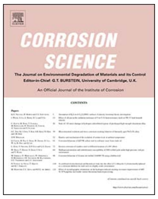
Corrosion Science 131 (2018) 174–186

Contents lists available at ScienceDirect

Corrosion Science

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



Effect of cyclic oxidation on the tensile behavior of a Fe-Cr-Si coated Nb-base alloy

Mahesh K. Kumawat, Md. Zafir Alam*, Dipak K. Das

Defence Metallurgical Research Laboratory, Hyderabad 500 058, India

ARTICLE INFO

Keywords:
A. Silicide coating
A. Niobium/Columbium alloy
B. Thermal cycling
C. Oxidation
C. Tensile properties

ABSTRACT

The room temperature tensile properties of Fe-Cr-Si coated C103 alloy are evaluated after cyclic oxidation at 1100–1300 °C for 30–180 min. The strength increased marginally (by 10–20 MPa) after oxidation at 1100 °C, whereas the ductility decreased by ~50%. Oxidation at 1300 °C for 180 min caused a greater increase in strength (by 10–15%) and deterioration in ductility to 9%. Localized embrittlement of the substrate sub-surface regions in the vicinity of cracks formed in the coating, HfO_2 precipitation at grain boundaries, and intergranular cleavage caused lowering of ductility during cyclic oxidation. Nevertheless, the coating prevented catastrophic oxidation and is indispensable for hypersonic applications.

1. Introduction

Nb-based alloys, such as C-103 and Cb-752, by virtue of their high melting temperatures, good high temperature strength, low density, low sublimation rates, and good weldability, are potential structural materials for use in strategic high-altitude aerospace applications involving high temperatures, hypersonic flow velocities, and low pressures [1–4]. However, these alloys exhibit extremely poor oxidation resistance, form loose oxide scales and undergo severe dimensional degradation above 900 °C in air [5–7], as shown for the bare alloy after oxidation at 1100 °C (Fig. 1). Oxidation resistant coatings such as silicides and Fe-Cr-modified silicides prevent catastrophic oxidation of these alloys and are indispensable for high temperature applications in air or oxidizing environments [8–14]. Previous thermal cycling studies in air have demonstrated that the silicide coatings provide excellent oxidation protection to the Nb-base alloys for 2–3 h at temperatures of 1300 °C [10–17]. The oxidation protection of these coatings is derived from the silicide phases ($NbSi_2$ and complex silicides of Nb-Fe-Cr) constituting the coatings, which form a protective layer of silica scale upon oxidation [10–17]. The microstructure of the coatings and the mechanisms for oxidation protection as well as coating degradation have been reported in previous literature [10–19].

The $NbSi_2$ and complex silicides constituting the coatings are intermetallic phases [11–17] and inherently brittle [20–24]. During the coating formation as well as thermal cycling, through-thickness cracks form in the coating due to thermal stresses which arise from the mismatch in coefficient of thermal expansion between the coating and the substrate [15,24,25]. The brittleness and the concomitant cracking of the coating can have adverse effects on the mechanical properties of the substrate. Sankar et al. have reported that, in the temperature range of 600–1200 °C, the ductility exhibited by the as-coated alloy after tensile testing in air was ~50% lower than that of the uncoated alloy tested in vacuum [26]. Furthermore, the Hf present in the C103 alloy is extremely reactive to oxygen and forms HfO_2 precipitates even during heat treatment at vacuum levels of 10^{-3} Pa (10^{-5} mbar) [27]. The HfO_2 precipitates induce embrittlement and cause deterioration in the tensile properties of the vacuum heat treated C103 alloy [27]. Therefore, since the coated C103 alloy is intended for use at high temperatures in air/oxidizing environments, ascertaining the effects of: (i) coating and (ii) oxidation, on the mechanical properties of the coated alloy is crucial. However, information on these aspects is extremely limited in the open literature. In consideration of the above, the present study examines the comparative tensile properties of Fe-Cr-modified silicide coated and uncoated C103 alloy at room temperature (RT). The effect of cyclic oxidation at 1100 °C and 1300 °C in air, for durations ranging between 30–180 min, on the RT tensile properties of the coated alloy has also been examined.

2. Experimental details

The Nb-base alloy, C103, having the nominal composition (in wt.%) Nb-10Hf-1Ti-0.7Zr-0.5Ta-0.5W was available in the form of 4 mm thick annealed sheets. The oxygen content in the alloy was less than 225 ppm. Flat tensile samples with gage length of 25 mm and thickness of 4 mm were fabricated using wire electrical discharge machining (EDM). The samples were subjected to acid pickling treatment for 2 min

---

* Corresponding author.
E-mail address: zafir.alam08@gmail.com (Md. Z. Alam).

https://doi.org/10.1016/j.corsci.2017.11.023
Received 1 May 2017; Received in revised form 14 November 2017; Accepted 22 November 2017

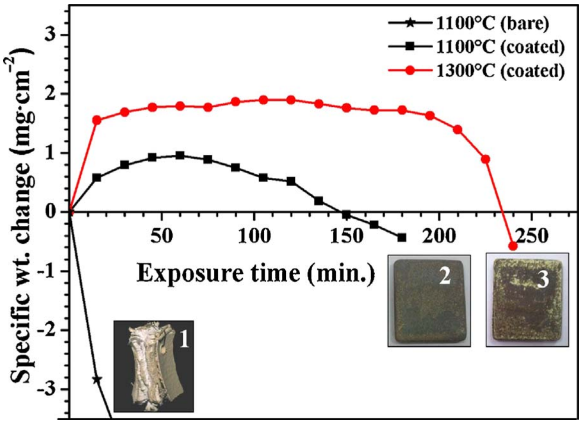


Fig. 1. Weight change plots for bare and silicide coated C103 alloy during cyclic oxidation. Inset 1 shows profuse scaling and dimensional degradation of the bare alloy after oxidation at 1100 °C for 30 min. Insets 2 and 3 show that the coated samples remain intact even after oxidation at 1100 °C and 1300 °C for 180 and 240 min, respectively. The data has been adapted from Ref. [15].

for removal of surface oxide films which form during the EDM. The pickling solution contained 10 ml water, 20 ml nitric acid, 20 ml sulphuric acid and 30 ml hydrofluoric acid. The concentrations of the acids used were (in vol.%): HNO_3 70%, H_2SO_4 98% and HF 40%. Subsequently, the samples were thoroughly cleaned, first in water and then in acetone. Some of the tensile samples were applied with a Fe-Cr-modified silicide coating using the dip slurry method, as described in the following text. Elemental metal powders of Si, Fe and Cr, each having purity of 99.99% and average practice size of −325 mesh, were obtained from American Elements Company, USA. The Si, Cr and Fe powders were mixed in the ratio of 60:20:20 (wt.%) in an attritor mill for 1 h. The above composition of the powders was selected because of its similarity with that of the R512E coating, i.e. 60Si-20Cr-20Fe (wt. %), used for aerospace applications [28]. Subsequently, a slurry was prepared by adding a suitable liquid binder to the powder mixture in the proportion of 1 ml of binder to 1 g of powder mixture and mechanical stirring for 15 min. For application of the coating, the samples were dipped in the slurry bath at a controlled rate of 1 mm/sec, held in the slurry for 30 s, and withdrawn from the slurry at a controlled rate of 1 mm/sec. The dipping process was repeated thrice with an intermediate hold time of 5 min between consecutive dips, which ensured proper drying of the slurry on the sample surface before re-dipping. Subsequently, the samples were diffusion heat treated at 1400 °C for 2 h at a vacuum level of 10^{-5} mbar.

Some of the uncoated and coated tensile samples were subjected to thermal cycling exposure in air at 1100 and 1300 °C in an automated thermal cycling furnace. The samples were initially weighed, their surface area measured using a micrometer, and placed in recrystallized alumina crucibles on the loading stage, which was initially outside the furnace hot zone. After the desired test temperature was achieved in the furnace hot zone, the loading stage was inserted into the hot zone. The sample temperature was continuously recorded by a thermocouple, which was placed on the sample stage in proximity to the samples. It took 5 and 7 min for the samples to attain the corresponding test temperatures of 1100 and 1300 °C after which, the heating time was counted. The samples were heated for 15 min and, subsequently, the loading stage was retracted from the hot zone. The samples were allowed to cool outside the furnace for 15 min. Subsequently, the samples were carefully taken out of the crucibles and weighed. The weight of any loose oxide powder formed and trapped in the crucibles was not considered. The samples were again placed in the crucibles and the above processes of heating, cooling, and weight measurement repeated. After each cycle, the specific weight change of the samples, i.e. the difference in the weight with respect to the initial weight per unit initial surface area, was measured. The cyclic tests were continued until the specific weight change of the samples became negative. The thermal cycling data for uncoated and coated C103 alloy, generated using the above approach, was reported in our earlier study [15] and shown in Fig. 1. The plot showed three distinct weight change regimes: (i) initial rapid weight gain, (ii) steady state weight change, and (iii) onset of rapid weight loss (Fig. 1) [15]. The weight gain indicated the formation of a protective oxide layer on the surface, whereas weight loss denoted spallation of the oxide layer off the sample surface. Therefore, in the present study, the tensile samples were thermal cycled at 1100 °C for 30, 75 and 120 min and at 1300 °C for 30, 90 and 180 min. These durations for thermal exposure correspond to the three distinct regimes of the oxidation life of the coated samples, as mentioned above. Thermal cycling of uncoated tensile samples was not carried out because their extensive oxidation and concomitant rapid dimensional degradation (typically shown Fig. 1) would have resulted in loss of sample thickness and made subsequent tensile testing unfeasible.

In order to examine the effect of vacuum heat treatment associated with coating formation on the microstructure and tensile properties of the substrate alloy, some of the uncoated tensile samples were subjected to vacuum heat treatment at 1400 °C for 2 h. Furthermore, for ascertaining the effect of thermal exposure (sans coating) on the microstructure vis-à-vis tensile properties of the substrate, some of the uncoated tensile samples, that had been vacuum heat treated at 1400 °C/2 h, were subjected to subsequent vacuum heat treatment at 1100 and 1300 °C for durations corresponding to that of the oxidation test durations. The vacuum level during the heat treatments was maintained at 10^{-5} mbar. The above samples, which were vacuum heat treated for various durations (sans coating), are referred to as dummy heat treated samples in the text. Table 1 presents the details of the various samples and their respective nomenclature used in the study. Tensile testing of all the samples, i.e. uncoated, coated, and after various dummy heat treatments (Table 1), was carried out at room temperature (RT) using a 200 kN Walter-bai Ag tensile testing machine. A constant cross-head speed of 1 mm/min was used for the tensile tests. At least two samples of each type were tested. The microstructure and fracture surface was examined using a Zeiss Supra-55 scanning electron microscope (SEM) equipped with Oxford electron back scattered diffraction (EBSD) and energy dispersive X-ray spectroscopy (EDXS) detectors operating at 20 kV. Cross-section samples were prepared from the gage portion of the failed samples for microscopic observation. An electroplated layer of Ni was applied prior to sample sectioning and mounting to prevent damage to the coating. Standard metallography polishing techniques were used for preparation of the coating cross-section samples. Wet chemical etching of some of the polished cross section samples was carried out using an acid solution comprising 30 ml HF, 15 ml HNO_3, 15 ml HCl and 10 ml water. The measurements for grain size in the various heat treated samples (Table 1) were carried out under a light microscope, Leica 4000DM, which had the provision for digital image acquisition. Lines, along the diagonals as well as joining the centers of the opposite edges, were drawn for the respective micrographs. The grain size was measured based on the number of grain boundary intercepts made with the total length of the line, i.e. by the linear intercept method [29]. This process allowed for the measurement of grain size for the various samples without any ambiguity. Microhardness measurements were also carried out in the vicinity of the crack tips, coating-substrate interface, and in the interior of the substrate (away from the coating) for the oxidized coated samples to ascertain the embrittlement caused by oxygen during thermal exposure. The microhardness tester of make Walter Uhl VMH104 was used for the indentation measurements. For each indent, the load was 5 gf whereas the indent speed and dwell time were 25 μm s^{-1} and 15 s, respectively. The instrumented micro hardness tester (Anton Parr, model CPX) was used for measuring elastic modulus of various layers of the coating. Indentation was carried out on the coating cross section using Vickers type indenter with maximum load of 1 N and dwell time of 10 s.