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The effects of temperature and oxygen pressure on the initial oxidation of stainless steel 441

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ABSTRACT

The oxidation behavior of the stainless steel 441 in the initial 2 h was investigated gravimetrically at 600 °C–950 °C under various oxygen pressures. The morphology, composition and the growth stress of the scale on the oxidized alloy were analyzed by SEM/EDS and Raman spectra. It was found that the performances of the scale degraded with the temperature and oxygen pressure increasing. The oxidation of stainless steel 441 presented a multi-stages behavior. It was suggested that the first chemical reaction determining stage was the nonselective oxidation of steel surface. The following stage in pure oxygen ambient was the formation of chromium-oxide-mainly-containing layer. Kinetic mechanism of second stage oxidation changed from diffusion determining step (600–800 °C) to interface chemical reaction (900–950 °C) due to the decline of the protection of the oxides layer. Only linear rate law was obeyed in the lower oxygen pressure atmospheres at 800 and 900 °C within the initial 2 h.

Introduction

Metallic interconnect can be used in the solid oxide fuel cells (SOFCs) when the operating temperatures is reduced, as the alloy has suitable coefficient of thermal expansion, low price, and good thermal conductivity etc. [1]. For example stainless steel 441, several investigations have been reported its performances as SOFC interconnect material at certain conditions [2–5]. In spite of the physical properties of alloy, high oxidation resistance is required as a key parameter to measure the possibility of one material used as interconnector.

Oxidation resistance of alloy can be evaluated by its mass gain at high temperature with the exposure time varied from seconds [4,6–10] to months [3,11]. The focusing points are different in two kinds of experiments. As for a long time

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Table 1 – Chemical composition of stainless steel 441.

Composition	Fe	Cr	Mn	Nb	Ti	Si	P	S	C
Mass%	Bal	18.3	0.2	0.5	0.2	0.3	0.022	0.002	0.008
Checked Mass%	Bal	20.46	0.063	0.25	0.17	0.34	0.013	0.0009	0.011

oxidation, the lifetime of alloy is examined, while for initial oxidation study, the oxidation resistance of the oxide scale formed above stainless steel is accessed, which is significant to the defending capacity of further oxidation.

Cr_2O_3 and $MnCr_2O_4$ are the main oxides in the initially formed scale during the alloy oxidation process. Besides, Chattopadhyaya et al. [12] also observed that Fe_2O_3 and Fe–Cr spinel were formed in the oxide films grown on Fe–Cr alloys (Cr = 5–30%) which were explored to oxygen at 600 °C within 15 min. Kuroda [9] reported that spinel phase was firstly observed on the oxidation of higher Cr alloys under air with partial pressure of 10^{-3} Pa in the temperature range of 700–800 °C. However, such spinel oxide was not appeared in Saeki's study [13].

In spite of the oxidation products varied according to the experimental conditions, the amounts of these compounds were also changed with condition. Srisrual et al. [4] observed iron based oxides, Cr_2O_3 as well as spinel phase $Mn_{3-x}Cr_xO_4$ within 5 min at 650 and 850 °C. By means of Raman spectra analysis, the samples oxidized at higher temperature and longer time exhibit stronger Cr_2O_3 peak and weaker iron oxides peaks. The formation processes of various oxides indeed were depended on the practical situations.

The initial oxidation process of Fe–Cr alloys can be classified to three stages: nucleation, transient and stationary stages. Duration time of the first two stages was very short. In the stationary stage, it was determined by the oxidation mechanism whether the parabolic rate law was followed or not [12,13].

In this study, the effects of oxygen partial pressure and temperature on the initial oxidation of 441 stainless steel at 600–950 °C were examined.

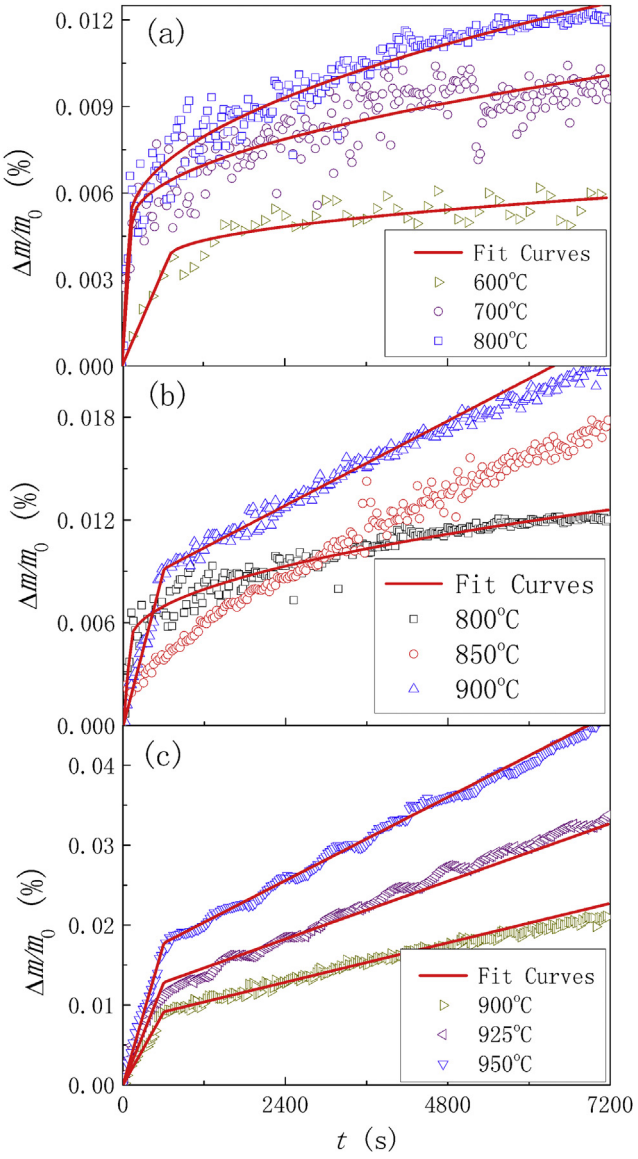

Fig. 1 – Oxidation kinetics of 441 alloy in pure O_2 at (a) 600–800 °C, (b) 800–900 °C, (c) 900–950 °C.

Experimental

Table 1 listed the chemical composition of 441 stainless steel supplied by HuaTsing Power Sci&tech Co. In order to confirm the exact 441 composition, it also has been analyzed by National Analysis Center of Iron and Steel of China, and the values listed in the same table.

Isothermal oxidation kinetics study of stainless steel 441 was carried out in a Netzsch STA449C thermal analysis system in the temperature range of 600–950 °C under different oxygen partial pressures: 33.3%, 66.6% and 100% O_2. The balance accuracy is within 1 μg. Before experiments, a sheet of 10 × 5 × 0.7 mm with specular gloss was cleaned by alcohol, and dried. Each sample was about 280 mg. The temperature was increased by 30 °C/min in pure argon gas with the flow rate of 20 ml/min. When arrived the target temperature, the pure oxygen or mixture of oxygen and argon gas was introduced with total follow rate of 60 ml/min. The mass gain of the sample was recorded during the oxidation. After the measurement, reaction gas was switched to pure argon gas (20 ml/min) and kept blowing till the specimen temperature was lower than 50 °C.

Morphologies of oxide scales were observed by scanning electron microscope (SEM, CARL ZEISS EVO MA 10/LS 10 JS) with energy dispersive spectrum (EDS, Thermo NORAN System). Raman spectrum (Horyba LabRAM HR Evolution) was also employed to investigate the component and growth stress of the oxidized specimen. The sample surface was probed with a 100 μm-spot-sized laser (532 nm laser in 25 mW).