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TEXTURE ANALYSIS IN ALUMINA PLASMA SPRAYED COATINGS

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Abstract

An original investigation of the crystallographic texture in alumina plasma sprayed coatings has been made by X-ray diffraction and transmission electron microscopy. A fibre texture has been revealed in these alumina coatings. The (100) base plane of γ Al_2O_3 is predominently parallel to the coating surface. The texture intensity increases from the surface in contact with the metal to the top surface of the coatings. After annealing the textured γ Al_2O_3 coatings at 1200°C, we have studied the relationships between γ and α Al_2O_3 phases.

Introduction

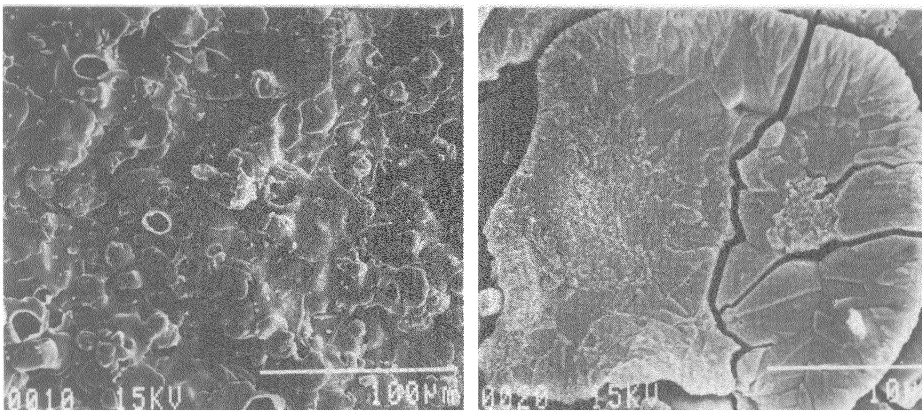
For orthopedic applications, a superficial porous ceramic layer may improve the fixation of metallic implants in bones. Alumina is often used as porous plasma sprayed coatings.

Adhesion of thick coatings is function of microstructure and residual stresses level. In X-ray diffraction analysis of residual stresses, crystallographic texture effects has been revealed. The crystallographic texture has to be taken into account in the X-ray diffraction determination of residual stresses. Then, the coating texture has been analysed by metallographic observations, X-ray diffraction and transmission electron microscopy.

Coating structure

In the plasma spraying process, α Al_2O_3 powders are injected in a plasma flame where they are changed into molten droplets. Droplets are shot on to a grit-blasted metallic substrate where they splash, cool and solidify.

As-sprayed coatings consist predominently of γ Al_2O_3 phase. The specific microstructure of alumina plasma sprayed coatings is formed of few hundred micrometers thick overlapping of solidified platelets (fig 1a). Their diameter is about 30 μm. The particles are bonded together by strong cohesive forces and they form a porous layer adherent to the surface of the substrate.



a) Overlapping of solidified platelets b) Microstructure of platelet

Figure 1 : Microstructure of coating

A chemical etching of the surface brings into view the microstructure of solidified platelets (fig.1b). It consists of elementary crystallites of about 1 μm in diameter. The crystallite morphology is not constant in a platelet. In the periferic area, they are radially elongated. They propagate from the core and terminate at the rim of the platelet. In the core area, they are equiaxial grains which correspond to a columnar solidification.

X-ray diffraction

i) X-ray texture analysis :

The crystallographic texture of a polycrystalline single phase material is defined by the orientation distribution function (ODF) of its crystallites [1] :

$$f(g) = (dV/V) / dg \qquad g = \{\varphi_1, \phi, \varphi_2\}$$

where dV/V is the volume fraction of material in which the crystal axes have the orientation g with respect to the macroscopic sample coordinate system. In the case of coatings, the sample coordinate system is given by longitudinal, transverse and normal directions. In the case of cubic γ Al_2O_3 the crystal coordinate system is chosen such that x = [100] and y= [010] . The relative orientation g of these two coordinate systems is specified by the Euler angles φ_1, ϕ, φ_2. The ODF cannot be measured directly. The distribution function f(g) can be calculated from several measured pole figures. X-ray diffraction gives the pole density functions (pole figure) :

$$P_h(w) = (dV/V) / dg \qquad g = \{\alpha, \beta\}$$

corresponding to the orientation distribution of particular crystallographic direction h, with respect to the various sample direction w represented by its spherical polar coordinates($\alpha = 0°$ is the substrate normal direction ; $\alpha = 90°$, $\beta = 0°$ is the longitudinal direction).

ii) Experimental results :

In our case, three pole figures (400), (440) and (444) of the γ Al_2O_3 phase were measured in steps of $\Delta\alpha = 4°$ and $\Delta\beta = 3.6°$ using Co Kα radiation.

The texture is apparently axisymmetric with respect to the substrate normal direction, as shown on figure 2.

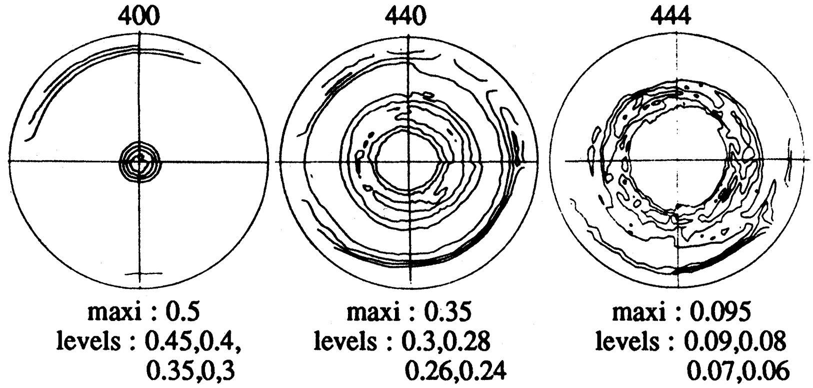


Figure 2 : Experimental pole figures of coating surface.

The ODF of an alumina coating is shown on figure 3. The distribution function has its maximum value at the line $\phi = 0°$ and $\varphi_2 = 0°$, and independent of the angle φ_1. This corresponds to the (100) base plane parallel to the coating surface. This texture type is called fibre texture. The textured material volume ratio ($\phi = 0° \pm 10°$ independent of φ_1 and φ_2) is about 35 %.

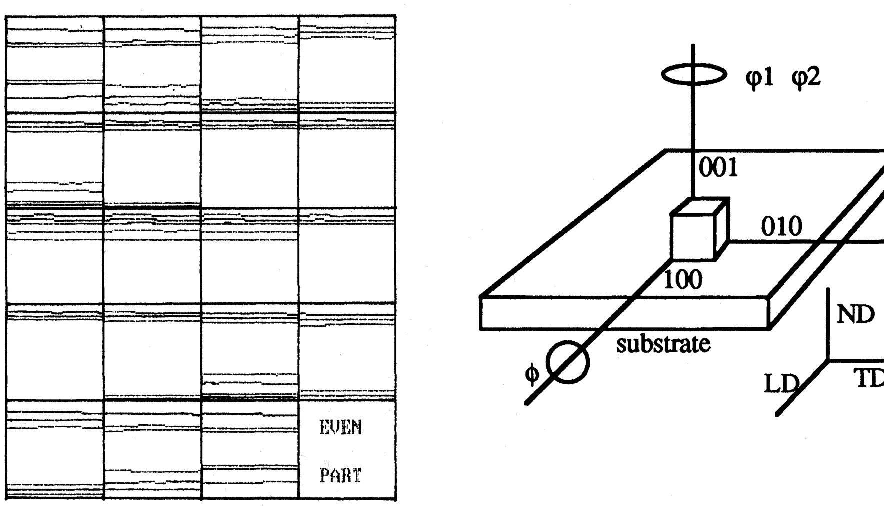
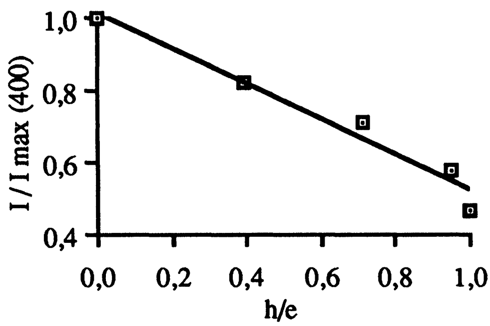


Figure 3 : Orientation distribution function (φ_2 Sections) :
Fmax = 3, levels (% of Fmax) = 90, 70, 50.

A coating has been removed from its metallic substrate by chemical etching. Then, the pole figures (400), (440) and (444) have been measured on the inner and outer surfaces. The same analysis has been made in the coating depth after succesive removing of layers by polishing. The corresponding one-dimensional sections through the (400) pole figures show that the texture intensity increases in the coating thickness from the inner surface to the outer surface. We have plotted X-ray diffraction intensity I for (400) plane versus analysis depth in the coating, on figure 4.



coating thickness e = 0.38 mm
X-ray penetration = 0.06 mm
h/e = 0 outer surface
h/e = 1 inner surface
h/e > 0.5 diffraction on outer surface
h/e < 0.5 diffraction on inner surface

Figure 4 : X-ray diffraction intensity I for (400) peak versus analysis depth.

Transmission electron microscopy

i) T.E.M. texture analysis :

First, we have obtained selected area diffraction (SAD) patterns on a group of adjacent crystallites. They show some anomalies on the density of the diffraction rings as result of a texture. Then, we have made a statistical study of the crystallographic orientation of a group of crystallites. For each crystallite, we have determined the [001] zone axis using the stereographic method; the stereographic projection has been established from the angular positions of three wave vectors of the crystals given by a rotation-tilt specimen holder. Thus, we determine the minimum angular distance of a (100) plane with respect to the coating plane for each studied crystallite.

ii) Experimental results :

It is very difficult to obtain a complete thinned alumina platelet of the coating layer prepared by mechanical thinning (dimple grinding) and ion milling at last. This is probably due to the high level of residual stresses in the coating bringing to the bending and fragmentation of thinned platelets.

However, T.E.M. observations of the platelet fragments reveal the elongated and equiaxial grains with very different sizes from 0.1 μm to 5 μm.(fig. 5).

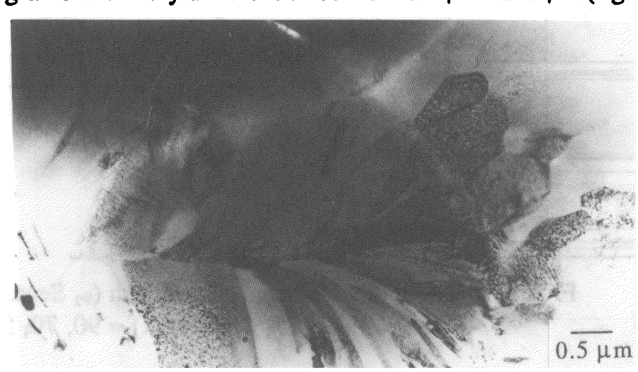


Figure 5 : TEM on a platelet fragment.

The smallest grains have not been investigated. Indeed, the minimum field of the selected area is 0.3 μm in diameter. The indexation of diffraction patterns has been carried out only on crystallites with a size larger than 0.3 μm.

Moreover, our observations reveal that the largest grains are slightly curved, so that they are not wholly in the exact Bragg position. Then, we have chosen to consider their medium orientation.

The specific orientation of about 50 crystallites has been determined. The ratio of the crystallites with an angular distance smaller than 10° of a (100) plane with respect to the coating plane is 30 %. This ratio of 30 % is significant. However, we can not consider this oriented crystallite ratio as a textured material volume ratio because of the large range of crystallite sizes.

Discussion

i) As-sprayed coating texture :

Some results have been published on the microstructure of plasma sprayed coatings [2,3]. By S.E.M. and T.E.M. we have shown the columnar microstructure of alumina plasma sprayed coatings. This can be explained by cooling mechanisms and heat flow directions when a droplet is solidifying [2].

In the core region (where there is a good adhesion on the substrate) the heat is extracted through the substrate, and the solid liquid interface moves parallel and away from the substrate. In the peripheral areas (where there is not a strong adhesion to the substrate), the heat is not extracted through the substrate, but rather through the core region. This is clearly indicated by the radially elongated grains which terminate at the rim of the platelets.

The (100) preferential crystallographic orientation, in our alumina plasma sprayed coatings, is known to be, in c.f.c. metals, the easiest direction of heat extraction [4]. In accordance with the projection conditions, we have been able to change the texture intensity in these coatings. Moreover, an additive of 3 % TiO_2 in the alumina powders enables to obtain a coating with no evidence (by X-ray diffraction) of a crystallographic texture in the γ Al_2O_3 phase. Perhaps, that is why a texture analysis by T.E.M. in alumina plasma sprayed coatings [3] has not shown any evidence of a crystallographic texture. Moreover, the texture intensity of our coatings is poorer than that of physical vapor deposited coatings and that of laminated metals.

We propose that the texture intensity gradient in the coating thickness is due to the variation of platelet coolings. For the first layers of platelets, the cooling is very rapid (on the cold substrate), without any possibility of a preferential crystallographic direction of solidification. When the coating thickness increases, the under layers form a thermal barrier which slows down the heat extraction of the new layers. Then, the preferential crystallographic direction of solidification (001) can appear.

ii) Relationships between γ and α Al_2O_3 phases :

By analogy with the Fe_2O_3 phase transformations, the following crystallographic relationships have been set up for $\gamma\ Al_2O_3 \rightarrow \alpha\ Al_2O_3$ transformation [5] :

$$\{1\,1\,1\}_\gamma \,//\, \{1\,1\,\bar{2}\,0\}_\alpha \quad \text{and} \quad \{1\,1\,1\}_\gamma \,//\, \{0\,0\,0\,1\}_\alpha$$

The alumina plasma sprayed coating gives the possibility of experimental verification.

The γ Al_2O_3 phase (c.f.c.) of the coatings can be transformed into α Al_2O_3 phase (h.c.) by annealing at 1200°C. Then, a different preferential crystallographic orientation appears in the annealed alumina coatings. This newly formed texture in the

α phase is poor. The (1 1 $\bar{2}$ 6) and (1 0 $\bar{1}$ 4) planes of the α phase seem to be parallel to the coating plane when the (1 0 0) plane of the γ phase was parallel to the as-sprayed coating plane.

The experimental relationship { 1 0 0 } γ // { 1 1 $\bar{2}$ 6 } α gives ;

$$\{111\}_\gamma / \{0001\}_\alpha = 12° \quad \text{and} \quad \{111\}_\gamma / \{11\bar{2}0\}_\alpha = 5°$$

and, the experimental relationship { 1 0 0 } γ // { 1 0 $\bar{1}$ 4} α gives :

$$\{111\}_\gamma / \{0001\}_\alpha = 16° \quad \text{and} \quad \{111\}_\gamma / \{11\bar{2}0\}_\alpha = 4°$$

The angular distances between (1 1 1) γ and (1 1 $\bar{2}$ 0) α from our two experimental relationships are 4° and 5°. These angular distances are small in comparison of experimental angular errors. Then, experimentally we are in good agreement with the following relationship of the literature :

$$\{111\}_\gamma \,//\, \{11\bar{2}0\}_\alpha$$

But, for alumina coatings a small rotation from exact topotaxy has been found experimentally for the second relationship of the literature :

$$\{111\}_\gamma / \{0001\}_\alpha = 15 \pm 5°$$

Conclusion

The possibility of a crystallographic texture in alumina plasma sprayed coatings has been revealed by X-ray diffraction and T.E.M.. This (1 0 0) texture is probably due to the combination of plastic deformation, during the flattening of molten droplets, and to the heat extraction on the substrate. A future EBSP (Electron Back Sctattered Pattern) -analysis will give the exact orientation of crystallites in the core and in the peripheral regions in a platelet. In fact, the coating is formed of textured platelets.

ODF will be introduced in theoretical models of mechanics. Then, we will be able to know if all problems in residual stress determination by X-ray diffraction are due to the texture effects.

Lastly, it seems that the residual texture in the annealed alumina coatings is a consequence of crystallographic relationships between α and γ alumina phase.

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