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Correlation between chromium physicochemical properties in silicate melts and the corrosion behavior of chromia-forming alloy

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HIGHLIGHTS

- Solubility limits of chromium in silicate melts are given for a wide fO_2 range.
- Diffusivity of multivalent chromium were determined by square wave voltammetry.
- Basicity and viscosity of the silicates affects the corrosion behavior of NiCr alloy.
- Dissolution of Cr_2O_3 is kinetically limited by the diffusion of Cr in silicates.

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ABSTRACT

The relationship between the corrosion behavior of a Ni-30Cr alloy and the physicochemical properties of chromium in silicate and borosilicate melts at 1150 °C has been investigated. Three glass compositions have been chosen in order to identify the effect of basicity and viscosity. The chromium solubility limits in borosilicate melts have been determined and compared with the basicity of the melts. The chromium diffusion coefficients in the melts have been determined with the square-wave voltammetry method. A strong impact of the melt viscosity has been found on the corrosion behavior of the Ni-30Cr alloy. This dependency indicates a mechanism involving a diffusion-limited process for the dissolution of the oxide.
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1. Introduction

Nickel-based alloys with a high chromium content offer useful properties for high temperature applications involving a metallic material in contact with a glass melt, e.g. for nuclear wastes vitrification [1] or glass fiber production [2,3]. Besides their good mechanical strength at high temperature, these alloys are able to develop a Cr_2O_3 protective oxide layer when oxidized. Chromium oxide provides a suitable protection against corrosion induced by glass melts due to the low solubility limit of chromium in silicate melts [4–6]. The stability of this Cr_2O_3 layer is therefore dependent on the physicochemical properties of the melt and of chromium in the melt. Indeed, the basicity of the melt affects the solubility of chromium. Dissolution of chromia in silicate melts has been well described by several authors with Eqs. (1)–(3) [5–8]. First, the dissolution of Cr_2O_3 into Cr^{III} follows an acid base reaction:

$$\frac{1}{2}Cr_2O_{3\ (s)} + \left(x - \frac{3}{2}\right)O^{2-} \leftrightarrow Cr^{III}O_x^{(2x-3)-} \quad (1)$$

Then, depending on the redox conditions, Cr^{III} can be either oxidized into Cr^{VI} or reduced into Cr^{II}:

$$Cr^{III}O_x^{(2x-3)-} + \frac{3}{4}O_2 \leftrightarrow Cr^{VI}O_y^{(2y-6)-} + \left(x - y + \frac{3}{2}\right)O^{2-} \quad (2)$$

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$$Cr^{III}O_x^{(2x-3)-} + \left(z - x + \frac{1}{2}\right)O^{2-} \leftrightarrow Cr^{II}O_z^{(2z-2)-} + \frac{1}{4}O_2 \quad (3)$$

The presence of the basic oxide ion O^{2-} in Eqs. (1)–(3) evidences the role of the melt basicity on the dissolution process of chromium in glass melts. Besides, a decreasing melt viscosity can lead to a faster diffusion of dissolved elements in the melt and may result in an accelerated corrosion rate, as it is the case for ceramic refractories [9]. Different studies have been focused on the effect of the melt basicity on the corrosion behavior of chromia-forming materials [10–12]. In the Na_2O-SiO_2 system, the increase of the corrosion rate of pure chromium with the melt basicity has been attributed to the increase of the Cr^{VI} solubility limit [10]. However, in these studies, the possible effect of viscosity has not been taken into consideration. Indeed, the more basic the glass is, the more depolymerized it is, with a low viscosity allowing a rapid diffusion in the melt, as illustrated by the value of diffusion coefficients of some elements in Na_2O-xSiO_2 melts by Von der Gönna and Rüssel [13,14].

As a consequence, in this paper, the corrosion behavior of a binary Ni-30Cr alloy in three different glass melts has been studied at 1150 °C with immersion tests and electrochemical measurements. In addition, the physicochemical properties of chromium in these glass melts, *i.e.* solubility limits and diffusion coefficients, have been determined. Eventually, a focus is made on the relationship between both the diffusion coefficients and solubility limits of chromium in the glass melts and the corrosion behavior of the alloy in these media.

2. Materials and methods

2.1. Alloy and glasses compositions

The synthesis and characterization of the Ni-30Cr (wt.%) alloy used for corrosion tests is described in a previous paper [15]. The composition of the alloy was assessed by EDX measurements and the Cr content is 30.5 ± 1.2 wt%. The microstructure of the alloy presents coarse grains of several hundred of micrometers. Rod-shaped samples were prepared by electro-erosion with a 25 mm length and a 5.5 mm diameter. The surface of the samples was then ground with a P1200 SiC paper and ultrasonically cleaned in ethanol.

Glasses were synthesized by the Cerfav (Centre Européen de Recherches et de Formation aux Arts Verriers) by mixing Na_2CO_3, H_3BO_3 and SiO_2 powders, and heating at high temperature. The compositions and properties of the three glasses used in this study are listed in Table 1. Glass compositions have been measured by EPMA with the analysis conditions listed in Table 2. Viscosity data are taken from experimental characterizations [16,17] when available, or calculated with the statistical model given by Fluegel et al. [18] or with Factsage software [19]. The optical basicity is considered as the basicity scale in this paper [20]. The optical basicity of glasses is calculated with Eq. (4):

$$\Lambda_{glass} = \sum_i X_i \Lambda_{(oxide\ i)} \quad (4)$$

where Λ (unit less) represents the optical basicity and X_i is the equivalent molar fraction of oxygen, *i.e.* the number of oxygen atoms brought by the oxide i on the total number of oxygen atoms in the glass composition.

N3S (Na_2O-3SiO_2) and 2.3NB5S (2.3Na_2O-B_2O_3-5SiO_2) glass compositions have same optical basicity and very different viscosity whereas the 0.75NB2.75S (0.75Na_2O-B_2O_3-2.75SiO_2) composition has a similar low viscosity to that of 2.3NB5S but is more acidic. Furthermore, at the temperature of 1150 °C, all these glass compositions are in a single-phased liquid state.

2.2. Corrosion tests

For corrosion tests of Ni-30Cr by simple immersion in silicate melts, Ni-30Cr samples were mounted in refractory mullite tubes and sealed with alumina cement (Resbond 989FS). Samples were then immersed in about 800 g of glass contained in a Pt-10%Rh crucible placed in a muffle furnace in laboratory air. Prior to immersion, Ni-30Cr samples were preoxidized in laboratory air above the glass batch for 2 h at 1150 °C in order to develop an initial Cr_2O_3 layer. The thickness of this preoxidation layer is about 2.6–4.4 μm (Fig. 1). Cross-sectional SEM observations were performed with a JEOL J7600F apparatus in BSE contrast mode.

2.3. Electrochemistry

Anodic polarization experiments were performed on Ni-30Cr samples immersed in the silicate melts in order to determine if a passivation domain can exist. Therefore, a three-electrode device was used for that purpose with Ni-30Cr rod as working electrode, yttria stabilized zirconia rod as reference electrode and a platinum plate as counter-electrode. A potential increase was imposed from −20 mV *vs.* open circuit potential up to +500 mV *vs.* ZrO_2 with a scan rate of 1 mV s^{-1}. For the anodic polarization experiments, no preoxidation treatment was performed on the samples. More detailed information about the device and apparatus can be found in Ref. [2].

A similar three-electrode device was also used for the determination of chromium diffusion coefficient in silicate melts with the aid of square-wave voltammetry, using a platinum wire as working electrode (length: 12 mm, diameter: 0.5 mm). After an initial polarization for 2 s at the starting potential, the

Table 1
Theoretical and measured compositions (mol.%) and physicochemical properties of the glasses at 1150 °C. Standard deviations are given as uncertainty.

		N3S	2.3NB5S	0.75NB2.75S
Na_2O	th.	25	28	16.69
	exp.	23.30 ± 0.31	26.28 ± 0.39	16.78 ± 0.23
B_2O_3	th.	–	12	22.23
	exp.	–	13.11 ± 0.30	22.54 ± 0.54
SiO_2	th.	75	60	61.08
	exp.	76.70 ± 0.14	60.61 ± 0.54	60.68 ± 0.54
Optical basicity (Λ) [20]		0.57	0.56	0.52
Viscosity (log η(dPa s))		2.89–2.97 [16,18,19]	1.42[a] [18] 1.98 [19]	1.57 [17] 2.09 [19]
Density ρ (g cm^{-3}) [21]		2.24	2.20	2.17

[a] Glass composition is slightly outside the model range proposed by Ref. [18].

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