Available online at www.sciencedirect.com

SCIENCE DIRECT®

Scripta Materialia 52 (2005) 809–814

Scripta MATERIALIA

www.actamat-journals.com

Effects of Fe on the oxidation/internal nitridation behavior and tensile properties of Cr and oxide dispersion ductilized Cr

M.P. Brady *, P. Sachenko

Division of Metals Ceramics, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6115, USA

Received 30 September 2004; received in revised form 3 January 2005; accepted 12 January 2005

Abstract

The addition of Fe to Cr and to oxide dispersion ductilized Cr alloys modified, but did not eliminate subscale internal nitridation on oxidation in air. The addition of 45 wt.% Fe increased the room-temperature tensile yield strength of Cr–6MgO from ~225 MPa to ~650 MPa, while still exhibiting 1–1.5% tensile elongation.

Keywords: Ductility; Chromium; Oxidation; ODS; Refractory metals

1. Introduction

Chromium has been of longstanding interest as a high-temperature structural material due to its combination of high melting point, moderate density, and good high-temperature oxidation and corrosion resistance in many environments [1–3]. However, these advantages are negated by inadequate high-temperature strength, a brittle to ductile transition temperature (BDTT) typically above room-temperature, and susceptibility to environmental embrittlement at elevated-temperatures in air by rapid Cr_2N subscale formation [1–4]. Impurities (particularly nitrogen and carbon) are a major contributor to the room-temperature brittleness of Cr [1]. Scruggs et al. [5,6] discovered that room-temperature tensile ductility could be achieved in commercial-purity Cr (i.e. high levels of impurities) by additions of MgO. Blended, sintered, and extruded powders of commercial purity Cr, MgO, and Ti in the range of Cr–(2–6)MgO–0.5Ti weight per cent (wt.%) exhibited room-temperature tensile elongations of up to 20% in the as-recrystallized state, and without electropolishing. During consolidation, much of the MgO converted to the $MgCr_2O_4$ spinel phase, which was hypothesized to getter nitrogen from the Cr, rendering it ductile. More recent study of these alloys confirmed the improvement in ductility via MgO additions, and found evidence that oxide dispersions in general in Cr, not just spinel, act as preferential sites for impurity segregation and impurity phase precipitation [4,7]. However, internal Cr-nitride formation was still observed in Cr–MgO base alloys on elevated temperature exposure in air [8] Based on our recent observation of changes in nitride subscale formation in Fe-modified Cr–Cr_2Ta base alloys [9], the effect of Fe additions to Cr and Cr–MgO on oxidation resistance and mechanical properties was investigated.

2. Experimental

Pure Cr and Cr–Fe base alloy samples were prepared by arc melting and drop casting in a chilled copper mold. The oxidation behavior of these alloys was studied in the as-cast condition. The baseline Cr–6MgO wt.% material was manufactured from oblique-blended

---

* Corresponding author. Tel.: +1 865 574 5153; fax: +1 865 241 0215.
E-mail address: bradymp@ornl.gov (M.P. Brady).

1359-6462/$ - see front matter © 2005 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.scriptamat.2005.01.019

commercial-purity Cr and MgO powders of nominal size 1–5 μm from Atlantic Equipment Engineers (AEE; Bergenfield, NJ, USA). The powders were hot-pressed under vacuum in a graphite die at ~1600 °C for 2 h at approximately 20 MPa (details are provided in Ref. [4]). The MgO powder was calcined and sieved prior to the mixing. To examine the effects of Fe, a composition of 55Cr–45Fe + 6MgO wt.% was selected for study (nominal composition of ~Cr–42.5Fe–5.5MgO wt.%). Commercial-grade Cr, Fe, and MgO powders of nominal 1–5 μm size were procured from AEE, oblique blended using zirconia balls, and then consolidated by hot pressing at 1450 °C for 1 h under Ar–4%H_2 in a graphite die. The different consolidation conditions used for Cr–45Fe + 6MgO were selected because of the potential for melting from interaction of the Fe powders with the graphite die, due to the Fe–C eutectic. Some local melting at the periphery of the 5 cm diameter compact did in fact occur, and use of different die materials is recommended for future work.

Disk-shaped oxidation specimens of approximately 8–13 mm diameter and 1 mm thickness were polished to a 600-grit finish using SiC paper. A short-term cyclic oxidation screening protocol was adopted, based on earlier work which found extensive subscale nitridation of Cr under these conditions [10]. The oxidation tests were conducted at 1100 °C in a tube furnace open to ambient air. The samples were placed in an alumina boat and inserted/removed from the furnace at temperature (air cooling) and weighed after intervals of 1, 4, 10, 30, 48, and 120 h of cumulative exposure. As expected for this temperature, there was some chromia volatility, as evidenced by green stains on the alumina boat. However, volatility-related weight loss did not appear to be significant. Tensile properties at room-temperature were obtained using sheet samples ~0.6–0.7 mm thick, with a gage length of 12.7 mm, prepared to a 600 grit surface finish. The cross-head speed was 2.54 mm/min (initial strain rate of $3.33 \times 10^{-3}\ s^{-1}$). Microstructures were characterized by optical microscopy, scanning electron microscopy, and electron probe microanalysis (EPMA) using pure element standards for metallic alloy components, a BN standard for N; and an Al_2O_3 standard for O.

3. Results and discussion

3.1. Oxidation

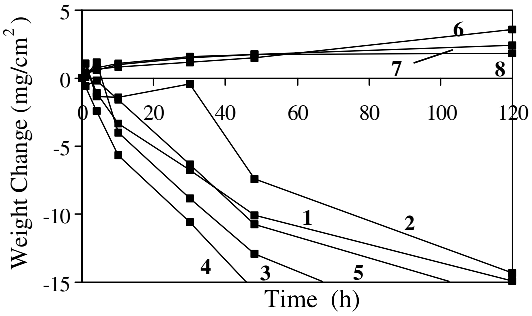

Fig. 1. Cyclic oxidation at 1100 °C in air. (1) Cr; (2) Cr–5Fe; (3) Cr–15Fe; (4) Cr–35Fe; (5) Cr–49Fe; (6) Cr–6MgO; (7) Cr–45Fe–6MgO; (8) Cr–45Fe–0.5La.

Specific weight change data for a series of Cr, Cr–Fe, Cr–6MgO, and Cr–45Fe + 6MgO alloys after a 6 cycle, 120 total hour cyclic oxidation screening at 1100 °C in air are shown in Fig. 1. Pure Cr and the Cr–Fe alloys all suffered from extensive spallation and weight loss during the course of this exposure. The addition of 6 wt.% MgO to Cr and Cr–45Fe significantly improved oxidation behavior under these conditions, with positive weight gains consistent with adherent Cr_2O_3-base scale formation (note that some minor scale spallation was observed for these alloys). The addition of 0.5 wt.% La to Cr–45Fe also significantly improved spallation resistance, with behavior similar to the MgO-modified alloys.

A SEM cross-section for cyclically oxidized pure Cr is shown in Fig. 2. No adherent Cr_2O_3 scale remained on the sample. A subscale region was present at the surface, and consisted of a continuous Cr_2N layer ~30–50 μm deep. Hardness in this region was in excess of 1400 Vickers and cracks were evident throughout. This rapid, brittle Cr_2N subscale formation is one of the key limiting factors for the use of Cr-base alloys at elevated temperatures in air [1].

In contrast, the cyclically-oxidized Cr–6MgO and Cr–45Fe + 6MgO alloys exhibited relatively intact, duplex oxide scales (Figs. 3 and 4). These consisted of an outer, Mg-rich region, consistent with the $MgCr_2O_4$ spinel phase, and an inner, continuous layer of Cr_2O_3. There was evidence of partial local spallation of the outer spinel layer, although it was not possible to defini-

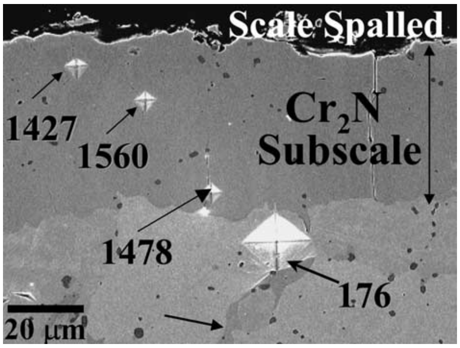

Fig. 2. SEM cross-section of pure Cr after 6 cycle, 120 h cyclic oxidation exposure at 1100 °C [10]. Numbers denote Vicker's hardness (100 g, 15 s). (Duplicate sample, similar weight change data as shown in Fig. 1.)