense coating modified by an overlay of Pt and Al. Such a coating would be generally fabricated using vacuum plasma spraying of the MCrAlY powder on the superalloy followed by a Pt electrolytic deposition, annealing at 1050-1100°C during several hours, and a vapor phase aluminisation during 1-3 h at about 1100°C. Pt and Al enrichments are realized to improve the oxidation and corrosion resistance of the MCrAlY coating [4]. With the SPS process, only one step of less than 1h is necessary to obtain a sample. Nevertheless, it was shown that this one-step process leads to a high level of Y and Pt segregation at the grain boundaries of the $\beta$-(Ni,Pt)Al top layer. This resulted in Y-rich oxide growth creating heterogeneities in the $\alpha$-alumina protective oxide layer. This could be detrimental during cyclic oxidation, but it has not yet been tested. Only isothermal tests at 1100°C were performed, and it was shown that the oxidation kinetics after 500 h at 1100°C were low [8], see Fig 5.

Fig. 3 shows an example of a TBC system including an AM1® superalloy substrate, a dense Pt-rich $\gamma/\gamma'$ bond coating and a YSZ porous top layer. It was obtained from the following stacking : AM1/ 5µm Pt / 2µm Al / Tosoh TZ8Y powder. An uniaxial force was applied, corresponding to a pressure of 50MPa. The stack was first heated up at 700°C during 10 min and then at 1150°C during 10 min. Heating rates were 100°C/min and cooling rate was 20°C/min. Only one SPS step was necessary to fabricate this system, nevertheless one additional step would be required to obtain RE-doped bond coating. In [2], the fabrication of a full TBC system including a Pt-rich $\gamma/\gamma'$ bond coating doped with a controlled quantity of metallic Y, Hf and Si was reported. The doped bond coating was obtained when the superalloy substrate was first coated with PVD thin layers of controlled thicknesses of metallic Y, Hf and/or Si before the SPS process. It can be noted also that for
the thickest bond coatings, it is also necessary to perform a final annealing of a few hours at 1100°C after SPS in order to obtain the Pt-rich $\gamma/\gamma'$ microstructure. It is remarkable here that SPS process can be conducted without oxidation of the RE elements (no interfacial RE oxide were observed). It is also shown that it is possible to obtain a fully dense bond coating together with a porous and adherent YSZ top coat. This was achieved using nanometric YSZ powder in order to enhance its sintering ability. Finally, it is shown that an interfacial TGO (thermally grown oxide) of alumina can be formed between the bond coating and the ceramic top coat during the SPS process [2, 11].

Another application of high temperature coatings on Ni-base superalloys concerns the abradable seals. The evaluation of the high temperature abradability of coated materials is complex and expensive. Then, it is interesting to test first the high temperature stability, oxidation and corrosion of new candidate materials. Fig. 4 reports a coating fabricated by SPS for this purpose. It consists in a mixture of natural talc and CoNiCrAlY powders. A perfect mixture of the powders could be obtained and a fully dense coating was produced with the SPS process, after 10 min at 1000°C under 100 MPa [10]. Then, the reaction between the talc and the CoNiCrAlY during SPS and during further annealing at high temperature could be studied, as reported in [10]. For example, Fig.4 shows the external surface of the cermet coating after 50 h at 1050°C in laboratory air. Experimental observations by optical and electron microscopy showed that the microstructure of the bulk specimen was constituted with CoNiCrAlY grains, showing a $\beta/\gamma$ structure, covered with fine layers of oxides resulting of the interaction between CoNiCrAlY and talc which decomposed at 1050°C. An external duplex protective oxide scale was also formed consisting in an external continuous layer of spinel MgAl$_2$O$_4$ lying on an internal continuous layer of Al$_2$O$_3$. The underlying CoNiCrAlY grains were depleted in Al leading to the $\beta$-phase dissolution.

After such rapid fabrication of these complex multi-layered systems, large amount of work is necessary to study the properties of these materials. Fig. 5 gathers some preliminary results on the oxidation resistance of the SPS fabricated coatings. The oxidation kinetics of the bulk CoNiCrAlY-talc based cermet was measured using thermogravimetry, but all the multi-layered systems were coated on one side only. Then, oxidation kinetics were evaluated by the measurement of the TGO oxide layer thickness, measured using the SEM on polished cross sections, as a function of time and assuming a parabolic behavior. When several oxidation durations were available, the local calculation of the parabolic constant $k_p$ [mg$^2$/cm$^4$/s] was performed using [12]:

$$e_2^2 - e_1^2 = F^2 k_p (t_2 - t_1)$$

where $e_2$ and $e_1$ are the oxide scale thicknesses at time $t_2$ and $t_1$, and where $F$ is a factor allowing the conversion from the scale thickness to the oxygen mass gain by unit surface area ($F$=0.185 mg/cm$^2$ for a 1µm thick $\alpha$-Al$_2$O$_3$ oxide layer). These evaluations were done after 500 h isothermal oxidation at 1100°C in laboratory air (MCrAlY-Pt-Al) or after 300x1h cycles at 1100°C (TBC systems with RE-doped Pt-rich $\gamma/\gamma'$ bond coatings). Results given in Fig. 5 show the good quality of the fabricated coatings. Indeed, they all demonstrate oxidation kinetics typical of $\alpha$-alumina formers, as it can be seen from the comparison with alumina growth kinetics measured on pure $\beta$-NiAl [13]. It can be seen also that very low oxidation kinetics can be obtained through Y doping of alumina formed on a NiCoCrAlYTa coating modified by Pt and Al which allows the formation of a continuous and protective alumina layer (and despite Y-rich pegs). Thanks to this coating processing, the reactive element co-doping (Y, Hf, Si) effect on high temperature oxidation of Ni-aluminides, including $\gamma/\gamma'$ bond coatings, can be studied in a systematic and reliable manner since the RE elements are added in controlled quantities and at their unoxidized state. This work is in progress.

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Figure 4: Cross section of a CoNiCrAlY+talc–based coating on AM3 superalloy forming an external duplex oxide scale of MgAl₂O₄/Al₂O₃ after 50h oxidation at 1050°C in laboratory air.

Figure 5: Parabolic rate constants of various coatings fabricated by SPS (see text). “85Y” stands γ/γ’ bond coating–base TBC system including a Y PVD coating of 85 nm. α, θ, γ-Al₂O₃ lines refer to oxidation kinetics of pure β-NiAl [13].

References