



Nano-crystalline coating to improve cyclic oxidation resistance of 304 stainless steel

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ABSTRACT

Cyclic oxidation of nano-crystalline 304SS coating was compared with that of conventional, micro-crystalline 304SS in both dry and wet (10% H₂O) air at 900 °C. The nanocrystalline alloys were prepared by direct current magnetron sputtering coating. Weight change kinetics were measured by continuous thermogravimetry. For micro-crystalline alloy in dry air, a small initial weight gain was followed by gradually increasing spallation. Addition of water vapour to air produced immediate spallation, and led to significant breakaway oxidation. Microstructural analyses revealed the formation of iron-rich oxides on the surface. The addition of water vapour also accelerated the development of internal oxidation in the form of fine spinel precipitates dispersed in the chromium depleted matrix. In contrast, nano-crystalline 304SS, underwent relatively rapid oxidation in the very early cycles of reaction, but then the reaction slowed down. No spallation was apparent in either gas. The weight gain was higher in wet air than in dry air. In both gases a dense and continuous chromium oxide layer was formed at the surface, together with other oxides distributed inside the coating layer. The effects of cyclic reaction, grain size and water vapour on the resistance of 304SS to breakaway oxidation are discussed.

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1. Introduction

It has long been recognised that refining the grain structure of an alloy can promote selective oxidation of its aluminium and/or chromium content [1,2]. This promotion effect becomes more significant when alloy grain sizes are reduced below about 100 nm. The effect is attributed to rapid diffusion of Al and/or Cr through the grain boundaries [3–5], which increases significantly the effective Al and/or Cr diffusion coefficient, and thereby reduces the critical aluminium/chromium concentration required for external alumina/chromia scale formation.

Another advantage of nano-crystalline materials is that their oxide scales show superior resistance to cracking and spallation. Cyclic and long-term oxidation resistance was significantly improved by applying nano-crystalline coatings on type 304 stainless steel [2,6], Ni–Cr–Al [3], Co–Cr–Al [7], and Ni–(Co)–Cr–Al [8–11]. In addition, the oxides formed on nano- and submicro-crystalline coatings are pegged onto the metal grain boundaries to form a convoluted interface. The so-called “micro-pegging” effect [5,12,13] of the inward-grown oxides results in better scale adhesion to the metal substrate.

Type 304 stainless steel exhibits good oxidation resistance at moderately high temperatures because of its ability to form a protective chromia scale at the alloy surface. However, the internal precipitation of chromium-rich compounds and repeated cycles of selective Cr₂O₃ scale formation and spallation reduce the chromium concentration at

the alloy surface to lower levels than that of the bulk alloy. When the protective chromia oxide scale fails and cannot heal because of chromium depletion, the alloy is susceptible to formation of a non-protective Fe-rich oxide scale. In this case, breakaway oxidation occurs. It has been reported that water vapour and cyclic reaction accelerate the onset of breakaway oxidation [14–16].

The effect of grain refinement on the resistance of 304 stainless steel to breakaway oxidation was investigated by comparing commercial, coarse-grained material with a nano-grained one under isothermal reaction conditions [6]. It was found that for the coarse-grained sample, catastrophic breakaway oxidation was not observed in dry air, but commenced in wet air after an incubation period. In contrast, the nano-grained steel did not suffer breakaway oxidation in either dry or wet air.

The present work was intended to provide further information on the oxidation of nano-crystalline 304 stainless steel under cyclic reaction conditions in both dry and wet air at 900 °C. The nanocrystalline alloys were prepared as coatings, by means of direct current magnetron sputtering (DCMS). The target alloy composition for coating was selected to be the same as that of the 304SS substrate to avoid inter-diffusion and reduce thermal stress between coating and substrate [5,8].

2. Experimental

The chemical composition of type 304 stainless steel used in this work was: Cr 18.39, Ni 8.11, Mn 1.84, Cu 0.41, Mo 0.36, Co 0.03, Si 0.46, C 0.05, P 0.032, S 0.001 and N 0.06 (all in w/o) with Fe the balance. Test sample coupons were cut into a rectangular shape, 20 × 10 × 2 mm.

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Samples used as substrates for coating were ground to an 800 grit finish and ultrasonically cleaned in acetone. Subsequently, they were DCMS coated in a vacuum chamber, using the same 304SS as the target material. During sputtering, the sample was rotating continuously to produce an even coating layer overall, with thicknesses up to about 30 μm . Details of processing parameters have been reported earlier [6].

The composition of both coating and the substrate were further analysed by SEM-EDS analysis. The average composition in weight percent for the substrate was Fe 73.54, Cr 16.7, Ni 8.2, Mn 1.1 and Si 0.5, and for the coating Fe 62.7, Cr 22.4, Ni 13.5, Mn 1.1 and Si 0.3. The coating is enriched in Cr and Ni. This difference presumably results from the sputter coating method, in a way which is not fully understood yet. However, both coating and the substrate are in the austenitic phase field at the reaction temperature of 900 $^{\circ}\text{C}$, according to Fe–Cr–Ni phase diagram [17].

Oxidation reactions were carried out at 900 $^{\circ}\text{C}$ in a thermal cycling apparatus. Temperature cycling was achieved by driving an electrically heated furnace at periodic intervals between two positions: one corresponding to the sample being located in the furnace hot zone and the other to the sample being outside the furnace. The cyclic operation was automatically controlled, and consisted of 50 min at reaction temperature and 10 min at ambient. The weight change of the sample during the whole process was monitored by thermogravimetric analysis (TGA) using a microbalance from which the sample was suspended by silica hooks. Continuous weight changes were recorded for each alloy for up to 100 cycles of reaction. The reaction gas, air, with a flowrate of 100 ml/min, was introduced either directly into the reactor for dry gas reaction, or through a water-vapour saturator hold at a temperature yielding the required 10% H_2O for wet gas reaction.

Reaction products were subsequently examined using X-ray diffraction (XRD), optical metallography (OM), and scanning electron microscopy (SEM) equipped for energy-dispersive X-ray spectroscopy (EDS).

3. Results

Nano-crystalline coatings prepared by direct current magnetron sputtering develop in the form of columnar crystallites oriented in the deposition direction. The typical coating structure is shown in the fracture cross-section in Fig. 1a and Fig. 1b shows a top view of these packed columns. The grain size normal to the deposition direction has been found by means of TEM to be in the range of 5–20 nm [6], whilst the grain size of the commercial 304SS used as substrates for coating and as a reference material for reaction was about 20 μm [6].

Weight change kinetics of micro- and nano-crystalline 304SS reacted at 900 $^{\circ}\text{C}$, in dry and wet air, are shown in Fig. 2a. Temperature changes produced discontinuous changes in the weight measurement, marking the periodic cycles.

The micro-crystalline steel in dry air slowly gained weight in the first 25 cycles of reaction. Then spallation was observed, and became significant after 40 cycles of reaction (Fig. 2a). In wet air, the spallation started in the first cycle of the reaction. After about 6 cycles of reaction, a sudden weight gain was observed, indicating the occurrence of break-away oxidation. Subsequently, extremely fast spallation was recorded (Fig. 2a).

Nano-crystalline 304SS gained weight rapidly in the first 5 cycles of reaction, and then reacted slower (Fig. 2b). There was no obvious spallation, such as observed for coarse-grained material. Weight gains were higher in wet air than in dry air, and both were higher than that for coarse grained steel in dry gas before the occurrence of spallation (Fig. 2a).

Fig. 3 shows a cross-section of nano-crystalline 304SS after 100 cycles of reaction in dry air. A dense, continuous oxide layer was formed at the surface with a thickness of about 3 μm . Underneath this oxide layer, many pores were present. In addition, oxide had formed within the coating layer, in elongated regions aligned vertically to the surface. Analysis by EDS of surface oxide and large oxide deposits within the coating layer showed that they are Cr and O only and confirmed by XRD as Cr_2O_3 . Addition of water vapour to the air did not produce significant change in the morphology of oxidised nano-coated 304SS (Fig. 4), which also formed Cr_2O_3 as the only reaction product. As seen in Fig. 4, oxide had also formed at local regions of the coating–substrate interface. The size of these oxide regions varied from place to place. This phenomenon perhaps reflects inadequacies in the coating–substrate bond.

Fig. 5 shows cross-sections of coarse-grained 304SS after 100 cycles of reaction in dry air. Clearly, there was no continuous protective oxide layer on the surface. Instead, non-uniform local attack and some external spalled oxides were observed. Analysis by EDS of the oxides in locally attacked areas showed that these oxides are Fe and Cr rich (Fig. 5d). Surface analysis by XRD showed the formation of Fe_2O_3 and FeCr_2O_4 . On this basis, the spalled oxides are identified as iron oxides and spinel.

Oxidation of the coarse-grained steel in wet air, produced a thick, rather uniform scale, as shown in Fig. 6a. At least two phases are present in the scale, the darker contrast phase being more aggregated in the outer part of the scale. EDS analysis showed clearly that this dark material is iron and chromium rich oxide (Fig. 6d). Similar analysis applied to the finely particulate oxides of the inner scale yielded the results in Fig. 6e, where nickel is also present, in addition to Fe, Cr and O. In all these cases, a small amount of Si was also detected. Surface analysis by XRD revealed the major product was FeCr_2O_4 together with some Fe_2O_3 . These results show that the dark oxide phase is FeCr_2O_4 .

Examination by SEM of an oxide surface grown on nanocrystalline material showed the very fine cuboidal chromium oxides ($\leq 0.5 \mu\text{m}$) formed over the whole surface after 100 cycles of reaction in dry air. These oxides grew faster along particular lines as shown in Fig. 7a, corresponding to surface convolutions with micro-cracks, as shown in Fig. 7b.

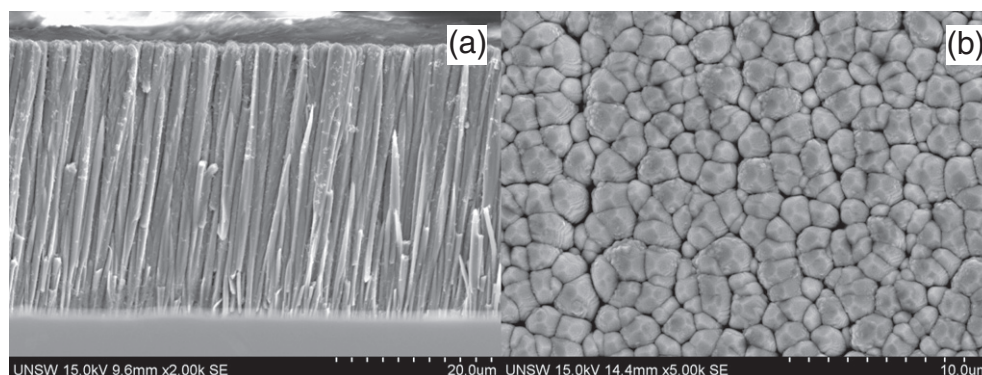


Fig. 1. SEM observations of sputter deposited 304SS: (a) cross-section and (b) top-view of the nano-coated structure.

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