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Temperature dependence of phase composition in W and Si-alloyed high chromium ferritic steels for SOFC interconnect applications

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Tungsten alloyed high-chromium ferritic steels such as the commercially available alloy Crofer 22 H have been proposed as construction materials for interconnects in Solid Oxide Fuel Cells. The background of the present study relates to the qualification of such alloys, especially with respect to a possible optimization of the tungsten concentration, aiming at formation of the strengthening intermetallic phases. For this purpose the chemical composition of intermetallic phases in a number of Fe-Cr-W-base model alloys after exposure at temperatures between 600 °C and 900 °C was measured by SEM/EDX and TEM/EDX. The obtained chemical and phase compositions were used for estimation of the iron-rich corner of the Fe-Cr-W system in the temperature range 600–900 °C. Finally, the experimental results were compared with values calculated using the Thermocalc software and the database TCFE 7. This comparison showed that in the temperature range 800 °C–900 °C the calculations gave a qualitatively correct description of phases present in the microstructure, however, substantial differences between calculations and experiments existed in the temperature range 600 °C–700 °C. Moreover, it was found that the solubility of silicon in the C14 Laves phase of the type Fe_2W is substantially smaller than that in the Fe_2Nb based laves phase present in Crofer 22 H.

1. Introduction

Aiming at increasing the creep strength of martensitic and ferritic steels, tungsten is a common alloying addition considered in many recent alloy development projects [1–4]. A number of these developments aimed at application of tungsten alloyed steels as construction materials for interconnects in solid oxide fuel cells (SOFC's) [3–6]. Tungsten addition results in solid solution strengthening and may also provide precipitation strengthening because the element forms binary intermetallic phases with iron and ternary intermetallic phases with chromium and iron [7–12]. The application as interconnect material in a SOFC imposes a number of additional requirements in respect to steel properties such as a high electrical conductivity of the surface oxide scales and a thermal expansion coefficient closely matching those of the ceramic parts of the SOFC stack [3–6]. Quadakkers et al. [3] and Froitzheim et al. [4] showed that the creep strength of high-chromium ferritic steels can be substantially increased by optimized, combined additions of niobium, tungsten and silicon. Solid solution strengthening was mainly obtained by tungsten addition and precipitation strengthening by niobium- and tungsten- containing Laves phase precipitates. By defining a precisely adjusted Si/Nb-ratio in the alloy [3,4], the adverse effect of niobium on the oxidation rates as well as the undesired subscale oxidation of silicon could be prevented [3–6,13]. These findings eventually resulted in the development of the ferritic interconnect steel Crofer 22 H [14].

The development and optimization of a material with a complex composition is a time and resources consuming task. Nowadays the process can, however, substantially be accelerated by application of thermodynamic software tools such as e.g. Thermocalc [15], which allow the calculation of equilibrium amount and composition of phases prevailing as a function of temperature in an alloy of given chemical composition. The main hindrance in applying such tools is the still existing inaccuracy of the thermodynamic databases. Consequently the theoretically predicted phase equilibria for a given alloy may substantially differ from the real ones and therefore improvement of thermodynamic databases requires continuous feedback of experimental results.

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Substantial differences between calculated and measured phase equilibria were identified in Refs. [16,17] dealing with the microstructural features in the ferritic steel Crofer 22 H and a number of niobium containing model alloys as a function of temperature. The mentioned commercially available ferritic steel as well as the studied model alloys did either have no tungsten addition or a maximum tungsten content of 2 wt.%.

In the frame of the project which eventually resulted in the development of Crofer 22 H, investigations were carried out to estimate whether adequate solid solution combined with precipitation strengthening could be obtained by omitting the niobium addition and increasing the tungsten content of 2 wt.% to substantially higher levels. Based on the phase diagrams known from literature [7–11], an intermetallic compound Fe_2W should form at sufficiently high tungsten addition. Omitting the niobium would have the advantage, that possible Fe_2Nb-formation at the scale/alloy interface [18,19], which may adversely affect the long term oxidation behavior, would be prevented [20].

Within the Crofer 22 H development project niobium-free variants with various tungsten contents were tested in respect to long term oxidation performance in the temperature range 600–900 °C in various gases. All these model alloys contained one or more of the minor additions (manganese, silicon, titanium and/or lanthanum) present in Crofer 22 H.

The present paper describes the microstructural features of three Fe – 22 Cr wt.% model steels with tungsten additions between 2.5 and 7 wt.% after the mentioned long-term exposures in the temperature range 600–900 °C. Oxidation features of these alloys were partly described elsewhere [21,22] and will not be discussed here. After exposure the compositions of the intermetallic phases were measured using energy and/or wavelength dispersive X-ray analysis (EDX/WDX). Thereby, the analyses were carried out in the specimen center i.e. a region which was not affected by oxidation induced microstructural and/or compositional changes. A number of specimens exposed at 600 °C and 650 °C could not be analyzed by SEM/EDX because of the limited size of the intermetallic precipitates. Therefore these specimens were analyzed by TEM/EDX. Finally, the compositions of the intermetallic phases formed at the various temperatures were calculated using the Thermocalc software (database TCFE 7 [23]) and compared with the experimental results.

2. Experimental

The materials used in the tests were three model Fe-Cr-W based alloys with minor additions of manganese, silicon, titanium and lanthanum. The minor alloying elements were considered because the alloys were part of the research program which eventually resulted in the development of the commercially available ferritic steel Crofer 22 H [14,24]. The detailed chemical compositions of the studied materials as determined by inductively coupled plasma - optical emission spectroscopy (ICP-OES) and hot gas extraction infrared absorption spectroscopy are shown in Table 1.

The investigated alloys were manufactured by VDM Metals GmbH in form of hot rolled sheets with approximately 2.5 mm thickness. Specimens of 20 mm × 10 mm × 2 mm were machined from the sheets by laser cutting. The prepared specimens were ground with SiC abrasive papers down to a 1200 grit surface finish and ultrasonically cleaned with ethanol. Subsequently the specimens were subjected to discontinuous high-temperature exposures in various environments (for details see Table 2). Resistance heated three-zone, tube furnaces were used for the tests. The furnaces were equipped with four type S thermocouples (one for each zone and one for the control of the sample temperature). The maximum temperature deviation was less than ± 3 °C.

Table 1
Chemical compositions of the investigated materials.

Alloy	Fe	Cr	W	Mn	Si	Ti	La	C	S	N	O
	Wt.%							ppm			
A	Bal.	20.7	2.6	0.53	0.04	0.11	0.13	20	15	60	50
B	Bal.	22.5	4.8	0.45	0.24	0.04	0.03	30	20	100	80
C	Bal.	22.7	7.0	0.45	0.25	0.04	0.03	30	21	60	60

After exposure, the samples were cross-sectioned and subsequently analyzed by scanning electron microscopy (SEM, Zeiss Supra 50VP) equipped with energy and wave length dispersive X-ray (EDX/WDX) analyzers (Oxford Instruments XMax 80, INCAWave and INCAEnergy EDX/WDX). The WDX analyzer was used only to proof the reliability of measurements of a new EDX system equipped with an 80 mm^2 detector, as will be illustrated in the next section. The vast majority of analyses for obtaining information about phase compositions, microstructure and grain orientation, was carried out using a combination of EDX with Electron Backscatter Diffraction (EBSD, Oxford Instruments Nordlys II Detector/Aztec). As mentioned in the introduction, the quantitative analyses were carried out in the center of the respective samples i.e. in areas which were not affected by subscale depletion processes resulting from the growth of surface oxide scales.

The phases observed in a number of samples after exposure at 600 °C and 650 °C were found to be too small to be analyzed by SEM/EDX. Therefore the respective samples were additionally analyzed by transmission electron microscopy (TEM, Zeiss Libra 200 CS) equipped with energy dispersive X-ray (EDX) analyzers (Oxford Instruments XMax 80/INCAEnergy). For preparation of the TEM lamella a focused ion beam system (FIB Zeiss Auriga Crossbeam) was used.

3. Phase analysis with EDX and WDX

In the present paper the chemical compositions of the phases formed in the investigated materials were measured virtually exclusively by SEM/EDX. This method exhibits obvious advantages, such as simplicity of handling and substantially shorter measurement time compared to WDX which is of special importance in case of multiple measurements. Its main disadvantage is the limited energy resolution of the EDX detectors of approximately 140 eV [25]. Consequently, the emission lines for some of the relevant elements cannot be properly resolved. This is for example the case for the silicon $K\alpha$ (1739 eV) and the tungsten $M\alpha$ (1774 eV) lines. However, recent EDX systems utilizing large surface silicon drift detectors (with an active surface of 80 mm^2 or more) combined with powerful algorithms for spectra deconvolution and simulation offer a possibility to overcome this limitation.

Table 3 shows compositions of the σ(FeCr)-phase formed in alloy C during 3000 h exposure at 650 °C measured with WDX and the new EDX system. Each value presented in Table 3 is an average of at least five measurements. It can be seen that, the concentrations of iron, chromium, tungsten and manganese measured by EDX and WDX are virtually identical. As expected, the largest deviation appeared for silicon. The concentration of this element measured by EDX is smaller than that measured by WDX. Considering that the absolute silicon concentration, in the range of 0.5 at.%, is very close to the detection limit of both methods used, it must be concluded that the applied EDX system provides reliable results especially for the major elements considered in the present paper i.e. iron, chromium and tungsten. Consequently the EDX system can apparently be used for quantitative analysis of phases containing elements such as silicon and tungsten together.