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Production of Al_2O_3/Ti/TiN functional materials by means of nitriding in ammonia salts of Al_2O_3/Ti composites

Elizabeth Refugio-García[a], José G. Miranda-Hernández[a], José A. Rodríguez-García[b] and Enrique Rocha-Rangel[b,*]

[a]*Departamento de Materiales, Universidad Autónoma Metropolitana, Av. San Pablo No. 180, Col. Reynosa-Tamaulipas, México, D. F., 02200, México*

[b]*Universidad Politécnica de Victoria, Av. Nuevas Tecnologías, Parque Científico y Tecnológico de Tamaulipas, Carretera Victoria-Soto la Marina Km 5.5, Cd. Victoria, Tamaulipas, México, 87138, México*

The production of Al_2O_3/Ti/TiN functional materials through the nitriding in ammonia salts of previously Al_2O_3/Ti fabricated composites was achieved. The matrix for the preparation of the functional materials is to create an Al_2O_3-based composite that presents a fine and homogeneous dispersions of very fine metallic particles of Ti. After the nitriding, microstructural observations were carried out on the transverse zone of the materials' surface showing the presence of a very thin film of about 20 μm of a constituent that was identified with the help of EDS as TiN. In addition, measurements of micro-hardness on the surface and in the core of the functional material were realized in order to determine the effect of nitride formation on the hardness.

Key words: Functional materials, Nitriding, Ammonia salts, Al_2O_3/Ti composites.

Introduction

Generally, ceramic materials are highly fragile, in the particular case of Al_2O_3 ceramics they are not an exception [1-2]. Ceramics can be toughened by the incorporation in their matrix of ductile metallic particles [3-6]. A functionally graded material (FGM) is a composite consisting of two components, characterized by the presence of a chemical gradient from one component to the other. By contrast, traditional composite materials are homogeneous mixtures; therefore cooperation between properties of the materials that generate the composite is required. Given the need to improve conversion efficiency in thermal cycles as in the case of turbines, this has provoked the necessity for new materials with the capacity to work at high temperatures without suffering damage in both; its structure and its chemical composition [7]. FGMs that consist of nitride and oxide ceramics have received special attention for use in those applications because they meet up with those characteristics [8]. The aim of this study is to produce an Al_2O_3-based functional material with a titanium nitride layer on its surface.

Experimental

The experimental route consisted of two stages; Stage 1 production of the Al_2O_3/Ti composite and stage 2 production of the Al_2O_3/Ti/TiN functional material. The raw materials for the first stage were: Al_2O_3 powders (99.9%, 1 μm, Sigma, USA) and titanium powders (99.9% purity, 1-2 μm, Aldrich, USA). The amount of powders used is one that allows at the end of the processing to obtain an Al_2O_3-10 vol.% Ti composite material. The powders were milled and dry mixed in a horizontal mill, using a rotation speed of 300 rpm, for 12 h, with the help of ceramic jars and using YSZ's balls as grinding elements, the relative weight of balls/weight of powder was 25 : 1. The powder mixtures were made into cylindrical samples by uniaxial pressing using 200 MPa with the following dimensions: 20 mm in diameter × 3 mm in thickness. Afterwards, the pressed samples were pressureless sintered at two different temperatures (1400 °C and 1500 °C) for 1 hour in an argon atmosphere. The rates of heating and of cooling were kept constant and equal to 10 K·minute^{-1}. The characterization of the synthesized products was the following: densities were evaluated by the Archimedes' method, microhardness measurements were evaluated with the help of a Vickers indenter. The microstructure of the composites was observed with a scanning electron microscope (SEM). In stage 2 for the formation of the FGMs, samples were submitted to a thermal treatment of nitriding in an ammonia salts bath, for 24 hours at a temperature of 570 °C. Finally, the microstructures of these samples were observed by a scanning electron microscope (SEM), this SEM was equipped with an energy dispersive X-ray spectrometer (EDS), to realize chemical analyses in the samples' microstructure, also measurements of microhardness in the transversal section of the same ones were carried out.

*Corresponding author:
Tel : +52(834) 172-03-83 ext. 2302
Fax: +52(834) 172-03-83 ext. 2302
E-mail: erochar@upv.edu.mx

Results and Discussion

Density

The relative densities reached by composites after stage 1 was 93.5% and 96% theoretical for composites sintered at 1400 ºC and 1500 ºC respectively. From these values it is evident that an increment in the sintering temperature favors consolidation of the samples. This must due to the activation of transport phenomena at high temperatures, which helps atom migration during sintering a situation that is reflected in better final densities.

Al_2O_3/Ti composite microstructure

Fig. 1 shows microstructural images taken with the help of SEM of the composites sintered at different temperatures. From these images both microstructures show the presence of two different phases, one gray phase that corresponds to the ceramic matrix and a white phase represented by small particles distributed in the matrix. At the same time it is possible to observe that second phase particles are localized at intergranular zones of the matrix. On the other hand, as expected it is possible to detect in the sample sintered at low temperature (1400 ºC) the presence of mayor porosity in comparison with the porosity displayed by the sample sintered at the higher temperature (1500 ºC). This confirms the measurements of density realized in both samples and previously reported.

On the basis of (EDS) analyses that are given in Fig. 2, it is deduced that the gray phase corresponds to the alumina matrix and the tiny white phase corresponds to the titanium added into the ceramic matrix. In this image it is evident that the metallic phase is localized principally at intergranular positions. The main titanium particle size has an average of 1 μm, whereas the main alumina grain size has an average of 10 μm.

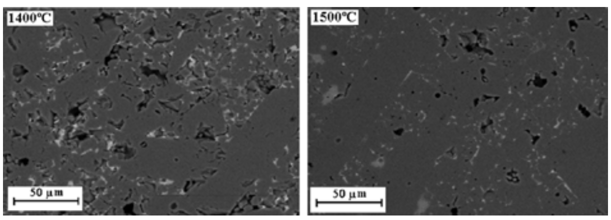

Fig. 1. Scanning electron images of the microstructures of Al_2O_3/Ti composites sintered at different temperatures.

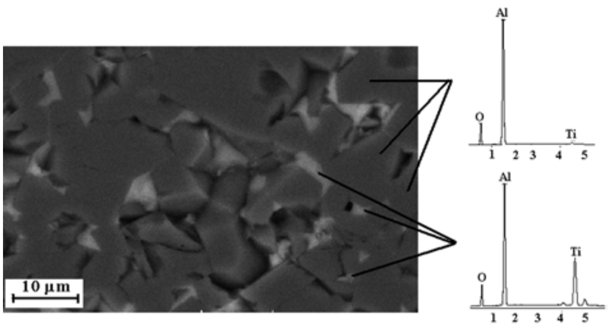

Fig. 2. EDS microanalysis realized in both: the gray phase and white particles of the Al_2O_3/Ti composite.

Al_2O_3/Ti/TiN functional material microstructure

As was commented before, the Al_2O_3/Ti composites fabricated in stage 1 were submitted to a thermal treatment of nitriding in ammonia salts, in which chemical reaction (1) took place, this reaction occurs between the fine titanium particles that are present close to the composite's surface and the nitrogen released by the ammonia salts. In this way Al_2O_3/Ti/TiN functional materials were obtained. These materials were also analyzed by SEM. Fig. 3 presents images of the surface of the new materials showing a very thin nitride film of about 20 μm thickness for both composites. In Fig. 3 there is a certain surface layer displaying a slightly different color contrast with respect to the Al_2O_3-bulk matrix. Such a contrast, in practice exhibited a similar texture to the nitride region. So that between the nitride layer and the non-nitride region, there is an intermediate zone which consists of partially-nitride Ti particles. Therefore, moving from the outermost surface part into the bulk of material, three specific regions have been detected, featuring: (1) fully nitride metal particles, (2) partially nitride particles and (3) metallic particles not being nitride.

$$Ti + N \rightarrow TiN \quad (\Delta G = -308\ kJmol^{-1}) \tag{1}$$

Hardness

Results of micro-hardness measurements performed in different zones on the transverse section of the composites are presented in Fig. 4. In this figure it is possible to

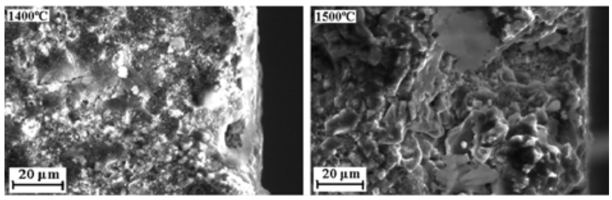

Fig. 3. Scanning electron images of the Al_2O_3/Ti/TiN functional materials produced by nitriding Al_2O_3/Ti composites in ammonia salts at 570 ºC for 24 h.

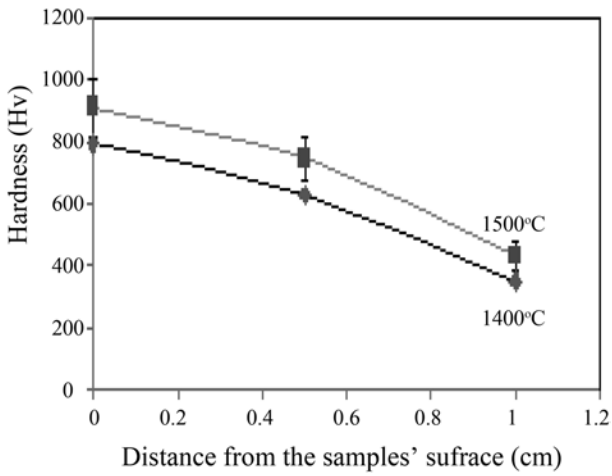

Fig. 4. Hardness results performed in different zones on the transverse section of the Al_2O_3/Ti/TiN functional material.

observe that the hardness of samples is reduced gradually from its surface to the core. This behavior is due to the formation of the TiN on the surface of the samples, which is harder than the Al_2O_3/Ti composite that is mainly present in the direction of the core, moving from the surface of the sample.

Conclusions

Hardened Al_2O_3-based composites can effectively be produced by inducing fine dispersions of TiN/Ti, through a combination of experimental techniques, such as; mechanical milling, pressureless sintering (in an argon-atmosphere) and a nitriding process in ammonia salts. The later provided that Al_2O_3, Ti and fine precursor powders are brought together to react upon sintering to forming a functionally-graded-nitride layer after nitriding. This *in-situ* synthesis method produces composites that are greatly sinterable and do exhibit enhanced hardness.

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