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The ability of silicide coating to delay the catastrophic oxidation of vanadium under severe conditions

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HIGHLIGHTS

- Oxidation protection is due to the formation of a pure silica layer.
- V–4Cr–4Ti with V_xSi_y silicide coating withstands 400 1-h cycles (1100 °C-T_{amb}) in air.
- Three-point flexure testing at 950 °C and 75 MPa does not induce coating breakdown.
- No delamination between coating and substrate is observed in any test.

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ABSTRACT

V–4Cr–4Ti vanadium alloy is a potential cladding material for sodium-cooled fast-neutron reactors (SFRs). However, its affinity for oxygen and the subsequent embrittlement that oxygen induces causes a need for an oxygen diffusion barrier, which can be obtained by manufacturing a multi-layered silicide coating. The present work aims to evaluate the effects of thermal cycling (using a cyclic oxidation device) and tensile and compressive stresses (using the three-point flexure test) on the coated alloy system. Tests were performed in air up to 1100 °C, which is 200 °C higher than the accidental temperature for SFR applications. The results showed that the VSi_2 coating was able to protect the vanadium substrate from oxidation for more than 400 1-h cycles between 1100 °C and room temperature. The severe bending applied to the coated alloy at 950 °C using a load of 75 MPa did not lead to specimen breakage. It can be suggested that the VSi_2 coating has mechanical properties compatible with the V–4Cr–4Ti alloy for SFR applications.

1. Introduction

Vanadium-based alloys are potential candidates for the core components of future innovative nuclear systems known as generation IV reactors [1]. These cross-cutting materials are also currently considered for fusion applications [1,2]. The V–4Cr–4Ti vanadium-based alloy has a low capture section (as vanadium generates no or few radioactive elements) for rapid neutrons and the capability to withstand high temperatures [2]. Unfortunately, the affinity of vanadium alloys for oxygen at moderate temperature (500–600 °C) has hindered their use, even in low-oxygen atmospheres [3,4]. Thus, the formation of a diffusion barrier for oxygen to avoid substrate oxidation and embrittlement is required.

Research on coatings for these new cladding materials led to the development of multi-layered silicides coatings [5]. It was demonstrated [6] by oxidation tests in air or low-O_2 environments and 1000 h immersion test in liquid Na (containing a few tens of wpm of dissolved oxygen) that these coatings are efficient diffusion barriers in the expected operating temperature range of 550–750 °C. The main silicide responsible for the high oxidation resistance in air at 650 °C was vanadium disilicide VSi_2. The coatings were shown to be fully adherent to the alloy substrate and did not suffer from pesting (rapid fragmentation of the coating into powder due to oxidation) even after 1500 1-h cycles at 650 °C.

To further valid the capability of this system for cladding application, its behaviour was also evaluated under severe conditions that could arise as accidental ones. However, the future design of cladding for sodium fast reactors is not yet defined, and the level of strain that must be withstood by the cladding material is also fairly unknown. It can only be supposed that these materials could reach temperatures as high as 1000 °C in liquid Na in the case of cooling device problems.

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This paper reports the results of two sets of harsh experiments conducted at up to pursue the characterisation of multi-layered VSi_2 coating system. Cyclic oxidation tests were performed up to 1100 °C in air. The three-point flexure tests were conducted at up to 950 °C. These testing conditions were chosen based on the accidental conditions that the zirconium cladding material withstands (1100–1200 °C in case of cooling failure in Pressure Water Reactors). In the same way, zirconium tubes at operating temperature in PWR (350 °C) are thought to experience strains as high as 150 MPa due to the volume increase of the combustible pellets; thus, this strain was chosen for flexure tests. Of course we have to keep in mind that the real conditions withstood by cladding materials can be different.

2. Experimental methods and materials

2.1. Manufacturing of VSi_2 coating

V–4Cr–4Ti substrate was provided by GfE Metalle und Materialien GmbH, Nuremberg, Germany; the manufacturing process is detailed elsewhere [7]. The samples were cut from a rolled plate and recrystallised at 1000 °C; their dimensions were approximately 10 mm × 10 mm × 1 mm for oxidation tests and 30 mm × 8 mm × 1.5 mm for three-point flexure tests. Surface preparation consisted of polishing down to 1200 grid and rounding the corners with SiC paper. The manufacturing of the coating by halide-activated pack cementation and the coating microstructure were previously described in detail elsewhere [4]. The coating consists of a stack of four vanadium silicides, with the outer, thicker layer being the vanadium disilicide VSi_2.

2.2. Oxidation tests

Cyclic oxidation tests were performed on the coated samples in a tubular furnace in air for a 1-h cycle at 950 and at 1100 °C. The specimens were then removed from the furnace, cooled for 10 min at room temperature and weighed by hand using an analytical balance with a precision of 0.1 mg. Cyclic oxidation conditions allowed for the evaluation, in a single experiment, of both the oxidation resistance of the coating and the effect of thermo-mechanical stresses applied to the coating-substrate system.

2.3. Three-point flexure tests

The three-point flexure test device is displayed in Fig. 1. This system, entirely made of alumina, is introduced in a muffle furnace with holes drilled in the bottom and top to pass two alumina rods. A constant load is applied at the middle of the specimen using the alumina road (from the top) cut into a V-shape. The movement of the specimen is registered by a displacement sensor of 5-μm sensitivity placed outside the furnace. The second alumina rod (from the bottom in Fig. 1) extended the sensor up to the specimen placed in the furnace. The flexure tests were performed at 650, 750, 850 and 950 °C. The load was chosen to reach a stress of 150 MPa for the first three temperatures listed. Based on the results, the test at 950 °C was conducted with a load corresponding to a stress of 75 MPa. The specimen for the flexure test was supported by two 1-mm-diameter alumina pins located 20 mm away from each other. The maximum vertical displacement for this device is approximately 1500 μm.

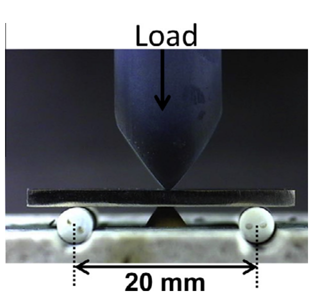

Fig. 1. Photograph of the three-point flexure device used in this study. The load is applied at the top using a V-shaped alumina rod. Displacement is measured at the bottom using an alumina rod placed on a displacement sensor located below the furnace.

2.4. Metallographic characterisation

Metallographic observations were performed using a JEOL JSM-7600F equipped with an SDD-type EDX detector coupled with an Oxford INCA WAVE WDS spectrometer. Metal disilicides (MSi_2 with M = V, Cr or Ti) were used as calibration specimens for the quantitative analysis.

Before cutting and grinding, the oxidised samples were covered by an electroplating layer of Ni to prevent the degradation of oxidation products. Next, the samples were cut transversally to characterise the cross-sections. They were embedded with a cold epoxy resin, ground from 240 to 2400 grid with SiC paper and polished using a colloidal SiO_2 suspension.

3. Experimental results

To appreciate the results presented in this section, it should be first mentioned that all tests were conducted in air. This is obviously not the environment of the fuel cladding in SFR operations. The growth rate of the protective oxide scale (a silica layer) is supposed to increase both with temperature and oxygen partial pressure [8]; thus, this environment is a very oxidative environment relative to the residual oxygen content which exists in liquid Na in SFR (less than 10 wpm). Therefore, the consumption of the VSi_2 coating by oxidation should be faster in our experiments (performed at 950 and 1100 °C in air) than under operating conditions (650 °C maximum, containing less than 10 wpm [O]). Moreover, the expected oxide of vanadium forming in air at or above 681 °C corresponds to liquid V_2O_5 [9]. Thus, the risk of contamination of the experimental devices by liquid V_2O_5 is high when performing the experiments at temperatures higher than 681 °C. This would occur in the case of coating rupture and would be, thus, a good experimental indicator of this phenomenon.

3.1. Cyclic oxidation behaviour of the VSi_2 coating in air

Coating behaviour was first evaluated at 650 and 750 °C, and the oxidation tests were stopped after 1600 and 840 1-h cycles, respectively, without having observed the end of life of the coated vanadium alloys [10]. The weight gain reached 1.2 and 1.8 mg cm^{-2}, respectively, after a few cycles and then ceased to evolve further. At these temperature, it is suggested that the thermo-mechanical strains are too low to observe coating degradation with a reasonable delay. This will be discussed further in the discussion section.

The results of the tests conducted at 950 and 1100 °C are reported in Fig. 2a and b, respectively. At these temperatures, cyclic oxidation tests were conducted up to the end of life of the system. In the present case, the end of life was peculiarly easy to locate because when the coating was no longer protective, the substrate quickly reacted with O_2 to form the liquid oxide V_2O_5.

At 950 °C, three coated specimens were tested for reproducibility. Their weight gains increased at the beginning (during the first 100 1-h cycles), after which the weight gains remained very low (<0.5 mg cm^{-2}) and quite constant up to their lifetime limit. As