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Effect of Mn on oxide formation by Fe-Cr and Fe-Cr-Ni alloys in dry and wet CO₂ gases at 650 °C

Thuan Dinh Nguyen, Jianqiang Zhang, David J. Young*

School of Materials Science and Engineering, University of New South Wales, Sydney, NSW 2052, Australia

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ABSTRACT

Model alloys Fe-20Cr-2Mn and Fe-20Cr-20Ni-2Mn (wt.%) were exposed to Ar-20CO₂-(20H₂O) gases at 650 °C. Oxide formation was affected by alloy Mn diffusion, reaction temperature and gas composition. In dry CO₂, both alloys initially formed thin scales of Mn₃O₄, Cr₂O₃ and MnCr₂O₄ layers. In wet CO₂, Fe-20Cr-2Mn formed a thin, duplex scale of (MnCr₂O₄ + Cr₂O₃). The Fe-20Cr-20Ni-2Mn alloy formed a thin Cr₂O₃ scale. In both cases, different oxides were observed over alloy grain boundaries. Oxide development is discussed in terms of changes to diffusion paths resulting from alloy microstructural features, and the presence in oxide grain boundaries of carbon and hydrogen.

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1. Introduction

Oxyfuel combustion is a new technology being developed and tested in coal-fired power plants to reduce CO₂ emissions into the atmosphere. In this process, coal is burned in pure oxygen mixed with some recirculated flue gas. Consequently, the flue gas consists mainly of CO₂ and water vapour. One of the most challenging technical problems is that this flue gas is highly corrosive to chromia-forming steels commonly used in heat exchangers [1–18], reducing their useful lifetime.

Corrosion resistance of Cr-bearing alloys relies on the formation and stability of chromia scales. It has been reported [5] that chromia scales grew faster during oxidation in CO₂ than in air, leading to greater Cr depletion in the alloy subsurface zone. Carbon can penetrate through chromia scales via grain boundaries [19], resulting in carburisation of the underlying alloy. Clearly, a single Cr₂O₃ scale is not always effective in protecting the alloys from oxidation and carburisation in CO₂ gas at high temperatures. An additional, stable oxide is desirable to improve the protective behaviour of the chromia scale.

The addition of a small amount of manganese (3%) to Ni-20Cr reduced its oxidation rate at 1200 °C in pure oxygen by forming a continuous MnCr₂O₄ spinel layer between a chromia layer and the alloy [20]. Scales on Fe-20Cr-2Mn after reaction for 240 h at 818 °C in dry CO₂ consisted of an outer MnCr₂O₄ layer and an inner

mixed (Cr₂O₃ + MnCr₂O₄) layer [5]. However, when water vapour was added to the reaction gas, the alloy formed an outer Mn₃O₄ layer over the inner mixed (Cr₂O₃ + MnCr₂O₄) layer [8]. In both cases [5,8], oxidation and carburisation resistance of the alloy were each improved significantly.

As reported earlier [10], adding 2% Mn to Fe-20Cr and Fe-20Cr-20Ni significantly improved oxidation resistance in dry CO₂ gas but had no effect in wet CO₂ at 650 °C. Thin scales formed on both alloys in dry gas and on Fe-20Cr-20Ni-2Mn in wet gas after 1000 h reaction were identified by XRD analysis as containing manganese oxide spinels and chromia [10]. However, little information on scale microstructure was reported. The aim of the present paper was to investigate the formation and stability of manganese spinels on Fe-20Cr-2Mn and Fe-20Cr-20Ni-2Mn in dry and wet CO₂ at the relatively low temperature of 650 °C. The results are also compared with those obtained at the higher temperature of 818 °C.

2. Materials and experiments

Two model alloys, Fe-20Cr-2Mn and Fe-20Cr-20Ni-2Mn, were prepared by arc melting pure metals Fe (99.97%), Cr (99.995%), Ni (99.95%) and Mn (99.9%) under a protective Ar-5%H₂ gas atmosphere, using a non-consumable electrode. The resulting buttons were annealed at 1150 °C for 50 h in flowing Ar-5%H₂ gas for homogenization. The alloy grain sizes after annealing were 2.6 ± 2 μm for Fe-20Cr-2Mn and 2.4 ± 1.8 μm for Fe-20Cr-20Ni-2Mn. Rectangular alloy coupons of dimensions (1.3 ± 0.3) mm × (6.5 ± 1) mm × (8.4 ± 1.6) mm were surface ground to a 1200-grit finish and ultrasonically cleaned in alcohol prior to

* Corresponding author.

E-mail address: d.young@unsw.edu.au (D.J. Young).

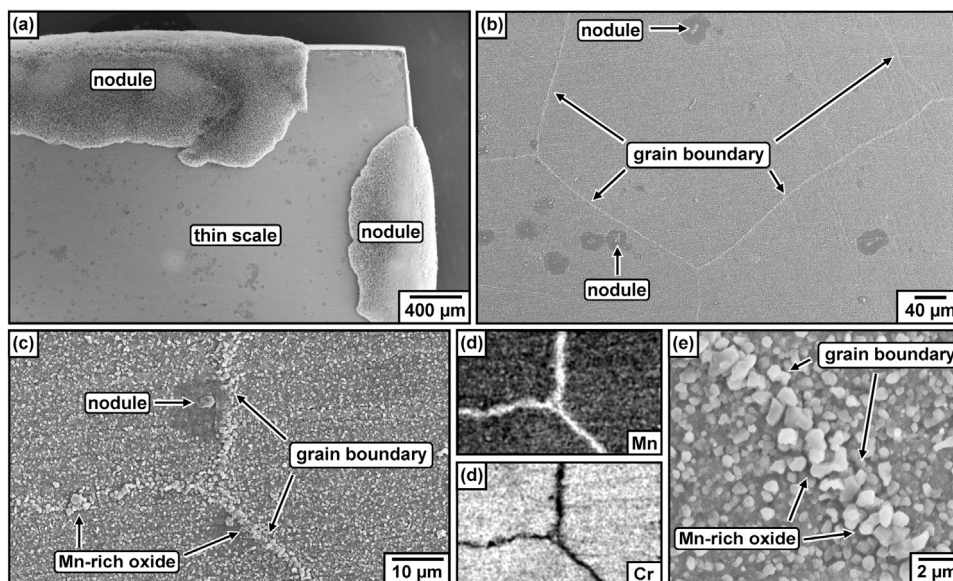


Fig. 1. Fe-20Cr-2Mn after reaction for 1000 h in Ar-20CO₂: (a) SE-SEM top view of the sample; (b) high magnification top view of the thin scale in (a); (c) SE-SEM image of grain boundaries in (b); (d) EDX mapping of (c); and (e) high magnification image of grain boundaries in (c).

reaction. Analysis by XRD confirmed that Fe-20Cr-2Mn was ferritic and Fe-20Cr-20Ni-2Mn austenitic.

All specimens were reacted at 650 °C in an Ar-20CO₂ or Ar-20CO₂-20H₂O (volume%) mixture with a linear flow rate of 2 cm/s and a total pressure of 1 atm. The water vapour content of the reaction gas was confirmed by a precision dew-point meter (Michell, S8000).

Corroded samples were characterized by scanning electron microscopy (SEM; Hitachi S3400) with an energy dispersive X-ray spectrometer (EDX, Bruker) and transmission electron microscopy (TEM; Philips CM200) operated at 200 kV. The TEM samples (about 100 nm thick) were prepared by a focused ion beam system (FIB, FEI Nova NanoSEM 230) with a maximum accelerating voltage of 30 kV. Phase diagrams of a Mn-Cr-O system were calculated by FactSage software (version 6.2), using databases Fact53 and FToxid.

3. Results

A principal point of interest concerns whether an alloy grows a thin, protective (or passivating) scale, or instead develops more rapidly growing nodules which eventually merge to form a thick scale. The latter state often evolves from a formerly protective state, and is here described as “breakaway”, regardless of the absolute reaction rate magnitude.

3.1. Corrosion of Fe-20Cr-2Mn in Ar-20CO₂

The scale surface morphology developed on Fe-20Cr-2Mn in reaction for 1000 h is shown in Fig. 1. The alloy formed large areas of thin scale, with coarse nodules located at the sample edges (Fig. 1a). The coarse nodules were identified by EDX (not shown) as iron-rich oxide [10]. Original alloy grain boundaries were visible in the thin scale (Fig. 1b), which also developed small, sparsely distributed nodules. A high magnification image of the thin scale surface (Fig. 1c) shows it to be fine-grained, whereas somewhat larger grains grew at alloy grain boundaries (Fig. 1e). The corresponding EDX mapping (Fig. 1d) shows that manganese-rich oxides were concentrated at the grain boundaries. Such manganese-rich oxide grains were also occasionally observed in regions far from the grain boundaries, as seen in Fig. 2.

Nodules formed on the thin scale (Fig. 1b) had different sizes and were surrounded by an intermediate zone of very flat oxide, as seen in Fig. 3a. However, zones of this sort without any nodule were also observed (Fig. 3a). A high magnification image of a fine nodule is shown in Fig. 3b. The smooth surface of the intermediate zone is seen to result from an absence of superficial fine oxide grains.

Scale cross-sections at visible alloy grain boundaries, nodules and regions far from the grain boundaries (Fig. 1b) were produced by FIB milling and examined by TEM.

A BF-TEM cross-section of the thin scale produced in reaction for 1000 h, far from any visible alloy grain boundary (Fig. 1b),

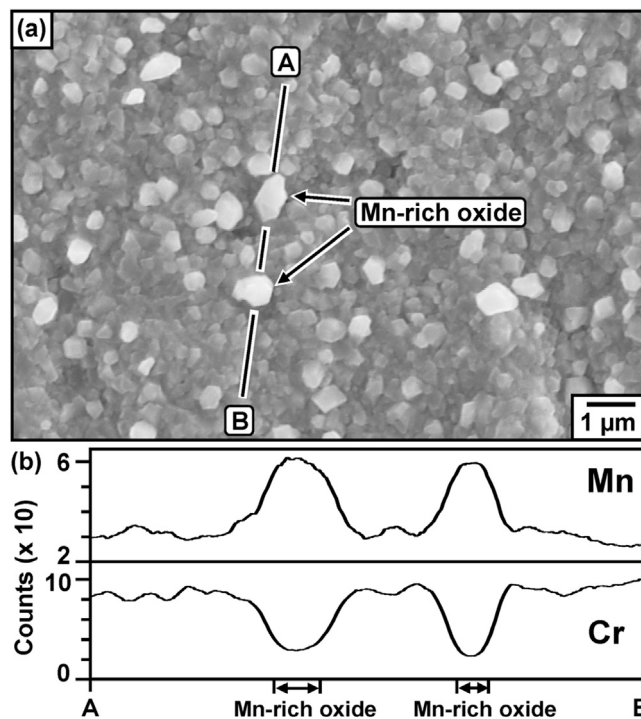


Fig. 2. Thin scale on Fe-20Cr-2Mn after reaction for 1000 h in Ar-20CO₂: (a) SE-SEM top view of grain regions far from the grain boundaries in Fig. 1 and (b) EDX line profiles along A–B in (a).

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