Characteristics and Sintering Behavior of Oxide Coated Iron Nanopowder Synthesized by Plasma Arc Discharge Process

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This paper investigates the effect of the surface oxide layer of Fe nanopowder synthesized by plasma arc discharge (PAD) process on the densification process in hydrogen atmosphere. The densification process was divided into two steps: rapid densification at low temperature and densification retarding at high temperature. The reduction process of the oxide layer was quantitatively analyzed, and it was observed that the reduction process dominantly affected the initial densification process at lower temperature. The volume shrinkage due to the reduction of the oxide layer corresponded to 75% of the initial volume shrinkage at low sintering temperature. The volume shrinkage of the reduced oxide layer and the densification rate were discussed in terms of microstructural evolution.

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1. Introduction

Nanostructured materials have been attracting much interest recently, and the consolidation of nanopowders and their application have been a growing issue in the industrial fields. Especially, the nano-sized Fe powder has been foot-lighted on high strength structural sintered parts. Unfortunately, however, the tendency of the nanopowder to form an agglomeration and the abrupt grain growth of Fe nanopowder during the sintering process have caused some limitations in obtaining full densification with fine grain size under a few hundred nanometers through the conventional compaction and pressureless sintering process. So attempts have been mainly made to consolidate Fe nanopowder by the pressure assisted sintering process, for example, hot press, hot isostatic press, spark plasma sintering, etc.¹⁻³⁾ But these pressure assisted sintering processes can achieve neither the near net shaping of small and complex shaped sintered parts nor mass production. Recently, it has been reported that the sinterability of nanopowder is closely related to the powder characteristics. Especially, the homogeneous pore distribution plays an important role in full densification of nanopowder.⁴⁾ In order to get homogeneous pore distribution, the powder has to have very fine size, and it has to be completely dispersed without agglomeration. In addition, the explosive oxidation on the surface of Fe nanopowder makes it impossible to reach the full densification because of the hard oxide phase. This oxide phase in sintered body can inhibit the densification process and decrease the final mechanical properties.

Recently, the authors have reported the consolidation of Fe nanopowder synthesized by plasma arc discharge (PAD) process.^{5,6)} As the Fe nanopowder synthesized by PAD process (this will be referred to as the PADed Fe nanopowder hereinafter) has fulfilled the above powder characteristics, *i.e.*, fine powder size, non-agglomeration, and uniform pore distribution in compact body, the PADed Fe nanopowder could be fully densified at a relatively low sintering temperature of 560°C by the conventional pressureless sintering process. Of course, the surface oxidation of PADed Fe nanopowder was unavoidable during the synthesis process, but the oxide layer was easily removed while sintering under

hydrogen atmosphere.

In this study, the effect of the oxide layer of the PADed Fe nanopowder on the low temperature sintering in hydrogen atmosphere has been investigated to consider microstructural evolution. Especially, the reduction process of oxide layer was analyzed quantitatively, and the densification process was characterized by using the volume shrinkage and densification rate at the hydrogen reduction temperature range.

2. Experimental Procedures

Fe nanopowders were fabricated by plasma arc discharge process as described in our previous work.⁷⁾ The Fe metal vapors evaporated by plasma arc heat in the reaction chamber collided with each other and condensed to form Fe clusters or nanoparticles. The plasma arc was generated in an atmosphere of $Ar+30\%H_2$ of 0.1 MPa. The applied current was 270 A. In order to prevent the explosive oxidation of Fe metal nanopowder, the synthesized Fe nanopowder was passivated in the collection chamber filled with Ar+1%O₂ mixing gas for 24 hours. The synthesized Fe nanopowder was characterized by using the X-ray diffractometer (X'Pert APD System, Philips Co., Cu K α , $\lambda = 1.54056$ Å) and Transmission Electron Microscope (TEM, 2000FX-II, JEOL Co.). The surface of PADed Fe nanopowder was analyzed by using X-ray photoelectron spectroscopy (EscaLab 250, Thermo VG Scientific).

To form disk shaped compact bodies (6 mm in diameter and 2 mm in height), the synthesized Fe nanopowders were uniaxially pressed under a pressure of 175 MPa in a cylinfdrical compaction die. The shrinkage behaviors of compacted bodies were measured by using a laser opto-dilatometry system.^{8,9)} The compacted bodies were heated up to 800°C under hydrogen atmosphere with various heating rates of 5, 10, 20 and 30°C/min. The dimensional changes in the diameter and height of each sample were measured and plotted with elevating temperatures. The microstructures of each sintered sample were observed by Field Emission Scanning Electron Microscope (FE-SEM, JSM-6700F, JEOL Co.), and the weight loss for hydrogen reduction was measured by thermo-gravimetry (DT-1500, Ulvac Shinku-Riko).



Fig. 1 TEM micrographs of PADed Fe nanopowder.



Fig. 2 X-ray diffraction patterns of PADed Fe nanopowder.

3. Results and Discussion

3.1 Characteristics of PADed Fe nanopowder

The TEM micrographs of PADed Fe nanopowder at the synthesis conditions of 250 A of applied current and 0.1 MPa of chamber pressure in Ar+30%H₂ gas mixture are shown in Fig. 1. It represents the fully dispersed spherical Fe nanopowder of 20–200 nm in size. In the highly magnified microstructure of Fig. 1(b), PADed Fe nanopowder was coated by the second phase to form a core/shell structure. In the phase analysis by X-ray diffraction in Fig. 2, the α -Fe phase and the iron oxide phase (Fe₃O₄) were observed at the same time. These results imply that the Fe₃O₄ oxide layer of around 5 nm in thickness coated the metallic α -Fe nanopowder.

For the detail analysis of the surface of PADed Fe nanopowder, X-ray photoelectron spectroscopy was used to elucidate the powder surface structure, and the results are depicted in Fig. 3. For the as-received powder specimen in Fig. 3(a), the Fe–O binding peaks were observed mainly at 710.5 eV for $2p_{3/2}$ and 724 eV for $2p_{1/2}$ (the theoretical binding energies of Fe–O are 710.9 eV for $2p_{3/2}$ and 724.5 for $2p_{1/2}$). While for the surface cleaned powder sample by sputtering in Fig. 3(b), Fe–O binding peaks disappeared, Fe



Fig. 3 X-ray photoelectron spectra of PADed Fe nanopowder, (a) as received and (b) surface cleaned samples.



Fig. 4 Thermo-gravimetric curve of PADed Fe nanopowder in hydrogen atmosphere with 10°C/min to 800°C.

binding peaks were observed at 707.1 eV for $2p_{3/2}$ and 720.2 eV for $2p_{1/2}$ (the theoretical binding energies of Fe are 707 eV for $2p_{3/2}$ and 720.1 eV for $2p_{1/2}$). With further sputtering on the powder surface, the Fe binding peak intensities increased. This reveals that PADed Fe nanopowders are composed of a surface oxide shell and a metallic Fe core, and it is expected that the oxide surface layer forms on the Fe core during the oxygen passivation process after the powder synthesis.

In order to analyze the amount of the oxide layer, the thermogravimetric experiment for PADed Fe nanopowder was performed under hydrogen atmosphere, and the result is presented in Fig. 4. The weight loss by hydrogen reduction of PADed Fe nanopowder occurred in the temperature range of $150-400^{\circ}$ C, and it was divided into two weight loss steps. The total weight loss for hydrogen reduction of PADed Fe nanopowder was 4.53%, and each weight loss for the first and second reduction steps was 1.02% and 3.51%, respectively. In general, Fe₃O₄ was reduced to metallic Fe through the following reduction processes under hydrogen atmosphere, and the experimental and theoretical weight losses are depicted in Table 1.

$$Fe_3O_4 + H_2 \rightarrow 3FeO + H_2O \uparrow \tag{1}$$

$$3\text{FeO} + \text{H}_2 \rightarrow 3\text{Fe} + 3\text{H}_2\text{O} \uparrow$$
 (2)

The experimental weight loss for the first reduction step had the value of 22.5%, and it agrees quite well with the theoretical value of 25%. This supports our argument that the first reduction process is caused by the reduction of Fe_3O_4 to the FeO intermediate oxide phase, according to eq. (1). And the experimental weight loss for the second reduction step was 77.5% and had a vale similar to the theoretical value of 75%. This also establishes that the second reduction step is caused by the reduction of the intermediate FeO phase to a metallic Fe phase according to reaction (2). So the surface coated oxide layer of PADed Fe nanopowders is reduced by

2

Table 1 The experimental and theoretical mass losses for the reductions of Fe oxides.

	Theoretical		Experimental	
	Mass Loss (%)	Fraction (%)	Mass Loss (%)	Fraction (%)
$Fe_3O_4 \rightarrow 3FeO$	9.6	25	1.02	22.5
$3\text{FeO} \rightarrow 3\text{Fe}$	28.6	75	3.51	77.5
$Fe_3O_4 \rightarrow 3Fe$	38.2	100	4.53	100

above two-step reduction process in hydrogen atmosphere. From the result of weight loss, the thickness of oxide layer on PADed Fe nanopowder is calculated to be 4.7 nm, and it agrees well with the result of TEM observation in Fig. 1(b). This surface coating oxide phase provides the Fe nanopowder with a resistance against explosive oxidation, and makes it possible to handle it easily in an ambient atmosphere condition.

3.2 Sintering behavior of PADed Fe nanopowder in hydrogen atmosphere

PADed Fe nanopowder compaction bodies were sintered under hydrogen atmosphere with different heating rates. The volume shrinkages of each sample were measured by a laseropto dilatometry system, and they are depicted in Fig. 5. The temperatures ranges of volume shrinkages and the densities for green and sintered bodies are also presented in Table 2. The starting temperature for densification of each sample had a quite similar temperature of around $260-270^{\circ}$ C, but the finishing temperature decreased as the heating rate increased. And the total volume shrinkages also decreased with the increasing heating rate. The maximum volume shrinkage was obtained in the low heating rate condition of 5° C/min sample, and the finishing temperature for densification and the sintered density for this condition were 550° C and



Fig. 5 Volume shrinkages of PADed Fe nanopowder compacts at different heating rates in hydrogen atmosphere.

Table 2 The temperature ranges for densification and the relative densities of green and sintered body of PADed Fe nanopowder at different heating rates.

Heating Rate (°C/min.)	Temperature Rage (°C)	Relative Density (%T.D.)		
		Green body	Sintered body	
5	271-550	43.8	90.56	
10	274–548	43.9	87.83	
20	265-520	43.7	85.87	
30	263-500	43.7	83.44	

90.5%T.D. (%T.D.; % of theoretical density), respectively. In a high heating rate condition, the finishing temperature for densification was around 500°C, but the sintered density was 83.4%T.D., showing a relatively low volume shrinkage. In authors' previous study,^{5,6)} this low sintered density for a high heating rate condition was proven to be caused by pore isolation during the rapid densification process. That is, the rapid pore isolation retards the complete reduction of the oxide phase on the surface of metallic Fe powder, resulting in remaining of an oxide phase inside the sintered body. So controlling the heating rate should be an important parameter in the sintering process of Fe nanopowder, because the surface of Fe nanopowder can be easily oxidized even in a careful powder handling step.

In Fig. 5, the densification was divided into two processes, *i.e.*, rapid densification at low temperature at first, and then the densification retarding at high temperature. The first rapid densification occurred at the temperature range of 260-380°C, and the sintered densities were around 70%T.D. for each sample. The densification rates for the first and the second steps calculated from the volume shrinkages ($\Delta V/V$) are presented in Table 3. For all the heating rate conditions, the densification rates for the first step had relatively higher than the second step. This means that densification is accelerated by certain effects, *i.e.*, temperature or phase transformation. Concerning the relatively lower temperature for the first step, the temperature effect was negligible in the densification acceleration. Then the volume shrinkage by phase transformation during the reduction of surface oxide to metal phase can be an available effect in the first densification step. So the weight loss of powder compact was measured by thermogravimetry in hydrogen atmosphere, and the result with the volume shrinkage curve is depicted in Fig. 6.

In the weight loss curve of Fig. 6, the first weight loss under 120°C was 1.2%, and this is caused by the desorption of water vapor on the powder surface. And the second weight loss in the 300–420°C temperature range was 7.5% corre-



Fig. 6 Thermo-gravimetric curve of PADed Fe nanopowder compact with volume shrinkage curve in hydrogen atmosphere with 10°C/min to 700°C.

Table 3 The densification rates of PADed Fe nanopowder compacts at different heating rates.

Heating Rate (°C/min.)	1st Densification		2nd Densification		Average Pate
	Temperature (°C)	Rate (min ⁻¹)	Temperature (°C)	Rate (min ⁻¹)	(min ⁻¹)
5	271-374	1.16×10^{-1}	374-550	0.89×10^{-1}	0.99×10^{-1}
10	274-364	3.01×10^{-1}	364–548	1.45×10^{-1}	1.96×10^{-1}
20	265-372	4.58×10^{-1}	372–520	3.72×10^{-1}	4.06×10^{-1}
30	263-331	10.8×10^{-1}	331–500	4.79×10^{-1}	6.49×10^{-1}

sponding to the reduction of Fe₃O₄ to metallic Fe. This reduction temperature agrees quite well with the first densification temperature range of 260-380°C. The slight shift of weight loss curve to the higher temperature region can be expected of the time delay for removing the generated water vapor from the compact body. From the total weight loss for oxide reduction (7.5%), the volume fraction of Fe₃O₄ phase was calculated to be 26.9 vol.% in the synthesized powder. Considering that the theoretical volume shrinkage for the reduction of Fe_3O_4 to Fe is 52.2%, the volume shrinkage by the reduction of the oxide layer is calculated to be 14.0%. This value is equivalent to around 24% of the total volume shrinkage for overall densification of the compact specimen. That is, the volume shrinkage for the densification of PADed Fe nanopowder is composed of 24% volume shrinkage for the oxide layer reduction and 76% volume shrinkage for the densification itself. This volume shrinkage for oxide reduction (24%) at the first densification step is considered to be sufficient for enhancing the densification rate even at a relatively low temperature. Considering the volume shrinkage of 32% for the first densification step, the volume shrinkage for the oxide layer reduction would be a dominant process in the first densification step.

The SEM microstructures for the fracture area of sintered specimens are depicted in Fig. 7. Figure 7(d) shows the SEM micrograph of the cross-section of the specimen sintered at 560°C after micro polishing and chemical etching. There are no big differences in microstructures between the compacted specimen [Fig. 7(a)] and the sintered specimen at 400°C after reduction [Fig. 7(b)], but slightly coarsened particles were observed as in Fig. 7(b). This is due to volume expansion of the reduced Fe particle to form a Fe oxide particle again when the reduced Fe particle is exposed to air atmosphere after being heated up in hydrogen. Nevertheless, each particle is homogeneously dispersed, and it keeps the spherical shape itself in the sintered body. This implies that the densification in the first step is dominantly controlled by volume shrinkage



Fig. 7 SEM micrographs of compact bodies of PADed Fe nanopowder (a) without sintering, (b) sintered body at 400°C, (c) sintered body at 500°C, and (d) sintered at 560°C in hydrogen atmosphere. Microstructure in Fig. (d) is of ground cross-section.

for the reduction of the oxide layer. However, with an increase in the sintering temperature, the particles get together with each other and form an agglomeration as can be seen in Fig. 7(c). Finally, in the specimen sintered at 560° C, the particles were connected by neck growth showing a densified microstructure with some pores in the sintered body [refer to Fig. 7(d)]. This explains the densification for the second step, which is controlled by the conventional sintering process, *i.e.*, neck formation and growth.

In conclusion, the surface oxidation of PADed Fe nanopowder enhances the initial densification rate at lower temperature by the innegligible volume shrinkage during the reduction of the surface oxide layer. And this can be expected to play an important role in reaching full densification and in inhibiting the grain growth during the densification process at a relatively low temperature. Practically, in authors' optimized consolidation condition, a fully densified sintered specimen (98.5% of theoretical density) with around 250 nm of grain size could be obtained at the sintering condition of 560°C for 1 hour in hydrogen atmosphere with a heating rate of 5°C/min.^{5,6)}

4. Conclusion

The PADed Fe nanopowder has good sinterability owing to its very fine powder size, homogeneous dispersion, and non-agglomeration as well as a surface oxide layer on the metallic Fe powder. Especially, the surface oxide layer has been revealed to accelerate the initial densification rate at a lower temperature by remarkable volume shrinkage for the reduction of the surface oxide layer. The volume shrinkage for oxide reduction occupies 75% of initial densification, which is faster than the second densification step. This rapid densification by oxide reduction can be expected to affect the total densification and grain growth processes at a relatively low temperature.

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