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Oxidation behavior and mechanism of porous nickel-based alloy between 850 and 1000 °C

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Abstract: The oxidation behavior and mechanism of a porous Ni−Cr−Al−Fe alloy in the temperature range from 850 to 1000 °C were investigated by optical microscopy, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) analyses and X-ray photoelectron spectroscopy (XPS). The results show that the oxidation kinetics at 950 and 1000 °C of this porous alloy is pseudo-parabolic type. Complex layers composed of external Cr_2O_3/$NiCr_2O_4$ and internal α-Al_2O_3 are formed on the surface of the oxidized porous alloys. γ' phases favor the formation of NiO/Cr_2O_3/$NiCr_2O_4$ during the initial oxidation. Many fast diffusion paths contribute to the development of the oxide layers. The decrease of the open porosity and the permeability with exposure time extending and temperature increasing can be controlled within a certain range.

Key words: porous alloy; high temperature oxidation; kinetics; oxide layer; diffusion

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1 Introduction

The porous metallic filters based on Fe_3Al alloys possess superior hot corrosion resistance properties, which have been used in the field of gas purification [1]. However, the poor room temperature ductility of the porous alloy and its insufficient strength above 600 °C make it difficult to withstand typical operating conditions. With the increasing requirements for energy crisis and environmental protection, more severe demands for filters are presented [2]. Nickel-based porous alloys exhibit good mechanical properties, excellent resistance to hot corrosion, low density, and high permeability, which are regarded as one of the candidate materials for filters applied to coal-fired power plants [3,4]. It has been demonstrated that alloys designed to develop surface layers of Al_2O_3 were more favorable than that of higher volatile Cr_2O_3 in oxygen-rich environments at high temperatures [5]. The oxidation behaviors of Ni−Cr−Al-based alloys have been reported since the last several decades [6−9]. The oxidation map for the Ni−Cr−Al alloys with normal grain size was also established [10].

Compared with bulk materials, larger surface area of porous alloys due to the presence of pores makes their applicability to filters enormously widening. However, the increasing mass gain per unit of the apparent surface implied that the real area of the alloy exposed to attack was dramatically increased [11]. The formation of less-protective oxides was also favored compared with that in the dense alloys under the same oxidation conditions [12]. Thus, the filter performance of the porous alloys would be significantly changed. In recent years, evaluations on the high-temperature oxidation properties of Ni-based [13−15] and Fe-based [16,17] porous materials have attracted more attention. PANG et al [13] synthesized the Ni−Cr−Fe alloy foams and compared the oxidation behavior of the foams with different compositions at temperatures of 800−1000 °C. CHOI et al [14] found that the decrease of pore size would result in lower high-temperature oxidation

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resistance of Ni−Fe−Cr−Al porous alloys. MICHAILIDIS et al [15] proposed that substrate composition and morphology had a significant influence on the grain size and oxide structure of high purity nickel and Inconel foams. BAUTISTA et al [16] characterized the oxides formed during high temperature oxidation of four Ni-based or Fe-based porous materials. Up to now, information about the oxidation behavior of porous Ni−Cr−Al-based alloys at elevated temperatures was still limited. As a basic system for developing more oxidation resistant materials used for the gas purification filters, systematically evaluations on its high-temperature oxidation properties are needed.

In this investigation, the oxidation behavior of a porous Ni−Cr−Al−Fe alloy at elevated temperatures was studied. The oxidation products and the structures of the oxide layers were systematically analyzed. Efforts were paid on discussing the differences of the oxidation mechanisms between the porous alloy and the dense alloy.

2 Experimental

Table 1 shows the nominal composition of the porous Ni−Cr−Al−Fe alloy used in this investigation. A conventional powder metallurgy process was employed to fabricate the porous alloys by using high purity water-atomized powders (99.99%). Oxidation tests were carried out on the porous alloys in a horizontal tube furnace with a nitrogen flow rate of 0.03 m^3/h. After holding at temperatures of 850−1000 °C for 2−8 h, the specimens were air-cooled to room temperature, and then the mass changes were measured by an electronic balance with an accuracy of 0.1 mg. The specific surface area of the porous alloy was measured using Brunauer−Emmett−Teller (BET) method [18]. The porosities of the porous alloys before and after oxidation were obtained according to Archimedes method. The air permeation rates were determined using an FBP−3 testing system for porous materials.

Table 1 Composition of porous Ni−Cr−Al−Fe alloy (mass fraction, %)

Cr	Al	Fe	Mn	Si	Y	B	Zr	C	Ni
16	9	3	0.05	0.2	0.01	0.01	0.1	0.05	Bal.

The morphologies on the surface and the cross-section of the porous alloys were examined by a Reichert MeF3A optical microscope and a Nova Nanosem 230 field emission scanning electron microscope (FESEM), respectively. A relatively rough surface with bumps and hollows is exhibited on the porous alloys (Fig. 1(a)), and a few micro pores are found inside the porous strut (Fig. 1(b)). Morphologies and chemical compositions of the oxides formed on the surfaces of the oxidized specimens were also analyzed by the Nova Nanosem 230 microscope equipped with an energy dispersive X-ray spectroscope (EDS). X-ray diffraction (XRD) analysis (Rigaku D/max−2550VB) was carried out using a Cu K_α radiation to identify different phases presented in the oxidized scales. A K_α 1063 X-ray photoelectron spectroscopy (XPS) instrument was further performed on the surfaces of the specimens oxidized at 1000 °C for 2 and 8 h, respectively. Al K_α (1486.6 eV) and Ar beam were selected as the excitation source and spray beam, respectively. The binding energy ranging from 0 to 1300 eV was then systematically scanned with a step size of 0.5 eV. The XPS lines of various elements in the porous alloys were recorded, namely, O 1s, Ni 2p, Cr 2p and Al 2p.

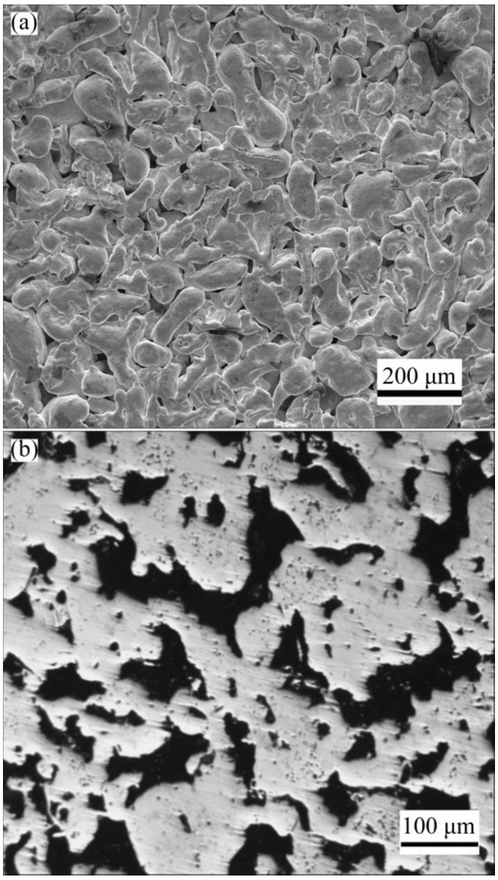

Fig. 1 Surface (a) and cross-section (b) morphologies of porous Ni−Cr−Al−Fe alloy

3 Results

3.1 Oxidation kinetics

The isothermal oxidation curves of the tested porous Ni−Cr−Al−Fe alloys at different temperatures are plotted in Fig. 2. The mass gain is found to increase as the oxidation temperature increases or the exposure time extends. It may be noted that the porous alloys oxidized at higher temperatures show much faster growth rates of