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CHARACTERISTICS OF THE POROUS BODY SINTERED BY NANO-SIZED Fe-Cr-Al ALLOY POWDER

CHARAKTERYSTYKA POROWATEGO KORPUSU SPIEKANEGO Z NANOMETRYCZNEGO PROSZKU STOPU Fe-Cr-Al

Porous metal with uniform honeycomb structure was successfully produced by sintering using Fe-Cr-Al nano powder, which was prepared by the pulsed wire evaporation (PWE) in ethanol. Its process consisted of the several steps; 1) coating on the surface of polyurethane sponge with the liquid droplets generated from the ethanol-based slurry where the Fe-Cr-Al nano powders were uniformly dispersed, 2) heat treatment of debinding to remove the polyurethane sponge and 3) sintering of the porous green body formed by Fe-Cr-Al nano powders. The strut thickness of porous Fe-Cr-Al was increased by the increase of spraying times in ESP step. Also, The shrinkages and the oxidation resistance of the sintered porous body was increased with increase of sintering temperature. The optimal sintering temperature was shown to 1450°C in views to maximize the oxidation resistance and sinterability.

Keywords: Fe-Cr-Al powder, Metallic sponge, Sintering temperature, Oxidation resistance

1. Introduction

Many researches for the development of particulate filter in automobiles have been actively concentrated on the improvement of the filtering performance in various exhaust filters. The materials applied to such filters should have the high oxidation resistance at an elevated temperature and the controls of shape and size of pores were also important factors for industrial application. The industry has usually employed the ceramic material for filtering materials because of its high thermal stability, but the application of metallic filter has comparatively increased owing to its good flexibility [1-3].

The main candidates of materials for metallic filters were Ni, Fe and stainless and they have been often fabricated by a simple sintering process, which was still caused in the limitation to enlarge the porosities and oxidation resistance. Therefore, it has been required to develop the new material and process to enhance the oxidation resistance in a high temperature and porosities, simultaneously [2-5].

We employed, therefore, 1) Fe-Cr-Al as filter material, 2) produced Fe-Cr-Al nano-powder from PWE (Pulsed Wire Evaporation) process, 3) sprayed the mixture solution with nano-sized particles on a PU (Polyurethane) sponge by ESP (Electro-Spraying) technique, 4) removed PU component by debinding heat treatment and finally 5) sintering of Fe-Cr-Al nano aggregate. And here, it was investigated the effect of ESP treating times and sintering temperatures on the strut thickness, shrinkage, porosity and oxidation behaviors in producing porous samples.

2. Experimental

Fe-22Cr-6Al wire was used as the starting material and its microstructure and particle size distribution were shown in Fig. 1. For ESP process, the ethanol based slurry mixed

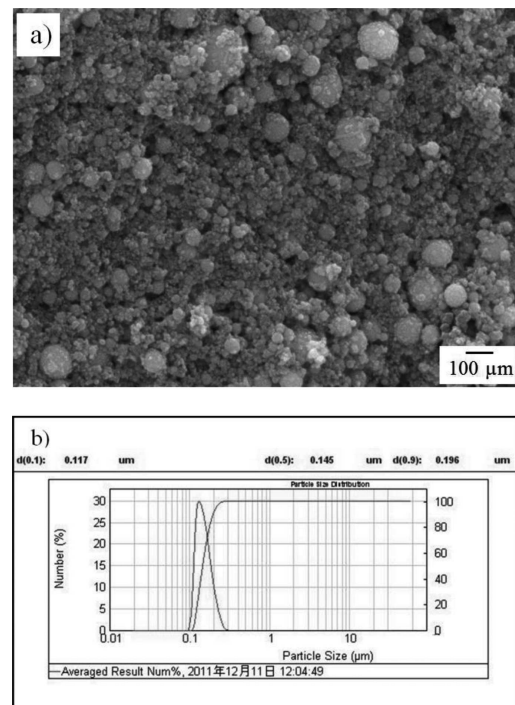


Fig. 1. FeCrAl alloy powder; a) SEM microstructure and b) analysis result of grain size

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with 10wt.% of powder was sprayed on the strut surface of PU sponge (average value of strut thickness: 30 μm) by Electro Spray Robot (ESR, ESR200R2, es-robot@, NanoNC Co., Ltd., Korea), which was constituted by the nozzle and line for transfer of slurry (Fig. 2b)). The spraying times were varied from 1 to 5 hours and other conditions such as distance of nozzle and applied voltage were fixed to 15 mm and 4.5 kV, respectively.

continuously in same furnace and atmosphere at the different temperatures from 1300°C to 1500°C for 2 hours (Fig. 2c)).

Porosities in sintered bodies were examined by micro computed tomography (Micro-CT, SKYSCAN 1172) and microstructures, and the thicknesses of the struts were analyzed in scanning electron microscope (Zeiss: SUPRA 55 VP-25-78). The oxygen contents were also measured by element analyzer (ELTRA 200 series I). The weight change in exposure at 1000°C in air atmosphere were measured to evaluate the oxidation resistance by thermo-gravimetric analyzer (SETARAM SYESIS Evolution).

3. Results and discussion

This study was tried to find the optimal conditions of the spraying time in ESP process and temperature in the sintering process after debinding. Fig. 3 shows that the bulk densities and strut thicknesses in the ESP-coating stage were increased with increase of spraying times. Here, the strut thickness formed by spraying time of 5 hours was shown to 130 μm , which included the strut thickness of PU sponge (30 μm) and it let us know that the true thickness made of the powders was about 100 μm . Also, as the spraying time above 6 hours was resulted in the blockage behavior of pores, the optimal spraying time in the ESP process was thought to be 5 hours.

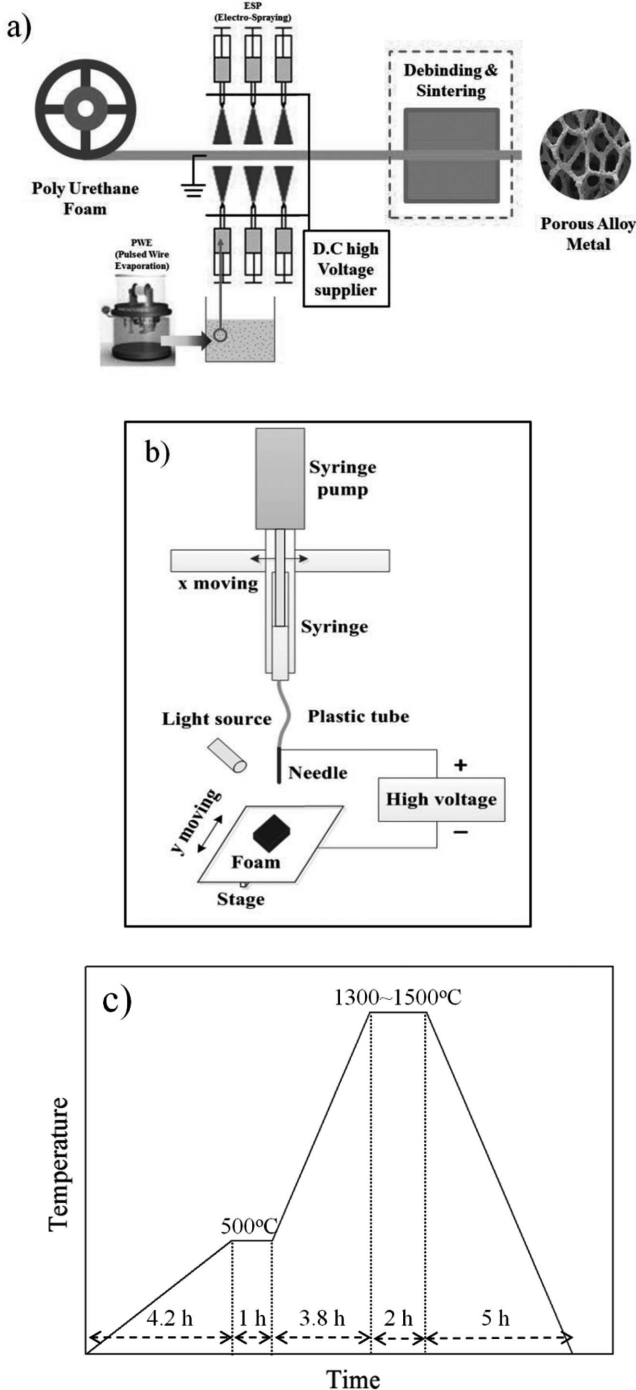


Fig. 2. Production procedures of porous metal; a) total process, b) electro-spraying and c) sintering condition

Coated preform prepared was placed in an alumina crucible and followed by debinding heat treatment to remove PU component. The debinding treatment was performed under hydrogen atmosphere at 500°C for one hour and it was sintered

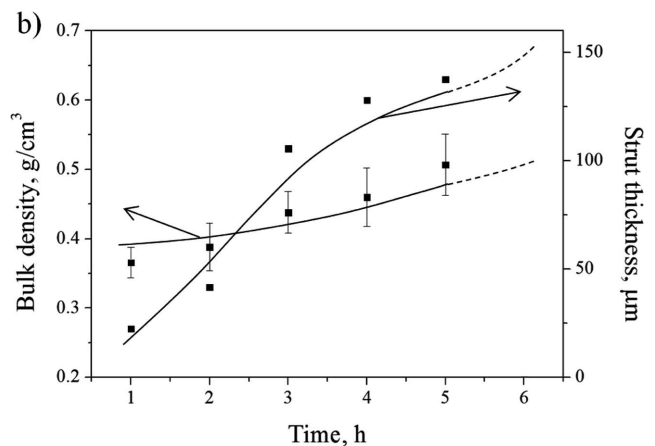
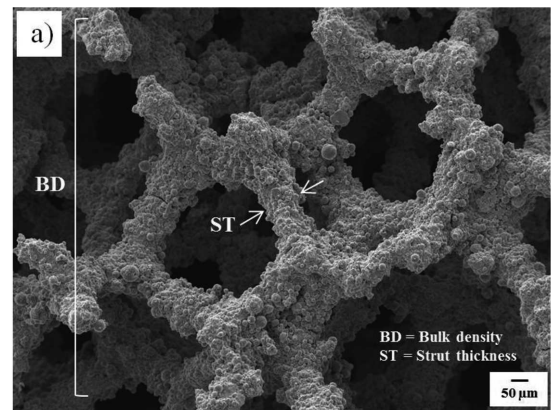


Fig. 3. a) SEM microstructure of metallic preform and b) analysis results of bulk density and strut thickness sintered by various spraying times

The sample appearance and X-ray diffraction patterns analyzed in porous Fe-Cr-Al bodies obtained after sintering were

shown in Fig. 4. The sintering of ESP-processed porous aggregate was caused in large shrinkage (Fig. 4a)) due to the nano-size effect and the diffracted patterns was shown to be similar in all samples produced with different sintering temperatures (Fig. 4b)).

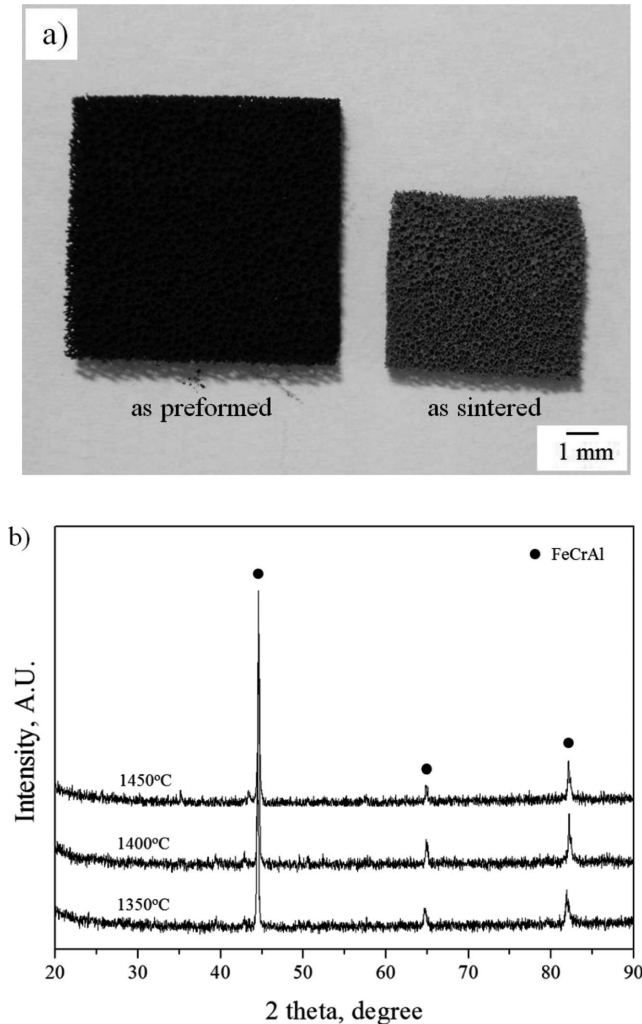


Fig. 4. a) Photo of metallic preform and sintered porous metal, and b) X-ray diffraction patterns of the porous FeCrAl alloy by sintering temperatures

The SEM microstructures of polyurethane porous body and the samples sintered at 1350°C and 1450°C were shown in Fig. 5. In sintering at 1350°C, the circular lumps were shown in the center of honeycomb structures, contrarily the good sintering behavior with densified and smooth surface was revealed at 1450°C.

Therefore, it was therefore required to observe the microstructures of the strut surface of the sintered Fe-Cr-Al in detail by a high magnification (Fig. 6). It can be known there that the aggregated structure (Fig. 6a)) formed with nano parties in as ESP-coated sample (Fig. 6a)) was gradually coarsened by the increase of temperatures in sintering stage (Fig. 6b) ~c)). However, it was found that giant pores existed locally in the samples sintered at 1350°C and 1400°C. On the other hands, the sample sintered at 1450°C, which was thought to be the optimal temperature, has shown well densified structure without any big pores like those shown in Fig. 6b) and c).

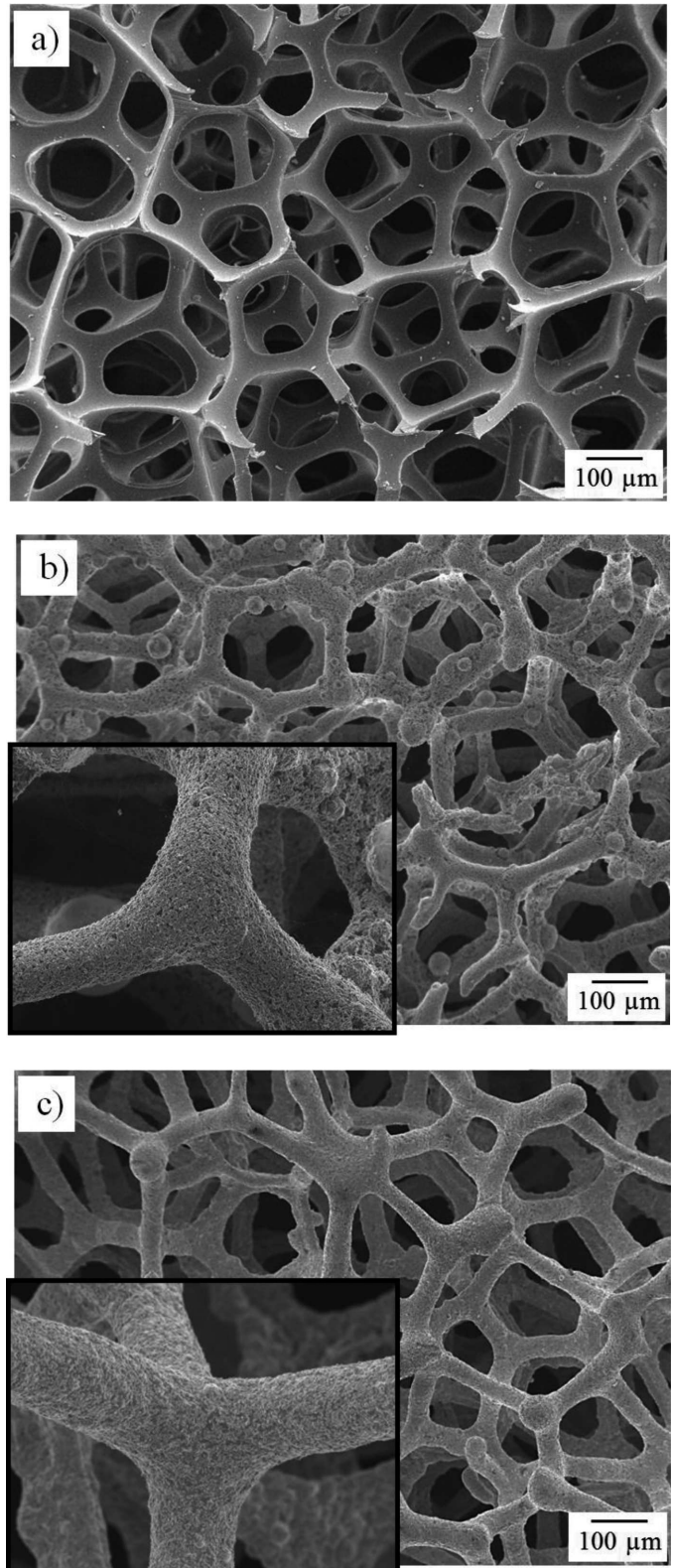


Fig. 5. SEM microstructures of a) polyurethane sponge and porous FeCrAl alloys sintered at a) 1350°C and b) 1450°C for 2h

The porosity and shrinkage of samples sintered at various temperatures were shown in Fig. 7. Firstly, the normal sintered sample could not be obtained at 1500°C due to the melting behavior locally. And we knew that the porosities was relatively largely dropped at 1400°C and contrarily, shrinkage increased.



Fig. 6. SEM microstructures of sintered porous Fe-Cr-Al alloys; a) as coated and sintered at b) 1350°C, c) 1400°C and d) 1450°C for 2h

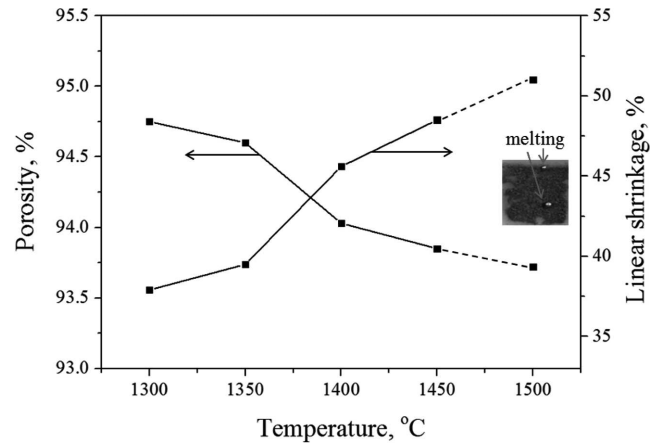


Fig. 7. Analysis results of porosity and linear shrinkage of porous Fe-Cr-Al alloys sintered by various temperatures

The oxygen content as one of impurities should be detected in produced samples because it can cause a brittleness of porous metal [6]. In the qualitatively analyzed results of oxygen contents by EDS technique (Fig. 8), we knew that they were increased from 3.1% to 11.4% as sintering temperature was increased from 1300°C to 1500°C. Such increasing tendency of oxygen content may be explained by the existence of a little oxygen gas inside the reactor as using normal purity, 99.9% of industrial hydrogen gas. Especially, such residual oxygen gas can cause the formation of oxide film on the surface of materials in a high temperature [7-8]. The Gibbs free energy for the formation of oxide phase in the surface of the porous body sintered at 1450°C were shown in Eq. (1)~Eq. (4).

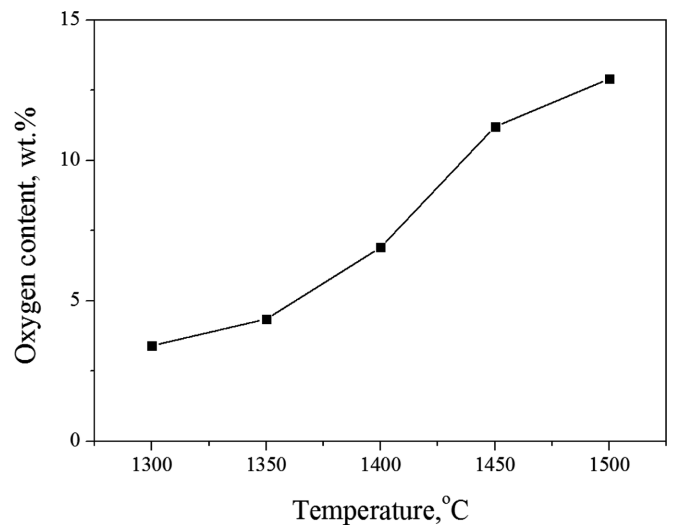
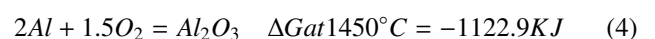
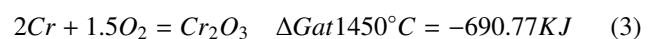
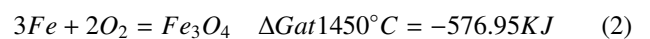
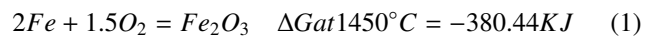


Fig. 8. The analysis result of oxygen content of porous FeCrAl alloys by sintering temperatures



4. Conclusions

By considering the values of free energy change, we can imagine that there is enough possibility for the formation of Cr_2O_3 or Al_2O_3 film on the porous body during sintering. In particular, such oxide film may provide us un-expected positive effect to enhance the oxidation resistance of metallic porous body [9-10]. So, it was required to check the oxidation resistance of porous samples produced in different sintering temperatures. For it, the weight changes by oxidation were measured by the thermo-gravimetric analysis with holding in air atmosphere at 1000°C for 24 hours (Fig. 9). It was found here that the weight of sample sintered at 1350°C was fully increased above 27% until short five hours of holding time. In the sample, 1400°C , the weight was initially restrained in the level of 2.5% and gradually mounted up to 20% during holding until 24 hours. Whereas the specimen weight sintered at 1450°C did not show such increase with keeping below 7% of the overall increasing level, which indicated us the high oxidation resistance. The reason why relatively better oxidation resistance shown in sample sintered at 1450°C , may be related with the existence of oxide film as mentioned above because whoever can imagine that the higher temperature can make the thicker oxide film. Another main reason can be also thought by the effect of decreasing specific surface area by sintering at relatively higher temperature. The nature of the oxide film and the density effect on the oxidation behavior are being investigated in detail.

Nano-sized powders of Fe-Cr-Al alloy were produced by PWE process and it was successfully electro-sprayed on the surface of a polyurethane sponge with different spray times and followed by debinding and sintering at $1300^\circ\text{C}\sim 1500^\circ\text{C}$. The total strut thickness coated for 5 hours was about $130\mu\text{m}$ including PU strut thickness. The control of sintering temperature from 1300°C to 1450°C gave us the different sintered structure, particularly in sample at 1450°C with showing the enough densified morphology without any giant pores. The linear shrinkage was increased from 36% to 52% and porosity was decreased from 94.8% to 93.8%. The oxidation content as impurity was also increased from 3.1% to 11.4% with increasing sintering temperature however it was positively affected to increase the oxidation resistance in the air at 1000°C especially in sample sintered at 1450°C .

REFERENCES

- [1] Do-Hyung Kim, Byung-Yong Yu, Pil-Ryung Cha, Woo-Young Yoon, Ji-Wong Byun, Sang-Hoon Kim, *Surf. Coat. Technol.* **209**, 169 (2014).
- [2] Su-In Lee, Jung-Yeul Yun, Tae-Soo Lim, Byoung-Kee Kim, Young-Min Kong, Jei-Pil Wang, Dong-Won Lee, *Thermochim. Acta* **581**, 87 (2014).
- [3] Ho-Jin Ryu, Yong-Heui Lee, Kwang-Ug Son, Young-Min Kong, Jin-Chun Kim, Byoung-Kee Kim, Jung-Yeul Yun, *J. Kor. Powder Metall. Inst.* **18**, 105 (2011).
- [4] Ho-Jin Ryu, Yong-Heui Lee, Kwang-Ug Son, Young-Min Kong, Jin-Chun Kim, Byoung-Kee Kim, Jung-Yeul Yun, *J. Kor. Powder Metall. Inst.* **18**, 112 (2011).
- [5] Kwang-Chul Oh, Chun-Beom Lee, Eui-Ju Lee, *J. Anal. Appl. Pyrolysis* **92**, 456 (2011).
- [6] Renate Fetzner, Alfons Weisenburger, Adrian Jianu, Georg Muller, *Corros. Sci.* **55**, 213 (2012).
- [7] Faug Liu, Krystyna Stiller, *Ultramicroscopy* **132**, 279 (2013).
- [8] Jae-Young Lee, Hyung-Giun Kim, Mi-Ri Choi, Chang-woo Lee, Man-Ho Park, Ki-Hyun Kim, Sung-Hwan Lim, *Appl. Surf. Sci.* **293**, 255 (2014).
- [9] D.W Lee, B.K. Kim, *Mater. Lett.* **58**, 378 (2004).
- [10] B.A. Pint, J.R. Martin, L.W. Hobbs, *Solid State Ionics* **78**, 99 (1995).

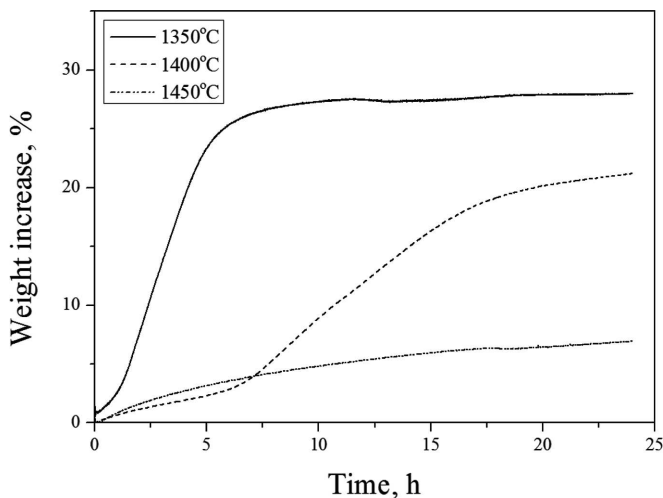


Fig. 9. Oxidation behaviors at 1000°C for 24h of porous FeCrAl alloys by sintering temperatures