INFLUENCE OF THE Fe22Cr5Al SUBSTRATE SURFACE FINISH, ON THE MORPHOLOGICAL TEXTURE OF Al$_2$O$_3$ GROWTH, STUDIED BY SEM-EDXS AND XRD

J. I. Guzmán-Castañeda[a], A. García-Bórquez[b]*, K. J. Lozano-Rojas[a], J. Tanori-Córdova[c]

[a]ESIQIE-IPN, Ed. 6-UPALM, 07738 México, D.F. [b]ESFM-IPN, Ed. 9-UPALM, 07738 México, D.F. [c]DIPM-UNISON, 83000 Hermosillo, Sonora.

*Corresponding author, E-mail: borquez@esfm.ipn.mx, phone, (55) 5729-6000 Ext. 55330.

ABSTRACT

Alumina may display a complex polymorphism depending on the production method. Starting from Al-solution, their amorphous or crystalline structures as well as its phase are strongly determined by the precursor, temperature, pressure, pH, etc. However, starting from Al containing solids, there is a lack of information about the procedure to obtain a determined phase and concerning the influence of its surface finish on the morphological texture of the alumina growth. In this work, Fe22Cr5Al plates were subjected to mirror polishing and mechanical erosion. The fractal dimension determined from optical images was 2.084 for mirror polished samples and 2.472 for the eroded ones; these values give a comparative element for the starting surface finishing, because a higher fractal dimension value means an increasing surface roughness. Thereafter, both samples were oxidized at 900 °C, 24 h in air. By SEM, the polished-oxidized samples show a passivation layer formed by agglomeration of relative small particles, of around 400 nm; whereas the eroded-oxidized samples show whiskers with 100 nm thickness. The fractal dimension determined from SEM images was 2.511 for the polished-oxidized samples and 2.582 for the eroded-oxidized ones. EDXS analysis detects Al and O enrichment at the surface and XRD identifies the θ and α phases of alumina, for both kind of surface finish. Results demonstrate that the difference found in the oxide morphology is directly related to the surface finish before oxidation. This in turn is attributed to the difference in the surface defects density acting as nucleation centers for alumina whiskers.

Keywords: Surface-finish, Morphological texture, Alumina-growth, Fractal dimension, SEM-EDXS, XRD.

INFLUENCIA DEL ACABADO SUPERFICIAL DEL SUSTRATO Fe22Cr5Al, EN LA TEXTURA MORFOLÓGICA DE CRECIMIENTO DE Al$_2$O$_3$, ESTUDIADA POR MEB-EDEX Y DRX.

RESUMEN

La alúmina puede mostrar un polimorfismo complejo según el método de producción. Partiendo de soluciones de Al, sus estructuras amorfa o cristalina, así como su fase son determinadas fuertemente por el precursor, temperatura, presión, pH, etc. Sin embargo, partiendo de sólidos conteniendo Al, no existe información sobre el procedimiento para obtener una fase determinada, ni de la influencia que el acabado superficial pueda tener en la textura morfológica del crecimiento de la alúmina. En este trabajo, placas de Fe22Cr5Al se sometieron a pulido especular y erosión mecánica. La dimensión fractal fue de 2.084 para las placas pulidas y de 2.472 para las erosionadas; esto da un punto de comparación del acabado superficial inicial, debido a que una dimensión fractal más alta significa una rugosidad superficial mayor. Ambas muestras se oxidaron a 900 °C por 24 h en aire. Las placas pulidas-oxidadas muestran una capa pasivante formada por aglomeración de partículas de 400 nm; mientras que las erosionadas-oxidadas muestran triquitas con espesores de 100 nm. La dimensión fractal fue de 2.511 para la superficie pulida-oxidada y de 2.582 para la erosionada-oxidada. En ambas superficies se detecta enriquecimiento de Al y O perteneciente a las fases θ y α de la alúmina. Se concluye que la diferencia en la morfología del óxido crecido, está directamente relacionada con el acabado de la superficie pre-oxidación. Esto a su vez se atribuye a la diferencia en la densidad de defectos en la superficie, los cuales actúan como centros de nucleación de las triquitas de alúmina.

Palabras claves: Acabado superficial, Textura morfológica, Crecimiento de alúmina, Dimensión fractal, MEB-EDEX, DRX.

INTRODUCTION

Current studies on surface in alloys, oxides, thin films etc., are directed to correlate changes in their physical or chemical properties with the modification in their morphology and continue to improve the methods of synthesis and processing. Oxides such as alumina, zirconia, cordierite, aluminum titanate, magnesia, calcite among others, have diverse applications due to its great stability to environment, by being more stable thermodynamically speaking, and easy to manufacture in comparison with other materials [1].

In particular alumina is applied in abrasives [2], thermal insulators, passivating protective layers, refractory materials, [3, 4, 5], catalytic supports [6, 7, 8, 9], biomedical materials, such as prostheses and implants [10], semiconductors with photoluminiscent [11] or photovoltaic [12] properties, dielectric materials [13] among many others. Each of these applications demands a different surface and therefore specific surface morphology of the alumina.

Alumina comes from a family of $Al \cdot (OH)_3$ of metastable transition and is formed through the increase of temperature in hundreds of Celsius degrees [14]. When the solution is heated in air, it decomposes in a microporous oxide having a surface area of hundreds of square meters per gram. Depending of pressure, PH and temperature [15], the four polymorphic transformations, γ, δ, θ and α, can be obtained with their respective structural changes; what occurs in this process is that firstly it losses its entire inner surface when it collapses, and finally reaches up to 1200 ºC, the stability of an extremely hard and crystalline phase, the alpha alumina or corundum, which has a melting point of 2100 °C [14].

In contrast, when the aluminum oxide is formed from aluminum or alloys aluminium content, the crystalline nature of the oxide is determined only by the temperature [16], but the surface finish where the oxide is generated, can greatly influence the morphological characteristics of the growth, as will be demonstrated in this paper.

MATERIALS AND METHODS

1. - **Surface polish:** To obtain near irregularities-free surfaces, samples of Fe22Cr5Al were polished to obtain a mirror-type surface by metallographic techniques, up to diamond paste.

2. - **Mechanical erosion treatment:** To create substantial amounts of defects and irregularities on the surface of samples of Fe22Cr5Al, these were roughed with abrasive paper of 500 μm average grain size.

3. - **Heat treatment:** Subsequently to steps 1 and 2 the samples were heat treated to perform an oxidation process, at a temperature of 900 °C for 24 hours. The muffle furnace used was Carbolite brand, model HTC 1500.

4. - **Morphological and composition characterization:** The samples surface was characterized before and after the steps 1, 2 and 3 using Optical Microscopy (OM), Scanning Electron Microscopy (SEM-FEG), Energy Dispersive X-ray Spectroscopy (EDXS) and X-Ray Diffraction (XRD).

RESULTS

Analysis by Optical Microscopy. The surfaces of the samples of Fe22Cr5Al were observed in the optical microscope Olimpos PM3 after the polish and mechanical erosion treatments, in order to compare the surface finish obtained in each of the preparations (Figure 1).
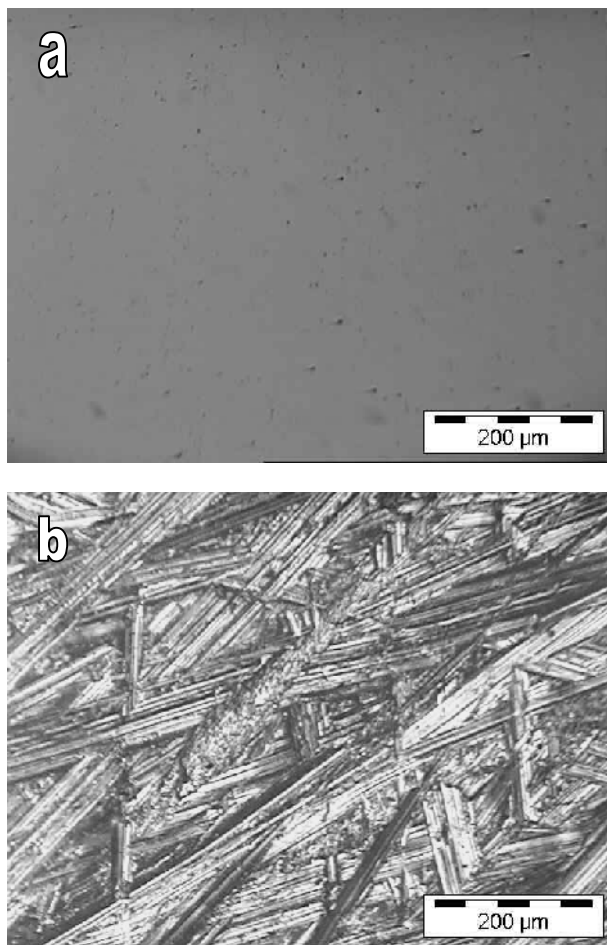
Fig. 1. Images by OM of Fe22Cr5Al plates, (a) after the polishing treatment and b) after the mechanical erosion treatment.

Fig. 2. SEM image of the surface of the Fe22Cr5Al plate after heat treatment. a) with polishing pre-treatment, and b) with mechanical erosion pretreatment.

Analysis by Scanning Electron Microscopy. The surface morphology of the samples was observed, after heat treatment in a Field Emission-Scanning Electron Microscope (FEG-SEM), FEI Sirion XL30. Figure 2a shows the pre-polished surface sample with thermal treatment and the formation of a surface layer constituted by agglomerations of small equiaxial grains is observed. While Figure 2b illustrates the pre-eroded surface sample with thermal treatment, where it is appreciated the growth of a great density of sharp sheets with 1-2 μm in length and few nanometer thickness, known in the literature as whiskers [17].
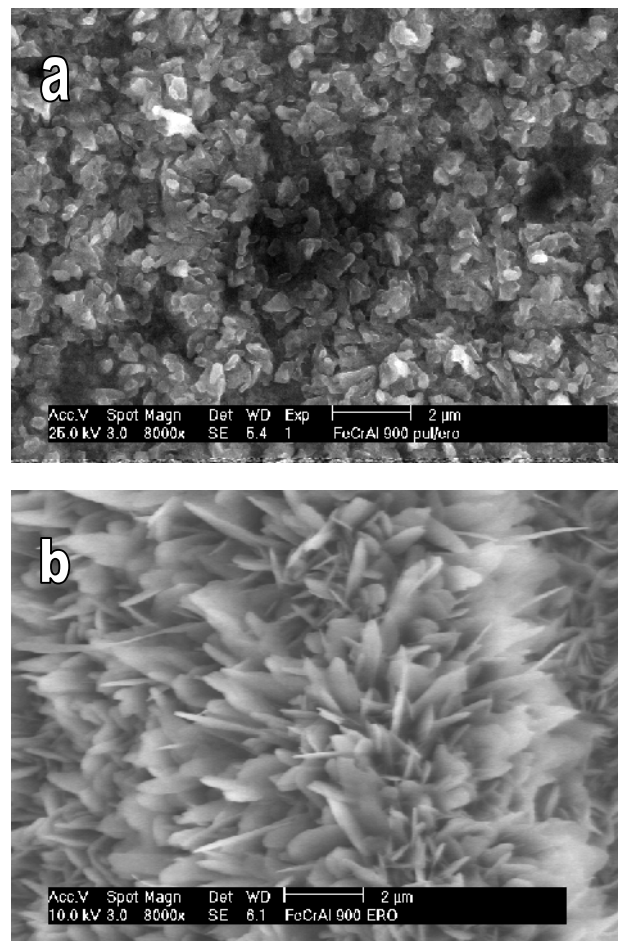
These different morphological textures were quantified, determining the fractal dimension of each surfaces, from the SEM images in Figure 2. To see more detail of the fractal dimension determination, it can be consulted the reference [18].

Analysis by Energy Dispersive X-ray Spectroscopy. With the aid of EDXS the chemical composition of the surface of the samples was determined before and after heat treatment using a 10 kV acceleration voltage. Figure 3a shows the composition spectrum of the alloy without any treatment, where it can be observed the elements that constitute the alloy: Fe, Cr and Al. In the spectra of

Figures 3b and 3c the analysis are depicted of the heat-treated samples, where it may be appreciated the considerable increase of the peaks belonging to Al and O. The small Fe and Cr peaks belong to the original substrate.
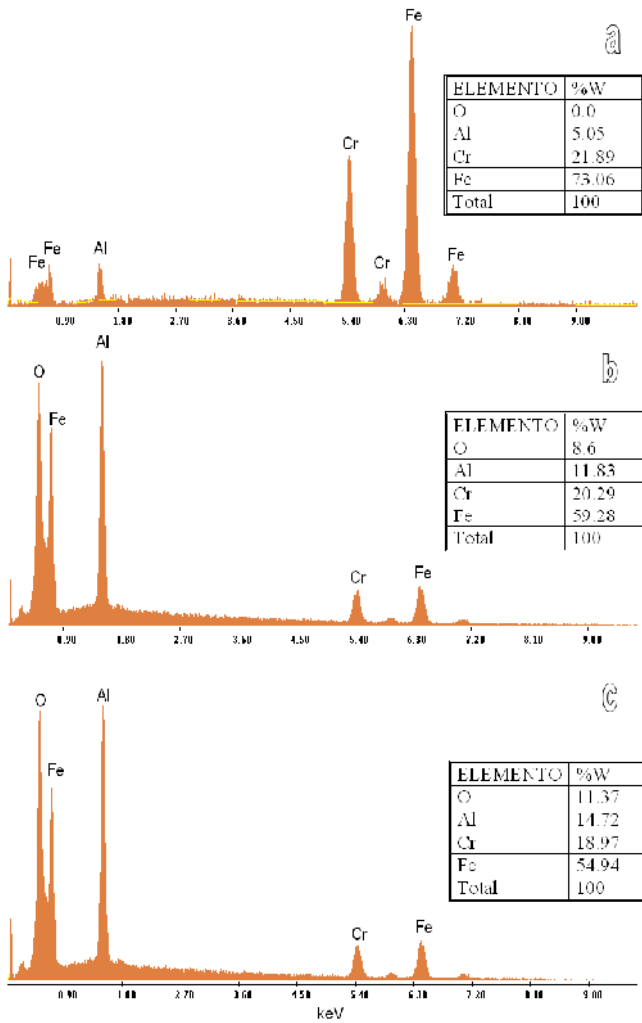
corresponding XRD-peaks more clear at the pre-polished sample. This is due to the great difference in roughness presented by each surface (fig. 2). The surface with whiskers has a higher ruoghness and thus higher diffuse scattering of X-rays is produced on it [19].
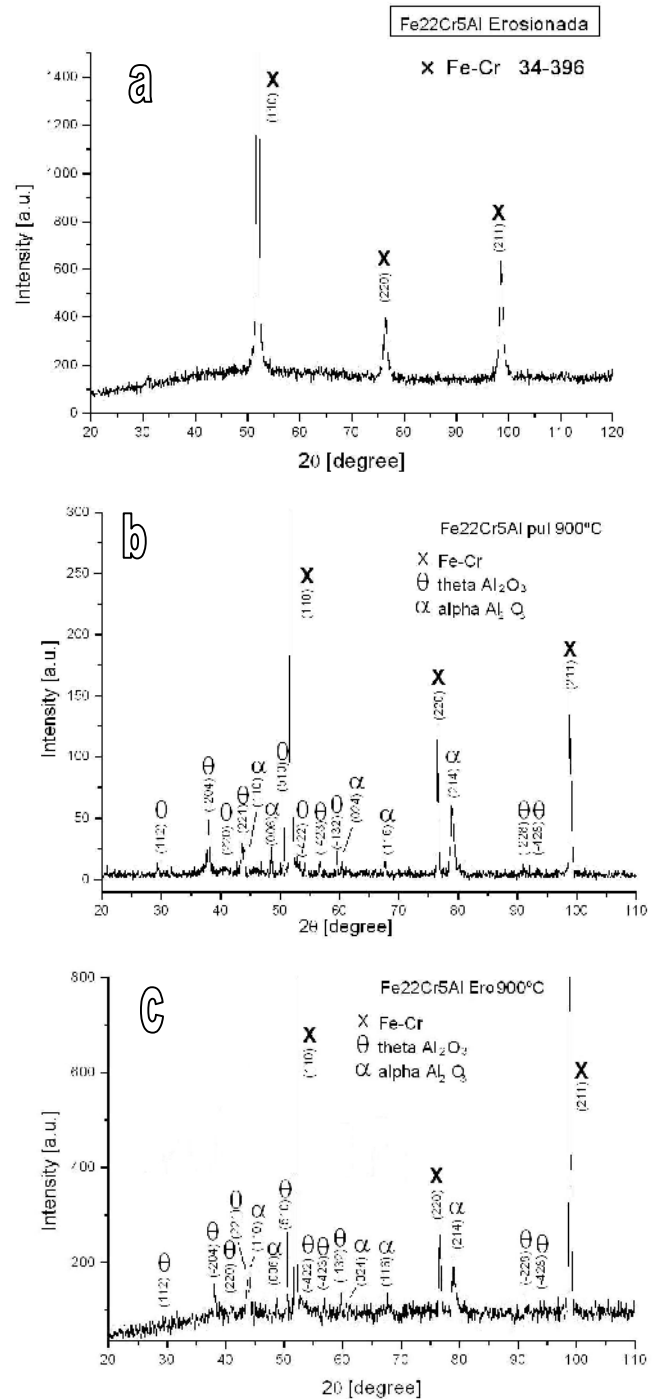

Fig. 3. EDXS analysis before heat treatment (a) and after heat treatment for the samples with previous polish (b) and mechanical erosion (c).

Analysis by X-Ray Diffraction. The XRD patterns of Figure 4 show substantial changes after the thermal treatment, when the emergence is observed of extra peaks to those of the alloy (Figure 4a), which belong to the θ and α phases of alumina (Figures 4b and 4c). The same alumina phases were detected for both pre-polished (fig. 4b) and pre-eroded (fig. 4c) samples, being the

Fig. 4. Diffractograms of Fe22Cr5Al alloy, before heat treatment (a) and after oxidation process for sample with previous polish (b) and mechanical erosion (c).

DISCUSSION

The discussion is handled in three parts; first: how the oxygen diffuse; second which oxide is formed and why; and finally which morphology adopts and why?

Oxygen diffusion. Usually metals absorb atoms different to those of cations to form the oxide (O anions) and subsequently the oxide absorbs cations of the same base metal. This ion exchange is a diffusive-type process in which there is a transfer of anions and cations that gives rise to the growth of the oxide [20, 21].

Thus the material is transported in the solids by diffusion on an atomic scale, atoms can move in the crystal lattices from one position to another, this process is generally activated by thermal energy, which provides vibration mobility to atoms [22, 23, 24]. The constant collisions and paths that atoms suffer during the diffusive phenomenon in solids are due to the increase of the thermal vibrations in the order up to 10^{12} - 10^{13} vibrations per second when an activation energy of 1 eV = 1.6 x 10^{-19} J is applied [23, 25], this is the minimal amount of energy that allows to an atom to move in the network. This process occurs through the surface, grain boundaries, dislocations, etc., depending on the crystal structure, atomic size of the elements involved and the extent of defects in the crystal. The vacancies on the metals for example are defects in equilibrium which favor the replacement diffusion of atoms. As temperature increases in the solid, there will be more vacancies and there will be more thermal energy available, therefore, the degree of diffusion is greater at higher temperatures, so that the activation energy necessary to form the vacancy and the activation energy required to moving it [23, 24, 26, 2 7] will depend largely on the temperature.

Oxide formation. Since diffusion is carried out in a spontaneous way, it must be seen as a process in which the free energy decreases or alternatively entropy increases. This eliminates the concentration gradients in an alloy, since there is a migration of atoms. The association of this with the variation of free energies for the oxides formation is direct, in our case it is possible to associate the energy of the oxides formation with values of -220, -150 and -110 $\Delta G°$ kcal for Al, Cr and Fe respectively, at a temperature of 900 °C [28]. These values indicate that aluminum reduces to Cr and Fe by preventing the formation of their oxides [28]. These two facts explain the enrichment of Al and O elements on the surface of the alloy of Fe22Cr5Al after the heat treatment.

Growth morphology. It is known that nucleation and growth of a phase require in firstly of pinning points such as grain boundaries, interfaces, dislocations and strain zones, where the energy is higher because there are unsaturated bonds, i.e. that they are not bonded but ready to react and interact [29].

Assuming the simplest case where nucleation is spherical (Figure 5), the contact angle θ is determined by mechanical balance of free surface energy of the oxide (γ_{ox}), of the substrate (γ_{sub}) and of the oxide-substrate interface (γ_{ox-sub}) as indicated by the follow equation [30]:

$$\gamma_{sub} = \gamma_{ox} \cos\theta + \gamma_{ox-sub.}$$

For this reason the polished samples present the morphology of equiaxial grain before forming the passivation layer.
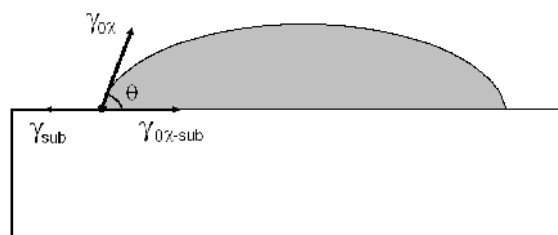

Fig. 5. Balance of free energies between the substrate and the formation of the new core.

The rough surfaces, in contrast, offer a greater number of irregularities (peaks and valleys) generators of stress and strain between the oxide layer and the substrate. This means that the layer formed in rough surfaces is not of the passivating-type, as in the polished surface, instead of that, a breakaway oxidation [31,32] take place, i.e., the oxide layer break up because inhomogeneous surface stresses. This is followed by the oxygen molecules penetrating in the crack and the oxide growth continues, generating therefore a greater surface vertically, as outlined in Figure 6.
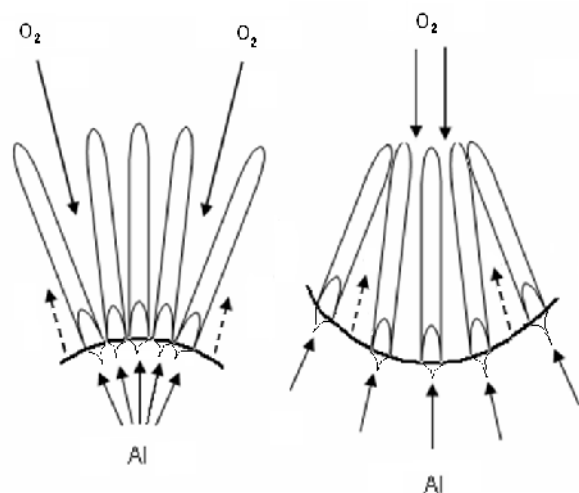

Fig. 6. Scheme of whiskers formation in peaks and valleys, because they are places of higher surface strain.

CONCLUSIONS

1. - Due to the mechanisms of diffusion of O and Al on the surface of the alloy and the lower free energy of the formation of the Al oxide in respect to Fe and Cr, the oxide layer formed is clearly of alumina.

2. – An oxide growth is propitiated with two different morphologies in spite of the samples being subjected to the same heat treatment, this was due to the different surface finishes: polished and eroded.

3. - The morphology of the equiaxial grains of the oxide in the polished surface gives rise to a passivating layer. The morphology of the oxide whiskers in the eroded surface gives rise to a layer with a high surface area.

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