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Electrochemical characterization of chromia- and alumina-forming nickel-based superalloys in molten silicates

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ABSTRACT

A comparison of the corrosion behaviour of simplified chromia- and alumina-forming alloys (Ni–30Cr and Ni–8Al–28Cr) in molten glass is performed via electrochemical methods. A pre-oxidation treatment in air prior to immersion ensured the formation of a 2-μm-thick oxide scale of Cr_2O_3 or Al_2O_3. The lifetime of Ni–30Cr depended on the competition between the oxide growth and its dissolution in the melt. For Ni–8Al–28Cr, the high solubility of alumina in the melt studied here led to severe aluminium loss in a few minutes and clearly demonstrated the higher efficiency of chromia-forming alloys for molten glass applications.

1. Introduction

The largest challenge faced during the production of glass is related to the lifetime of the glass-processing equipment, which is in contact with molten glass. This equipment is expected to have the ability to withstand harsh environments and thus to resist high-temperature corrosion. The protection of metallic materials is generally achieved by forming a protective oxide layer. Due to their refractory properties and their low solubility in molten silicates [1], many oxides are suitable in applications involving contact with these media [2–5]. Ni-based superalloys with high chromium contents (25–30 wt.%) are generally employed for these high-temperature applications because they have the capability (i) to develop a protective chromia (Cr_2O_3) layer when they are exposed to hot air and (ii) to maintain this protection when they are immersed in molten glasses [6,7]. In all cases, chromia-forming alloys exhibit rather good performance as long as they are pre-oxidized before immersion in the melts [6–8].

Aluminium is also frequently added to the composition of refractory alloys, as it can also develop a thermodynamically stable and protective oxide layer (i.e., Al_2O_3). Dutta et al. [9] reported the high stability of thermally oxidized aluminide coatings on a superalloy 690 substrate in a borosilicate melt at 1248 K. They attributed this stability to a change in the glass composition close to the interface due to the partial dissolution of alumina in the melt, thus increasing its viscosity and limiting the diffusion of aluminium in the melt. However, the performance of Al-containing alloys in molten glass is not so widely documented [9,10].

Consequently, this study aims to compare the corrosion behaviour of chromia- and alumina-forming alloys in contact with molten glass. As previous studies dealing with the interactions between alloys combining multiple elements and glasses containing several oxides [7–9] exhibited the complexity of such systems, binary and ternary model alloys and a simplified ternary glass were implemented here. The model materials have compositions of Ni–30Cr and Ni–8Al–28Cr (wt.%) and are chromia- and alumina-forming alloys, respectively [11]. The ternary glass used here corresponds to the soda-lime silicate mixture $Na_2O–CaO–3SiO_2$ (mol.%), noted NC3S.

First, the oxidation behaviour of the two alloys has been characterized using thermogravimetry under isothermal conditions (1100 °C) in air in order to determine the growth kinetic constants for the development of chromia and alumina on Ni–30Cr and Ni–8Al–28Cr, respectively. These data give access to the theoretical

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oxide thicknesses formed for each alloy after a given duration of air pre-oxidation at 1100 °C.

Then, a systematic procedure was used to characterize the corrosion caused by molten glass for both alloys. The as-prepared and pre-oxidized alloys were immersed in molten NC3S for times up to 24 h. The *post mortem* characterization provided information about the morphology of the corroded alloy. This information was completed by an in situ electrochemical characterization, providing information about the chemical mechanisms involved in the corrosion process.

2. Experimental procedures

2.1. Materials preparation

The glass material, Na_2O–CaO–$3SiO_2$ (molar composition), was provided by CERFAV (Centre Européen de Recherche et de Formation aux Arts Verriers). The glass composition has been verified by EPMA (Electron Probe Micro-Analysis), which yielded molar ratios of Na/2Ca = 1.1, Si/Ca = 3.3 and 2Si/Na = 3.1. These values are close to those expected from the theoretical formulation of NC3S.

High-frequency induction melting was used to prepare Ni–30Cr (wt.%) and Ni–8Al–28Cr (wt.%) from metal flakes of nickel (Alfa Aesar 99.5%), aluminium (Alfa Aesar 99.9%) and chromium (Alfa Aesar 99.5%). The required amounts of the metallic elements were weighed and placed in the induction furnace. The melting occurred in a water-cooled copper crucible under an argon atmosphere. To obtain a rod shape with the dimensions required for electrode preparation, a silica tube (inner diameter = 6 mm, length ~300 mm) was attached to the pumping system of the furnace. The silica tube was then immersed in the molten alloy, and the pressure was carefully controlled while sucking the alloy into the tube. After the synthesis, the alloy rods were cut into pieces before being annealed at 1200 °C for 24 h to reach a homogeneous microstructure. The heat treatments were performed in silica tubes sealed under vacuum (10^{-6} atm).

2.2. Thermogravimetric assessment

The isothermal oxidation tests were performed at 1100 °C for 100 h in dry air using a SETARAM SETSYS thermobalance. The samples were hung in the hot zone of the thermobalance furnace with a platinum wire. Dry air was introduced into the reaction chamber with a flow rate of 1.5 L h^{-1}. The samples were heated at 20 K min^{-1} until reaching the test temperature and then cooled to room temperature at a rate of 5 K min^{-1}. The curves presented here only show the mass gain once the temperature dwell was reached. The mass variation of the hanging system was subtracted from the raw data.

2.3. Electrochemical measurements

Due to their structure and composition, glass media exhibit acido-basic properties as they allow the exchange of oxide ions (O^{2-}) [12,13]. Furthermore, the presence of dissolved oxygen (O_2) in the medium, depending on the conditions of the glass preparation, provides oxido-reducing properties [14–17]. Because glass is a corrosive medium acting as an electrolyte, an electrochemical characterization can be performed by adapting the electrochemical equipment to high temperatures, providing access to better knowledge of the mechanisms involved in the corrosion of the alloys by molten glass.

The experimental apparatus was previously described by Di Martino et al. [6,7]. From 1 to 1.5 kg of glass contained in a fused-cast Al_2O_3–ZrO_2–SiO_2 crucible was placed in a high-temperature furnace. The three electrodes were immersed in the molten glass through the top of the furnace and electrically linked to an acquisition system. The electrodes were fabricated in the laboratory using specific materials such as mullite tubes, platinum wires, and refractory cements. The working electrodes consist of the Ni–30Cr or Ni–8Al–28Cr rods (diameter = 5.5 mm, ground with 1200 grid SiC paper). The same method was used to prepare the platinum counter electrode (surface ~1 cm^2) used for the current collection. The reference electrode consists of a platinum wire connected to a yttria-stabilized zirconia (YSZ) stick (diameter = 5 mm), as this material is a good conductor of O^{2-} ions at high temperature. The reference electrode was flushed with air (P_{air} = 1 bar) through a syringe needle. The reference used for the electrochemical potentials is the O_2/O^{2-} couple. All of the potential values given in the present study are reported vs. this reference electrode.

The measurements were performed using a Potentiostat/Galvanostat model 263A interfaced with EG&G Perkin Elmer M352 software. The electrochemical behaviour of the alloys was characterized by measuring the polarization resistance (R_p). The polarization resistance was evaluated by polarizing the working electrode from −10 mV to +10 mV around the open circuit potential with a scan rate of 0.166 mV s^{-1}. The intensity vs. potential curve was plotted from the open circuit potential up to 0.5 V with a scan rate of 1 mV s^{-1}.

2.4. Immersion tests

The electrochemical measurement is a destructive method; therefore, the surfaces of the studied materials can be strongly modified after the high polarization applied to draw the intensity vs. potential curves. Therefore, immersion tests were systematically coupled with the electrochemical measurements. The experiments were performed by immersing the alloys in an alumina crucible that was filled with glass. After the desired time, the alloys were removed from the molten glass and quenched in air. A heat-shrinkable tube was applied to the sample when it was at a temperature of approximately 300 °C in order to preserve the glass surrounding the corroded specimen.

2.5. Samples characterization

The sample's surface topography and composition were determined using a scanning electron microscope (SEM) (JEOL JSM-7600F) equipped with both an energy-dispersive spectrometer (EDS) and a wavelength-dispersive spectrometer (WDS). The analyses were performed with an accelerating voltage of 15 kV and a beam current of 6 nA.

The chemical analyses were performed using an electron probe micro-analyser (CAMECA SX 100) that was equipped with wavelength-dispersive spectrometers (WDS). The glass composition analyses were performed using a spot size with a diameter of 20 μm in order to minimize the Na loss from the samples, whereas focalized analyses were performed on metallic parts of the samples. The acceleration voltage and beam current used were 15 kV and 10 nA, respectively.

The phase identification was realized by X-ray diffraction analysis (XRD) with a goniometer-type Philips X'PERT PRO that operates in the θ–2θ mode. This device is equipped with a copper anticathode ($\lambda K\alpha_1$ = 1.5406 Å). The studied angular domain is in the range of 25° and 140° (in 2θ) with a step of 0.01671°. The indexing of the X-ray peaks was performed by module EVA with Diffract Plus software equipped with the JCPDS database.