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Morpho-chemical investigations and thermodynamic study of Nb-rich passive nodules grown on AISI 441 oxidized in wet atmosphere

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ABSTRACT

AISI 441 sheets were oxidized from 4 to 24 h at 800 °C in wet atmosphere. Micrometric oxide nodules containing Ti, Nb, Cr and Mn were observed to form on the passive scale. The internal microstructure of these objects was investigated using STEM–EDX and FIB-SEM tomography. Experimental results reveal a complex microstructure linked with the presence of Si and Nb and their competition for interfacial oxidation. Eventually, the chemical compositions of the nodule and of the oxidation affected zone in the nodule vicinity are discussed in relation with thermodynamic calculations investigating the stability of the different oxides.

1. Introduction

AISI 441 ferritic stainless steel fulfills interconnectors requirements for Solid Oxide Fuel Cells (SOFCs) applications at operating temperatures in the range of 600–800 °C [1]. AISI 441 contains around 0.5 wt.% of Nb which enables the stabilization of the ferritic structure and a reduction of creep [1–3]. Nb addition, from 0.5 to 2 wt.%, prevents unwanted precipitates of Cr-rich carbides by formation of stable NbC. Nb is also known to form Fe_2Nb Laves phase particles precipitation of which along the grain boundaries combined to solid solution strengthening leads to a reduction of creep [1,4,5].

Nb occurrence reduces Si activity. Si is incorporated into intermetallic Laves phase as $(Fe,Si)_2Nb$ which hinders the formation in service of a thick insulating subscale of SiO_2 beneath the oxide scale [1]. As a consequence, the formation of $(Fe,Si)_2Nb$ Laves phase particles in the bulk results in a non uniform distribution of Si oxide at the metal/oxide interface [6]. On the other hand, addition of Si decreases the activity of Nb in solid solution. Increased Si concentration promotes the precipitation of Laves phase particles and lowers the amount of Nb in solid solution [7]. At high temperature, Nb and Si segregate and form oxides at the metal/oxide interface. Their competition for interfacial oxidation modifies the oxide scale composition. Nb interfacial segregation is believed to restrain the internal diffusion of oxygen and decrease oxygen activity below the oxide scale [8]. The formation of a discontinuous SiO_2 scale results in a reduced formation of Nb-rich oxides (NbO, NbO_2, Nb_2O_5) [6,8,9]. SiO_2 at the metal/oxide interface acts a partial barrier to diffusion thus slows the growth rate of Cr_2O_3. Si-rich metal/oxide interface is believed to increase the Mn to Cr ratio in the oxide scale [9].

The growth of the regular $Cr_2O_3/MnFe_{2-x}Cr_xO_4$ duplex oxide scale on ferritic stainless steels has been widely described in the literature [10–14], as well as the possible development, in various atmospheres, of iron containing oxide nodules leading to catastrophic oxidation [15–23]. Oxide nodules containing mainly Ti, Nb, Cr, Mn and almost no Fe have been observed to form on the passive scale [24–27]. They are believed to lower oxide scale adhesion [28]. Their formation is probably linked with the oxidation of Nb-rich carbides present near the surface [24].

The present paper aims at discussing the growth and the fine composition of these (Ti, Nb, Cr, Mn)-rich nodules in relation with the presence of Si and Nb in the alloy and with their competition for interfacial oxidation. Oxidations were performed on as-received AISI 441 at 800 °C in wet atmosphere (5% H_2O in O_2) up to 24 h. Chemical and morphological characterizations were performed with scanning transmission electron microscopy and energy dispersive X-ray spectroscopy (STEM–EDX) on a cross-section thin lamella and with 3D

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Table 1
Chemical composition of AISI 441 stainless steel [wt.%].

Element	Cr	Mn	Si	Al	Ti	Nb	Mo	C	Fe
AISI 441	17.83	0.24	0.60	0.006	0.13	0.55	0.01	0.01	Bal.

reconstructions in backscattered electron (BSE) mode obtained using dual focused ion beam scanning electron microscopy (FIB-SEM). STEM–EDX and FIB-SEM tomography are complementary techniques allowing investigation of both morphology and chemistry of heterogeneous objects with a micrometric size. Eventually, the chemical compositions of the nodule and of the oxidation affected zone in the nodule vicinity are discussed in relation with thermodynamic calculations investigating the stability of the different oxides.

2. Material and methods

1 mm thick sheets of AISI 441 in as-received industrial state (cold rolled, annealed, etched and skin-passed) were supplied by APERAM. The composition, measured by Fluorescence Spectroscopy Analysis and conductimetric techniques, is displayed in Table 1. Samples with 20 mm × 15 mm × 1 mm dimensions were cleaned with ethanol in an ultrasonic bath for 5 min and dried before thermal treatment. They were introduced in a cold furnace set at 40 °C. Isothermal oxidations were performed in a 5% H_2O–95% O_2 atmosphere at 800 °C for either 4, 14 or 24 h. The experimental set-up has been described in a previous paper [24]. The heating rate was fixed to 20 °C min^{-1}. The samples were cooled in the turned off furnace. The wet gas flow was maintain during cooling until the furnace temperature reaches 500 °C.

Transversal cross-sections of the nodules were investigated using FIB-SEM (Zeiss Cross Beam NVision 40). For EDX maps at high resolution, standard cross-section lamella was prepared with a volume of about 20 µm × 10 µm × 5 µm. The lamella, fixed to a Cu grid, was thinned until a thickness of about 100 nm with a final length of about 10 µm. STEM observations coupled to EDX investigations have been conducted on a Field Emission Gun Transmission Electron Microscope at 200 keV (FEG-TEM, Jeol 2100F). EDX maps have been recorded with a spot size of 1 nm using the X-ray energies reported in Table 2.

FIB-SEM tomography was conducted using a FIB box of 10 µm × 10 µm. Stacks of BSE images were recorded by serial sectioning the box into thin layers with a step of 20 nm. Fiji software [29] was used to compute 3D reconstructions with a voxel resolution of 20 nm^{-3}. For clarity purpose, the electron beam induced carbon deposit used to protect the surface of the sample during the FIB processing has been virtually removed.

Thermodynamic calculations were performed using Thermo-Calc software with TCFE7 database [30,31]. This database covers a major part of the systems involved in the oxidation of stainless steels, with assessed data for pure phases and multi-element metallic and oxide solid solutions. In the present case, seven elements were taken into account: Fe, Cr, Si, Nb, Mn, Ti, C, with their actual molar fraction in the steel. The ultra-minor elements Al and Mo were omitted for clarity purposes. The nature and composition of equilibrium phases were determined for O_2 activities increasing from 10^{-30} to 1. Results are given in terms of nature of stable phases with elemental composition for corundum, spinel and rutile oxide phases.

Table 2
X-ray energies used for EDX maps.

Element	O	Si	Ti	Cr	Mn	Fe	Nb
Emission line	K_α	K_α	K_α	K_α	K_α	K_α	L_α
Energy (keV)	0.523	1.740	4.510	5.414	5.898	6.403	2.166

3. Results

3.1. FIB-SEM cross-sectional investigations

FIB cross-sectional views (SEM in BSE mode) of nodules grown on AISI 441 at 800 °C in wet atmosphere (5% H_2O in O_2) for 4, 14 and 24 h are displayed in Fig. 1. The nodules present a complex structure in two parts: a dark gray outer part above the sample surface and a light gray inner part embedded in the bulk alloy. Microstructural and chemical features of each part will be fully discussed in the following. The interface between the inner and the outer parts is highlighted by a dotted line in Fig. 1. The contrasted gray levels in the inner part reveal a complex chemistry and microstructure linked with the presence of Nb (appearing in bright). Cavities and Laves phase precipitates are observed along the metal/nodule interface. The chemical and microstructural analyses of the “base oxide” have been described in a former paper [25].

After 4 h of oxidation (Fig. 1a), the interface between the inner and the outer parts is at the level of the sample surface. This interface moves upward whereas the metal nodule interface move downward with increasing oxidation time. After 24 h of oxidation, the inner part breaks through the outer part up to the nodule/gas interface (white area in Fig. 1c). In the following, microstructural and chemical investigations are focused on experiments performed for 24 h.

3.2. STEM–EDX characterizations

SEM and bright field STEM images of a longitudinal cross-section prepared by FIB on a nodule grown on AISI 441 at 800 °C in wet atmosphere (5% H_2O in O_2) for 24 h are shown in Fig. 2a and b respectively. According to SEM image in Fig. 2a, the dark gray outer part, of about 1.5 µm thick, is composed of micrometer sized oxide grains. The compact inner part is about 3 µm length. A large cavity and numerous Laves phase particles can be seen along the metal/nodule interface. This large overview as well as two regions of interest were investigated by STEM–EDX spectroscopy: (i) the interface between the external and the internal parts (region no. 1 in Fig. 2b) and (ii) the metal/nodule interface (region no. 2 in Fig. 2b).

Fig. 2 shows EDX maps of O + Cr (c), Cr (d), Mn (e), Ti (f), Fe (g), Si (h) and Nb (i) of a nodule grown on AISI 441 at 800 °C in wet atmosphere (5% H_2O in O_2) for 24 h. The nodule is composed of O as non-metallic elements (Fig. 2c). The upper part of the nodule is composed of large oxide grains containing either Ti and possibly Nb (area A in Fig. 2f and i) or Cr and Mn (area B in Fig. 2d and e). According to Fig. 2g, Fe is not detected at this point in the upper part of the nodule. In the lower part of the nodule, Cr, Mn and Nb are distributed everywhere. As detailed in the following, Cr is distributed uniformly, whereas Mn and Nb seem to be complementary (area C in Fig. 2e and i). Ti and Nb enrichments happen at the lower edge of the nodule inner part (Fig. 2f and i). According to Fig. 2h, Si is mainly located along the metal/nodule interface and in the Laves phase precipitates.

3.2.1. Interface between the inner and the outer parts of the nodule (region no. 1 in Fig. 2b)

Fig. 3 shows bright field STEM image (a) and EDX maps of Cr (b), Fe (c), Ti (d), Mn (e) and Nb (f) located at the interface between the inner and the outer parts of the nodule (region no. 1 in Fig. 2b). The analysis at higher magnification on the Ti-rich outer part of the nodule reveals additional small regions localized along the pores rich either in Cr, Mn and Fe (area A) as well as Fe oxide filaments (area B). Nb can be clearly linked to Ti (area C) but its presence is not extended to the full outer part of the nodule but rather limited to the interface with the inner part. The inner part is composed of small particles (average size less than 100 nm) containing either Nb and Ti (area D) or Mn enriched Cr oxides (area E).