Materials Science & Engineering A 594 (2014) 372–380

Contents lists available at ScienceDirect

Materials Science & Engineering A

journal homepage: www.elsevier.com/locate/msea

Development of high chromium ferritic steels strengthened by intermetallic phases

B. Kuhn [a,*], M. Talik [a,b], L. Niewolak [a], J. Zurek [a], H. Hattendorf [c], P.J. Ennis [a,1], W.J. Quadakkers [a], T. Beck [a], L. Singheiser [a]

[a] *Forschungszentrum Jülich GmbH, Institute for Energy and Climate Research (IEK), Microstructure and Properties of Materials (IEK-2), 52425 Jülich, Germany*

[b] *Czech Technical University in Prague, Zikova 4, 160 00 Praha 6, Czech Republic*

[c] *Outokumpu VDM GmbH, Kleffstraße 23, 58762 Altena, Germany*

ARTICLE INFO

Article history:
Received 15 April 2013
Received in revised form
12 November 2013
Accepted 14 November 2013
Available online 21 November 2013

Key words:
High Cr ferritic steel
Creep strength
Precipitation
Intermetallic phases
Steam oxidation

ABSTRACT

Microstructural features, mechanical and steam oxidation properties of ferritic 18–23 wt% chromium model steels, strengthened by the precipitation of intermetallic phases, were investigated. The behavior of the commercially available ferritic steel Crofer® 22 H [1–4], originally developed for the application in automotive solid oxide fuel cell (SOFC) powered auxiliary power units (APUs) [5–7], was compared with that of optimized model alloys with systematic variations in Cr, Nb, W and Ti content. The main aim of the studies was the estimation of the potential suitability of these steels as construction materials in power plants with live steam temperatures around 600 °C.

Some of the optimized trial alloys demonstrated remarkable characteristics at 600 °C. Results of constant load creep experiments and steam oxidation tests indicate the potential of these alloys as candidate materials for application in highly efficient steam power plants with steam temperatures above 620 °C. At high stress levels some of the presented alloys, especially those containing enhanced levels of W and Nb, even exhibit higher creep strength than standard ferritic–martensitic steel P92. The amount of strengthening $(Fe,Si,Cr)_2(W,Nb)$ – Laves phase particles is found to correlate well with the level of W- and Nb-alloying and in contrast to ferritic–martensitic steels, the formed Laves phase particles are highly stable at elevated temperature. Owing to the high contents of chromium, the model alloys have excellent steam oxidation resistance. A way to preserve favorable steam oxidation properties and diminish undesirable (Fe,Cr)-σ-phase formation is outlined.

1. Introduction

Resource protection and decrease of CO_2 emissions by efficiency increase of energy conversion systems are the main driving forces for the development of highly heat resisting construction materials. Most state of the art steam power plants employ ferritic–martensitic 9–12 wt% Cr steels, in some cases – particularly in superheaters and reheaters – also austenitic steels. For a further improvement in efficiency to about 50%, a further increase of steam parameters to approximately 650 °C/300 bar [8,9] would be necessary. Owing to its confined creep strength, but even more because of its steam oxidation resistance being limited by the relatively low chromium content, the concept of ferritic–martensitic 9–12 wt% chromium steels seems to hit technological limitations [10]. Creep strengthening of these materials is mainly obtained by microstructural stabilization due to distribution of fine carbide and nitride precipitates. The limited thermodynamic stability of the strengthening precipitates, as well as poor steam oxidation resistance, restrains the use of the well known ferritic–martensitic steel P92 to temperatures of about 620 °C [9]. Adequate steam oxidation resistance, up to temperatures of about 650 °C, would require significantly increased chromium contents [11,12]. Newly developed steels with higher chromium contents from 11 to 12 wt%, such as VM12 [13], NF12 [14] and T122 [14], exhibited an accelerated decrease in creep strength upon long-term operation. Because of the high chromium content, which is beneficial for oxidation resistance, these materials are prone to increased precipitation of the undesirable Z-phase (Cr(V,Nb)N) [14]. The Z-phase occurs at the expense of the strengthening MN-nitrides (M=V, Nb), resulting in a reduction of strength in the long term [15]. Thus, the operating temperature of currently available ferritic–martensitic steels is, depending on the actually prevailing component, limited to about 610 °C– 630 °C [9,10,16]. All together, the martensitic steels used in

---

[*] Corresponding author. Tel.: +49 2461 61 4132; fax: +49 2461 61 8284.
E-mail address: b.kuhn@fz-juelich.de (B. Kuhn).

[1] Now visiting Professor at University of Leicester, University Road, Leicester LE1 7RH, United Kingdom.

0921-5093/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.msea.2013.11.048

Table 1
Chemical compositions of the selected trial materials (wt%).

Group:	Batch ID:	C	N	Cr	W	Nb	Si	Mn	La	Fe	Ti
"Crofer® 22 H"	Specification	≤ 0.03	≤ 0.04	22.00 ± 2	2.00 ± 1	0.2–1.0	0.1–0.6	≤ 0.8	0.04–0.2	R	0.02–0.2
	1.75W0.57Nb	0.003	0.014	22.56	1.75	0.57	0.24	0.45	0.01	R	0.039
	2.02W0.48Nb	0.002	0.007	22.32	2.02	0.48	0.27	0.43	0.09	R	0.065
"Zero Ti"	Specification	–	–	22.00	2.00	0.5	0.25	0.45	–	R	< 0.02
	2.1W0.49Nb0Ti	0.002	0.004	23.08	2.10	0.49	0.24	0.45	0.12	R	0.003
	2.5W0.57Nb0Ti	0.004	0.008	22.95	2.5	0.57	0.20	0.46	0.03	R	0.004
"Low Cr"	Specification	–	–	18.00	2.00	0.50	0.25	0.45	–	R	–
	18Cr	0.002	0.005	18.50	1.98	0.51	0.24	0.44	0.12	R	0.057

today's power plants do exhibit more or less serious disadvantages and for this reason it seems hardly possible to achieve further improvement in creep strength and oxidation resistance, necessary for a highly efficient 650 °C steam power plant, on this technological base. A paradigm shift in alloy development – away from improving creep resistance with steam oxidation resistance as a secondary goal – towards combined improvement of oxidation and creep resistance, therefore seems mandatory.

In the year 2001 the Japanese National Institute of Materials Science (NIMS) published its concept of a ferritic 15 wt% Cr steel [17], strengthened by the precipitation of intermetallic phases. During the last decade several variants with promising 650 °C creep properties [18,19] were developed, some of them equaling, others even outbalancing current creep strength enhanced ferritic–martensitic (CSEF) materials like P92 [19–21]. Because of the precipitation of a large number of strengthening intermetallic particles, which consume chromium from the steel matrix, the remaining chromium reservoir is likely to drop to values below 13 wt% [20] and thus may appear to be relatively low to provide sufficient long-term resistance against steam oxidation at 650 °C [11].

At the same time, the Institute for Energy and Climate Research, Microstructure and Properties of Materials (IEK-2) of Forschungszentrum Jülich and ThyssenKrupp VDM (now Outokumpu VDM) developed high chromium (22 wt% Cr), ferritic stainless steels for the application in high-temperature solid oxide fuel cell (SOFC) stacks [22–26]. This collaboration resulted in the now commercially available interconnector steels named Crofer® 22 APU [27] and Crofer® 22 H [1]. Fuel cell application at operating temperatures in the range of 700 °C–800 °C requires the formation of an electrically conductive oxide scale at the surface. Standard deoxidants like Al or Si therefore have to be avoided in the melting of Crofer® 22 APU, because these elements would form electrically insulating sub-surface oxides beneath the external chromia base scale during fuel cell operation. Consequently Crofer® 22 APU is produced by comparatively expensive vacuum induction melting processes. The alloy variant Crofer® 22 H is a logical further development of the original material Crofer® 22 APU. Development goals were the reduction of production costs, while maintaining or improving all fuel cell relevant properties like low thermal expansion, oxidation and creep resistance as well as electrical conductivity of the surface oxide scale in the temperature range from 700 °C to 800 °C. All these goals were achieved by combined alloying of relatively small amounts of tungsten (2 wt%), niobium (0.5 wt%) and silicon (0.25 wt%). Compared to Crofer® 22 APU a reduction of the minimum creep rates of at least an order of magnitude was achieved [3] by combined solid solution strengthening and the precipitation of intermetallic $(Fe,Cr)_2(Nb,W)$ – Laves phase particles, finely dispersed in the fully ferritic matrix. It was proposed [25] that the addition of Nb decreases the activity of Si in the ferrite matrix, which is partly related to the fact that the Laves phase exhibits a substantial solubility for silicon [3,28]. In this way electrically insulating subscale silica formation beneath the external chromia scale during actual service at, e.g. at 800 °C is prevented. Consequently, minor amounts of silicon may be added as de-oxidants during the alloy melting process, thus allowing the use of conventional, cost effective manufacturing processes for Crofer® 22 H. Some of the advanced model alloys, which were further optimized starting from the technological base of the commercial Crofer® 22 H grade, show very promising creep properties in the temperature range relevant for supercritical steam power plants (600 °C–650 °C). Moreover, they exhibit excellent steam oxidation resistance, owing to their sufficiently high chromium contents of 18–23 wt%.

In the present study the creep and steam oxidation properties and corresponding microstructures of optimized model alloys are outlined and compared to state of the art CSEF steels.

2. Experimental

2.1. Materials and preparation

All presented model alloys were manufactured by Outokumpu VDM (formerly ThyssenKrupp VDM) by vacuum melting of approximately 10 kg ingots (initial thickness: 80 mm) with subsequent annealing at 1080 °C for 2 h, followed by hot rolling at 980 °C down to a final plate thickness of 16 mm and subsequent air cooling. The chemical compositions are given in Table 1 and were analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

The first group, consisting of two alloy batches, is characterized by a composition according to the commercial "Crofer® 22 H" – specification with nominally 22% Cr, 2% W, 0.5% Nb, 0.25% Si (all values are given in wt%, cf. Table 1) and distinct variations in tungsten and/or niobium contents. The second group ("zero Ti") differs from the first by minimized titanium content only. Compared to this, the "low chromium" ("low Cr") variant features a reduced chromium content of nominally 18 wt%, in order to minimize the formation of the intermetallic FeCr-(σ)-phase at temperatures from 600 °C to 650 °C (cf. Fig. 1a).

2.2. Alloy development

Thermodynamic equilibrium calculations were performed, employing the software package Thermocalc® (database TCFE6.2), for nominal compositions of both the commercial Crofer® 22 H (22 Cr, 2 W, 0.5 Nb, 0.25 Si; Fig. 1a) and the low chromium (18 Cr, 2 W, 0.5 Nb, 0.25 Si; Fig. 1a) variant. Because of its brittleness and high Cr-content (resulting in lowered Cr content of the ferrite matrix) the topologically close packed (Fe,Cr)-σ-phase is usually considered to be disadvantageous for ambient temperature ductility, hot-working, welding, corrosion resistance and long-term thermomechanical fatigue properties [29–32] of components manufactured from high chromium steels. Fig. 1a shows a reduced amount of this undesired phase, accompanied by an increase in Laves phase fraction (Fig. 1a), accomplished by decreasing the Cr