Characterization of Si_3N_4-Al interface after corrosion tests
(Caracterização da interface Si_3N_4-Al após testes de corrosão)

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Abstract

Silicon nitride is a covalent ceramic material of high corrosion resistance and mechanical stability at elevated temperatures. Due to these properties, its use in metallurgical processes, such as the casting of alloys, is increasing. Therefore, the characterization of the interface between Si_3N_4 and the casted metal is of great importance to investigate possible interactions, which might deteriorate the ceramic mould or contaminate the metal. In this work, the use of Si_3N_4 as crucible material for Al-casting has been studied, by investigating the corrosion attack of liquid Al at a temperature of 1150 °C during 30 days in air. The interface was characterized by X-ray diffraction, scanning electron microscopy and energy dispersive spectroscopy. It has been found that due to superficial oxidation two oxide layers form – SiO_2 on Si_3N_4 and Al_2O_3 on Al – which effectively hinder further reactions under the conditions studied, confering high corrosion resistance to the Si_3N_4 crucible.
Keywords: silicon nitride, corrosion behavior, scanning electron microscopy, X-ray diffraction.

Resumo

Nitreto de silício (Si_3N_4) é um material cerâmico covalente de elevada resistência à corrosão e estabilidade mecânica em temperaturas elevadas. Devido a essas propriedades, sua utilização em processos metalúrgicos, tais como em fundição de ligas metálicas, é crescente. Desta forma, a caracterização da interface entre Si_3N_4 e metais fundidos é de grande interesse para investigar possíveis interações as quais poderão deteriorar o material cerâmico e/ou contaminar o metal. Nesse trabalho o uso de Si_3N_4 como material base de cadinhos para fundição de alumínio foi estudado, pela investigação do ataque corrosivo de Al líquido a 1150 °C durante 30 dias, ao ar. A interface foi caracterizada por difração de raios X, microscopia eletrônica de varredura e espectroscopia de energia dispersiva. É encontrado que devido à oxidação superficial dois óxidos se formam - SiO_2 no Si_3N_4 e Al_2O_3 no Al - os quais evitam possíveis reações sob as condições estudadas, conferindo alta resistência à corrosão aos cadinhos de Si_3N_4.
Palavras-chave: *nitreto de silício, comportamento de corrosão, microscopia eletrônica de varredura, difração de raios X.*

INTRODUCTION

Silicon nitride (Si_3N_4) is used as a structural ceramic material with interesting characteristics for high temperature applications, such as wear and corrosion resistance [1-4]. One of the many fields of application as structural ceramic is in metallurgical processes as refractory material, thermocouple protection or casting valve [5, 6]. The corrosion behavior of this material has been mainly studied on metal/ceramic junctions under inert atmospheres [7-11], thus avoiding oxidation common in industrial processes.

The phase identification by mass contrast, using emission of backscattered electrons in SEM, is an important tool in situations where the phases present have an accentuated difference of their atomic number. Even so, it should be noticed that the use of X-ray diffraction analysis for the final phase identification is indispensable.

In the Al/Si_3N_4 system, due to the adherence of Al_2O_3 originating from the aluminum surface, on the surface of Si_3N_4, the difficulty of chemical attack of this oxide and the small thickness of the interfacial layer formed, it is extremely difficult to affirm if new phases are formed at the interface. Thus, it is necessary to ally those characterization techniques to the chemical analysis of the energy dispersive spectroscopy (EDS), in order to identify new phases formed during the tests and to determine possible chemical reactions and the mechanisms that act during corrosion.

The purpose of this work is to demonstrate that the characterization techniques association is an effective tool to characterize ceramic-metal interfaces.

EXPERIMENTAL

Materials

Crucibles with high relative density (98%) were produced using a ceramic powder mixture composed of 86 vol.% of ζ4 Si_3N_4 (UBE Industries-Japan) and 14 vol.% of ζ4 Al_2O_3 (BAIKALOX- Germany) and a mixed concentrate of yttrium and rare earth oxides, CTR_2O_3 (FAENQUIL-DEMAR-Brazil, obtained by alcaline fusion of the mineral xenotime, precipitation by oxalic acid and subsequent calcination), in the stoichiometry of the intergranular phase $Y_3Al_5O_{12}$. This mixture was milled for 6 h (1000 rpm) and compacted by isostatic

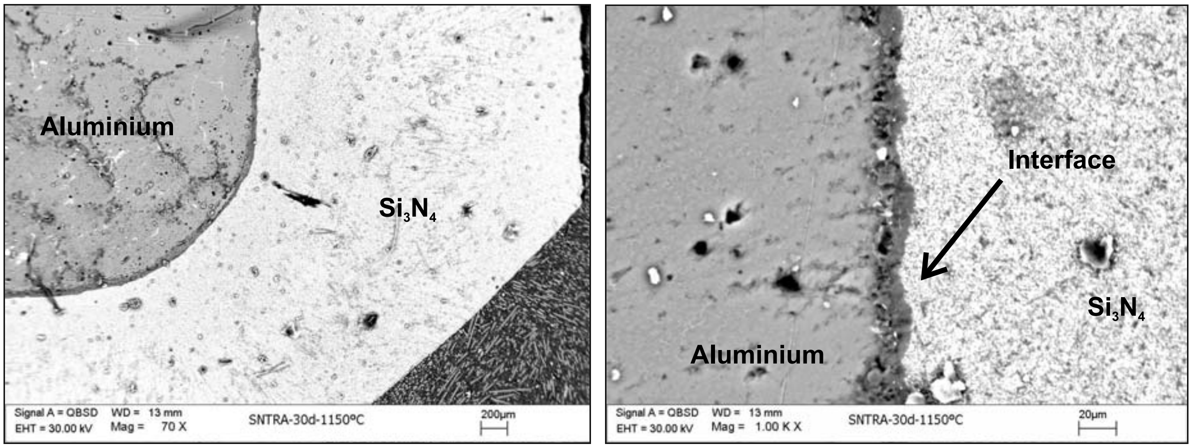


Figure 1: Interface Al/Si_3N_4 after testing during 30 d at 1150 °C in air.
[Figura 1: Interface Al/Si_3N_4 após testes por 30 dias a 1150 °C ao ar].

pressing (100 MPa). After this step the compacts were sintered under 1.5 MPa of N_2 atmosphere at a heating rate of 10 °C/min up to 1800 °C, with an isothermal holding time of 30 min and subsequently heating up to 1900 °C with an isothermal holding time of 2 h. After sintering, the samples were submitted to a heat treatment for devitrification of the intergranular phase at 1400 °C during 24 h, under 0.1 MPa of N_2 atmosphere [1, 12].

Corrosion Tests

In the sintered crucibles, aluminum bars were melted and treated during 30 d at 1150 °C in air. The objective of these tests was to verify the behavior of the dense Si_3N_4 ceramics in similar conditions to industrial aluminum melting, at temperatures where the chemical reactions between Si_3N_4 and aluminum are favored thermodynamically [7, 9]. For the accomplishment of the tests, the aluminum bars had their surfaces cleaned by pickling with a NaOH solution (10%) during 20 min. The crucibles with aluminum were put into an electric furnace, in air. After testing, the crucibles were cut and the cross-section embedded in phenolic resin for the metallographic preparation by grinding and polishing to a 1 σm finish.

After the corrosion tests, the internal surface of the crucibles was analyzed by X-ray diffraction (XRD) with the objective to identify phases in the system, using $Cu_{k\zeta}$ radiation, at 0.05 degree/s and 2χ between 10∀ and 80∀.

The microstructural evaluation of the Si_3N_4/Al interface of the samples was examined using mixed emission of backscattered electrons (BSE) and secondary electrons (SE) [13] in a LEO 1450VP Scanning Electron Microscope, and chemical analysis by energy dispersive spectroscopy (EDS) in the contact region.

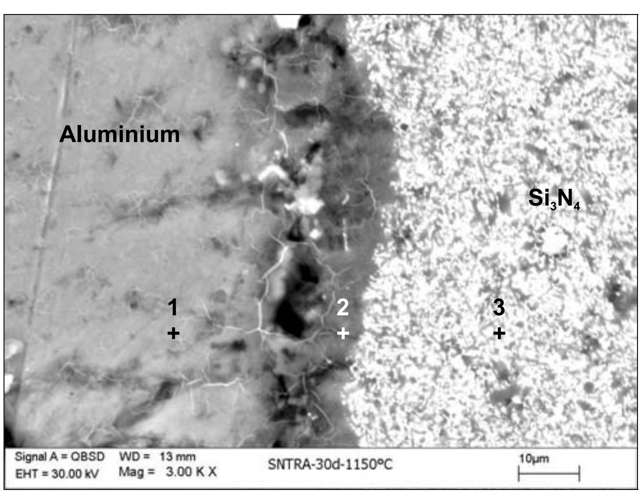


Figure 2: Regions analyzed by EDS.
[Figura 2: Regiões analisadas por EDS].

RESULTS AND DISCUSSION

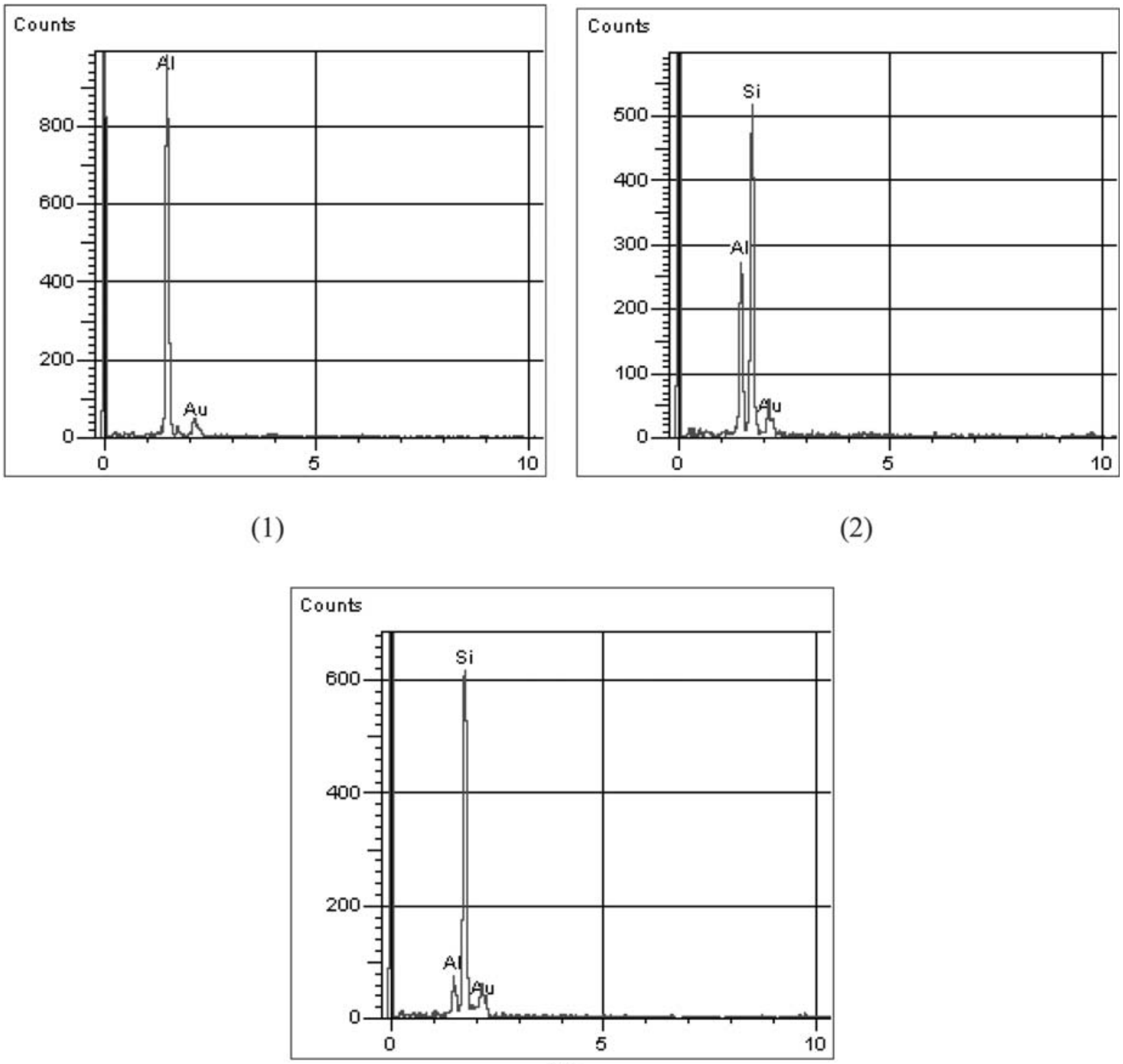
Microstructural Analysis

The crucibles were cut and the cross sections were ground and polished as described previously. Fig. 1 presents the microstructures of the cross sections of crucibles tested during 30 d, at 1150 °C, focusing on the contact area between aluminum and the Si_3N_4 crucibles.

The presence of three well defined phases is observed, being the central phase, probably, the result of the corrosion between aluminum and Si_3N_4. It is noticed, that the central film, of darker tonality, is uniform and with a thickness of approximately 10 σm. By this phase tonality, it is supposed that the atoms composing this phase have smaller atomic numbers than the one of the Si_3N_4 with intergranular phase ($Z_{interface} < Z_{Si3N4+Al203+CTR203}$), since darker phases are due to smaller atomic numbers [13].

Chemical analysis by energy dispersive spectroscopy (EDS) was used to identify the elements and the quantity of each element in the region analyzed, besides verifying spectrum differences among the three areas analyzed, with prominence for the central area. Fig. 2 presents the microstructure of the contact region Al/ Si_3N_4, indicating the areas analyzed by EDS.

Based on Fig. 2, EDS measurements were carried out and the results in form of EDS spectra are presented in Fig. 3.



(1) (2)

(3)

Figure 3: EDS spectra of the regions 1 to 3 (Fig. 2).
[Figura 3: Espctros de EDS das regiões 1 a 3 (Fig. 2)].

In region 1 of Fig. 3, EDS analysis shows the presence of Al confirming that this is the region where aluminum was deposited into the crucibles for the corrosion tests. The Au peak in the spectrum is due to the recovering used in the samples metalization. The identification of only Al in region 1 is insufficient to affirm that only pure aluminum exists in this area. The elements O and N are not identified with clarity by EDS analysis [13]. Thus, also in this area oxides such as Al_2O_3 can exist. This hypothesis is reinforced by the fact that aluminum is oxidized easily in contact with the atmosphere, even at room temperature [14].

Region 3, shown in Fig. 2, corresponds to the Si_3N_4 crucibles. The presence of the Si is observed, as justified by the chemical composition of Si_3N_4. The presence of the Al in this region is due to the intergranular phase formed during sintering, since a relatively large amount of Al_2O_3 has been used as additive. The other oxide used as additive was Y_2O_3 whose element Y possesses identical relative position to Si, thus difficulting the identification of these elements.

Fig. 3.2 shows the spectrum corresponding to the interface. A large signal is observed corresponding to Si and a small signal to Al. Comparatively, it is observed that the intensity of the Al peak is much smaller than that of the region 3.

This takes us to believe that a different phase is present in that region, composed for the major part of Si, and due to the tonality of this phase, and this new formed phase possesses $Z < Z_{Si3N4}$. Besides, the Al can be some residual content or some interference during the scan, since, in spite of the EDS analysis has been executed pontually, this kind of analysis detects chemical elements present in the interaction volume, i.e. in an area of 1.5 σm on the surface and 3 σm depth of the sample.

X-ray Diffraction

The X-ray diffraction technique was used to complement the corrosion interface analysis in the samples tested during 30 d at 1150 °C. Two different regions were analyzed after the tests: 1) the surface of the crucibles subjected to oxidation without contact with aluminum during the corrosion tests and; 2) the region in contact with aluminum during the corrosion test. Fig. 4 presents a layout with the regions analyzed by XRD, microstructure of the surface oxidation and the diffraction patterns corresponding to the analyzed regions.

The SEM images of this region present typically SiO_2 in the form cristoballite [15-17]. This microstructure originates from the Si_3N_4 oxidation that is thermodynamically favored at this temperature and atmosphere [15, 16]. The X-ray diffraction pattern of this region confirms this supposition. The presence of SiO_2 and Si_2N_2O is verified, demonstrating that the Si_3N_4 crucibles have been oxidized, according to proposed reactions (equations A and B) [16].

$$Si_3N_{4(s)} + 3/4O_{2(g)} \longrightarrow 3/2Si_2N_2O_{(S)} + 1/2\,N_{2\,(g)} \quad (A)$$

$$Si_2N_2O_{(s)} + 3/2O_{2(g)} \longrightarrow 2SiO_{2(s)} + N_{2\,(g)} \quad (B)$$

The second observed region presented a dark and adherent film. During cooling, the solid Al formed shrinks more than the Si_3N_4 crucible due to the higher thermal expansion coefficient and can be easily retrieved. This Si_3N_4 surface was analyzed by XRD. In region 2 the diffraction pattern shows a degree of underground noise, characteristic for the presence of amorphous phases, and Al_2O_3 in several structures, denominated transitory aluminas that are intermediary phases for the crystallization of ζ-Al_2O_3 [14]. This indicates that, in the internal surfaces of the crucibles, aluminum has been oxidized forming the transitory phases of Al_2O_3. The Si_3N_4 peaks identified in this diffraction pattern correspond to the crucible material.

Final discussion

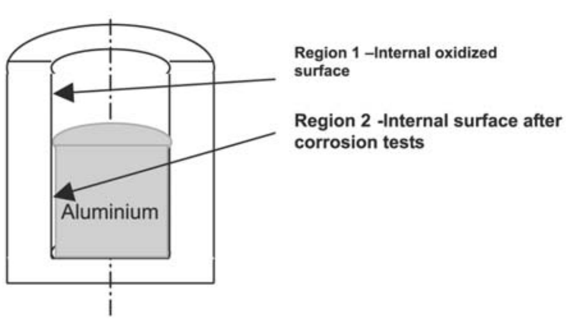
Gathering the information generated by the various characterization techniques, we propose a theory to describe the process of corrosion in the Si_3N_4 crucibles: the crucibles were heated under oxidizing atmosphere and solid aluminum bars were deposited, with superficial Al_2O_3 already present. This solid and resistant Al_2O_3 film represents a barrier for the contact between liquid Al and solid Si_3N_4. On the other hand, the Si_3N_4 surface during heating up to 900 °C also oxidized. In this way in the accomplished corrosion tests, the true contact interface was Al_2O_3/SiO_2. For the microstructural analysis (Fig. 1), three different phases are observed.

By the observed tonality differences (identification of atomic number of the phases), we propose that supposedly Al_2O_3 in the area of Al, due to the sample was exposed to atmosphere oxidizer, during the preparation of the samples (sanding and polish), the enough time to oxidize the aluminum surface. Comparing the tonality of the intermediary phase (interface) with the two majority regions, we identified, by difference of atomic number, which the presented phases: Al_2O_3 has Z = 50, while for Si_3N_4 Z = 70.

Starting from the microstructural analysis and the X-ray diffraction results, for the SiO_2 presence, (Z = 30), we can affirm that the interface presented in Figs. 1 and 2 is an Si_3N_4 oxidation film composed mainly of SiO_2 ($Z_{SiO2} < Z_{Al2O3} < Z_{Si3N4}$), which was formed in the contact region of Al/Si_3N_4, and that was formed due to the presence of oxygen in the system, motivated by the lack of existent contact of solid phases.

CONCLUSIONS

High corrosion resistant Si_3N_4 ceramics crucibles were produced using an alternative sintering additive, CTR_2O_3, produced at this laboratory. This corrosion behavior for liquid aluminum, at 1150 °C, in air, is due to the oxidized surface layer



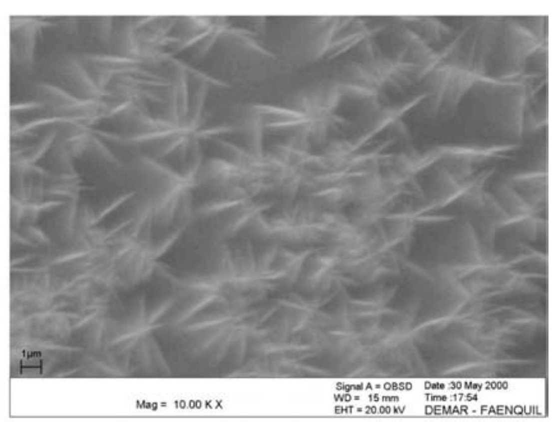


Figure 4: Oxidized surface of the crucible (Region 1).
[Figura 4: Superfície oxidada dos cadinhos (Região 1)].

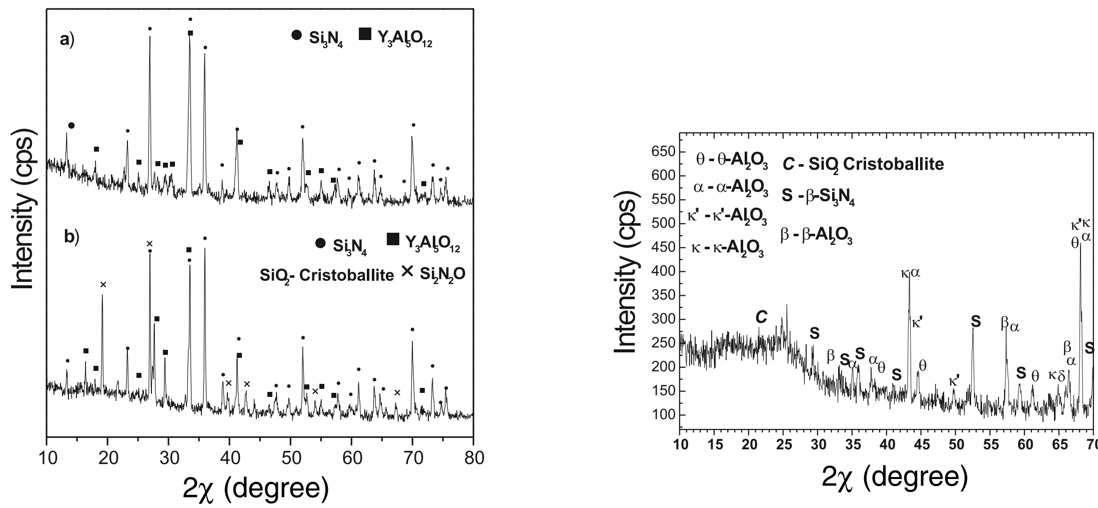


Figure 5: X-ray diffraction patterns of the crucibles surface: Region 1: a) before the corrosion tests; b) after corrosion tests for 1150 °C, in air; Region 2: surface of the crucibles, in contact with melted aluminum.

[Figura 5: Difratogramas de raios X das superfícies dos cadinhos: Região1: a) antes dos testes de corrosão; b) após testes de corrosão a 1150 °C, ao ar; região 2: superfície dos cadinhos em contato com o alumínio fundido].

of SiO_2, stable and adherent, that promotes the adherence of Al_2O_3 present on the aluminum surface. Starting from the scanning electronic microscopy characterizations, the chemical analysis for energy dispersive spectroscopy, and phase analysis by X-ray diffraction, the detected phases could be identified and the mechanisms present during the corrosion tests were defined.

ACKNOWLEDGEMENT

The authors would like to thank to FAPESP (Processes 99/08976-8 and 01/08682-6) for financial support.

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(Rec. 25/02/03, Ac. 18/07/03)