Influence of process parameters on the microstructural and mechanical properties of plasma sprayed nanostructured YSZ coatings

C. Lamuta, G. Di Girolamo, P. Caliandro and L. Pagnotta

Abstract — Plasma sprayed ceramic coatings can be used for thermal protection of hot-section metal components of turbine engines, in order to improve their durability and efficiency. The presence of nanostructures, deriving from partial melting of agglomerated nanostructured particles, represents an interesting technological solution in order to improve their functional characteristics. In this work nanostructured yttria stabilized zirconia (YSZ) coatings were deposited by plasma spraying. The influence of the main process parameters on their microstructural and mechanical properties was investigated by scanning electron microscopy (SEM) and indentation techniques at micro- and nano-scale. Their porous microstructure was composed of well melted overlapped splats and partially melted nanostructured areas. This bimodal microstructure led to a bimodal distribution of the mechanical properties. An increase of plasma power and spraying distance was able to produce denser coatings, with lower content of embedded nanostructures, which exhibited higher elastic modulus and hardness. With increasing the indentation load the mechanical properties decreased, due to the influence of microstructural defects.

Keywords— hardness, indentation, plasma spraying, thermal barrier coatings, Young’s modulus, zirconia

I. INTRODUCTION

Ceramic coatings are suitable to be employed for thermal protection of Ni-based superalloy turbine components operating in power plants and aircraft engines. Their application allows to improve their high-temperature capability and durability, by reducing the heat flux and the temperature at the metal surface. Significant improvements in terms of engine efficiency and lower pollution are then expected [1]-[2]. A thermal barrier coating (TBC) is usually composed of a metal substrate, a metallic bond coat and a ceramic top coat [4]. The intermediate bond coat (MCrAlY) plays a meaningful role on the adhesion of the ceramic top coat and provides better resistance to the attack typically promoted by oxygen and molten salts in severe working environments [4]. Ceramic materials with low thermal conductivity and heat capacity are good TBC candidates.

Partially-yttria stabilized zirconia (8YSZ) is the most common used TBC material, owing to its satisfactory thermal and mechanical properties (low thermal conductivity, relatively high thermal expansion coefficient, low Young’s modulus, high hardness and toughness) [5]-[6].

It has been reported that significant enhancements can be achieved by using nanostructured materials in substitution of conventional ones. Indeed, the reduction of the grain size typically involves better mechanical strength and toughness [7]-[8].

Plasma spraying is suitable for fabrication of thick porous coatings on complex metal parts. In such process powder particles are injected in the plasma jet by an inert gas, melted and accellerated toward the substrate, where they impact at high speed and quench, thus producing the build-up of a coating with typical microstructural defects such as splat boundaries, pores and microcracks [9]. It is worth noting that single nanoparticles cannot be carried by plasma jet and deposited on the substrate, so that they are commonly pre-synthesized in micronsized particle agglomerates. To this purpose, these agglomerates should be only partially melted to preserve part of their starting nanostructure. On the contrary, if the agglomerates are totally melted, grain growth occurs and the final microstructure resembles that of a conventional coating [10].

In the present work different process parameters were employed for coating manufacturing, in order to control the degree of melting of the powder particles and to obtain coatings with well-tailored characteristics. The morphology and the microstructure of nanostructured YSZ coatings were investigated by scanning electron microscopy (SEM), while Nano and Micro Indentation (NI, MI) were employed to study the evolution of the main mechanical properties, such as Young’s modulus and hardness. A statistical approach was used to study the mechanical properties of YSZ coatings and their relationship with the microstructure.

II. MATERIALS AND METHODS

A. Plasma spraying

Six different sets of YSZ ceramic coatings were deposited on Ni superalloy disks (IN738, φ = 25 mm, thickness = 4 mm). The substrates were sand blasted using an alumina abrasive powder to increase their surface roughness and to improve the mechanical interlocking between coating and substrate. The
substrate roughness, measured using three dimensional optical surface profilometry, was found to be 6.9 ± 1.1 μm. An atmospheric plasma spraying equipment, with a 4F-MB plasma torch with 6 mm internal diameter nozzle, was used for coating deposition. A metallic CoNiCrAlY coating (Amdry 995C, Sulzer Metco) with thickness of 150 μm was previously applied as bond coat on the substrate surface.

Nanostructured partially yttria stabilized zirconia TBCs were then deposited using the nanostructured ZrO$_2$-7wt% Y$_2$O$_3$ powder feedstock (Nanox S4007, Inframat, US). The final thickness of the coatings was of about 300 μm. Six different sets of parameters were employed: three different values of arc current (500 A, 565 A and 630 A) and two levels of substrate-torch distance (80 mm e 100 mm). The other parameters were kept constant and can be summarized as follows: primary gas flow rate (Ar) 40 slpm, secondary gas flow rate (H$_2$) 12 slpm, powder flow rate 28.5 g/min, substrate tangential speed 2086 mm/s. The cross sections of the coated samples were prepared using standard metallographic procedure for ceramic coatings, including low-speed sectioning, cold mounting in vacuum in two-part epoxy resin, grinding, polishing and finishing to 0.25 μm.

B. Microstructure

The morphology and the microstructure of powder feedstock and as-sprayed YSZ coatings were analyzed by scanning electron microscopy (SEMLEO 438 VP, Carl Zeiss AG, Oberkochen, Germany). The SEM pictures were then processed by image analysis software (Image J, U.S. National Institutes of Health, Bethesda, MD, USA) to measure the percentage of molten and semi-molten areas embedded in coating microstructure, and the distribution of the nanostructured areas. The size of the regions used for porosity measurements was 350 x 250 μm$^2$.

C. Mechanical properties

The mechanical properties of YSZ coatings were determined by Micro and Nano Indentation tests. A measuring system of CSM Instruments SA, Peseux, Switzerland, equipped with three objective lenses (with magnitude of 5x, 20x e 100x) was used. The indentations were performed on a portion of the ceramic top coat containing areas with different melting degree and were equally spaced (40 μm for NI and 60 μm for MI) in order to avoid the mutual influence of consecutive indentations [11]. Due to the presence of microstructural defects such as pores and poorly compacted areas, an Adjust Depth Offset operation was set every ten indentations in order to find the height position of the sample surface (acronym ADO in Fig. 1).

NI tests were performed according to a 4x10 matrix (with lines parallel to the substrate) by using a Berkovich tip, a loading and unloading speed of 3 mN/s, a hold time of 10 s and two different values for the maximum load: 8 and 100 mN. MI, distributed according to a 3x10 matrix, were also performed by using a Vickers microindenter with maximum loads of 50 gf and 100 gf and a hold time of 10 s.

Fig. 1 disposition of NI on the top coat cross section. Starting from the top: epoxy resin, top coat, bond coat and metallic substrate (magnitude 5x)

The values of reduced Young’s modulus $E_r$ and hardness $H$ were obtained by load-depth curves, according to Oliver and Pharr theory [12]-[13], and then the experimental data were analyzed by assuming a two-parameters Weibull statistical distribution [14].

III. RESULTS AND DISCUSSION

A. Microstructure

Fig. 2 shows the cross sectional SEM microstructure of nanostructured YSZ coatings produced at the spraying distance of 80 mm and using different values of plasma current (500, 565 and 630 A). The plasma current is proportional to the plasma power and to the temperature of the sprayed particles, so that it can be used to have a good control on the degree of melting of the particle agglomerates. All the coatings exhibited a bimodal microstructure composed of well melted splats (dark grey dense areas in the pictures) and partially melted nanostructured areas (light grey areas) possessing an intrinsic porosity derived from their pre-agglomeration, as shown in Fig. 3 (a). The nanostructured areas are composed of loosely bound nanostructured particles.

Fig. 3 (b) shows the morphology of the related powder particles, so that it can be deduced that the nanostructured zones retained in the final coatings were not affected by complete melting during processing. The inset shows some clusters of nanograined particles with size close to 100 nm. During processing the hot plasma gas penetrated inside the agglomerated particles of the powder feedstock, melting their surface, while their core remained unmelted. The low heat transfer associated to their intrinsic porosity, the short residence time of the same sprayed particles in the plasma jet and the high quenching rate of the solidified splats at the substrate surface are able to reduce the mechanism of grain growth and nucleation, thus preserving great part of the starting nanostructure in the final coating.
As well displayed in Fig. 2, the well melted areas cement the loose microstructure, providing good mechanical integrity. The distribution of the nanostructured areas is more uniform for lower values of plasma current. For increasing values of this parameter the melting degree of the powder particles enhances, thus leading to denser coating with lower content of nanostructured areas. The flight path and the temperature history of the agglomerated particles in the plasma jet affect their distribution in the final coatings. The melting process is strongly related to the temperature distribution in the plasma jet and to the heat transfer to the porous agglomerates.

Table I reports the amount of retained nanostructured areas measured by image analysis along the cross section of nanostructured YSZ coatings produced using different process parameters. At constant spraying distance the percentage of nanozones decreases with increasing the plasma current, due to the better melting of the particle agglomerates, so that denser coatings are produced. This effect is more pronounced at 80 mm. The effect of spraying distance is more pronounced at the lowest value of plasma current. Higher spraying distance involves higher residence time of the sprayed particles in the plasma jet, better melting and thus higher deposition efficiency and higher coating thickness.

Table I. Fractions (%) of retained nanostructured areas measured in YSZ coatings produced using different process parameters (plasma current and spraying distance)

<table>
<thead>
<tr>
<th>Distance/current</th>
<th>500 A</th>
<th>565 A</th>
<th>630 A</th>
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<tr>
<td>80 mm</td>
<td>36 ± 4</td>
<td>23 ± 1</td>
<td>20 ± 4</td>
</tr>
<tr>
<td>100 mm</td>
<td>31 ± 2</td>
<td>25 ± 4</td>
<td>21 ± 1</td>
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It is worth noting that the percentage of nanostructured areas embedded in coating cross section can be properly optimized based on the application the coating is addressed to.

High retention of nanozones (30-40 %) is particularly desired for manufacturing of abradable coatings with relatively low mechanical integrity. These coatings can be used in turbine engines to minimize the bypass flow of hot combustion or cold compressor gases through the spaces between the rotating blade tips and the walls of the shroud, in order to provide seal and improve the efficiency.

On the contrary, lower retention of nanostructures (20 %) is preferable for development of thermal barrier coatings with low thermal conductivity, high structural integrity and resistance to the infiltration of oxygen and molten salts in severe working environments (stator turbine blades and vanes). The presence of nanostructured areas with low sintering rate can counteract the high-temperature densification of YSZ coatings, which negatively affect the compliance and the thermal property, thus retarding extended microcracking and TBC delamination [10].

To this purpose, it has been reported that the presence of nanozones plays a significant role on the thermal shock resistance and durability of TBCs, because they act as crack arresters in the case of microcracking promoted by thermal stresses produced by thermal expansion mismatch between overlapped layers, thus increasing the fracture toughness [7]-[15]. Otherwise, microcracks tend to easily grow in more dense areas.

Fig. 4 shows the fractured cross section of the nanostructured YSZ coating: the morphology of well melted areas can be appreciated in.

![Fig. 2 cross sectional SEM microstructure of nanostructured YSZ coatings deposited at spraying distance of 80 mm and various plasma current levels (a) 500 A, (b) 565 A and (c) 630 A](image1.png)

![Fig. 3 (a) cross sectional SEM microstructure showing the morphology of retained nanostructured areas; (b) a view of agglomerated nanoparticles in the powder feedstock with detail of zirconia clusters](image2.png)
Columnar grains with diameter in the range from 50 to 300 nm are detectable. They are oriented along the direction of grain growth and derived from heterogeneous nucleation at splat boundary produced by the heat flow released by the crystallization of the previous deposited splats. Some equiaxed grains can be also observed at splat boundary. They are produced by homogeneous nucleation, occurring when the heat loss promoted by cooling at substrate is higher than the heat released by crystallization [15].

B. Mechanical properties

Tables II and III summarize the values of Young’s modulus, micro and nanohardness measured on the cross sections of nanostructured YSZ coatings, deposited at spraying distance of 80 and 100 mm, respectively, and using different values of plasma current parameter. The measured values magnitude is in good agreement with that of results in literature [16]-[17].

It should be noted that the mechanical properties tend to increase with increasing the plasma current and the spraying distance. Specifically, at constant spraying distance, for increasing values of current, an average increase of 9% and 30% for Er and 13% and 60% for H was observed, from nanoscale to microscale, respectively. Instead, the influence of spraying distance is less prominent. At constant current value, for increasing values of torch-substrate distance, an average increase of 4% and 7% for Er and 3% and 34% for H was recorded, from nanoscale to microscale. It should also be noted that the values of mechanical properties exhibited large scattering.

Fig. 5 shows the load-depth (P-d) curves obtained by nanoindentations performed in the melted areas (grey line) and in partially melted ones (black line), respectively. The curves refer to coatings produced at 500 A and 100 mm, but similar behaviour was noticed for all the other samples. The parameters used for NI were: maximum load 100 mN, loading and unloading speed 3 mN/s, hold time 10 s.

It is possible to observe that in the melted phase lower maximum penetration was noticed (709 nm versus 2056 nm in the partially melted phase) as well as a higher unloading curve slope. This suggests that the melted phase is characterized by higher stiffness and hardness in comparison with the partially melted area [12]-[13].

Indeed, as shown in Fig. 6, the size of the imprint is bigger in partially melted area. The nanostructured areas are characterized by porosity at nanoscale which reduces the cohesion between the agglomerated nanostructured particles. In addition, curves in Fig. 5 show that melted phase doesn’t reveal any creep phenomenon, whereas the unmelted one is affected by it: in fact, it presents a depth increase during the hold time at the maximum load. Based on the observations herein reported, one can conclude that the increase of the mechanical properties, observed in Tables II and III, is related to the increase of the melted fraction in YSZ coatings when higher values of current and distance are employed (Table I).
The usage of increasing current values involves higher plasma power, higher temperature of the sprayed particles and therefore lower retention of nanostructured areas and higher coating density. As previously reported, higher distance involves higher residence time of the sprayed particles in the plasma jet and better degree of melting, even if the effect of distance on the experimental trend of the mechanical properties was not always consistent, probably because of a kind of mutual influence with current. This aspect could be analyzed in future works by performing an experimental plan that provide a third level of torch-substrate distance and more in-depth analysis. As clearly observed in Tables II and III, the values of the mechanical properties measured at microscale are lower than those obtained at nanoscale, because of the larger analyzed volume and the higher influence of typical defects embedded in coating microstructure, such as coarse pores, splat boundaries and microcracks.

Moreover, for each Indentation technique employed, as the indentation load rises the analyzed volume grows and the same microstructural defects becomes more significant, enough to bring down the mechanical properties, that result always more averaged and far from those of bulk stabilized zirconia [10]-[11].

Further analysis showed that the mechanical properties don’t change across coating thickness and their variation is so small to be covered by the high scattering of the results (related to the different characteristics between melted and partially melted phases). In order to understand the reasons of this high scattering, two series of NIs were performed on the areas with different morphology, by using a maximum load of 8 mN and a time for loading and unloading of 10 s. Fig. 7 shows some of the load-depth curves obtained.

It is interesting to notice that the curves related to the melted area (continuous lines) are very close and reproducible, whereas the curves acquired during indentation in the unmelted area (dashed lines) are somewhat different and dispersed. The well melted area is, in fact, characterized by lower scattering in the mechanical properties, whereas the second one exhibits widely scattered data (Table IV), typical of structures produced by nanostructured agglomerates assembly and characterized by intrinsic porosity.

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Table IV summarizes the mean values and the standard deviations of the elastic modulus and hardness for both these areas.

<table>
<thead>
<tr>
<th>Mechanical properties</th>
<th>Melted area</th>
<th>Unmelted area</th>
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<tbody>
<tr>
<td>$E_r$ (GPa)</td>
<td>196 ± 29</td>
<td>131 ± 61</td>
</tr>
<tr>
<td>$H$ (GPa)</td>
<td>15.8 ± 2.3</td>
<td>9.0 ± 7.8</td>
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</table>

These data can be used to predict the mechanical properties of nanostructured coatings, by using the typical mixture law: $X = X_m * v_m + X_{nm} * v_{nm}$, where $X$ represents $E_r$ or $H$ of the coating, $X_m$ and $X_{nm}$ Er and H of the melted and unmelted phases, respectively, $v_m$ and $v_{nm}$ the corresponding volumetric...
fraction. Indeed, the nanostructured coatings can be considered as a composite consisting of two materials, melted and partially melted phases.

Fig. 8 shows the distribution of Er and H, in a bilogarithmic scale [14], for the well melted and unmelted areas, by assuming a two parameters Weibull distribution for the mechanical properties. The data can be approximated with a linear regression curve. On the same graph, the values of shape and scale parameters are reported. According to the previous assertions, the melted phase, characterized by less scattered data, presents greater values of \( m \). The probability density functions of Er and H are plotted, respectively, in Figs. 10 (a) and (b), in grey for the melted area and in black for the partially melted one.

The sample obtained by merging the experimental data related to melted and unmelted areas can be considered like a coating with the 50% of the two phases. The analysis of the distributions concerning this kind of sample can be very useful for the prediction of the mechanical properties of any other nanostructured coating. For this purpose, in Fig. 9, Er and H Weibull plot of this simulated coating are shown, while Figs. 10 (a) and (b) show (dashed lines) the related probability density function (obtained as a weighted average of the probability density of the data referred to single zones). It can be noted that the points related to partially melted phase are so scattered that they contaminate the data of the second section, concerning the melted area, and go also beyond this region (in this example it is just a point). The slope of the mixed section (the second one) increases by decreasing the level of contamination. Despite the data merging, the bimodal behaviour of the coating can be clearly observed, due to the change in the slope of the Weibull plot. In order to find the transition point between the two regions the \( R^2 \) statistics analysis can be used [10]. It should be noted that the presence of points above the mixed zone may generate incorrect interpretations of the data distribution, by suggesting, erroneously, the existence of a third phase, and then a trimodal distribution. Fig. 11 shows the trends of the mechanical properties for all the coatings produced in this work and tested by Nano Indentation at 8 mN.

In all the cases a bimodal Weibull distribution can be noticed, as also observed in any previous works [10]-[16]. The zone in the graph characterized by lower values of H or Er reflects the mechanical behavior of the partially molten phase and it is characterized by lower slope, owing to greater scattering, whereas the second one is characteristic of the mixed area. It is interesting to notice that, at constant torch-substrate distance, as current value rises the slope of the second regression line increases: this is caused by the increase of the degree of melting of the sprayed particles which results in lower probability of contamination of the data pertaining to the molten zone. Note that, at constant current level, the increase of the torch-substrate distance produces different trend, but the results are in good agreement with the volume fractions of nanostructured areas listed in Table I.

The results obtained by NI tests performed at maximum load of 100 mN showed similar behaviour but less noticeable changes in slope between the interpolating sections were detected. This effect is the consequence of the greater size of the volume involved during NI at higher load, which mediates the local properties and makes the bimodality of the distributions more difficult to be observed.

In turn the results obtained by Micro Indentation for the coatings produced at 500 A and 100 mm are shown in Fig. 12. The second region of the distributions of MI data exhibit lower slopes with respect to the first one, unlike NI tests, and in agreement with the data reported in literature [10]-[16].

This behaviour can be addressed to the scale effect for which microcracks and globular pores embedded in the molten...
areas are responsible of data scattering, since higher volume of material was under analysis [10].
Therefore at higher indentation loads the data distribution is almost single-mode, as shown in Fig. 12 (b). Similar behaviors was observed for the other five specimens produced with different values of current and torch-substrate distance.

IV. CONCLUSION

In this work the influence of some process parameters (plasma current and stand-off distance) on the microstructural and mechanical properties of nanostructured YSZ coatings was investigated. The partial melting of the nanostructured particle agglomerates produced the formation of a bimodal microstructure composed of well melted splats and semimolten areas. Columnar and equiaxed grains were observed in melted splats, while the partially melted areas did not suffer grain growth and retained porosity at nanoscale. An increase of plasma current promoted the increase of the particle temperature, improving their melting degree and the density of the coatings.

The reduction of the retained nanostructured areas produced significant increases of Young’s modulus and hardness values. The effect of the torch-substrate distance was more significant at lower current values. The Nano and Micro Indentation tests, performed at various loads, in conjunction with Weibull statistical approach, revealed that the bimodal microstructure involved a bimodal distribution of the mechanical properties, which tended to disappear with increasing the indentation load. The elastic modulus and the hardness decreased with increasing the indentation load, because of higher analyzed volume and stronger influence of the microstructural defects.

This is particularly promising in the purpose to predict the mechanical behaviour of nanostructured coatings.

The development of a reliable procedure allowing a proper control of the percentage of the nanostructured areas embedded in coating microstructure in the purpose to obtain well determined mechanical characteristics, is not easy to be achieved and will require further investigations.

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