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High temperature oxidation behavior of silicon carbide-carbon coated nanostructured ferritic alloy composites in air + water vapor environment

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A B S T R A C T

Oxidation behavior of silicon carbide (SiC) - carbon coated nanostructured ferritic alloy (C@NFA) composites was investigated in an air + 45 vol% H_2O atmosphere at 500–1000 °C. All the composites show an oxidation structure with an outer Fe-rich layer and an inner Cr-rich layer, as well as internal oxidation along grain boundaries. Oxidation resistance increases with SiC addition. The corresponding fundamental mechanism is proposed. The improved oxidation resistance for the higher SiC content composites is attributed to a delay in 'breakaway oxidation' due to improved kinetics for the formation of dense Cr_2O_3 and SiO_2 protective layers.

1. Introduction

The widespread use of nuclear energy strongly depends on enhanced safety of reactors. The latest nuclear disaster at the Fukushima-Daiichi power plant blackout was caused by excessive hydrogen gas evolution due to the reaction between the steam and the zirconium alloy based cladding material [1–4]. Following this incident, there has been significant research in either modifying or replacing current zirconium based alloy as fuel claddings [3,5–7]. The main requirements of the cladding materials are high irradiation and creep resistance and good high temperature oxidation resistance under harsh steam containing nuclear environments [8–11].

Nanostructured ferritic alloy (NFA) [5,12,13] and silicon carbide (SiC) [2,14,15] are being widely considered as potential candidates to replace current zirconium based cladding materials, such as Zircaloy. The excellent irradiation resistance and high temperature mechanical properties of NFA are attributed to homogeneously distributed Y-Ti-O nanoclusters with a high density [2,13]. These nanoclusters can trap helium at their interface and significantly increase void swelling resistance [16–18]. This entrapment reduces accumulation of helium gas at interphase grain boundaries, and greatly improves creep resistance and fracture strength [18]. The nanoclusters also obstruct the motion of dislocations and ultimately strengthen the NFA material [2]. SiC is considered as a desirable high temperature stable nuclear material, especially for fusion reactors [19,20] and high temperature gas reactors [21]. SiC and its composites are attractive claddings in light water reactors because of their high irradiation resistance, slow oxidation kinetics, and good high temperature strength [22,23]. Based on the above considerations, NFA-SiC composite has been studied as fuel cladding materials owing to the combined advantages from both materials [24–28]. Such composite is expected to provide good high temperature mechanical performance, strong oxidation and irradiation tolerance, and improved manufacturability.

High temperature oxidation behavior of cladding materials in water vapor containing nuclear environment is a basic concern and requires more in-depth fundamental understanding in the search for effective solutions. Chromium containing steels rely on the formation of an external chromia (Cr_2O_3) layer to improve the oxidation resistance [29–32]. A water vapor containing environment can cause breakaway oxidation on chromium containing steels, and lead to the failure of the protective chromia layer and produce extensive oxidation damage at high temperatures of 600–800 °C [29,31,33,34]. Excessive chromium loss occurs due to the reaction between chromia and water vapor, which results in volatile species such as CrO_3(g), $CrO_2(OH)_2$, $CrO_2(OH)$, etc. [29,35]. Alloying elements, such as Al and Si, can enhance the oxidation resistance of steel by forming additional Al_2O_3 and SiO_2 protective layers [1]. Ueda et. al. [36] reported diffusion reduction and ionization of iron due to Si enrichment in an internal spinel oxide layer.

This work focused on the effects of thermal treatment on the SiC-C@NFA composites at 500–1000 °C in an air + 45 vol% H_2O vapor environment. The oxidation resistance was studied based on weight change and oxidized layer thickness. The oxide layer microstructures, phase compositions, and surface morphologies were characterized and investigated. The overall oxidation mechanism was elucidated from a thermodynamic point of view.

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Table 1
Relative densities of the SPS sintered composites [24,27].

Sintering temperature (°C)	Sample	Relative density (%)
850	Pure NFA	95.60 ± 0.50%
	5 vol% SiC-C@NFA	87.42 ± 0.22%
	15 vol% SiC-C@NFA	89.83 ± 0.16%
	25 vol% SiC-C@NFA	96.84 ± 0.14%
950	Pure NFA	98.70 ± 1.10%
	5 vol% SiC-C@NFA	99.33 ± 0.17%
	15 vol% SiC-C@NFA	99.33 ± 0.17%
	25 vol% SiC-C@NFA	99.57 ± 0.14%

2. Experimental procedures

Our previous work has detailed the preparation method, density, and microstructural evolution of the SiC-C@NFA composites [27]. In brief, carbon coated NFA powder (C@NFA, NFA with a composition of Fe-9Cr-2 W-0.4Ti-0.2 V-0.12C-0.3Y_2O_3) was mixed with 5, 15, and 25 vol% SiC powder and then densified using spark plasma sintering (SPS) at 850 °C and 950 °C for 10 min with 100 MPa pressure and 50 °C/min heating/cooling rate. The relative densities of the pure NFA and 5–25 vol% SiC-C@NFA composites are listed in Table 1.

In this work, the pure NFA and 5–25 vol% SiC-C@NFA composites were thermally treated in an air + 45 vol% H_2O atmosphere. The samples were cut into 5 mm × 5 mm × 3 mm sizes and the surfaces were polished using SiC papers (grit size: 180, 400, 600, 800, 1200) and an alumina suspension (size: 1 μm) before the thermal treatment. It was carried out in a tube furnace (1730-20 HT Furnace, CM Furnace Inc., Bloomfield, NJ) at temperatures of 500 °C, 750 °C, and 1000 °C for 50 h. The air + 45 vol% H_2O atmosphere was generated by passing air through a water jar before it reached the tube furnace. The water in the jar was maintained at 80 °C and generated the saturated vapor pressure of 355 mmHg, which corresponded to ~45 vol% of water vapor. The weight changes of the samples were tracked using a balance before and after the thermal treatment in the air + 45 vol% H_2O atmosphere. Normalized weight changes with respect to sample areas were obtained for all the samples.

The phase compositions of the oxidized sample surfaces were examined using an X-ray diffractometer (XRD, PANalytical B.V., Almelo, Netherlands) with Cu-Kα radiation at an operating condition of 45 kV/40 mA. Scanning electron microscopy (SEM, FEG ESEM QUANTA600, FEI Company, Hillsboro, OR, USA) was performed to characterize the surface morphology and cross section microstructure of the oxidation layers. Elemental distributions along the cross section of the oxide layers were analyzed using an energy dispersive spectrometer (EDS) (model of BRUKER) attached to the SEM.

The oxidation behavior of the samples was studied based on the Thermo-Calc® software. The corresponding phase diagrams and elemental diffusion coefficients (D_{Cr} and D_{Fe}) at the thermal treatment conditions were obtained. The average elemental compositions in each composite were calculated by considering contributions from SiC, C-coating, and NFA.

3. Results and discussion

3.1. Physical changes

Fig. 1 shows the effect of SiC addition on the mass changes for the 850 °C and 950 °C sintered pure NFA and 5–25 vol% SiC-C@NFA composites during the thermal treatment in the air + 45 vol% H_2O atmosphere. There are three major factors that contribute to the mass changes during the oxidation process: oxide layer formation, oxide layer spallation, and volatile species formation and depletion. The oxide scale formation contributes to the mass gain due to oxygen uptake during metal-oxygen reactions. The difference in thermal expansion coefficients between the oxide scale and the substrate at high temperatures results in the oxide layer spallation and concurrent mass loss. The chemical reactions between the oxide layer and the atmosphere (more specifically H_2O vapor) also lead to the formation of volatile species such as metal hydroxides, which again contribute to the mass loss.

As shown in Fig. 1a, the 850 °C sintered pure NFA and 5–25 vol% SiC-C@NFA composites after the thermal treatment in air + 45 vol% H_2O at 500 °C and 750 °C have significantly less mass gains (0.4–15 mg/cm^2) compared to that of the 1000 °C treated composites except for the 25 vol% SiC composites. (The marginal increase in the mass gain for the 850 °C sintered 15 vol% SiC-C@NFA composite after the 500 °C thermal treatment is probably because of sample quality variation derived from sintering, and it does not alter the overall trend in this work). For the 500 °C thermal treated samples, the 25 vol% SiC-C@NFA sample shows the lowest mass gain of 0.38 mg/cm^2 as compared to 1.15 mg/cm^2 for the pure NFA. While for the 750 °C thermally treated samples, the mass gain decreases from 14.6 mg/cm^2 for the pure NFA to 4.5 mg/cm^2 for the 25 vol% SiC-C@NFA. The mass gains after the 1000 °C thermal treatment show considerable decrease from 111.9 mg/cm^2 for the pure NFA to 8.5 mg/cm^2 for the 25 vol% SiC-C@NFA. Less than 1/10 of the mass gain for the 25 vol% SiC-C@NFA composite than that for the pure NFA means that the high SiC content with 25 vol% addition significantly improves oxidation resistance of the SiC-C@NFA composites. All the 950 °C sintered pure NFA and 5–25 vol% SiC-C@NFA composites show negligible mass gains after the 500 °C and 750 °C thermal treatments (0.03-3.5 mg/cm^2) as shown in Fig. 1b. There is no obvious correlation with the SiC addition in the samples. The 950 °C sintered samples also show better oxidation resistance than the 850 °C sintered samples at the same thermal treatment condition. The 950 °C sintered pure NFA and 5–25 vol% SiC-C@NFA composites show a decreasing trend in mass gain, similar to the 850 °C sintered composites after the 1000 °C treatment. The mass gain for the 950 °C sintered pure NFA is comparable to that of the 850 °C sintered condition (~107 vs ~111.9 mg/cm^2 respectively) after the 1000 °C treatment. However, the 950 °C sintered 5 and 15 vol% SiC-C@NFA composites have much lower mass gains (84.5 vs 23.2 mg/cm^2) than that of the 850 °C sintered 5 and 15 vol% SiC-C@NFA composites (111.7 vs 86.2 mg/cm^2). The 950 °C sintered 25 vol% SiC-C@NFA composite shows significantly lower mass gain (7.8 mg/cm^2) compared to that of the pure NFA (107 g/cm^2) as well as that of the 5 and 15 vol% SiC composites (84.5 and 23.2 g/cm^2) during the 1000 °C treatment. The 950 °C sintered samples have better oxidation resistance than the 850 °C sintered samples at the same treatment condition, which is attributed to the higher densities derived from the sintering temperature. As shown in Table 1, the higher sintering temperature of 950 °C produces a higher relative density for the same composition sample. The denser samples tend to have fewer defects, which can hinder oxidant diffusion and benefit the oxidation resistance.

3.2. Phase composition

Fig. 2 shows the XRD patterns of the 850 °C and 950 °C sintered pure NFA and 5–25 vol% SiC-C@NFA composites after the thermal treatments. All the samples show mainly hematite phase after the thermal treatment between 500–1000 °C. For the 500 °C thermal treatment condition, the pure NFA and 5–25 vol% SiC-C@NFA composites show the hematite phase without preferential growth. For the 750 °C thermal treatment condition, the XRD peaks of the (300) plane from the hematite phase in the pure NFA and SiC-C@NFA composites have higher intensity, meaning that the hematite phase has preferential growth along the (300) plane. For the 1000 °C thermal treatment condition, the pure NFA and 5 vol% SiC-C@NFA composite show preferential growth of the hematite phase along the (600) plane, while the 15 vol% and 25 vol% SiC-C@NFA composites have no preferential growth of the hematite phase. The same phenomenon has been observed in our