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## MANUFACTURING AND HIGH TEMPERATURE OXIDATION PROPERTIES OF ELECTRO-SPRAYED Fe-24.5%Cr-5%Al POWDER POROUS METAL

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Fe-Cr-Al based Powder porous metals were manufactured using a new electro-spray process, and the microstructures and high-temperature oxidation properties were examined. The porous materials were obtained at different sintering temperatures (1350°C, 1400°C, 1450°C, and 1500°C) and with different pore sizes (500  $\mu\text{m}$ , 450  $\mu\text{m}$ , and 200  $\mu\text{m}$ ). High-temperature oxidation experiments (TGA, Thermal Gravimetry Analysis) were conducted for 24 hours at 1000°C in a 79% N<sub>2</sub>+ 21% O<sub>2</sub>, 100 mL/min. atmosphere. The Fe-Cr-Al powder porous metals manufactured through the electro-spray process showed more-excellent oxidation resistance as sintering temperature and pore size increased. In addition, the fact that the densities and surface areas of the abovementioned powder porous metals had the largest effects on the metal's oxidation properties could be identified.

*Keywords:* Powder porous metal, Electro-spray process, Electric wire explosion, Fe-24%Cr-5%Al, High temperature oxidation

### 1. Introduction

Porous materials or porous metals refer to structures in which pores accounting for 15~95% of the volumes of the materials are irregularly or regularly dispersed. Porous materials have such advantages as larger specific surface areas compared to existing bulk materials, ultra-light weight, excellent energy absorbing ability, distinctive thermal and electric conductivity, and excellent liquid or air permeability [1].

Attempts have been made recently to apply porous metals to uses such as car filters, catalyst carriers, and exhaust gas purification systems, utilizing these metals' good machinability, ultra-light weight, large specific surface areas, and high thermal conductivity [1]. Among porous metals, existing powder porous metals manufactured using powder processes can be manufactured by coating alloy powder on the foam frames of pure metals and implementing post-heat treatment processes, and they generally have sponge-form, three-dimensional network structures [2]. However, the abovementioned current manufacturing process [2] for powder porous metals is a complicated process that involves high production costs, as well as having the disadvantage that filter efficiency and high-temperature durability may be reduced since uneven composition and phase distributions occur in porous metals

because the sizes of powder particles are several tens of  $\mu\text{m}$ , on average.

In this study, attempts were made to manufacture powder porous metals using ultra-fine alloy powders and new processes (submerged electric wire explosion process and the electro-spray process etc.). The basic properties and microstructures, according to sintering temperatures and pore sizes of the new Fe-Cr-Al powder porous metal, were examined. In addition, through high-temperature oxidation experiments, attempts were made to figure out the effects of sintering temperatures and pore sizes on the high-temperature oxidation of the Fe-Cr-Al powder porous metals manufactured through the new process.

### 2. Experimental

A submerged electric wire explosion process and an electro-spray process were used to manufacture new powder porous metals based on Fe-Cr-Al. As an initial material for powder manufacturing, 0.1 mm diameter FeCrAl alloy wires having a composition of Fe-24.5%Cr-5%Al (wt.%) were used. A powder was manufactured using these wires by implementing the submerged electric wire explosion process several times with PNC (plasma nano colloid system) equipment [3]. The average particle size used in this study was 168 nm. Afterward,

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a nano colloid at 0.05~0.5 wt.% concentrations was produced by adjusting the weight ratio between the ultra-fine alloy powder and ethanol. The first form of the powder porous metals was manufactured by coating the manufactured Fe-Cr-Al nano colloid on PU (polyurethane) foam [4]. After that, the foam (cell size: 500  $\mu\text{m}$ ) was sintered under an  $\text{H}_2$  atmosphere at each of four different temperatures of 1350°C, 1400°C, 1450°C, and 1500°C. The sintering was implemented for two hours at each sintering temperature in a box furnace. In addition, to examine the effects of pore sizes on high-temperature oxidation, porous metal with average pore sizes of 200  $\mu\text{m}$  and 450  $\mu\text{m}$  was additionally manufactured and sintered at 1450°C. The Fe-Cr-Al powder porous metals were manufactured in the form of 1.28~1.9 mm-thick sheets.

To examine the high-temperature oxidation property of the manufactured powder porous metals, thermo gravimetric analysis (TGA) experiments were conducted using Rigaku TG-1280. The materials, in the form of sheets, were processed into a size of 5 mm  $\times$  10 mm and used as oxidation specimens. The oxidation test were conducted under a high-temperature oxidation condition at a temperature of 1000°C while having 79%  $\text{N}_2$ + 21%  $\text{O}_2$  environment similar to the air atmosphere flow at a speed of 100 mL/min. The specimens were heated from room temperature to the desired temperature at 10°/min., and the same temperature was maintained for an oxidation time of 24 hours. SEM and EDS analyses were used to examine the microstructures. The kinds of oxides formed and the shapes of oxidized layers were examined through X-ray diffraction analysis (XRD) and EPMA analysis to compare and analyze those before and after the oxidation test.

### 3. Results and discussion

Figure 1 shows images of the powder porous metals manufactured through the abovementioned processes. The porous metals shown in Figure 1, (a) 500  $\mu\text{m}$  (pore size), 1350°C (sintering temperature), (b) 500  $\mu\text{m}$ , 1400°C, (c) 500  $\mu\text{m}$ , 1450°C, and (d) 500  $\mu\text{m}$ , 1500°C, will be referred to as A1350, B1400, C1450, and D1500, respectively, hereafter. In addition, the powder porous metals with different pore sizes manufactured under the conditions (e) 200  $\mu\text{m}$ , 1450°C, and (f) 450  $\mu\text{m}$ , 1450°C, will be referred to as E200 and F450. The manufactured powder porous metals consisted of three-dimensional network structures in which irregular open pores were connected with each other. However, due to the powder porous metal manufacturing processes attempted for the first time, some “pore clogging” and “cracks” on the strut were observed. The results of examination of the physical characteristics (pore size, strut thickness, etc.) of the powder porous metals through an image analyzer are shown in Table 1. It was apparent that the structures became denser as sintering temperatures and pore sizes increased. It could be seen that since the manufacturing process used in this study constructed struts only with the binding of powder particles, the spaces between round powder particles appeared as pores after sintering, and the pores were changed into closed pores as sintering temperatures increased.

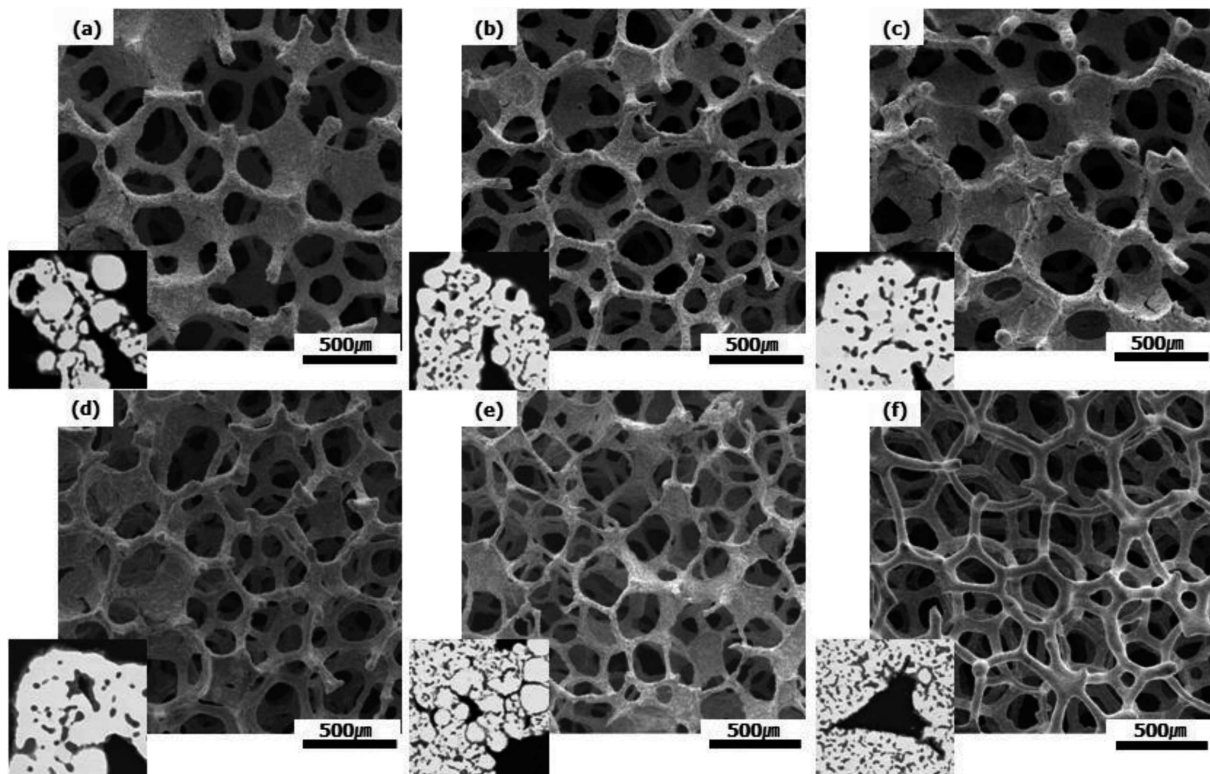


Fig. 1. Morphology of newly manufactured Fe-Cr-Al powder porous metals; (a) 500  $\mu\text{m}$  (cell size), 1350°C (sintering temperature), (b) 500  $\mu\text{m}$ , 1400°C, (c) 500  $\mu\text{m}$ , 1450°C, (d) 500  $\mu\text{m}$ , 1500°C, (e) 200  $\mu\text{m}$ , 1450°C, and (f) 450  $\mu\text{m}$ , 1450°C

TABLE 1  
The characteristics of Fe-Cr-Al powder porous metals used in this study

PU foam cell size ( $\mu\text{m}$ )	500				(e)200	(f)450
	(a)1350	(b)1400	(c)1450	(d)1500	1450	
Sintering temp. ( $^{\circ}\text{C}$ )	(a)1350	(b)1400	(c)1450	(d)1500	1450	
Cell size ( $\mu\text{m}$ )	509	505	492	471	201	449
Strut thickness ( $\mu\text{m}$ )	69.0	61.6	60.2	58.4	43.4	58.3
Apparent density ( $\text{g}/\text{cm}^3$ )	0.21	0.37	0.38	0.40	0.26	0.28

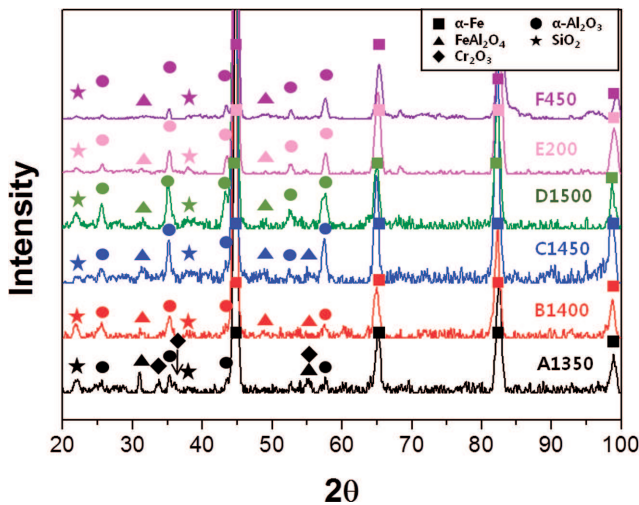


Fig. 2. XRD analysis results of newly manufactured Fe-Cr-Al powder porous metals

The results of XRD analysis (before the oxidation experiments) of the manufactured powder porous metals according to the sintering temperatures and pore sizes are shown in Figure 2. In all specimens,  $\alpha$ -Fe and oxide  $\alpha$ - $\text{Al}_2\text{O}_3$  were main peaks, and  $\text{SiO}_2$  and  $\text{FeAl}_2\text{O}_4$  were additionally detected.  $\text{Cr}_2\text{O}_3$  additionally appeared in A1350 that was manufactured at relatively low sintering temperatures.

For clearer phase analysis, EPMA mapping analysis was conducted for the cross-sectional microstructures of the porous metals sintered at  $1350^{\circ}\text{C}$  (A1350) and  $1500^{\circ}\text{C}$  (D1500), and the results are shown in Figure 3. In both specimens, Fe and Cr components were evenly distributed throughout the strut, and Al appeared in the same positions as O. In the case of the manufactured Fe-Cr-Al powder porous metals,  $\alpha$ - $\text{Al}_2\text{O}_3$  existed on the surface and inside of the strut, and the matrix structure is considered to be an  $\alpha$ -Fe phase in which Cr was solid-dissolved. Some  $\text{Cr}_2\text{O}_3$  was detected in  $1350^{\circ}\text{C}$  sintered specimens (A1350). In addition, under both sintering conditions,  $\text{FeAl}_2\text{O}_4$  and  $\text{SiO}_2$  appeared in mixtures with  $\alpha$ - $\text{Al}_2\text{O}_3$ , although the quantities were very small. Meanwhile, at the high sintering temperature of  $1500^{\circ}\text{C}$ , approximately  $1\ \mu\text{m}$  thick  $\alpha$ - $\text{Al}_2\text{O}_3$  oxide was formed in layers on the surface of the porous metal separately from the inside.

The oxidation results of new powder porous metals are illustrated in Figure 4. The oxidized weight increased rapid-

ly after beginning and gradually showed parabolic oxidation behaviors thereafter. From the oxidation time of 800 minutes, a breakaway behavior was shown in which only A1350 ( $500\ \mu\text{m}$ ,  $1350^{\circ}\text{C}$ ) specimens showed rapid increases in oxidized weight. Continuous decreases in oxidized weight and oxidation rate (increases in oxidation resistance) could be seen as sintering temperatures increased (Figure 4 (a)). The oxidized weight gain and oxidation rate increased as pore sizes decreased (Figure 4 (b)). As a result, among the manufactured powder porous metals, the one sintered at  $1500^{\circ}\text{C}$  showed the most excellent oxidation resistant properties (an oxidized weight gain of 2.57%). In the case of Fe-Cr-Al powder porous metals (average pore size,  $580\ \mu\text{m}$ ) [5] manufactured through existing manufacturing processes, an oxidized weight gain value of 3.01% has been shown under the same oxidation conditions.

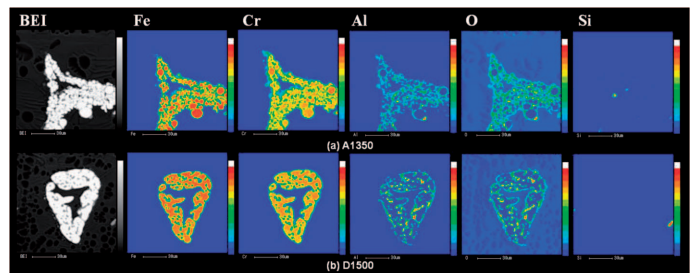


Fig. 3. EPMA mapping analysis results with different sintering temperatures of (a)  $1350^{\circ}\text{C}$  and (b)  $1500^{\circ}\text{C}$

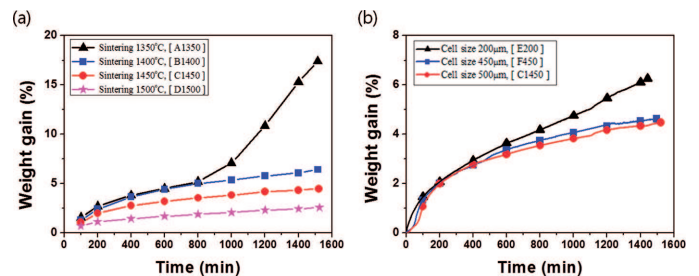


Fig. 4. TGA results of newly manufactured Fe-Cr-Al powder porous metals; (a) sintered at different sintering temperature ( $500\ \mu\text{m}$ ), and (b) with different cell size

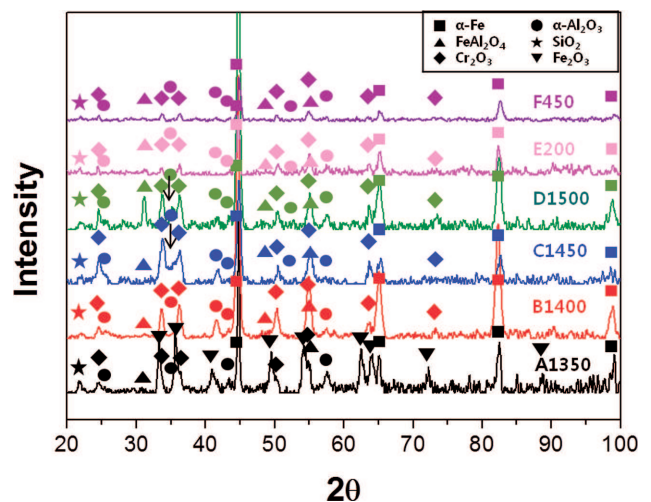


Fig. 5. XRD analysis results of Fe-Cr-Al powder porous metals after the TGA test



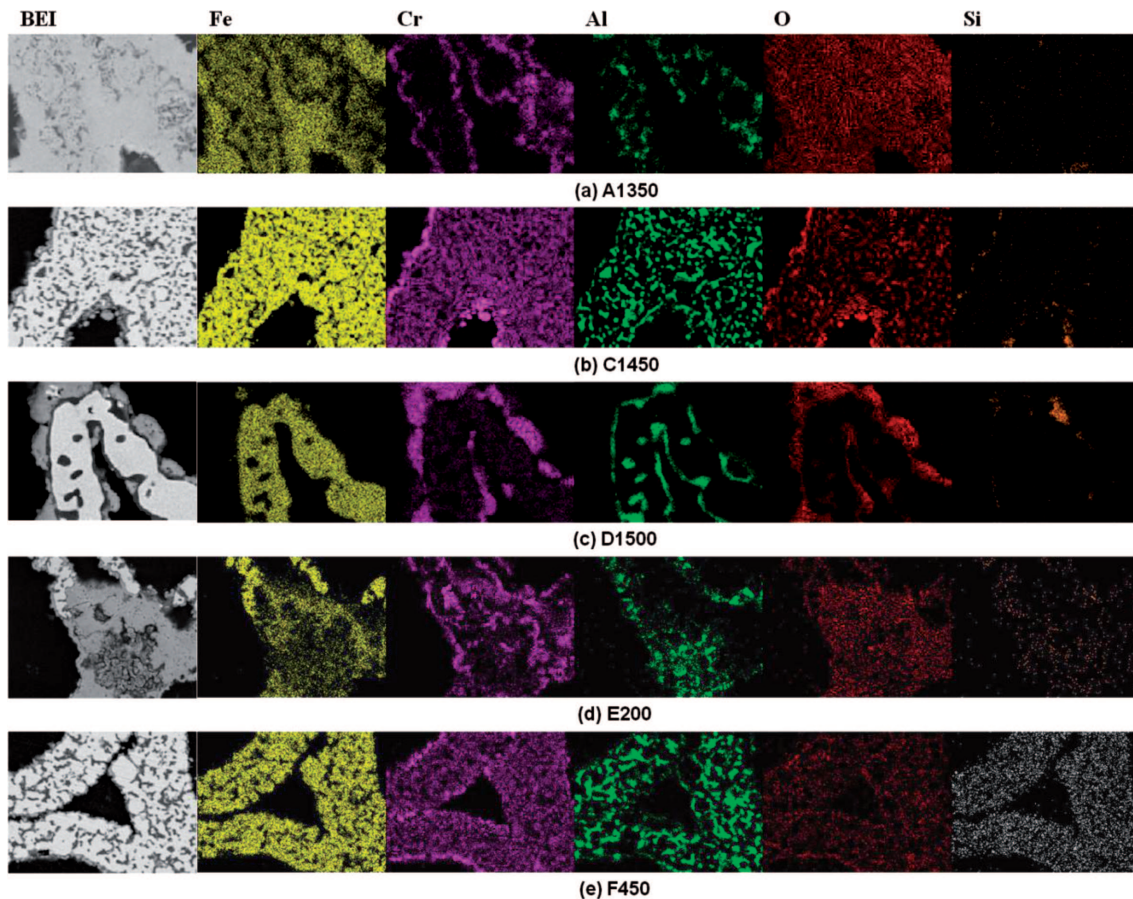


Fig. 6. EDS mapping analysis results after the TGA test

The results of XRD analysis of the specimens subject to the oxidation experiments are shown in Figure 5. In specimens under all conditions, along with the  $\alpha$ -Fe,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and FeAl<sub>2</sub>O<sub>4</sub> that had existed from before the oxidation experiments, new Cr<sub>2</sub>O<sub>3</sub> peaks clearly appeared. Meanwhile, in the case of the A1350 specimens in which Cr<sub>2</sub>O<sub>3</sub> had already been formed before the oxidation experiments, Fe<sub>2</sub>O<sub>3</sub> was additionally formed.

The results of Fe, Cr, Al, Si, and O element EDS mapping analyses for the oxidized specimens of the powder porous metals are shown in Figure 6. (a) is A1350, (b) is C1450, (c) is D1500, (d) is E200, and (e) is F450. In the case of (a) sintered at a relatively low sintering temperature, and (d) with small pore sizes, Cr<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> were formed in layers on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> on the surface of the powder particles that had existed in the strut, and Fe-based oxides appeared inside the strut too. In the case of (b), (c), and (e), in addition to the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> existing in the strut,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> formed continuous oxidized layers on the surface of the strut and Cr<sub>2</sub>O<sub>3</sub> was formed on the top of the oxidized layers. Oxidation-resistant properties could be improved, if structures among powder particles became denser and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> oxidized layers were evenly formed on the surface to suppress the formation of additional oxide during the oxidation experiments, and in particular, to effectively delay the formation of Fe<sub>2</sub>O<sub>3</sub>. In addition, the differences in pore sizes of porous metals manufactured under the same conditions showed differences in the quantities and kinds of oxides and oxidation-resistant properties, mainly due to the difference

of interior surface area. Meanwhile, through a previous study, these researchers reported that in the case of powder porous metals manufactured through existing manufacturing processes, oxidation-resistant properties were weakened as pore sizes decreased [6].

As the equilibrium oxygen partial pressure of Fe based, Cr based, and Al based oxides increases in the order of Al<Cr<Fe at high temperatures, the driving force of oxidation increases in the order of Fe<Cr<Al [7]. Therefore, Fe-Cr-Al based alloys forms oxides step by step in the order of Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub>. In general Fe-Cr-Al based alloys, most Al in metals is consumed in the early stage of oxidation, and oxidation reactions occur in the interface between metals and oxidized layers due to the diffusion of Al and oxygen. However, in the results of this study, in the case of the powder porous metals manufactured through the electro-spray process, Al<sub>2</sub>O<sub>3</sub> was formed during the manufacturing process and during the oxidation experiments; high-temperature oxidation behavior was shown after the formation of Al<sub>2</sub>O<sub>3</sub> in states where the early stage of oxidation behavior had already been undergone. Few cracks or stripping of Al<sub>2</sub>O<sub>3</sub> were observed in the oxidized layers, and the thickness of the oxidized layer increased over oxidation time as Cr<sub>2</sub>O<sub>3</sub> was additionally formed. Specimens sintered at a low temperature (1350°C) in which the area in contact with oxygen was relatively large and the continuous surface Al<sub>2</sub>O<sub>3</sub> layers that can suppress oxidation didn't exist, showed rapid oxidized weight gains along with the formation of Fe<sub>2</sub>O<sub>3</sub> and runaway oxidation behavior.

#### 4. Conclusions

Fe-Cr-Al powder porous metals were manufactured using new manufacturing processes. Those powder porous metals that had small pore sizes and had been sintered at low temperatures showed incomplete bindings between powder particles, and the structures of the porous metals became denser as sintering temperatures and pore sizes increased. Those porous metals that had been manufactured through the electro-spray process showed more-excellent oxidation-resistant characteristics as sintering temperatures and pore sizes increased. However, porous metals with small pore sizes sintered under low sintering temperature conditions showed increased areas of reactions with oxygen due to large surface areas and loose microstructures, and also showed rapid breakaway behaviors because Fe-based oxides were formed. On the contrary, those porous metals sintered at high temperatures that had denser structures, continuous protective films, which are  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> oxidized layers formed on their surfaces, showed stable high-temperature oxidation behaviors.

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