

Residual Stress Analysis on Oxide Layers Obtained by High Temperature Oxidation of Chromia-Forming Alloys

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Abstract: The oxide layers formed during high temperature oxidation of metallic alloys depend on experimental conditions (oxidation gas composition, gas pressure, temperature, duration etc...) and often with complex structure or multilayer structure. Residual stress can be generated not only due to oxide growth at high temperature (growth stress) but also during cooling of layer/metallic alloy system after oxidation (thermal stress). The determination of the level and the distribution of the residual stresses in oxide layers are very important to determine the influence of oxidation condition in one hand and to estimate the mechanical component's durability at high temperature in the other hand. Two Chromia-forming alloys have been studied: a nickel based Inconel 600 alloy (Ni-17%Cr-8%Fe-1%Mn) and a ferritic AISI 430 steel (Fe-17%Cr-1%Mn). Oxidation test has been carried out at different temperatures (from 600°C to 900°C) for various durations (from 2 h to 96 h) under different absolute humidities (from 0% to 19%). After oxidation of Inconel 600, the oxide layers are composed essentially by an external NiO layer and by an internal spinel NiCr₂O₄ layer. While the AISI 430 steel forms an external spinel Mn_{1.5}Cr_{1.5}O₄ layer and an internal Cr₂O₃ layer. The residual stresses (RS) have been analyzed by X-Ray Diffraction (XRD) method in each of oxide layers after oxidation tests. In oxide layers, the RS are compressive and the RS levels are more important in internal layer than those in external layer. Overall, the compressive RS in oxide layers increase with oxidation temperature, oxidation duration and absolute humidity.

Introduction

At high temperature, almost all metals are not thermodynamically stable in air or in atmosphere where oxygen exists, and a solid oxide scale will form on the surface. Oxidation of Chromia-forming alloys has drawn lots of attention in recent years, for their good oxidation resistance and low cost. It is true that lots of studies have been done to study the oxidation behavior of Chromia-forming alloy in dry air, but humidity exists in all stages of oxidation in reality. Therefore, studying the influence of water vapor on Chromia-forming alloys oxidation at high temperature has great importance. Some works have been done to study the influence of water vapor on oxidation [1-6], and several mechanisms have been proposed to explain the influence of water vapor on oxidation, such as Fuji and Meussner [2] proposed a dissociation mechanism, and suggested that hydrogen appears to play an important role in the oxidation process as an oxygen carrier between the separated inner and outer scale layers. Shen Jianian [3] suggested that breakaway oxidation happened in the water vapor containing atmosphere is the result of formation of microcracks and microchannels during oxidation. H. Asteman [4, 5] observed the evaporation of Chromia hydroxide. According to J. Ehlers the entry of molecular H₂O into the oxide scale was the main process leading to breakaway oxidation [6]. Obviously, the mechanism of Chromia-forming alloys oxidation with water vapor is still a contentious question.



It has been known that the residual stresses in the oxide scale are closely related to oxidation kinetic and the microstructure. Although some research works were already performed for Chromia-forming alloys to determine the residual stresses in the oxide scale after oxidation under dry air [7, 8], very few works were focused on residual stresses after oxidation in atmosphere with water vapor.

The purpose of this work was to investigate the influence of water vapor on Chromia-forming alloys at high temperature, and AISI 430 and Inconel 600 alloys were selected.

Experimental

The nominal chemical composition of the materials used in this study is listed in Table 1. Before oxidation, the samples were cut into a dimension of 10mm x 10mm x 1mm. All 6 surfaces of the samples were polished by SiC paper followed by silicon solution to make all the samples have the same surface state. Oxidation experiments were performed by thermal gravimetric analysis (TGA) (model SETARAM 92-16.18) under artificial air with different absolute humidity, and the precision of TGA analysis is more than 10^{-6} g. For AISI 430 alloy, the oxidation temperature is 700°C-800°C, and for Inconel 600 alloy the temperature is 600°C-900°C. The regulation of absolute humidity is realized by using a vapor generator (SETARAM D/WETSYS-2F) and the sensibility of regulation is about 1.5% in relative humidity. To ensure the reliability of the experiments, every oxidation conditions has been conducted at least 2 times and the results were reproducible.

After oxidation, the samples were investigated by using FEG-SEM (Field Emission Gun-Scanning Electronic Microscope) / EDX (Energy-dispersive X-ray spectroscopy) (ZEISS SUPRA 55VP) to study the surface morphology and the cross section, and by Grazing Incident X-ray diffraction (GIXRD) to identify the oxide phase formed during the oxidation.

In this study, European standard NF EN 15305 (version of April 2009) [9] has been applied to determine the residual stresses levels in different oxide layers. In our experiments, a high resolution configuration XRD system (Panalytical X'Pert MRD Pro) was used under Copper radiation ($\lambda=0.154$ nm), whatever the relative low diffraction angle 2θ , the determined peak position error is smaller than 0.005° in 2θ . For each selected plane family, more than 13 peaks are recorded. The calculation of the residual stress was performed via X'Pert Stress software. The precision for stress determination is about 30 MPa under our experimental conditions. The details of the operation parameters for determining residual stresses by XRD method is given in Table 2.

Table 1 Chemical composition of AISI 430 and Inconel 600 alloys (weight %)

	Fe	Cr	Mn	Si	S	C
AISI 430	Bal.	16-18	< 1.00	< 1.00	< 0.03	< 0.08
Inconel 600	6-10	14-17	< 1.00	< 0.5	< 0.015	< 0.15

Table 2 Operation parameters for determining residual stresses by XRD method

Analyzed zone	2mm x 2mm
ψ angle amplitude	$[-60^\circ ; 60^\circ]$
Number of ψ angle	13
diffraction angle 2θ	33.6° for $\{104\}_{Cr_2O_3}$, 35.1° for $\{311\}_{Mn_{1.5}Cr_{1.5}O_4}$, 63° for $\{110\}_{NiO}$, 57° for $\{511\}_{NiCr_2O_4}$
2θ step	0.04°
Acquisition time	15s/step
Peak position error	0.005°
Young's modulus (GPa)	Cr_2O_3 : 280 [10]; $Mn_{1.5}Cr_{1.5}O_4$: 250 [11]; NiO: 190 [10]; $NiCr_2O_4$: 280 [10]
Poisson's ratio	Cr_2O_3 : 0.29 [10]; $Mn_{1.5}Cr_{1.5}O_4$: 0.27 [11]; NiO: 0,25 [10]; $NiCr_2O_4$: 0,29 [10]

Results and discussion

AISI 430 alloy. Figure 1 gives the 2° GIXRD patterns of AISI 430 alloy after oxidation in air with different humidity at 700°C, 800°C for 96h. It is clear that the oxide scales are mainly consisted of Cr₂O₃ and Mn_{1.5}Cr_{1.5}O₄ whatever the oxidation atmospheres, indicating that the water vapor doesn't affect the scale composition. The intensity of substrate peaks is larger in the atmosphere containing water vapor because the oxide scales formed during the oxidation are thinner than them formed in the dry air.

Observation of the cross section after oxidation in air with 5% absolute humidity at 800°C for 48h by FEG-SEM is given in Figure 2, and it shows clearly that the oxide scale consisted of two layers. With the FEG-SEM observation and XRD analysis, we can conclude that the outer layer is Mn_{1.5}Cr_{1.5}O₄ (with little Fe incorporation) and the inner layer is Cr₂O₃. Moreover, formation of thin and discontinuous SiO₂ was also observed at the scale/substrate interface. Isolated voids were found at the scale/substrate interface, which may be result from outward diffusion of ions.

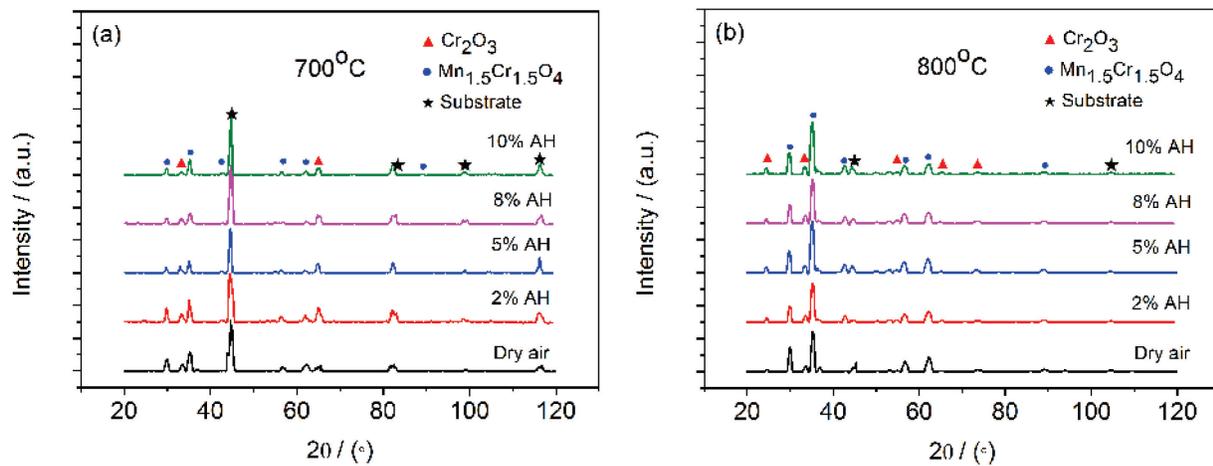


Figure 1 2° GIXRD pattern of AISI 430 after oxidation in air with different absolute humidity (AH) at 700°C for 96h (a), at 800 °C for 96h (b)

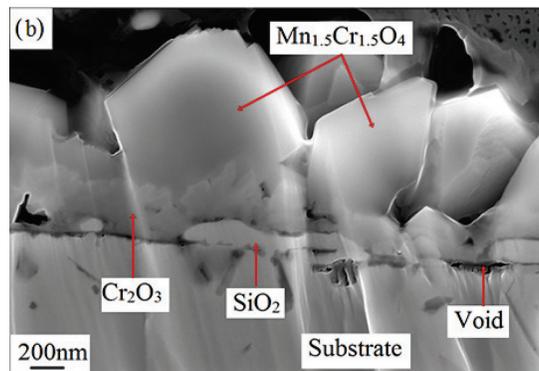


Figure 2 Cross section of the AISI 430 alloy oxidized in air with 5% humidity at 800°C for 48h

Residual stresses in protective Chromia layer after oxidation in air with different absolute humidity at different temperature are given in Figure 3. It is clear that the concentration of water vapor in the atmosphere can affect the residual stresses levels in the Chromia layer. At 700°C, the compressive residual stresses increase with the increase of water vapor. For 800°C, the higher the concentration of water vapor, the bigger the residual stresses at first 24h and smaller the residual stress after 48h. With the presence of water vapor, stresses relief was observed at 800°C.

Figure 4 shows the residual stresses in spinel layer after oxidation in air with different absolute humidity at different temperature, indicates that the residual stresses in this layer are increased with

the introduction of water vapor in the oxidation atmosphere. At all temperatures studied, the higher the concentration of water vapor, the bigger the level of residual stresses. The stresses relaxation is also observed in this layer, this might be due to the effect of accommodation between the two oxide layers. The stresses in spinel layer decrease with the decreasing of stress in the Chromia layer.

The residual stress values in Chromia layer is more important than those in $Mn_{1.5}Cr_{1.5}O_4$ spinel layer because the Chromia is in inner layer and the RS are generated not only by oxide formation but also by ion diffusion and the external layer formation. With the increase of absolute humidity (AH), the RS level increases in compression and it is probably related especially to oxide layer formation kinetics. Until now, there is no convincing argument to explain the role of the humidity for RS evolution. After 24h oxidation at 800°C, the residual stresses are relaxed and their level is reduced slowly.

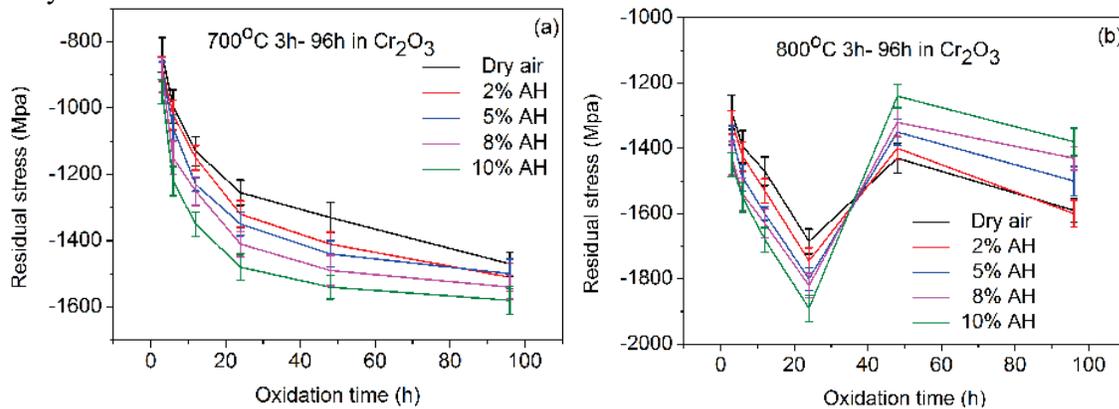


Figure 3 Residual stresses in chromia layer after oxidation in air with different absolute humidity (AH) at 700°C (a) and 800°C (b)

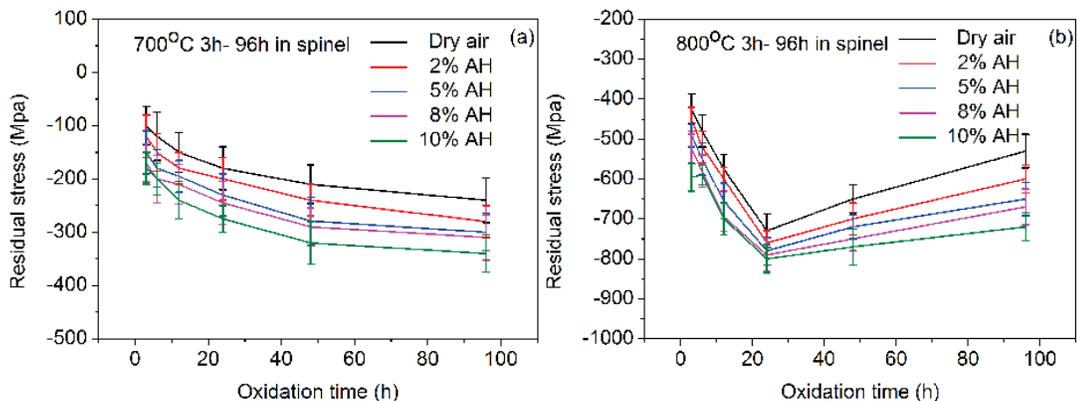


Figure 4 Residual stresses in spinel layer after oxidation in air with different absolute humidity (AH) at 700°C (a) and 800°C (b)

Inconel 600 alloy. Figure 5 gives the 2° GIXRD patterns of Inconel 600 alloy after oxidation in air with different humidity at 700°C, 800°C for 24h. The oxide layers obtained with or without water vapor contained the same mixture of phases (NiO , Cr_2O_3 and $NiCr_2O_4$), but the peak of NiO is more intense than that of Cr_2O_3 and $NiCr_2O_4$. The presence of water vapor has no effect on the nature of the phases in the oxide layer formed on the substrate.

Cross section of the Inconel 600 alloy oxidized at 800°C for 24h in dry air and in air with 5% absolute humidity is given in Figure 6. It is clear that there are two different oxide layers on the substrate, and the inner layer is thicker than the outer layer. The outer layer is mainly composed of Ni and O , but in the inner layer, the concentration of Cr increased obviously. With the XRD analysis, we can conclude that the outer layer is NiO and the inner layer is likely to be a mixed oxide of spinel type $NiCr_2O_4$ ($NiO + Cr_2O_3$) and Cr_2O_3 .

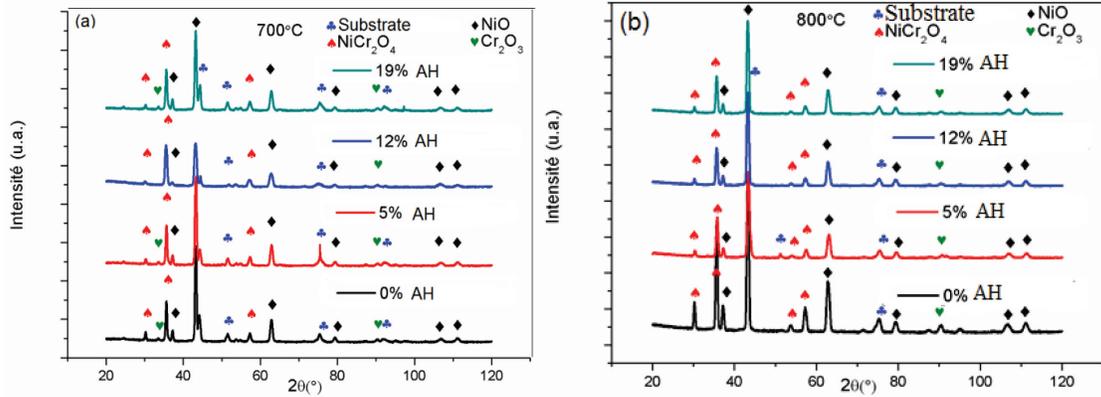


Figure 5 2° GIXRD pattern of Inconel 600 alloy after oxidation in air with different absolute humidity (AH) at 700°C for 24h (a), at 800 °C for 24h (b)

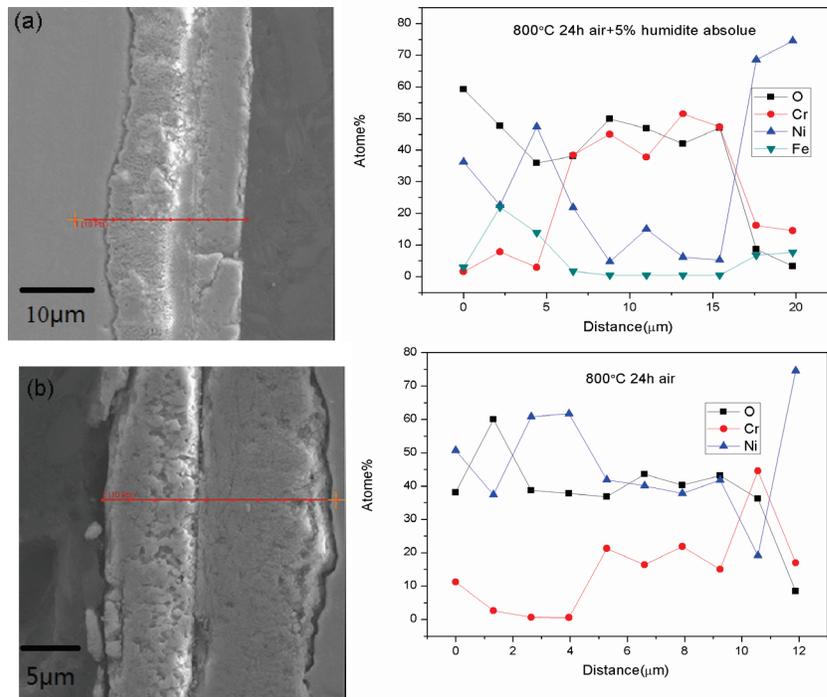


Figure 6 Cross section photos and EDX profiles of the Inconel 600 alloy oxidized at 800°C for 24h in air with 5% AH (a); in dry air (b)

The in-plane residual stresses levels in NiCr_2O_4 and NiO layers after oxidation in air with different absolute humidity at different temperatures are shown in Figure 7, indicating that the residual stresses in both layers are compressive. At 900°C, compared to other three temperatures, a significant increase of the stresses levels in the two oxide layers was observed. At 600°C, with or without water vapor, residual stresses in the layer of NiO are larger than those at 700°C and 800°C.

In addition, with the introduction of water vapor at 700°C and 800°C, the levels of residual stresses in the NiCr_2O_4 spinel oxide layer are quite similar to those in dry air; but at 900°C, the residual stresses in the NiCr_2O_4 spinel phase are much higher than those measured at 800°C.

The residual stress levels in NiCr_2O_4 spinel inner layer is more important than those in NiO external layer because the RS in inner layer are generated not only by oxide formation but also by ion diffusion and the external layer formation. With the increase of oxidation temperature, the RS values increase in compression and it is related directly to the increase of oxide layer thickness. There are less evolutions of residual stress when the absolute humidity is more than 5%; this is due to perhaps

the relative short time of oxidation. With the increase of oxidation time, the RS levels can be relaxed and reduced.

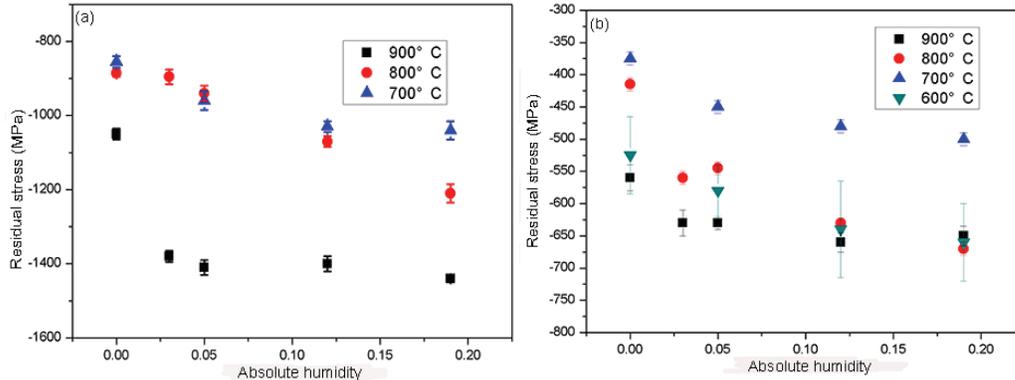


Figure 7 Residual stresses after 24h oxidation in air with different absolute humidity (AH) at different temperature in NiCr₂O₄ inner layer (a); in NiO external layer (b)

Conclusions

The oxidation of AISI 430 and Inconel 600 alloys have been carried out in air with different absolute humidity at different temperatures, the basic conclusions from this work can be given as follows:

- (1) For AISI 430 alloy, the oxide scale is consisted of an inner Cr₂O₃ layer and an outer Mn_{1.5}Cr_{1.5}O₄ layer; and for Inconel 600 alloy, the oxide scale is composed of outer NiO layer and inner NiCr₂O₄ spinel layer;
- (2) With the introduction of water vapor in the oxidation atmosphere, the composition of the oxide scale is not changed for these two alloys. But the water vapor can affect the surface morphology.
- (3) For both alloys, with or without water vapor, the residual stresses in oxide scales are always compressive. The water vapor has obvious influence on residual stresses levels.

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