Alumina-based composites strengthened with titanium and titanium carbide dispersions

ENRIQUE ROCHA-RANGEL ▪ Universidad Politécnica de Victoria
DAVID HERNÁNDEZ-SILVA ▪ Departamento de Ingeniería Metalúrgica
EDUARDO TERRÉS-ROJAS ▪ Laboratorio de Microscopía Electrónica de Ultra Alta Resolución
ENRIQUE MARTÍNEZ-FRANCO ▪ CIITEC-IPN
SEBASTIÁN DÍAZ-DE LA TORRE ▪ CIITEC-IPN

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The synthesis of Al_2O_3-based composites having different amount of fine titanium and titanium-dispersed carbide reinforcement-particles has been explored. Two experimental steps have been set for the synthesis; namely, solid sintering of Al_2O_3-titanium powders which were thoroughly mixed under high energy ball-milling, pressureless-sintered and then for the second step it was induced formation of titanium carbide at 500 °C by the cementation packing process. SEM analyses of the microstructures obtained in cemented bodies were performed in order to know the effect of the activated carbon used as cementant on the microstructure of titanium for each studied composite. It was observed that a titanium carbide layer growth from the surface into the bulk and reaches different depth as the titanium content in the composites was increased. The use of reinforcing titanium significantly enhanced density level and fracture toughness of the composites.

Keywords: ceramic-matrix composites, particle-renforcements, fracture toughness

Dr. Enrique ROCHA-RANGEL
Actually is titular professor at the Politechnique University of Victoria in Tamaulipas Mexico. He has gotten his bachelor and master in Metallurgical Engineering by the IPN. His doctoral was in the field of Metallurgy and Materials in the IPN. Also he has had Research Stay and Postdoctoral Studies in The Toyohashi University of Technology, Japan and Oak Ridge National Laboratory, USA respectively. His main field of work is the study of composite materials reinforced with different metals, ceramics and polymers, from where he has written several works.

Dr. David HERNÁNDEZ-SILVA
Actually is titular professor at the Metallurgy Engineering Department of the National Institute Politechnique (IPN) in Mexico City. He has gotten his bachelor and master in Metallurgical Engineering by the IPN. His doctoral was in the field of Metallurgy in the Max Plan Institute of Germany. His main field of work is the study and characterization of composite materials and the superplasticity of metals, from where he has written several works.

Dr. Eduardo TERRÉS-ROJAS
Actually he has a research position in the Mexican Institute of Petroleum. He has gotten his bachelor in Physical Engineering by the UAM, his master was in the field of ceramic materials in the Materials Institute of UNAM, and his doctoral studies was in the field of nanomaterials in the IPICyT, all of these Institutions are localized in Mexico. His main field of work is the study and characterization of composite materials, from where he has written several works.

Dr. Enrique MARTÍNEZ-FRANCO
Actually is titular professor in the Research and Innovation Technology Center of the IPN. He has gotten his bachelor and master in Metallurgical Engineering by the IPN. His doctoral was in the field of Ceramic Materials in the Hamburg Technology from Germany. His main field of work is the study and mechanical characterization of composite materials, from where he has written several works.

Dr. Sebastián DIAZ-DE LA TORRE
Actually is titular professor in the Research and Innovation Technology Center of the IPN. His bachelor studies were in the field of the Chemistry Engineering by the Autonomous Zacatecas University in México. He has gotten his master degree in Metallurgical Engineering by the IPN. Whereas, his doctoral studies were in the field of the Materials Processing in the Kyoto University, Japan. He had worked for more than 10 years as an invited researcher in the Technological Research Institute of Osaka, Japan. His main field of work is in the referent to production and characterization of structural materials, from where he has written several works.

Introduction

Al_2O_3 is considered a valuable industrial material and the most widely used ceramic. It possesses good mechanical properties such as: high hardness, high compressive strength, good chemical and thermal stability [1–2]. However, its applications as a structural material have been limited by its low fracture toughness and low-fracture strength. This is because cracks easily propagate in this ceramics and therefore they might fail unpredictably in service. The incorporation of several reinforcement materials such as; ceramics, metals and intermetallics into an Al_2O_3 matrix forming a composite material has been proved to be an effective experimental route which improves toughness and mechanical strength of the composites matrix [3]. Thus, composites can be constituted in some cases of carbide ceramics, oxide ceramics and metals, and they can be used, for example in application at high temperatures such as in the construction of gas turbine engines in order to increase their thermal cycle efficiency [4–5]. Therein, the mechanical and physical properties of such type of composites have been studied, as well as their production processes [6–8]. In spite of this, the high temperature cementation of metal-dispersed carbide composites has not been investigated in detail and there are not sufficient reports on the high temperature cementation of thermal barrier composite-coatings [9].

The Pack Cementation process has been used for many years to develop protection coating in different materials. Here the body is essentially heat treated in a reactive environment as to chemically alter the surface region, thus forming ceramic compounds that improve corrosion and heat resistance behavior. Variables that affect the quality of coating include body composition, powder bed composition, and heat treating conditions such as temperature, time and furnace atmosphere.

Since elemental carbon may diffuse throughout an oxide matrix at high temperatures, the metallic particles dispersed in a matrix can consequently be cemented. In turn, the crystallographic volume of such metallic-oxide´s dispersions will expand, thus inducing micro stresses accumulation in the surrounding matrix. As result, fissures can nucleate in the neighboring matrix upon the stresses fraction generated by the volume expansion. The later is particularly true if the magnitude of compressive stresses reaches the ultimate fracture strength. Inevitably, after multiple cracks formation, the composite undergoes catastrophic fracture. It is then important designing composites for high temperature applications, and so does their analysis behavior at high temperature-cementation. The later is the experimental aim of this work.

Experimental procedure

Composite materials were prepared using two consecutive steps. First, titanium-dispersed oxide aluminium composites were prepared using precursor powders of Al_2O_3 (99.9%, 1 µm, Sigma, USA) and Ti (99.9%, 1–2 µm, Aldrich, USA). The amount of powder was selected as to obtain Al_2O_3-based composites having 0.5, 1, 2 and 3 vol% of Ti. The powder mixture was ball-milled in a commercial high energy mill (Simoloyer) using ZrO_2 media (with Si_3N_4-inner coating to avoid contamination), the rotational speed of which was set to 400 rpm for 8 h. The ball-to-powder volume ratio was set to 20:1. Using milled powder mixtures, cylindrical samples of 2 cm in diameter and 0.3 cm thick were fabricated by uniaxially pressing 2 grams at 250 MPa. Cold-pressed green samples were then pressureless sintered PLS in an electric furnace using argon atmosphere. Heating rate was set to 5 °C min^{-1}, sintering temperature was 1500 °C and holding time 1 h. After sintering, furnace was turned off and samples were left inside it for gradual cooling. Then for second step the composites were cemented in vacuum as follows. The composite powder produced as described before was placed inside a graphite-made container as it can be seen in *Fig. 1*. Inside the container the sintered-compact sample was totally surrounded by the cementing medium (powdered activated carbon) and then heated in vacuum up to 500 °C for 1 h. The later set arranged in order to induce carbon diffusion into the sample and to cement metallic particles that are found near the surface of the composite, before being allowed to cool down inside the furnace.

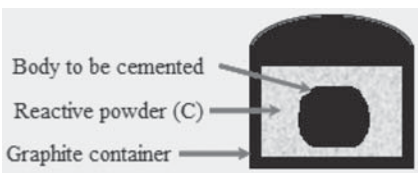

Fig. 1. Schematic configuration set for inducing cementation on the test-specimens
1. ábra Az indukált cementálás megvalósítására szolgáló kísérleti berendezés

The specimen's characterization was conducted as follows. Density of fired specimens was determined using the Archimedes' method. Cemented samples were analyzed using scanning electron microscopy SEM (XL30 ESEM, Philips) and energy dispersive spectroscopy EDS (Noram), to observe their microstructure and chemical composition, respectively. Thickness of the carbide (cemented) layer as a function of the titanium-carbide content in each sample was also determined by using these techniques. Microhardness of the obtained specimens was evaluated using *Vickers* indentation in a microhardener (Buehler Micromet 2003), whereas their toughness was estimated following the fracture indentation method, the most widely used technique in the literature for assessing the fracture toughness directly from indent cracks utilizes the *Vickers* indenter. First proposed in the late 1970's, this technique was developed to estimate the fracture toughness of ceramic materials by measuring the lengths of cracks emanating from *Vickers* indents [10]. *Evans et al.* modeled the elastic-plastic behavior under the indent, assuming that a median/radial crack system is created due to tensile stresses that form during unloading. They derived the expression:

$$K_{IC} = 0.16\,(c/a)^{-1.5}\,(Ha^{1/2}) \qquad (1)$$

where K_{IC} is the fracture toughness, H is the hardness, c is the length of the surface trace of the half crack measured from the center of the indent and a is the length of the indentation mark.

Results and discussion

The cross section view of prepared composite-specimens is shown in *Fig. 2.*, as a function of the Ti content and after completing their cementation process at 500 °C for 1 h. These fractographs reveal general features of the microstructure and larger grains for the 2 and 3 vol% Ti specimens. It is evident the formation of homogeneous specimens, because the Ti particles (typically disclosed by SEM as tiny white dots), which retained their very fine sizes were well distributed in the alumina matrix (gray-dark phase). In general the resulting microstructures displayed few pores left in the matrix after sintering. In these pictures, it can also be observed that there are no Ti particles in the surface region to a depth of about 50, 83, 107 and 119 µm for samples with (0.5), (1), (2) and (3) vol% of titanium, respectively. The local region in which Ti-particles have reacted with diffusing carbon is defined to as the cemented zone, whose thickness turns into layer depending on the gradient concentration and sintering time. A common factor in all pictures shown in *Fig. 2.* relates to the fact that Al_2O_3-based composites do not fracture by the Ti-cementation.

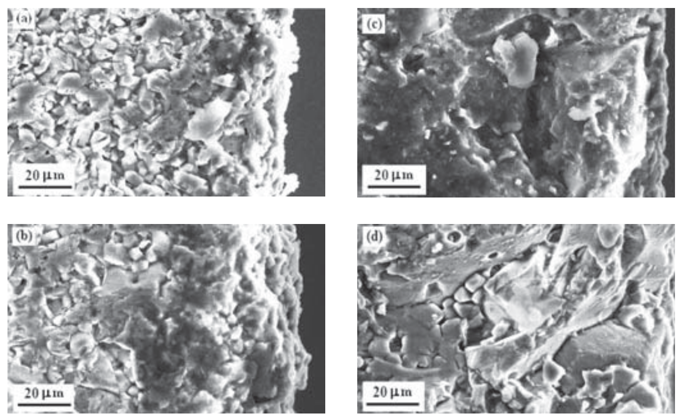

Fig. 2. Cross section view of the functional graded material´s resulting microstructures. The right side of each fractograph corresponds to its outermost part or external surface.
(a) 0.5, (b) 1, (c) 2 and (d) 3 vol% Ti
2. ábra A funkcionális rétegszerkezetű anyag keresztmetszeti mikroszerkezete. Minden egyes törési kép jobb oldala a minta legkülső felületét mutatja; a Ti-tartalom tf%-ban: (a) 0,5, (b) 1, (c) 2 és (d) 3.

Fig. 3. shows a cross section SEM-view of the 2 vol% Ti specimen after sintering. EDS-microanalysis conducted both at the white particles at the edge and in the core of the sample confirmed the existence of elemental carbon, particularly being more concentrated at the specimen´s edge. As long as the qualitative analysis is conducted at inner zones of the composite the carbon concentration diminished. Not evident from this picture but there is a certain surface layer displaying a slightly different color contrast with respect to the Al_2O_3-bulk matrix. Such contrast, in practice exhibited similar texture to the cemented region. So that between the cemented layer and the non-cemented region, there is an intermediate zone which

consists of partially-cemented Ti particles. Therefore, moving from the outermost surface part into the bulk of material, it has been detected three specific regions, featuring: (1) fully cemented metal particles, (2) partially cemented particles and (3) metallic particles not being cemented.

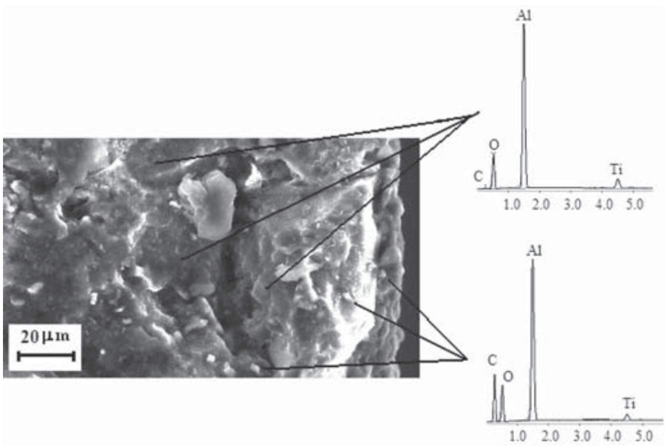

Fig. 3. EDS microanalysis conducted both at the white particles placed in the edge (near external surface) and in the core of specimen containing 2 vol% Ti
3. ábra A 2 tf% titánt tartalmazó minták EDS mikroelemzésének eredményei; az elemzéseket a minta fehér, a legkülső felülethez közeli részén, valamint azok belsejében is elvégeztük

Fig. 4. shows depth of the cemented layer as a function of the titanium content supplied into the alumina-based composites. There is an evident increment on the layer´s depth as the Ti concentration rises. This on-growing behavior is not lineal and the curve´s trend suggests eventual saturation of titanium at the surface, which accounts for its composite-nature. From the same figure it is also clear the toughening effect that results on the composites derived from the formation of TiC, i.e., as long as the cement layer gets thick. To explain toughening in these composites we assume the crack-bridging effect operating, which often occurs when dispersing metals into ceramic matrix [3]. Thus, when enough external energy is conferred to the composite material, micro cracks or remaining micro pores act arresting it and avoid fracture, to some extent. The Ti ligaments present in the ceramic matrix absorb part of the fracture energy.

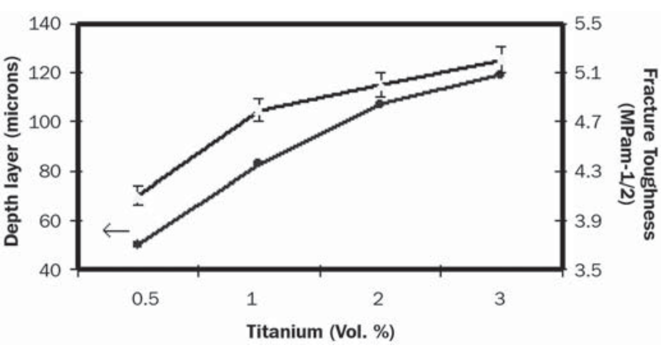

Fig. 4. Thickness of the cement layer plotted as a function of Ti content in the Al_2O_3 matrix
4. ábra A cementált réteg vastagságának változása az Al_2O_3 mátrix Ti-tartalmának függvényében

Table 1. summarizes the relative density and some mechanical properties measured on the studied material. It can be observed that density increased as Ti content was rose in the composites. It is worth noting that microhardness was evaluated by indenting two different zones on the specimens. First testing was carried out at the edge of the sample whereas others were practiced near to its core. Microhardness for all studied samples with Ti is larger at the edge of specimens than that observed at their core. This behaviour is due to the formation of hard TiC near to the edge of samples. The later takes place through the reaction: Ti + C → TiC. This chemical reaction is thermodynamically favored since its free energy of formation is – 43.2 Kcal/mol [8]. The TiC formation takes place with carbon gas diffusing through the specimen´s edge into the bulk. Cementation degree depends on the temperature and gas concentration. In practice, it is thus possible to fabricate Al_2O_3/TiC/Ti - composites.

System (vol% Ti)	Relative density (%)	Edge hardness (GPa)	Core hardness (GPa)	K_{IC} ($MPa\cdot m^{-1/2}$)
0	94.95	11.97 +/- 0.5	11.94 +/- 0.5	3.2 +/- 0.2
0.5	97.64	9.76 +/- 0.3	6.80 +/- 0.3	4.1 +/- 0.2
1.0	97.75	10.01 +/- 0.4	9.13 +/- 0.3	4.8 +/- 0.1
2.0	97.93	10.34 +/- 0.4	9.69 +/- 0.4	5.0 +/- 0.1
3.0	99.76	10.17 +/- 0.5	7.09 +/- 0.3	5.2 +/- 0.1

Table 1. Relative densities and mechanical properties measured in the studied composites
1. táblázat A vizsgált kompozitok relatív sűrűségei és mechanikai tulajdonságai

The magnitude of fracture toughness K_{IC} attained in the studied materials is reported in Table 1. For all studied cases, this strength parameter is superior to that of the pure alumina which is of about 3.2 $MPa\cdot m^{-1/2}$ [3], see Table. It is concluded that the metallic particle´s dispersion into a ceramic matrix, as conducted in this work may increase its toughness. Some authors have reported that the reinforcing mechanism operating here is associated to the crack bridging phenomena triggered by ductile metallic ligaments [8, 11]. The high densification level conferred to the composites is another factor that greatly influences their toughness value. Catastrophic cracking of specimens usually takes place as large voids are left in it.

Conclusions

Strengthened Al_2O_3-based composites can effectively be reinforced by inducing fine dispersions of TiC/Ti, throughout a combination of experimental techniques, such as; mechanical milling, pressureless sintering PLS (Ar-atmosphere) and cementation process (vacuum). The later provided that Al_2O_3, Ti and activated carbon fine precursor powders are bring together as to react upon sintering forming a functionally-graded-cemented layer. This *in-situ* synthesis method produces composites that are greatly sinterable and do exhibit enhanced toughness, as compared to monolithic-Al_2O_3 ceramics. This toughening improvement technique offers the possibility of a low synthesis cost, turning into an attractive synthesis route for scaling the process up to a pilot plant-level.

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Titán- és titán-karbid diszperziókkal erősített alumínium-oxid alapú társított anyagok

Különböző mennyiségű, kis szemcseméretű titán és titán-karbid erősítőfázist tartalmazó, Al_2O_3 alapú társított anyagok előállítását vizsgáltuk. Az előállítás két lépésből áll: az első lépésben az Al_2O_3–titán porelegyet nagy energiájú golyós malomban végzett őrléssel összekeverjük, majd nyomásmentesen, szilárd fázisban szintereljük. A második lépésben 500 °C-on cementáljuk a mintát a titán-karbid képződés elősegítésére. A cementált próbatestek mikroszerkezetét SEM módszerrel vizsgáltuk. A vizsgálatok célja annak felderítése volt, hogy a mintába cementáló anyagként bevitt az aktivált szén miként befolyásolja a titán mikroszerkezetét. Azt találtuk, hogy a titán-karbid réteg a felületről kiindulva növekszik, és onnan halad az anyag belseje felé, és a behatolási mélység a titán tartalommal változik. A titán, mint erősítőfázis bevitele jelentősen növelte a kompozitok sűrűségét és törési szívósságát.

Kulcsszavak: kerámia mátrixú kompozitok, részecske-erősítés, törési szívósság

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