

Stabilization of MgCr_2O_4 spinel in slags of the SiO_2 -CaO-MgO- Cr_2O_3 system*

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Abstract

The objective of this study is to analyze the effect of MgO content and the slag basicity on the stability of the mineralogical species of the SiO_2 -CaO-MgO- Cr_2O_3 system. Slag samples were prepared in equilibrium at 1600 °C under reducing conditions ($p\text{O}_2 = 10^{-9}$ atm). The MgO content ranged from 0 to 12 mass%, Cr_2O_3 was 10 % and the slag basicity was held at 1 and 1.5. A thermodynamic analysis was carried out to estimate the most stable mineral phases in the slag. Experimental and calculated results show that Cr_2O_3 is mainly bound into MgCr_2O_4 spinel phase, even at low MgO content. SEM-EDS results show the evidence of three crystalline structures: (A) Octahedrons which correspond to MgCr_2O_4 spinel-type compound; (B) Elongated crystals which belong to calcium silicate compounds and (C) Massive grains that correspond to calcium silicates with impurities of Mg and Cr that did not crystallize completely.

Keywords

Spinel. Slag.

Estabilización de la espinela MgCr_2O_4 en escorias del sistema SiO_2 -CaO-MgO- Cr_2O_3

Resumen

El objetivo de este estudio es analizar el efecto del contenido de MgO y la basicidad de la escoria sobre la estabilidad de las especies mineralógicas del sistema de escoria SiO_2 -CaO-MgO- Cr_2O_3 . Se realizaron ensayos al equilibrio a 1600 °C bajo condiciones reductoras ($p\text{O}_2 = 10^{-9}$ atm). El contenido de MgO fue de 0 a 12 % masa, el Cr_2O_3 de 10% y la basicidad de 1 y 1,5. También se realizó un análisis termodinámico para determinar las fases mineralógicas más estables en la escoria. Los resultados experimentales y calculados muestran que el Cr_2O_3 se encuentra principalmente ligado en una fase espinela MgCr_2O_4 , incluso a bajos contenidos de MgO. Los resultados obtenidos por microscopia electrónica de barrido (MEB-EDS), muestran la evidencia de tres estructuras cristalinas: (A) Octaedros, los cuales corresponden a la espinela MgCr_2O_4 , (B) Cristales alargados que corresponden a la formación de silicatos cálcicos y (C) Matriz de silicatos cálcicos con impurezas de Mg y Cr que no cristalizaron por completo.

Palabras clave

Espinela. Escoria.

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1. INTRODUCTION

Chromium losses are one of the main concerns in ferrochromium and stainless steel production since it is one of the major constituents of these materials and represents a large portion of the raw materials cost. It is important to save costs and energy as well as to reduce eventual polluting effects of chromium containing slags and wastes. To come close to the goal of zero chromium waste, some researchers have worked either on decreasing the scorification of chromium or on the neutralization of the chromium in the slag. The first objective is fulfilled by decreasing the chromium content in the slag by the use of reducing agents during melting such as silicon, aluminum and calcium^[1]. The second objective can be achieved through bounding the chromium into stable spinel phases in the slag. Some spinel formers such as Al_2O_3 and MgO have high bounding efficiency, which results in lowering the chemical activity of chromium^[2 y 3].

Magnesium has been used as a reducing agent of niobium oxide and other metallic oxides. However, very few works have been carried out on the reduction of metallic oxides in steelmaking slags using magnesium^[4 y 5]. Magnesium is used in steelmaking processes mainly as deoxidation agent and sometimes to modify inclusions. In addition, a MgO -based slags can be used to diminish the leaching behavior of chromium through the formation of stable spinels which do not leach any of their compounds as has been reported elsewhere^[6]. It has also been reported that magnesium-based slags reduce the refractory lining attack due to its own magnesia contribution what it means a real protection of the furnace walls^[7].

The purpose of this study is to determine the effect of MgO content and slag basicity on the stabilization of the MgCr_2O_4 spinel and other mineralogical species in slags of the SiO_2 - CaO - MgO - Cr_2O_3 system. This includes mineral identification and mineral morphology by the X-Ray diffraction and Scanning Electron Microscope (SEM). A thermodynamic analysis is also carried out to estimate the most stable mineral phases in the slag system.

2. MATERIALS AND EXPERIMENTAL PROCEDURE

The experiments were carried out at $1,600 \pm 5^\circ\text{C}$ using 4 g of slag and a platinum crucible with 25 mm inner diameter and 35 mm height. The slag was prepared with laboratory reagent-grade oxides (CaO , MgO , SiO_2 and Cr_2O_3) which were previously ground into fine powder whose particle size was between 45 and 74 μm . The required powders were homogeneously mixed and placed into the Pt crucible. The working cru-

cible was placed in a corundum protecting crucible. The MgO content ranged from 0 to 12 mass%, Cr_2O_3 was 10 % and the slag basicity B , defined as the ratio of $\text{CaO}+\text{MgO}$ content to the SiO_2 content (all mass%), was held at 1 and 1.5.

The experimental system consisted of a horizontal electric resistance furnace heated by MoSi_2 heating elements, an argon purification line and a CO-CO_2 line. Temperature was measured by a PtRh30-PtRh6 thermocouple. The overall error in the measurement and control of the temperature was less than $\pm 5^\circ\text{C}$.

The reaction system was protected by purified argon gas during the heating process with a flow rate of 0.5 l/h. After the slag melted and reached the desired temperature ($1,600^\circ\text{C}$) the argon gas was switched to the 93 % CO -7 % CO_2 mixture to produce the desired oxygen pressure $p\text{O}_2 = 10^{-9}$ atm (1.013×10^{-4} Pa). Equilibrium relations involving chromium oxide-containing systems have been reported to be dependent on the oxygen partial pressure by Pretorius *et al.*^[8]. In addition, Jahanshahi and Sun^[9] reported that dissolution rate and desintegration of refractories depend on the oxidation state of the slag. Then we have chosen a relatively low oxygen pressure which can be found in steelmaking processes.

The oxide mixture were reacted and equilibrated at 1600°C for about 12 h in the furnace. Previous trials were carried out to be sure that 12 h were enough to reach the equilibrium. Then after the equilibrium was reached, the crucible was pulled out of the hot zone of the furnace and quenched rapidly by jetting argon gas. In order to identify the equilibrium phases the quenched specimen were ground into fine powder and subjected to the X-ray diffraction analysis using a Rigaku DMAX2200 X-ray diffractometer. Other slag samples were cut into pieces of about 0.5 cm, mounted and analyzed with a Jeol 6300 Scanning Electron Microscope (SEM) with energy dispersive spectra (EDS) employing an accelerating voltage of 25 kV. SEM was also used to study the morphology and composition of mineral phases.

3. THERMODYNAMIC ANALYSIS

The FACTSage computational thermodynamic package^[10] was used to determine the equilibrium species in the slag since it contains an extensive optimized solution database. FACTSage system uses the quasi-chemical approximation^[11] for the liquid oxide-based slags. The general free energy minimization method is used to estimate the equilibrium concentration once the models and the thermodynamic properties of the species in the system have been selected. For a given set of constraints (such as fixed temperature, pressure and overall concentration), the free energy minimiza-

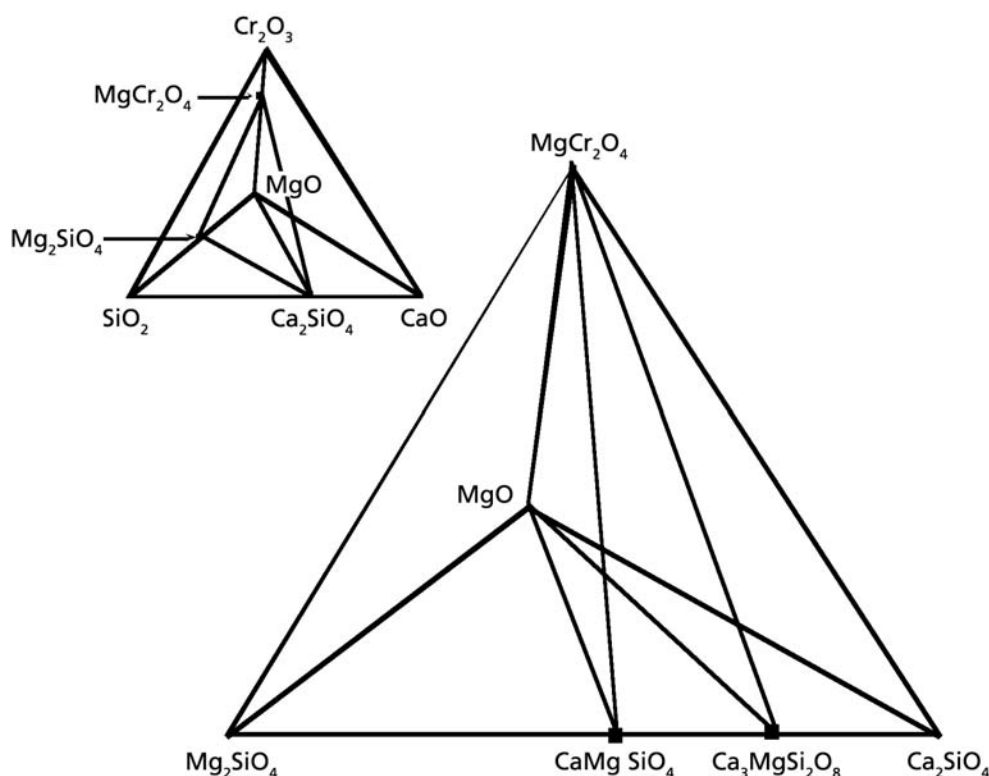


Figure 1. Schematic diagram of the MgCr_2O_4 - Mg_2SiO_4 - Ca_2SiO_4 - MgO system.

Figura 1. Diagrama esquemático del sistema MgCr_2O_4 - Mg_2SiO_4 - Ca_2SiO_4 - MgO .

tion algorithm finds the set of mole numbers of each species as well as the compositions of all solution phases which globally minimize the free energy function.

The equilibrium computations were performed to analyze the effect of MgO and Cr_2O_3 content as well as the slag basicity on the stability of the mineralogical species. The equilibrium calculations were performed at 1,600 °C with an atmosphere with $p\text{O}_2=10^{-9}$ atm. The input in mass places 4 g of slag containing MgO content ranged from 0 to 16 mass %, Cr_2O_3 was from 0 to 25 % and the slag basicity ranged from 0.5 to 2.0. Data are automatically retrieved from databases for the liquid slag phase and pure chemical species. Gibbs energy minimization then gives the equilibrium slag composition along with the probable solid oxide species present in the system.

Figure 1 shows the schematic diagram of the MgCr_2O_4 - Mg_2SiO_4 - Ca_2SiO_4 - MgO system and the solid state compatibility of MgCr_2O_4 with phases in the quaternary system having mol ratio $\text{CaO}/\text{SiO}_2 \leq 2$. Insert diagram shows position of this tetrahedron in the CaO - MgO - SiO_2 - Cr_2O_3 quaternary composition volume^[12]. Figure 1 is included to have a better comprehension of the stability diagrams.

Figure 2 shows the estimated phase stability diagrams at four basicities (0.5, 1, 1.5 and 2). As can be seen, the mineralogical phases of the system are highly dependent on its basicity and slag composition. As a

general trend, lower slag basicities diminish the melting point of slags; thus, the liquid phase is stable in higher ranges of Cr_2O_3 and MgO contents. The thermodynamic analysis predicts that the MgCr_2O_4 spinel is one of the most stable solid phases at all basicities (from 0.5 to 2) even at low MgO content. This spinel phase appears once the liquid slag becomes unstable. The CaCr_2O_4 phase is also stable at high basicities and relatively low MgO content. Other main solid components in the system are the calcium silicates (Ca_2SiO_4 and CaSiO_3). Free MgO occurs only at basicities higher than 1.5 and at high MgO content, whereas free Cr_2O_3 occurs at low MgO content. It must be stressed that these diagrams are calculated at 1,600 °C and do not predict the phases that can be formed during the cooling of the slag system. These thermodynamic results show that chromium is mainly bound into stable spinel phase (MgCr_2O_4 and CaCr_2O_4), even at low MgO content in the slag and at basicities from 0.5 to 2.

4. RESULTS AND DISCUSSION

4.1. X-Ray diffraction pattern

The X-ray diffraction patterns for the slags with basicity fixed at 1 are shown in figure 3. As can be observed, the crystallization process is carried out at 1,600

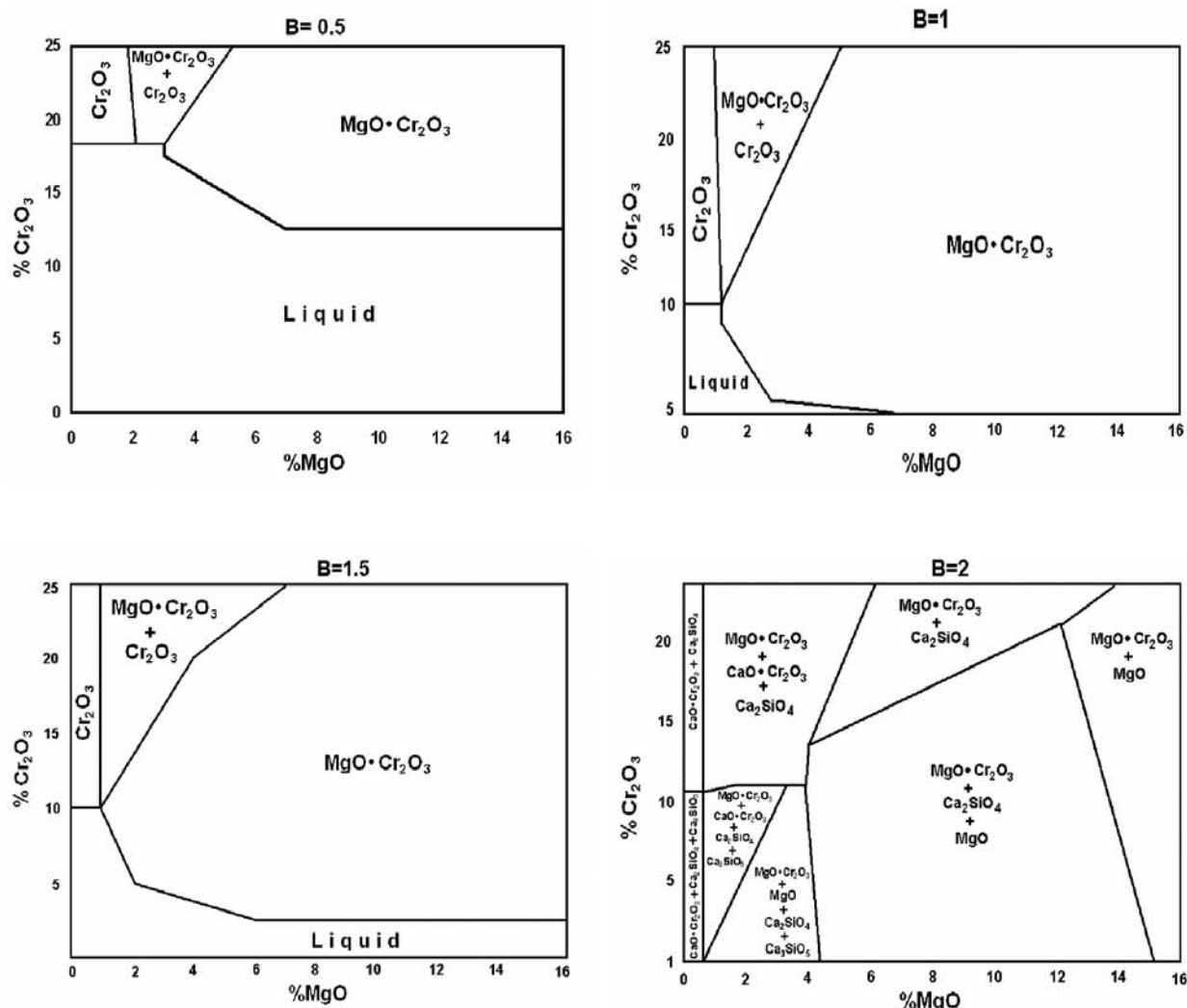


Figure 2. Phase stability diagrams at 1,600 °C for the SiO_2 -CaO-MgO- Cr_2O_3 system (mass %) as function of slag basicity.

Figura 2. Diagramas de estabilidad de fases a 1.600 °C para el sistema SiO_2 -CaO-MgO- Cr_2O_3 (% masa) en función de la basicidad de la escoria.

°C when the MgO content in the slag is higher than 6 %. The X-ray patterns for the samples with % MgO = 0, 3 and 6 show that the products obtained are “amorphous” to X-rays, or contains a few very weak reflections of Ca_2SiO_4 and CaSiO_3 . This means that the liquid slag became a glassy slag when the specimens were quenched with argon gas. This is in agreement with the thermodynamic results shown in figure 2 which indicates that at low slag basicity and low MgO content, the liquid slag is more stable than the crystalline phases at 1,600 °C.

Figure 3 shows that more clear X-ray diffractions were obtained for samples with 9 and 12 % MgO content. These samples are mainly constituted by calcium silicates (Ca_2SiO_4 and CaSiO_3) and the MgCr_2O_4 spinel, with minor amounts of free SiO_2 and CaO. It was also observed some fainter peaks of free Cr_2O_3 and CrO. The presence of CrO in the slag is in agreement with the work of Xiao *et al.*^[13] who reported that at

low oxygen partial pressure and low slag basicity, divalent and trivalent chromium coexists in the slags.

Figure 4 shows the X-ray diffraction patterns for the slags with basicity equals 1.5. It can be seen that the diffraction patterns are complicated since many mineral species can be formed in the system. The results show that the samples exhibit a higher degree of crystallization at this basicity. It is also observed that the main species are calcium silicates (Ca_2SiO_4 , CaSiO_3 and Ca_3SiO_5), free Cr_2O_3 and the MgCr_2O_4 spinel. It was found in this work that the free Cr_2O_3 becomes more stable than CrO when the slag basicity is increased, which is in agreement with the results of Tanahashi *et al.*^[13]. The ternary compound (merwinite) $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$ was found at high MgO content. The CaCr_2O_4 spinel was not detected by X-ray diffraction. It is possible that the peaks of this compound are too close to the MgCr_2O_4 phase. Fainter peaks were detected for free SiO_2 and CaO.

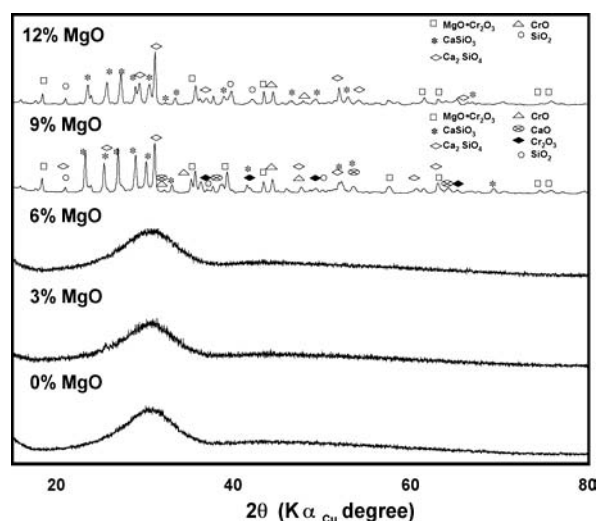


Figure 3. Observed X-ray diffraction patterns for the slags with basicity equals 1.0.

Figura 3. Patrón de difracción de rayos X para las escorias de basicidad igual 1,0.

4.2. Microanalysis results

Another experiment was conducted in order to identify the crystalline structure and composition of the species using the scanning electron microscope with energy dispersive-spectra (SEM-EDS) and in this way to support the thermodynamic and X-ray diffraction results. In this trial the slag contained 6 mass % MgO , 10

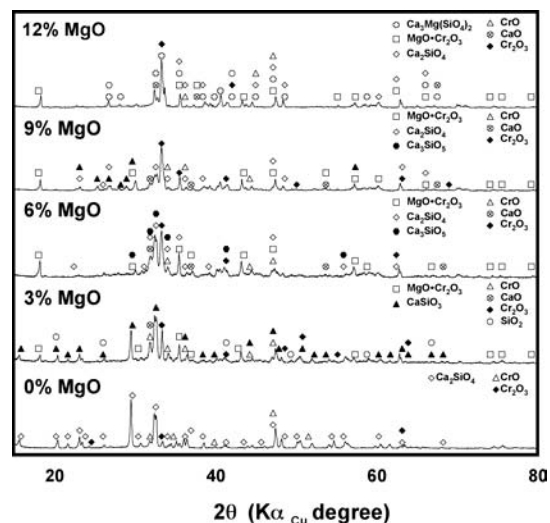


Figure 4. Observed X-ray diffraction patterns for the slags with basicity equals 1.5.

Figura 4. Patrón de difracción de rayos X para las escorias de basicidad igual 1,5.

% Cr_2O_3 and the basicity was 1.5. After the equilibrium was reached at 1,600 °C the furnace was turned off and the sample was cooled down slowly to room temperature inside the furnace in order to promote the formation of well defined crystalline structures.

The sample was mounted and the microstructure was examined in detail using optical microscopy as well as SEM coupled with EDS analysis. The SEM mi-

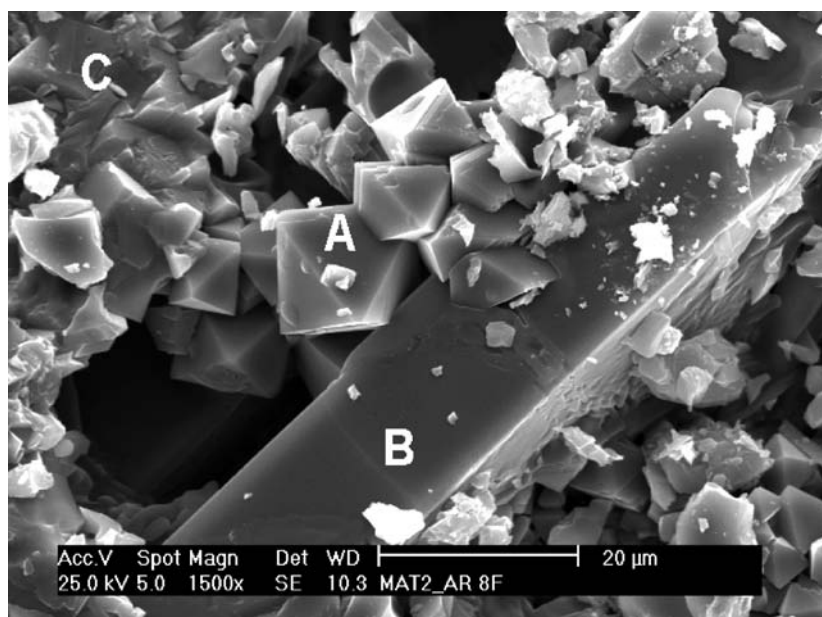


Figure 5. SEM micrograph for the slag constituted by 6 % MgO , 10 % Cr_2O_3 and $(\text{CaO}+\text{MgO})/\text{SiO}_2 = 1.5$. (A) Octahedrons, (B) Elongated crystals, (C) Massive grains.

Figura 5. Micrografía de MEB para la escoria constituida por 6 % MgO , 10 % Cr_2O_3 y $(\text{CaO}+\text{MgO})/\text{SiO}_2 = 1,5$. (A) Octaedros, (B) Cristales alargados (C) Granos masivos.

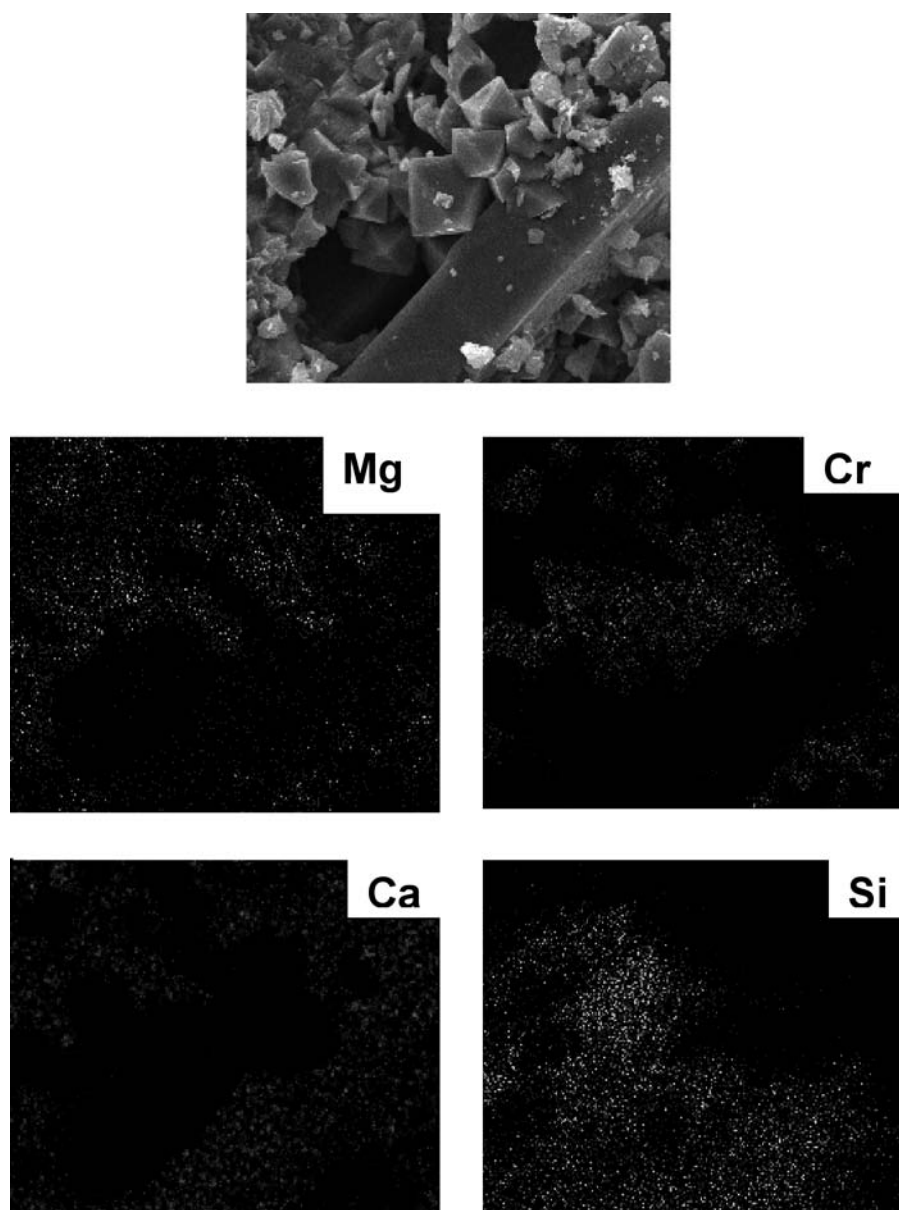


Figure 6. X-ray mapping images for the Mg, Cr, Ca and Si elements.

Figura 6. Imágenes de rayos X de mapas de distribución para los elementos Mg, Cr, Ca y Si.

crograph in figure 5 shows the evidence of the following three main kinds of crystalline structures: (A) Octahedrons which corresponds to the isometric crystal system, with a size from 5 to 20 μm , (B) Fibrous masses of elongated crystals which belong to the triclinic crystal system, (C) Massive grains lacking apparent structure.

Figure 6 shows the X-ray mapping images for the Mg, Cr, Ca and Si elements. The X-ray image shows a contrast due to element concentration gradient. For example, in the X-ray image for magnesium, the bright areas correspond to magnesium rich zones and the dark areas correspond to magnesium poor zones. The crystals labeled A in Figure 5 present a high

her concentration of chromium and magnesium; thus, it is believed that this corresponds to the MgCr_2O_4 spinel-type phase. In addition, it has been reported^[15] that magnesiochromite or similar minerals crystallize in cubes or octahedrons, such as those that were found in this sample. The X-ray mapping shows that crystals B contain mainly calcium and silicon and probably they are calcium silicates, Ca_2SiO_4 and CaSiO_3 . Finally, the massive grains, labeled C, present calcium and silicon as main elements and small amounts of magnesium and chromium. Then, it is assumed that they correspond to calcium silicates with impurities of magnesium and chromium that did not crystallize completely.

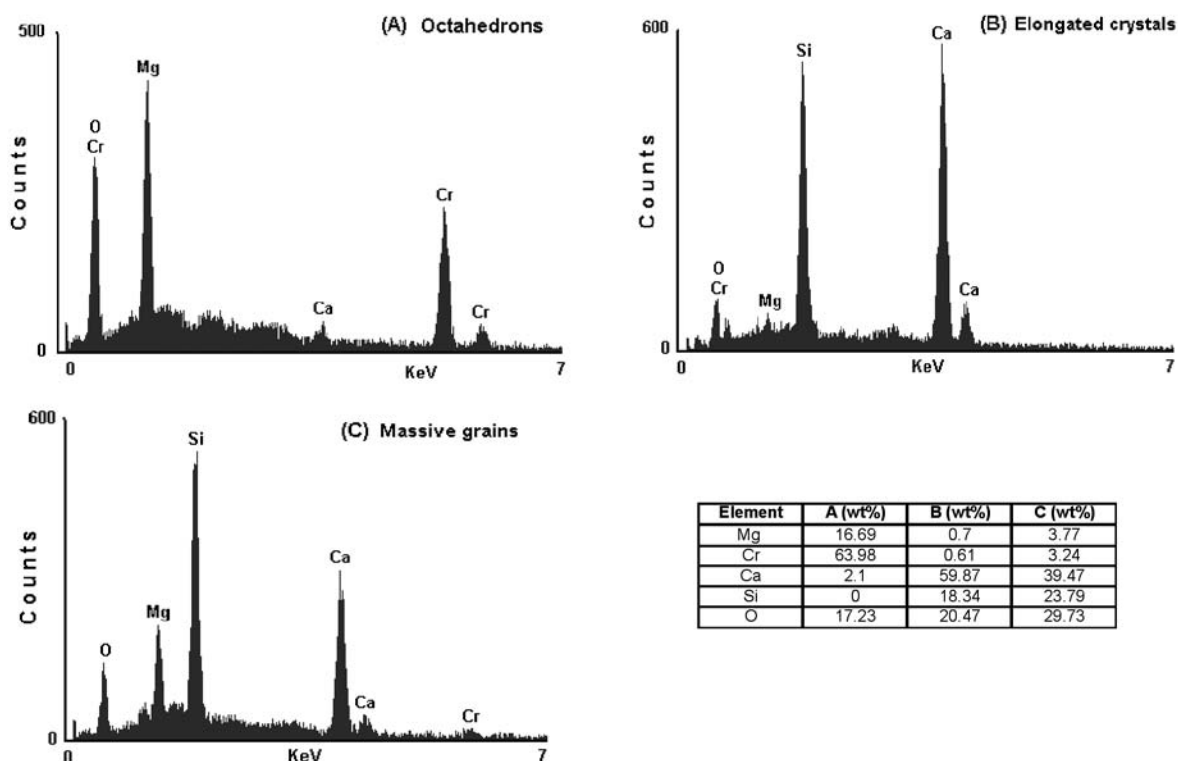


Figure 7. EDS analysis of the crystalline phases: (A) Octahedrons, (B) Elongated crystals, (C) Massive grains.

Figura 7. Análisis por EDS para las fases cristalinas: (A) Octaedros (B) Cristales alargados, (C) Granos masivos.

This sample was also analyzed in the SEM-EDS system to estimate the concentration of elements in each kind of crystals. Figure 7 shows X-ray spectra and the composition of phases obtained by this semi-quantitative method for the crystals labeled A, B and C. By examining these results, it can be seen that the octahedrons correspond to a magnesium, chromium and oxygen rich element, probably MgCr_2O_4 compound. The elongated crystals correspond to Ca, Si and O rich species, Ca_2SiO_4 and CaSiO_3 .

The SEM-EDS results confirm the X-ray identification results and the thermodynamic analysis which show the existence of MgCr_2O_4 , Ca_2SiO_4 and CaSiO_3 . Then, it is concluded that MgO-based slags can be used in stainless steel production to bound the remaining chromium into spinel phases in the slags and wastes. It is expected that this Mg-Cr phase diminish the leaching behavior of chromium; however, further experimental research must be carried out on the environmental behavior of this kind of slags to estimate the polluting effects of chromium.

5. CONCLUSIONS

Thermodynamic analysis of the SiO_2 - CaO - MgO - Cr_2O_3 slag system was carried out at 1600 °C to analyze the

effect of MgO and Cr_2O_3 content as well as the slag basicity on the stability of the mineralogical species. Experimental and calculated results show that Cr_2O_3 is mainly bound into MgCr_2O_4 spinel phase, even at low MgO content in the slag and at basicities from 0.5 to 2.

SEM-EDS results show the evidence of three crystalline structures: (A) Octahedrons which correspond to MgCr_2O_4 spinel-type compound; (B) Elongated crystals which belong to calcium silicate compounds and (C) Massive grains that correspond to calcium silicates with impurities of Mg and Cr that did not crystallize completely.

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