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Oxidation kinetics of Fe- Cr- and Fe-Cr-Ni alloys for SOFC interconnect applications at temperatures from 600ºC to 800ºC [(b)]

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Abstract

Metallic interconnects in solid oxide fuel cells (SOFCs) are exposed to a reducing environment, hydrogen, on one side and an oxidizing environment, air, on the other side at elevated temperatures. To further understand the suitability of Fe-Cr-base and Fe-Ni-Cr-base alloys for solid oxide fuel cell interconnect applications, three commercial Cr-base alloys, AISI 430, AISI 316 L, and CROFER® were selected and evaluated for oxidation behavior at temperatures from 600°C to 800ºC. The oxidation kinetic of alloys was studied.

Introduction

Significant progress in the research and development of solid oxide electrochemical devices to convert chemical reaction energy directly into electrical energy without combustion process has been made for several years (1). Solid oxide fuel cells generate very low levels of pollutants with a high power density. A SOFC is composed of two porous electrodes, an anode and a cathode, separated by a gas imperviousness ion-conducting electrolyte. The interconnection provides electrical connection between anode of one individual cell and the cathode of the neighboring one. It also acts as physical barrier to avoid any contact between reducing and oxidizing atmospheres.

Over the past years, advances in materials and cell fabrication technology have led to a steady reduction in SOFC operating temperatures to the intermediate range of 650°C-800ºC (2). Consequently it has become possible to consider high temperature oxidation-resistant alloys as the stack interconnect materials, instead of lanthanum chromites (3-6).

Only the chromia-forming alloys are generally considered for interconnect applications, as low electrical resistivity is required to minimize ohmic losses within the stacks (2). Among the chromia-forming oxidation-resistant alloys, the body-centered-cubic (BCC) ferritic stainless steels (FSS) demonstrate good oxidation resistance and the ability to match the coefficient of thermal expansion (CTE) of adjacent cell/stack components (2, 7-9). However, FSS has some disadvantages such as difficulty of reach long-term surface stability, increasing electrical resistance due to scale growth during prolonged stack operation, and low high temperature mechanical strength. In comparison, the face-centered-cubic (FCC) Ni-Fe-Cr- base alloys are much stronger and more oxidation resistant in the SOFC interconnect operating environment (10).

In this work, the kinetic oxidation behavior of a Cr-base and Ni-Cr-base alloys was studied. This is a preliminary study of the oxidation kinetics of the Cr-base alloys, which are materials

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that can be used as interconnecting in SOFCs. Other Cr-base alloys will be studied such as the AISI 444 steel, Haynes 230, and Hastelloy S.

Methodology

Commercial Cr-base steels, AISI 430, AISI 316 L, and CROFER® steels were selected and evaluated for oxidation behavior at temperatures from 600ºC to 800ºC. Sample dimension are 4 mm x 4 mm x 4 mm for the AISI 316 L steel, and 10 mm x 10 mm x 1 mm for the AISI 430 steel. The area of samples of CROFER® steel is 2 cm^2.
The chemical composition of the steels was measured by using plasma spectroscopy and was shown in Table 1.
Five samples of each steel were tested at the following temperatures: 600ºC, 700ºC and 800ºC.
The steel sample was heated in a porcelain crucible in an oven. For each temperature, the steel sample was heated for 5 minutes and then removed of the oven and cooled in air, up to the testing time reaches 30 minutes. For test times from 30 minutes up to 5 hours, the samples were heated in oven at intervals of 30 minutes. For testing times from 5 up to 20 hours, the steel sample was heated in oven for one hour, removed of the oven and cooled, up to the testing time reached 20 hours.
The cooling time was 5 minute for an oxidation time of 5 minutes. When the samples were heated for 30 or 60 minutes, the cooling time was 20 minutes.
Curves of mass gain versus time were obtained for each temperature studied, and linear regression technique was employed to adjust the results to a given function. This regression method models the relationship between a dependent variable Y, independent variables X_i, I= 1, …, p, and a random term ε.

Results and Discussion

Curves of mass gain versus time for the alloys oxidized were obtained. There are three main equations that relate the mass gain with time of oxidation: linear, parabolic and logarithmic. The data obtained in this work were analyzed in order to find the best equation that fit the data. The oxidation process of the Cr-based steels studied in this work was a cyclic process, which is more aggressive than the continuous oxidation.
A cubic kinetic was observed for the oxidation of AISI 430 steel at 600ºC.The AISI 430 steel oxidized at 700ºC showed a logarithmic kinetic (Figure 1). The initial corrosion rate is high, decreases, and there was a trend to stabilize. The logarithmic kinetic is observed when the oxide layer is almost impermeable and usually occurs in the initial oxidation of several metals such as iron, zinc, nickel, and aluminum (11). The analysis can also indicate a behavior related to a polynomial equation of second degree after the initial period. Pérez et al (12) reported a similar behavior for the AISI 430 steel submitted to a cyclic oxidation at 900ºC. However, Pérez et al (12) did not observe the final oxidation stabilization, but a linear kinetics after 250 cycles of one hour oxidation.
A polynomial equation of third degree fit to the data of oxidation of AISI 430 steel at 800ºC. The curve was a sigmoid, and then a stabilization of mass change occurs after 12 hours of oxidation.

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A parabolic kinetic was observed for the oxidation at 600ºC of the AISI 316 L steel as shown in Figure 2. In this case, the ion diffusion or the electron migration through the oxide layer is controlled and the oxidation rate is inversely proportional to the thickness of the oxide film. The oxidation behavior of 316 L steel heated at 700ºC showed several stair landings at 5, 12.5, and 20 hours. The initial period seems to be a logarithmic kinetic behavior, and then the oxidation stabilizes at five hours. After 7.5 hours of oxidation, the oxidation rate increases, and then stabilizes near to 12.5 hours of heating. After 15 hours of test, the oxidation rate increases and trends to stabilize after 20 hours. The rupture of the stabilization can occur due to failures of the oxide layer. Literature (1) reported the poisoning of the electrodes of SOFCs due to the oxidation gaseous species (CrO_3 or $CrO_2(OH)_2$) at temperatures close to 1000ºC and higher, but also observed at lower temperatures due to the severe operation conditions such as the presence of water vapor. This last hypothesis can have occurred in this work, generating the systematic oxide layer breaking. At 800ºC there was a higher dispersion of results, but the parabolic kinetic was the better fit to the results.

The oxidation kinetic behavior showed by the CROFER® steel at 600ºC and 800ºC (Figure 3) was logarithmic. The logarithmic kinetic is usually found when the oxide film is thin and not much permeable.

A parabolic kinetic was found for the oxidation in air of CROFER® steel at 700ºC. This kinetic behavior is presented by metal such as iron and chromium at high temperatures. As the temperature increases, the oxide layer becomes thicker and the ionic and electronic diffusion is more difficult.

Conclusions

A cubic kinetic was found for the AISI 430 steel oxidized at 600ºC.The AISI 430 steel oxidized at 700ºC showed a logarithmic kinetic. The curve of mass change versus oxidation time for the AISI 430 steel oxidized at 800ºC was a sigmoid, and a stabilization of mass change occurs after 12 hours of oxidation.

The oxidation behavior of 316 L steel heated at 600ºC, and 800ºC showed a parabolic kinetic.

The oxidation behavior of 316 L steel heated at 700ºC showed several stair landings at 5, 12.5, and 20 hours.

The oxidation kinetic behavior showed by the CROFER® steel at 600ºC and 800ºC was logarithmic. A parabolic kinetic was found for the oxidation in air of CROFER® steel at 700ºC.

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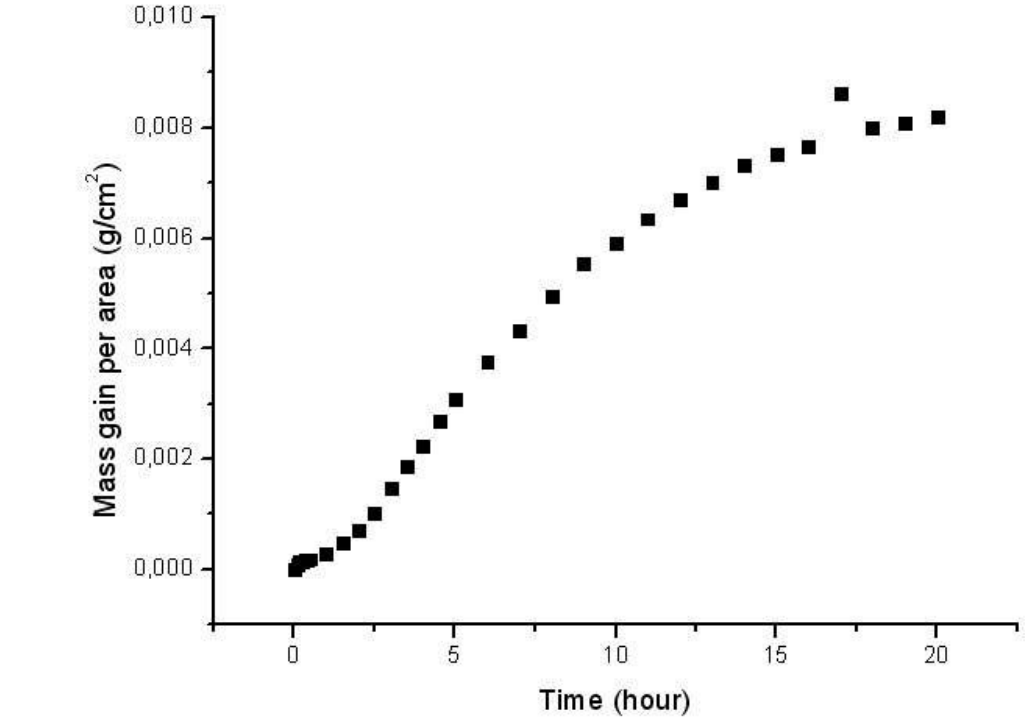

Figure 1 – Mass gain of AISI 430 steel oxidized at 700ºC

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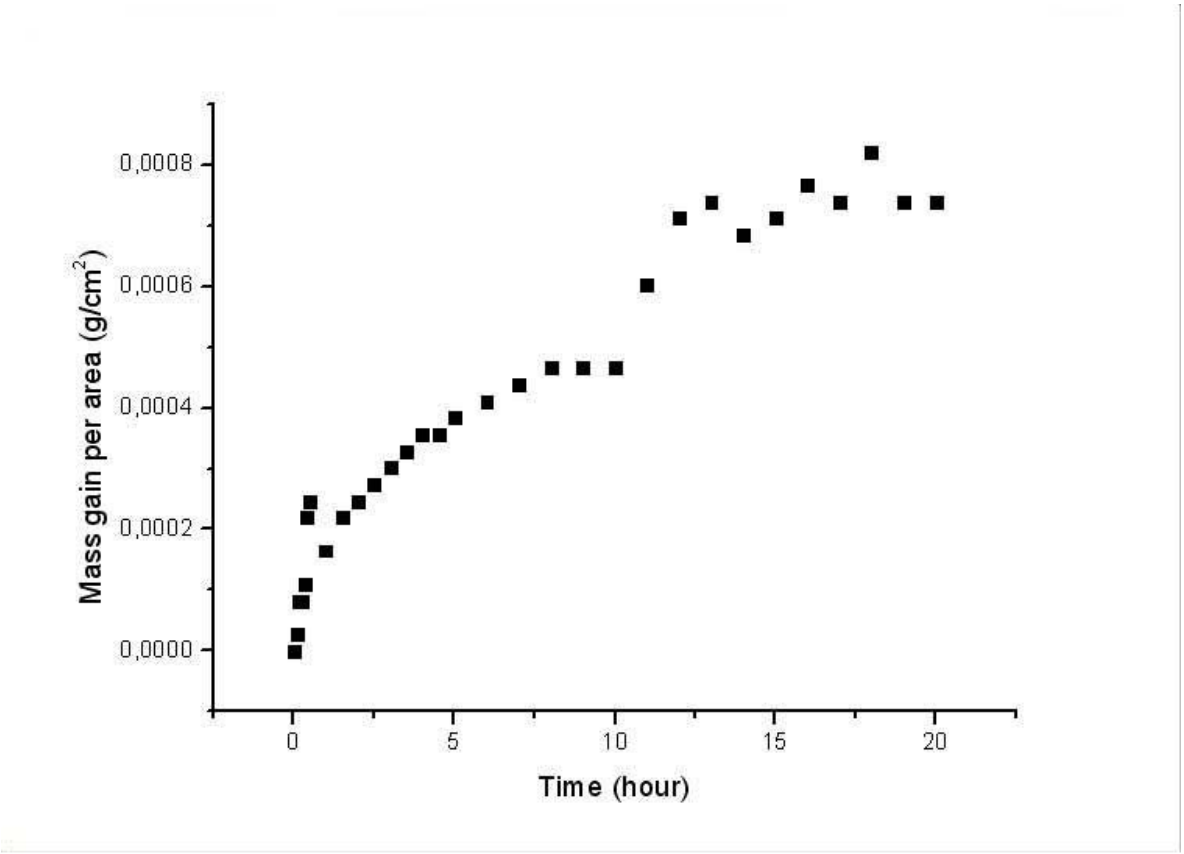

Figure 2 – Mass gain of the AISI 316 steel oxidized in air at 600ºC

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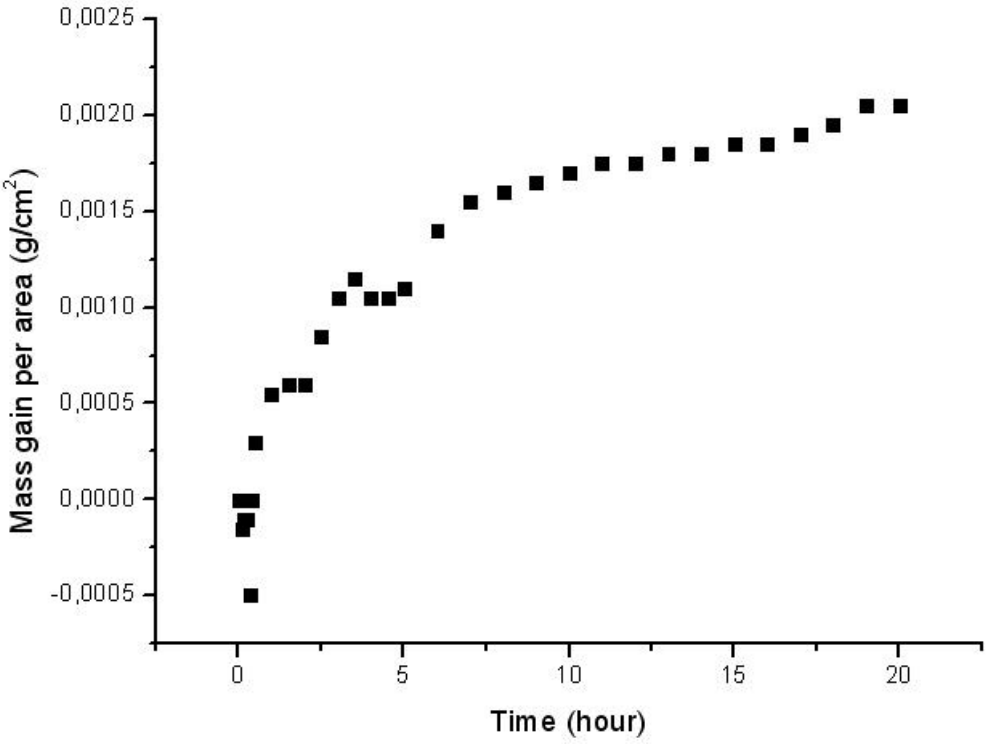

Figure 3 – Mass gain of the CROFER® steel oxidized at 800ºC in air

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Steel	C (%)	Mn (%)	Cr (%)	Ni (%)	Mo (%)	Si (%)	S (%)	P (%)
430	0.12	0.55	20.4	0.14	0.03	0.75	0.03	0.04
316 L	0.03	1.56	20.5	11.02	2.02	0.75	0.03	0.045
CROFER®	0.03	0.80	30.0	---	---	0.50	0.02	0.05

Table 1 – Chemical composition of steels

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