



Incipient oxidation kinetics and residual stress of the oxide scale grown on Haynes 230 at high temperatures

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ABSTRACT

Incipient oxidation kinetics of alloy 230 in air in the temperature range of 850–1000 °C was investigated by in situ thermogravimetry. A two-stage oxidation kinetics was observed; each stage followed Wagner's parabolic law. The activation energies for the first and the second stages are 246.5 and 212.1 kJ/mol, respectively. Grazing incidence X-ray diffraction showed that two types of oxide phases existed: Cr₂O₃ and MnCr₂O₄. Cr₂O₃ was the dominated phase. Structural characterization revealed that Cr₂O₃ and MnCr₂O₄ are mixed with each other and uniformly distributed throughout the scale. The results of residual stress measurements showed that the intrinsic residual stresses of the scale are highly tensile, ranging from 648.9 to 1308.4 MPa. The stress state of alloy 230 near the scale/substrate was found to be tensile, which is opposite to the stress state in the oxide scale, such that the forces balanced.

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1. Introduction

The Very High Temperature Reactor (VHTR) is the lead Gen-IV nuclear systems, owing to its highly efficient heat-electricity conversion along with the capability of hydrogen production [1]. Since the VHTR is expected to be operated at temperatures up to 950 °C and pressures up to 7 MPa for a design life of 60 years, the structural metallic components must withstand long-term severe operating conditions. Therefore, structural materials must possess excellent high temperature mechanical properties and withstand corrosive conditions due to active impurities in the He gas coolant. Small amounts of gaseous impurities, such as CO, CO₂, H₂O, H₂, and CH₄, will be present in the He during the operation of the VHTR. The environment may cause the gas-metal interactions, which may lead to oxidation, carburization and decarburization of the materials [2–4]. The corrosion issues may be detrimental to the mechanical behavior of the materials [5–7].

Alloy 230 is a promising candidate material for hot gas ducts and intermediate heat exchangers (IHX) used in VHTR [8]. Due to its high chromium content (20–24 wt%), the alloy usually develops chromium-rich surface oxide under high-temperature oxidation conditions. It has been suggested [9] that surface chromia formed within slightly oxidizing environments may act as an effective barrier to minimize environmental degradation of the materials in the VHTR environment and reduce negative synergistic effects to degrade mechanical properties (e.g. tensile and creep) under these

conditions. Therefore, the oxidation characteristics of alloy 230 are of particular importance at temperatures up to 1000 °C. However, there is very limited information concerning the oxidation behavior of alloy 230 at high temperatures [10,11]. In a study by Li et al. [10], multi-stage oxidation kinetics was observed at temperatures ranging from 650 to 850 °C and it was found that two oxide phases (Cr₂O₃ and MnCr₂O₄) were formed. England et al. [11] reported that the selective oxidation of Mn occurred in thin foils of alloy 230. More recently, it was suggested [12] that MnCr₂O₄ was formed on top of Cr₂O₃ layer for alloy 230 oxidized up to 1000 h at 900 °C. These results indicated that the oxidation kinetics and the resulting microstructure of oxide phase for alloy 230 exposed at high temperatures are complicated.

An additional aspect of high temperature oxidation which has received very little attention is the development of residual stresses in the oxide and substrate. Residual stresses in the oxide layer may cause cracking and/or spallation of the protective oxide layer. Loss of the protective layer may enhance the oxidation rate and reduce the materials lifetime. Previous study [13] showed that the measured residual stresses are compressive and might originate mostly from thermal stresses between the oxide and the substrate.

The purpose of this study is to investigate incipient oxidation kinetics of Haynes 230 in air at 850, 900, 950 and 1000 °C. The resulting microstructures of the scale are characterized. The interplay between the oxidation kinetics and the microstructures is also examined. Residual stress measurements were performed to obtain the residual stress of the oxide scale and alloy 230. The relevant mechanism regarding the residual stress of the oxide generated is also described and discussed.

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2. Experimental details

Haynes alloy 230 provided by Haynes International, Inc. was used in this study. The chemical compositions are listed in Table 1. Coupons of 10 mm × 15 mm × 1 mm were prepared from the as-received material, and were polished down to a 600 grit SiC paper, followed by an ultrasonic cleaning process, which used acetone and ethanol and then dried in a vacuum dryer.

The Cahn Thermax 500 Thermogravimetric Analyzer (TGA), manufactured by Thermo Fisher Scientific Inc., was employed to study in situ incipient oxidation kinetics. The accuracy of the balance was 1 μg. The samples were heated in air with a tube furnace at 850, 900, 950 and 1000 °C, respectively. The heating rate was 25 °C/min. Oxidation time of 6 h for the samples exposed to air was used at temperatures from 850 to 950 °C. For the temperature of 1000 °C, 3 h oxidation time was used. The weight change was monitored over the entire exposure period with measurements every second. After oxidation exposure, phase identification of the oxide scale grown on the substrate was characterized by grazing incidence X-ray diffraction (GIXRD) with an incident angle of 2° (X'Pert MRD Pro, PANalytical). X-ray diffraction (XRD) was used to obtain the integrated intensities of the diffraction peaks to calculate the relative crystalline phase ratio of MnCr₂O₄. The ratio of the phase was defined by

$$\frac{\sum I_{\text{MnCr}_2\text{O}_4}}{\sum I_{\text{MnCr}_2\text{O}_4} + \sum I_{\text{Cr}_2\text{O}_3}},$$

where I is the integrated intensity of the corresponding peaks. A scan rate of 1.2°/min was used for $\theta/2\theta$ scan, where the 2θ ranged from 20° to 80°. X-ray photoelectron spectroscopy (XPS, model PHI5400 from Physical Electronics) was used to calculate the Mn content by deconvolution of Cr 2p_{1/2} and 2p_{3/2} peaks. The photoelectron spectra were excited by soft X-ray using Mg anode at 1253.6 V. To eliminate the surface contamination, the specimen was sputtered with 3 KeV Ar⁺ ions for 20 s. The compositional depth profiles of the oxide scale/substrate specimens were determined by Auger electron spectroscopy (AES, model PHI 660 from Physical Electronics). The interface between the substrate and the scale was defined by the intersection of concentration of oxygen and nickel detected. From the results of AES, the uniformity of each composition can be obtained. Thickness of the oxide scale was observed using the FEI StrataTM DB235, which is a dual beam system combining a scanning electron microscope (SEM) and a focused ion beam (FIB) with gallium metal ion beam source for cutting. The 10 thickness measurements were made and the average value was reported.

The residual stresses of the Cr₂O₃ and the substrate were determined by modified sin²ψ method using a four-circle diffractometer with psi-goniometer geometry [14]. In order to increase the diffraction volume of the oxide scale, an incidence grazing angle of 2° was used for the Cr₂O₃ oxide phase and the substrate. The (1 1 6) peak of the Cr₂O₃ was used for the residual stress measurement because it provided sufficient intensity for precise determination of the peak position. For the substrate, the diffraction peak of (2 2 0) was used. Using the method, the residual stresses of the substrate near the scale/substrate interface can be obtained.

3. Results and discussion

3.1. Microstructure

Fig. 1 depicts the XRD patterns for all specimens. Since there are few diffractions peaks in the spectra, GIXRD patterns were used for phase identification (Fig. 2). The results of GIXRD revealed that the oxide phases observed were Cr₂O₃, and spinel-type MnCr₂O₄ using JCPDS file no. 38-1479 and 75-1614, respectively. As shown

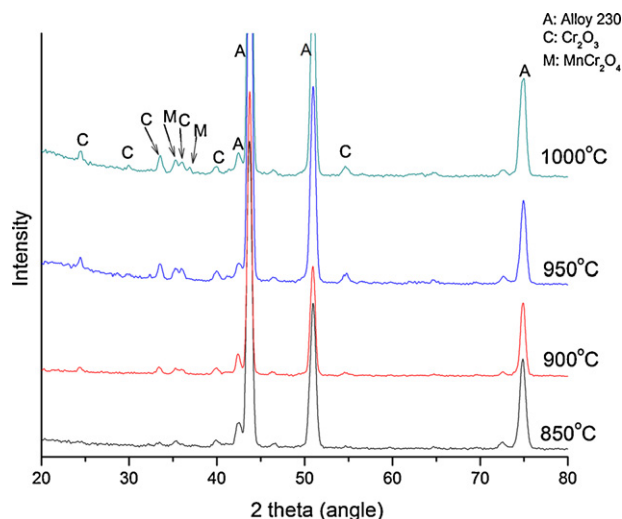


Fig. 1. The XRD patterns for the specimens oxidized at 850, 900, 950 and 1000 °C.

in Figs. 1 and 2, the diffraction peaks become more distinct as the oxidation temperature increases. The fraction of MnCr₂O₄ ($= \sum I_{\text{MnCr}_2\text{O}_4} / (\sum I_{\text{MnCr}_2\text{O}_4} + \sum I_{\text{Cr}_2\text{O}_3})$) for each oxidation temperature is listed in Table 2. It can be seen that the dominated oxide phase is Cr₂O₃. In addition, the MnCr₂O₄ fraction is found to be nearly constant across all of the exposure temperatures.

To examine the distribution of the two oxide phases, compositional depth profiles of the oxidized specimens were acquired using AES. Two representative AES spectra are shown in Fig. 3(a) and (b). The results indicated that Cr and Mn are distributed nearly uniformly throughout the oxide scales following oxidation. The microstructures of the scales, shown in Fig. 4(a)–(d), show a homogeneous oxide layer grown on the substrate. No significant distinction can be made for the separation of the two oxide phases. The results of GIXRD, AES and the microstructure suggest that the two oxide phases mix randomly with each other and are uniformly distributed throughout the scale. It is noted that for all specimens, the scale grown on the substrate is dense and maintains good adhesion at the interface over the entire temperature range (Fig. 4(a)–(d)). This should provide good oxidation resistance for alloy 230 over this range of application temperatures.

The amount of Mn measured by AES ranged from 1.9 to 3.3 at% for all the specimens. The results obtained by XRD and XPS were used to further confirm the atomic concentrations of Mn. Using

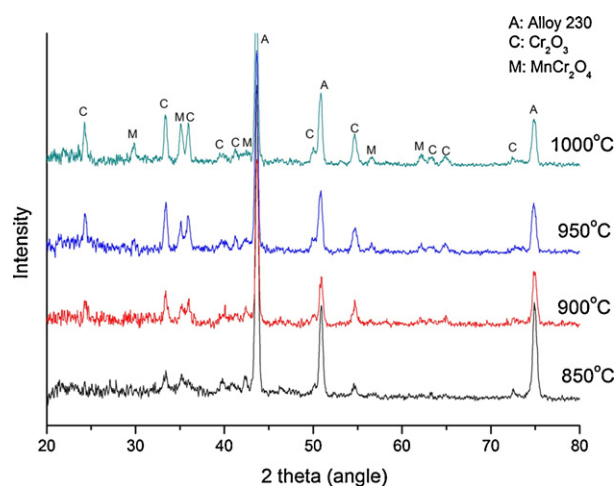


Fig. 2. The GIXRD patterns for the specimens oxidized at 850, 900, 950 and 1000 °C.

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