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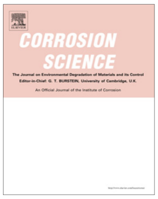

Isothermal oxidation behavior and growth kinetics of silicide coatings formed on Nb–1Zr–0.1C alloy

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ABSTRACT

Isothermal oxidation behavior of the single layer $NbSi_2$ and the double layered ($NbSi_2 + Nb_5Si_3$) silicide coated Nb–1Zr–0.1C (wt.%) alloys has been studied between 800 and 1300 °C in static laboratory air. The single layer coated alloy shows a lower weight gain as compared to the double layer coatings at all temperatures. The formation of amorphous silica scale embedded with Nb_2O_5 oxide particles is observed beyond 1100 °C, and a superior oxidation resistance is detected between 1100 and 1300 °C. A kinetic equation relating the thickness of the coating layer with the various process parameters for pack siliconizing of Nb-alloy has been established.

1. Introduction

Advanced high temperature nuclear reactors require the structural materials capable of withstanding the aggressive environmental conditions with respect to stress, temperature, liquid metal corrosion, and irradiation etc. for longer period of time. Nb–1Zr–0.1C (wt.%) alloy is the most suitable candidate as it offers superior creep properties, excellent liquid metal corrosion resistance, relatively lower density, and good fabricability [1,2]. However, the alloy has inferior oxidation resistance at high temperatures due to the non-protective nature of the oxide (Nb_2O_5) scale. Niobium-silicide based in-situ composites are under development to replace the Ni-based super alloys at the hottest locations of airfoils of advanced gas turbine engines. These Nb-silicide based alloys comprising of a niobium solid solution Nb_{ss} with Nb_3Si and/or Nb_5Si_3 silicides possess lower density, adequate room-temperature fracture toughness and good high temperature mechanical properties [3–6]. A lot of research has been reported to improve the oxidation resistance of these materials by alloying additions with Ti, Hf, Cr, Al, B, Sn, Ge etc. [7–15]. Although, a significant improvement in oxidation behavior is observed with the alloying additions, it is difficult to avoid the oxidation of these materials as Nb_{ss} forms the matrix phase. Therefore, formation of suitable protective coating is considered essential for application of the Nb base materials at high temperatures.

Silicide and aluminide coatings on Nb-base alloys were found to be suitable for improving their high-temperature oxidation performance by forming the protective oxide scales such as SiO_2 and Al_2O_3, respectively [16–19]. The attempts were made to improve the oxidation behavior of protective SiO_2 scale of silicide coated alloy by doping with Al, Y, B, Cr, Hf, Ge etc [20–28]. Multilayer Mo–Si–B [29] and Nb–Fe–Si [30] based coatings were also investigated for improving oxidation resistance of Nb and Nb–Si based composites. Different coating techniques were explored to produce uniform, adherent, and crack-free coatings. Halide activated pack cementation technique is found to be the most potential process for the production of desired coatings on different geometries. During the formation of silicide coatings on Nb-based materials, it was observed that the niobium di-silicide ($NbSi_2$) phase is formed in the outer layer. The effects of minor alloying additions were studied for improving the oxidation behavior of the $NbSi_2$ phase. Therefore, the coating of $NbSi_2$ would remain the primary focus for designing the Nb-based materials for high temperature applications. Our earlier work [31] showed that the two layered-coating structures comprising of a thin Nb_5Si_3 inner layer and a thick $NbSi_2$ outer layer is formed on Nb–1Zr–0.1C (wt.%) alloy substrate beyond 1300 °C. In the present work, the detailed isothermal oxidation studies of both the single layer ($NbSi_2$) and the double layer (Nb_5Si_3 and $NbSi_2$) coatings were carried out between 800 and 1300 °C. A kinetic model has been derived to predict the growth kinetics of the $NbSi_2$ phase in the pack siliconizing process. A large number of coating experiments were conducted in a broader temperature range from 900 to 1500 °C by

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varying the processing parameters to arrive at the actual model equation.

2. Experimental procedure

Nb–1Zr–0.1C (wt.%) alloy was prepared by adopting reduction and melting approach. Aluminothermic co-reduction was carried out using the mixture of oxides comprising of Nb_2O_5, ZrO_2 and C to produce Nb–Zr–Al alloy. Pyro-vacuum treatment and electron beam melting technique was adopted for purification of the alloy with respect to metallic and non-metallic impurities to achieve the desired composition. Small samples of dimensions 3.5 mm × 2.5 mm × 2 mm were sliced from the cast ingot using EDM wire cutting. The specimens were subsequently ground and polished to 1 μm diamond finish and cleaned ultrasonically. Pack siliconizing coating experiments were carried out at 1000 °C (to be identified as Si-1000) and 1300 °C (designated as Si-1300) for 6 h using a pack composition of $10Si–5NH_4F–85Al_2O_3$ (wt.%). Thermogravimetric analysis (TGA) of the coated samples was carried out using a Setaram, France make TGA apparatus (Model-Setsys Evolution). The samples were kept in a platinum crucible through platinum suspension wires inside the analysis chamber. The coated specimens were initially heated at 20 °C/min to the desired temperatures and isothermally held for 24 h in static air. Isothermal oxidation tests were conducted at 800 °C, 1000 °C, 1100 °C, 1200 °C and 1300 °C. The as-coated and oxidation tested specimens were characterized using scanning electron microscopy (CamScan MV 2300CT/100) and energy dispersive X-ray spectroscopy (Oxford X-Max 80).

For analyzing the kinetics of the coating growth process, the alloy specimens were cut into the coupons of dimensions 15 mm × 10 mm × 5 mm. The pack mixtures were prepared by mixing appropriate amounts of Si, Al_2O_3 (filler) and NH_4F (activator) powder. The packs were prepared by filling and tapping the powder mixture around the Nb–1Zr–0.1C alloy substrates in a cylindrical alumina crucible of 36 mm diameter and 48 mm length. The crucible was then sealed with an alumina lid using alumina base cement. The cement sealing was dried for 24 h at room temperature followed by controlled heating inside the alumina tube furnace under argon flow. After providing a cement-curing treatment, the temperature of the furnace was raised to the actual coating temperature at a rate of 4 °C min^{-1} and held for a desired time. The furnace was subsequently cooled to room temperature at a slow rate. The coating experiments were conducted at seven different temperatures between 900 and 1500 °C for 6 h using the pack composition of Al_2O_3 – 85%, Si – 10% and NH_4F – 5% (wt.%). Applying the same pack composition, the next sets of experiments were carried out at 1300, 1400 and 1500 °C by varying the dwell time between 6, 9, 12 and 15 h. Further experiments were conducted at 900, 1000, 1100 and 1200 °C for 6 h by varying Si and NH_4F contents in the pack keeping constant NH_4F and Si percentages in respective cases. After cooling and taking the samples out of the furnace, the coated samples were washed in water jet to remove any loosely adherent powder from the surface. Weight and thickness measurements of the coated specimens were conducted. The specimen weight gain in mg cm^{-2} was estimated. The cross-sectional microstructure and chemical composition of the coated specimens were analyzed using SEM and EDS. Using the weight gain and thickness data; the actual kinetic model was derived.

3. Results and discussion

3.1. Formation of coating

Fig. 1(a) and (b) represent the cross-sectional BSE images of the specimens coated for 6 h at 1000 °C and 1300 °C, respectively. It is clear from Fig. 1(a) that the coating formed at 1000 °C (Si-1000) consists of a single layer, while two layers are formed at 1300 °C (Fig. 1b). The concentration profiles (X-ray counts in cps) of the elements (Nb, Si etc.) across the interfaces of the coated layers for Si-1000 and Si-1300 are presented in Fig. 1(c) and 1(d), respectively. It has been confirmed from the quantitative EDS analysis that Si-1000 coating consists of one layer of niobium di-silicide ($NbSi_2$) phase (Fig. 1c). Fig. 1(d) shows two layers composed of the inner Nb_5Si_3 and the outer $NbSi_2$ phases for Si-1300 samples. A black layer comprising of aluminum–silicon oxide type phase is observed at the outer-most layer formed at 1300 °C (1d). This layer is normally observed at and beyond 1300 °C, which is due to the formation of a low melting eutectic between the instantaneously formed silica with the alumina present in the pack. It has been observed that for the maximum process duration of 24 h, silicide coatings consist of a single layer of $NbSi_2$ below 1300 °C, and double layer of Nb_5Si_3 and $NbSi_2$ beyond this temperature. In general, coatings produced by high activity pack cementation technique consist of multiple layers. The surface layer shall be rich in coated element. This is a result of dominant inward diffusion of coating material from the pack into the substrate. Subsequently, during the coating process, the major element present in the substrate reacts with the major element present in the surface-coated layer, and it produces the intermediate or second layer which will have low concentration of coating element in comparison to top coating surface layer. The formation of intermediate layers is guided by the temperature and time of the coating process. Therefore, during pack siliconizing of Nb based alloy the silicon-rich phase $NbSi_2$ is formed first. Subsequently, the intermediate Nb_5Si_3 layer is formed by outward diffusion of Nb from the substrate and the reaction between Nb and $NbSi_2$ at the Nb/$NbSi_2$ interface ($3NbSi_2 + 7Nb \rightarrow 2Nb_5Si_3$). It was observed that kinetics of growth of inner Nb_5Si_3 layer is very slow and existence of this layer was not detected below 1250 °C for the coating-process duration of 24 h. The thickness of the $NbSi_2$ layer formed at 1300 °C is much higher than that of Nb_5Si_3 layer indicating faster growth kinetics of $NbSi_2$ phase as compared to Nb_5Si_3 phase. Nb–Si diffusion couple experiments also show such differential growth kinetics of these two phases at higher temperatures [32,33]. Fig. 2(a) and (b) show the two layered coated structures formed at 1300 and 1400 °C for longer time. Columnar grain structure formation was observed in the $NbSi_2$ phase at 1300 °C. The grains were oriented along the direction of inward diffusion of Si along the $NbSi_2$ phase toward the Nb substrate. A clear transition from columnar to equiaxed type of morphology at the outer side of the $NbSi_2$ layer is observed at 1400 °C (Fig. 2b). Growth of the $NbSi_2$ phase from two different interfaces namely Si/$NbSi_2$ and Nb_5Si_3/$NbSi_2$ has been reported as the probable reason for the duplex morphology of $NbSi_2$ phase [33]. The fraction of the equiaxed grain morphology in $NbSi_2$ phase is increased with higher temperatures as evident from Fig. 2(a) and (b). Nb_5Si_3 layer contains a much finer grain structure due the slower growth kinetics of this phase.

3.2. Isothermal oxidation behavior

For isothermal oxidation tests, the single layer ($NbSi_2$) coated and the double layer coated (Nb_5Si_3 and $NbSi_2$) Nb–1Zr–0.1C alloy specimens were selected. Fig. 3 shows the weight change behavior of the silicide coated specimens produced at 1000 °C (Si-1000) and 1300 °C (Si-1300). Here, it is mentioned again that Si-1000 contains about 58 μm thick single $NbSi_2$ layer, while Si-1300 is comprised with about 125 μm thick $NbSi_2$ outer layer and about 3 μm thick inner Nb_5Si_3 layer. Fig. 3(a) indicates a linear weight gain behavior of both Si-1000 and Si-1300 specimens at 800 °C. Si-1000 specimen showed much improved isothermal oxidation