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Corrosion of nickel aluminate by Ca, Fe, Mg and V oxides and synthetic slags

R. Allende-Mata, J.M. Almanza-Robles*, J.C. Escobedo-Bocardo, D.A. Cortés-Hernández

Centro de Investigación y de Estudios Avanzados del IPN, Av. Industria Metalúrgica 1062 Parque Industrial Saltillo-Ramos Arizpe, Ramos Arizpe, Coahuila 25900, Mexico

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ABSTRACT

The corrosion resistance of a stoichiometric $NiAl_2O_4$ spinel was studied. $NiAl_2O_4$ spinel samples were exposed to either CaO, Fe_2O_3, MgO, V_2O_5 or synthetic slags at 1450 °C for 6 h. Two different synthetic slags were used, one containing high amount of Fe_2O_3, SiO_2 and MgO and other with high amount of CaO and Al_2O_3. In most the cases, $NiAl_2O_4$ spinel was not chemically stable and, depending on the nature of the corrosive agent, several corrosion products were formed. The higher reactivity was observed for the system where a synthetic slag with high content of Ca and Al was used. Using the corrosion results and thermodynamic equilibrium calculations (FactSage 6.2) it was possible to elucidate the corrosion mechanisms.

1. Introduction

Magnesium spinel-based refractories have been widely used in different applications such as cement rotary kilns, sidewalls of steel teeming ladles and in the checker work of the glass tank furnace regenerators [1,2]. This spinel possess several properties that make it suitable for refractory applications: high melting point, high mechanical strength, high hardness, good thermal shock resistance and high resistance to chemical attack [2–4]. One of the main characteristics of these refractories is their chemical stability. The chemical resistance of the spinel-based refractories has been extensively studied, recently the chemical resistance of magnesium spinel in contact with high MnO slag [5], sulfur-containing slag [6] and a melting salts bath [7] has been reported. In order to reduce costs during high temperature process, petcoke has been used as an alternative fuel in several industries [8]. One of the drawbacks of alternative fuels is the impurities content. These fuels contain mainly V_2O_5, SiO_2, Al_2O_3, CaO, Fe_2O_3 and, in minor quantities, MgO, TiO_2 and K_2O [9–11]. These oxides are dragged out by the combustion gases and are deposited on the refractories walls initiating a complex corrosion process. Fernández et al. [12] studied the corrosion mechanisms of magnesium spinel with NiO, Fe_2O_3, V_2O_5 and a vanadium slag at 1400 °C. They found that the more severe attack was produced by V_2O_5 since a low melting point magnesium vanadate was formed. On the other hand, in the group of spinels, nickel spinel shows excellent properties to be considered as a refractory material. Nickel aluminate spinel possess good mechanical strength, high melting point and chemical stability [13] making this material suitable for high temperature applications. Recently, $NiAl_2O_4$ spinel has been extensively studied due to its properties. Nickel aluminate shows catalytic behavior and it is used for diesel steam reforming [14] and H_2 production [15–17]; additionally, it has been used as a support composite for thin films in solid oxide fuel cells [18] and as a reinforcement in alumina membranes [19]. The nickel spinel has been used as a sidewall lining for aluminum smelters, this spinel showed good chemical stability in contact with cryolite at 980 °C [20]. Depending on the application, $NiAl_2O_4$ spinel is synthetized by different methods: sol-gel [21], polymeric precursor [22], auto-combustion [16,23], co-precipitation [14], nitrate route [17], and solid-state reaction [24,25]. In order to evaluate the use of this spinel as a refractory material it is important to determine its chemical stability in contact with different oxides. In this work, the corrosion mechanisms of $NiAl_2O_4$ spinel synthetized by solid-state reaction in contact with V_2O_5, Fe_2O_3, MgO, CaO and two different synthetic slags were studied.

2. Experimental procedure

Calcined alumina (99.7 wt%, Almatis), NiO, MgO, Fe_2O_3, V_2O_5, CaO, MnO, TiO_2 and Cr_2O_3 (analytical-grade chemicals, Sigma Aldrich) were used as raw materials in the present work. The $NiAl_2O_4$ spinel was prepared from a mixture of 57 wt% Al_2O_3 and 43 wt% NiO. Powders of these reagents were homogenized by ball-milling in a plastic container during 12 h using acetone. The homogenized product was then dried in an oven at 100 °C during 8 h. Homogenized powders were uniaxially pressed at 300 MPa to produce cylindrical specimens of 1 cm in diameter and 1 cm in height. Specimens were heat treated at 1550 °C in air for 6 h. Samples were analyzed by X-ray diffraction (XRD) and scanning

* Corresponding author.
E-mail addresses: rene.allende@cinvestav.edu.mx (R. Allende-Mata), manuel.almanza@cinvestav.edu.mx (J.M. Almanza-Robles), jose.escobedo@cinvestav.edu.mx (J.C. Escobedo-Bocardo), dora.cortes@cinvestav.edu.mx (D.A. Cortés-Hernández).

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Table 1
Composition of the synthetic slags (wt%).

	Slag 1	Slag 2
Fe_2O_3	24.5	5.5
SiO_2	25.1	5.8
V_2O_5	8.9	–
TiO_2	3.3	–
Al_2O_3	10.2	32.9
MnO	1.6	2.5
Cr_2O_3	8.7	–
MgO	15.8	3.4
CaO	1.9	49.9

electron microscopy (SEM) after sintering.

Two synthetic slags of the composition shown in Table 1 were also prepared using the raw materials. One of the slags was prepared with high amounts of iron oxide and silica and the other with high amounts of calcium oxide and alumina. Cylindrical specimens of 1 cm in diameter and 1 cm in height were prepared following the procedure described above. Slag samples were heat treated at 1500 °C for 2 h, ball-milled (< 45 µm) and analyzed by XRD.

Corrosion tests were carried out using alumina crucibles containing the $NiAl_2O_4$ spinel samples. Spinel disks were cross-sectioned, one-half of the disk was placed over the other half, and 1 g of the corrosive powder (oxide or synthetic slag) was placed in the middle. Thus, samples were in contact with either Fe_2O_3, V_2O_5, MgO, CaO, or a synthetic slag respectively at 1450 °C for 6 h. The corroded specimens were analyzed by XRD and cross-section samples were analyzed by SEM and energy dispersive spectroscopy (EDS). In order to identify plainly the products after the reaction that takes place between spinel and slags, further investigation was performed. Two samples of $NiAl_2O_4$ powder were mixed with each one of the slag powders in a weight ratio 1:1. Powder mixtures were uniaxially pressed at 300 MPa, heat-treated at 1450 °C for 6 h and analyzed by XRD.

3. Results and discussion

Fig. 1 shows the XRD patterns corresponding to the synthetic slags after heat treatment.

After heat treatment, slag 1 formed phases such as anorthite, pseudobrookite, frustrated spinel (AlV_2O_4) [26], SiO_2 and Fe_2O_3. For the slag 2, the main components were CaO, Al_2O_3 and $Ca_2Fe_2O_5$. These components were used for the thermodynamic calculation to predict the equilibrium phases when these slags are in contact with $NiAl_2O_4$ spinel at high temperature.

The XRD patterns corresponding to the $NiAl_2O_4$ spinel before and

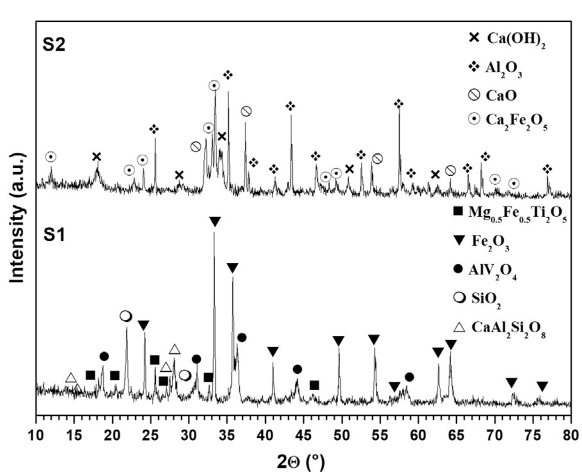

Fig. 1. XRD patterns of synthetic slags after heat treatment; S1: slag1, S2: slag2.

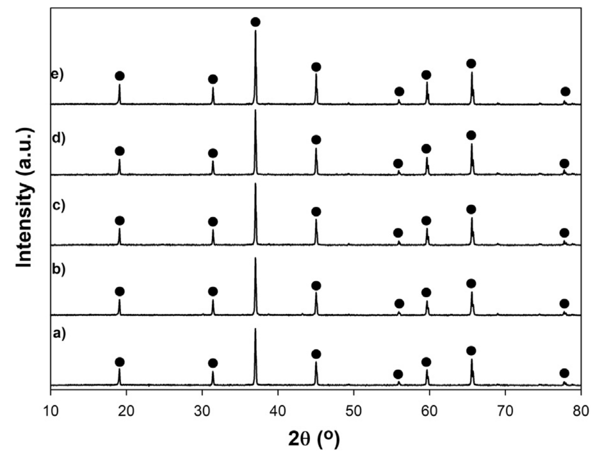

Fig. 2. XRD of $NiAl_2O_4$ (a), $NiAl_2O_4$-CaO (b), $NiAl_2O_4$-Fe_2O_3 (c), $NiAl_2O_4$-MgO (d), and $NiAl_2O_4$-V_2O_5 (e) after the corrosion test at1450 °C for 6 h.

after corrosion testing using simple oxides are shown in Fig. 2.

In all the cases, a single phase corresponding to $NiAl_2O_4$ spinel (JCPDS 71–0964) was detected. According to these results, there is no indication of a reaction among the spinel and single oxides. However, taking into account that this technique cannot detect phases in a content below 3 wt%, samples were also analyzed by SEM-EDS and some changes were observed.

Fig. 3 shows the reaction layer of the $NiAl_2O_4$ spinel in contact with CaO. Two phases can be observed in the compact reaction layer. The white one is a bright phase that it is composed mainly by Ni and O and a grey continuous phase is composed by Al, Ca and O. The grey phase may correspond to calcium aluminate and the bright phase to NiO.

The $NiAl_2O_4$ spinel sample, after corrosion testing in contact with Fe_2O_3, is shown in Fig. 4. A corrosion layer of about 100 µm in thickness has been formed. The EDS analysis showed that the corrosion layer is composed mainly of Fe, Ni, Al and O. According to the Al_2O_3-Fe_2O_3 phase diagram [27] the stable phases are hematite and corundum in solid solution. No intermediate phases are reported in the phase diagram.

Fig. 5 shows an SEM image and corresponding EDS spectrum of the $NiAl_2O_4$ spinel after the corrosion test in contact with MgO. There is no evidence of chemical attack. Magnesium and nickel possess the same valence and have similar ionic radii. Thus, the formation of $MgAl_2O_4$, in a similar behavior to that observed when using CaO, was expected. However, Mg was not detected by EDS.

The SEM image and corresponding EDS spectra of the $NiAl_2O_4$-V_2O_5 system after corrosion testing are shown in Fig. 6. As observed in the EDS results, the main phase may be $NiAl_2O_4$ and some Al-rich particles were also observed, which may correspond to Al_2O_3. Additionally, a V, Ni-rich compound was also detected which may correspond to a vanadate phase. According to the EDS analysis and based on the NiO-V_2O_5 phase diagram [27], this phase may correspond to NiV_2O_6. This observation may indicate that vanadium oxide infiltrated the sample and reacted with the $NiAl_2O_4$ spinel. Thermodynamic calculation was made in the aim to clarify the results obtained.

Fig. 7 shows the corrosion test results of the $NiAl_2O_4$ spinel-synthetic slags systems, where a different behavior occurred resulting in severe morphological changes. A major change for the system with the slag that contains high amount of calcium was observed. Due to the complexity of reactions that are taking place, it is not possible to imply the phases formed. The possible corrosion products for these systems are discussed below based on thermodynamic calculations.

For the $NiAl_2O_4$ spinel-slag 1 system, Ni, Al, O and Si were detected indicating a less severe reaction. Since this slag contains more components, many phases in small amounts which are not easily detected may be formed. For the $NiAl_2O_4$ spinel-slag 2 system that contains higher