Role of Equilibrium Pressure of Gas in Sintering Densification of Carbonyl Iron Powder for Metal Injection Molding*

Koji Hayashi** and Tai-Whan Lim***

The incomplete densification in vacuum-sintering of carbonyl iron fine powder having a small amount of carbon impurity (0.03 mass%) was examined, with the result that the cause was considered to be the high equilibrium pressure of CO gas which was formed by the reduction reaction of the oxide with the carbon impurity and was trapped in closed pores. The addition of the metals which produce a stable oxide having low standard free energy of formation was found to be effective for the complete densification.

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I. Introduction

Metal injection molding (MIM) has recently drawn a great deal of attention as a shaping technology for metal powders, because of the relative freedom to shape intricate geometries which are not easily fabricated by conventional unidirectional die-pressing⁽¹⁾. The powders used for MIM are, in general, fine powders of smaller than 15–20 μm having high sinterability, because the relative density of the green compact (D_g) fabricated by the MIM process is as low as 50–60% at maximum due to the use of a large amount of binder (about 35–55 vol%), and therefore the compact must be made to densify as much as possible by sintering in order to get attractive properties. The design criterion like this is in sharp contrast to that in the fabrication technology of sintered machine parts; coarse powders having low sinterability are used, the green compacts with D_g of as high as 85–92% are produced by die-pressing and the densification of the compact by sintering should be avoided as much as possible to get good dimensional tolerance of the parts.

The relative density of the MIM sintered compacts (D_s), however, are not 100% in general⁽¹⁾, in spite of the above design criterion. The present authors' previous studies^{(2)–(5)} on the H_2 -sintering of Cu, Cu–Ni and Cu–Sn fine powder compacts with D_g of about 60% showed that the D_s peaked at about 95% even when no binder or lubricant was added. This incomplete densification could be explained by assuming the following; (1) a small amount of copper oxide or oxygen (about 0.02 mass%) is retained even after the isolation of pores, (2) the oxide is reduced by the H_2 gas of the sintering atmosphere, producing

H_2O gas which is entrapped in the existing closed pores or forms new closed pores around the oxide particles, (3) the equilibrium pressure of the H_2O gas in closed pores is high enough to exceed the surface stress ($\sigma = 2\gamma/r$, where γ is the surface tension and r is the radius of the closed pore) which is the driving force for the pore shrinkage. The keypoint of our new hypothesis is that the "equilibrium pressure" of the H_2O gas which is formed by the reduction reaction of oxides and trapped in closed pores, plays an important role in whether the densification in the solid phase sintering becomes incomplete or complete.

The D_s of the MIM sintered compact of Invar, Permalloy, etc., the main components of which are iron and nickel, have been reported to be also below 100%⁽¹⁾. The equilibrium pressure of the H_2O gas in the reduction reaction of iron oxide with H_2 is calculated to be as low as 0.07 MPa at the sintering temperature, although that of nickel oxide is as high as 100 MPa. Therefore, the D_s of a fine iron powder at least was expected to become 100% judging from the above hypothesis. An unexpected result, however, was obtained for carbonyl iron powder which is widely used for MIM at present; the D_s ceased to increase at about 95% in sintering in a vacuum as well as in a H_2 atmosphere. This incomplete densification was investigated from various viewpoints, with a conclusion that it could be explained by the high value of the equilibrium pressure (in closed pores) of CO gas produced by the reduction reaction of the oxide with the carbon impurity. This paper will report the details.

II. Specimens and Experimental Procedures

The iron powder used was of a commercial variety produced by the carbonyl method. The average grain size was 5.3 μm , and the oxygen and carbon contents were about 0.40 and 0.03 mass%, respectively. The contents of volatile components such as sulfur and phosphorus

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** Institute of Industrial Science, the University of Tokyo, Tokyo 106, Japan.

*** Graduate Student, the University of Tokyo.

were as little as 0.005 and 0.001 mass% respectively. Another iron powder, i.e., reduced iron powder having carbon content of as little as about 0.0059 mass% (25 μm ; 0.44 mass% O; the contents of both sulfur and phosphorus were nearly the same as the carbonyl iron powder) was also used when deemed necessary. The master alloy powders such as Fe-Al, -Cr, -Mn, -Mo, -Nb, -Si, -Ti, -V, and -W were used. The properties of these powders were as follows; the contents of alloying elements were 51, 62, 71, 60, 66, 43, 43, 51, 77 mass%, respectively; the average grain sizes were all under 44 μm ; the oxygen contents were in the range of 0.4–1.5 mass%; the carbon contents were 0.6–0.7 mass% for Fe-Mn and Fe-W powders and 0.03–0.1 mass% for the other powders.

The carbonyl iron powder and each master alloy powder were dry-mixed with each other so that the alloying element was 4 mass% in general. The mixed powders were compacted by die-pressing without a binder or a lubricant to avoid the effect which the gases evolved from them have in the densification process. The D_g was about 59% and the sizes of the compacts were $\phi 19 \times \text{H}7.6$ mm. The compacts were heated at a rate of 0.17 K s^{-1} , kept for 7.2 ks at a temperature (973–1273 K) below which the shrinkage is small, and then sintered at various temperatures ranging from 1273 K to 1773 K for 3.6 ks. The sintering atmosphere was a vacuum of 10^{-3} Pa in order to avoid the formation of H_2O gas. For each sintered compacts, the relative density (D_s), the optical or SEM microstructure (pores and crystal grain size) and the contents of oxygen and carbon were investigated.

The results on D_s were discussed from various densification parameters such as the crystal grain size, the solidus temperature, the diffusion rate of iron atoms and the calculated value of the equilibrium pressure of CO gas inside closed pores in the reduction reaction of oxides with the carbon impurity.

III. Experimental Results and Discussion

Figure 1 shows the effect of the addition of various metals on the relation between the D_s of a carbonyl iron sintered compact and the sintering temperature (T_s). The upper diagram shows the results on sintered compacts, the D_s of which were below 100%. The carbonyl iron compact continued to densify with increasing temperature up to about 1700 K, but leveled off at 94% above about 1700 K in a vacuum as well as in H_2 gas. In other words, as previously stated, the densification was incomplete. The addition of 4 mass% of Cr, Mn, Mo, Si or W did not change the D_s substantially; the densification of these compacts were also incomplete. On the other hand, the D_s of the compacts shown in the lower diagram reached 100% at about 1670 K; the compacts densified completely by the addition of Al, Nb, Ti and V. The minimum amounts of Al, Nb, Ti and V needed for the complete densification were clarified to be about 1.5, 3.0, 2.0 and 3.0 mass%, respectively. The same results were obtained, even when the D_g of green compacts were in-

Fig. 1 Effects of 4 mass% addition of various elements and sintering temperature (T_s) on relative density (D_s) of carbonyl iron vacuum-sintered compact. The result of Fe compact sintered in H_2 gas is also shown. D_g and t_s in the figure are relative density of green compact and sintering time, respectively.

creased up to about 90%.

Figure 2 are the optical micrographs of the compacts sintered at 1673 K, the D_s of which peaked at about 96% or reached 100%. The upper micrographs in each sintered compact are those of as-polished specimens. The lower micrographs are those of etched specimens. The pores are certain to be observed for the specimens, D_s of which are below 100%. In the compacts with a D_s of 100%, small gray particles were judged to be oxides by a comparison of SEM and X-ray images of metal and oxygen, as shown in Fig. 3 which is an example of a Ti-added compact.

The cause of why the above differences in the densification were observed among those compacts was discussed from the following densification factors; (1) the liquid formation⁽⁶⁾, (2) diffusion rate of iron atoms⁽⁶⁾, (3) the crystal grain size or density of grain boundaries as a sink for atomic vacancies⁽⁶⁾, and (4) the equilibrium pressure of gas trapped in closed pores^{(2)–(5)}.

Table 1 shows the ratio of T_s/T_{sol} , where T_s is 1673 K at which the densification faltered or became complete and T_{sol} is the solidus temperature in each alloy system⁽⁷⁾. There is a lack of a correlation between the ratio (or liquid formation) and complete densification.

The diffusion rate or diffusion distance ($\sqrt{Dt_s}$, where the D is the diffusion coefficient at 1673 K and t_s is the sintering time which equals 3.6 ks) of iron atoms in each alloy system which was calculated from the activation energy and frequency factor for diffusion⁽⁸⁾ is also shown in Table 1. No correlation is observed between the diffusion distance and the D_s .

The phenomenon that the densification ceases below 100% in solid phase sintering is generally explained from the grain boundary separation from pores due to large

Fig. 2 Examples of optical microstructures of various compacts sintered at 1673 K, showing that pores disappear by the addition of Al, Nb, Ti and V. Upper microstructure for each compact; as-polished, $\times 600$. Lower; etched, $\times 35$ for Fe, Fe-Cr and $\times 150$ for the others.

Fig. 3 SEM micrograph and Ti and O X-ray images of 4 mass% Ti added sintered compact. ($\times 1500$)

Table 1 The ratio of T_s/T_{sol} , calculated values of diffusion distance ($\sqrt{Dt_s}$ at 1673 K for 3.6 ks) of iron atom, and oxides formed for each alloy system.

	Fe	Fe-Cr	Fe-Mn	Fe-Mo	Fe-Si	Fe-W	Fe-Al	Fe-Nb	Fe-Ti	Fe-V
T_s/T_{sol}	0.92	0.93	0.94	0.93	0.97	0.93	0.94	1.01	1.00	0.93
$\sqrt{Dt_s}$ (cm)	1.5×10^{-2}	4.1×10^{-3}	1.6×10^{-3}	3.1×10^{-2}	2.0×10^{-2}	—	1.5×10^{-2}	—	2.0×10^{-2}	1.5×10^{-2}
Oxides	FeO	FeO	(Fe, Mn) ₃ O ₄	Fe ₂ MoO ₄	FeO + Fe ₂ SiO ₄	FeWO ₄	Al ₂ O ₃	NbO ₂	TiO ₂	VO

grain growth⁽⁶⁾. Figure 4 shows the D_s versus the iron crystal grain size (d) of the sintered compacts. The iron crystal structure (bcc or fcc) at T_s of 1673 K does not change during cooling except for Fe, Fe–Cr and Fe–Nb sintered compacts⁽⁷⁾. There is not a good correlation between them. Furthermore, it can be observed in Fig. 2 that many pores are on the grain boundaries in the incompletely densified compacts. These indicate that the incomplete densification in this case can not be explained by the grain boundary density or the separation of the grain boundaries from the pores.

Then, the incomplete or complete densification was discussed from the viewpoint of the equilibrium pressure of gas. The gas was assumed to be CO gas which was formed in the reduction reaction of oxides with the carbon impurity and trapped in closed pores. This is because carbon and oxygen are contained in the starting powder and a part of the carbon as well as the majority of the oxygen are retained in the sintered compacts as shown in Table 2.

The equilibrium pressure of the CO gas (P_{co}) was estimated as follows: The P_{co} in the reduction reaction of $FeO + C \rightarrow Fe + CO$ can be calculated by using the formula of $\Delta G^\circ = -RT \ln (a_{Fe} \cdot P_{co} / a_{FeO} \cdot a_c)$ ⁽⁹⁾, where ΔG° is the standard free energy change in the reduction reaction, and a_{Fe} , a_{FeO} and a_c are the activities of the Fe, FeO and carbon in the system, respectively. The ΔG° is equal to $(\Delta G_{f,CO}^\circ - \Delta G_{f,FeO}^\circ)$ where $\Delta G_{f,CO}^\circ$ and $\Delta G_{f,FeO}^\circ$ are the standard free energy of formation of CO and FeO (-516 and -313 kJ/mol, O_2), respectively. The a_{Fe} is naturally equal to one, and a_{FeO} is also equal to one, because the solubility of oxygen in iron at the sintering temperature of 1673 K is about 0.06 mass%. The calculated value of P_{co} is as high as 148 MPa (1470 atm) in the case of $a_c = 1$. Actual carbon activity (a_c) in the iron sintered compact with 0.03 mass% C, is calculated to be as low as

1.73×10^{-2} , taking into consideration the carbon content and the two phase diagram of Fe–C⁽⁷⁾ and assuming that a_c varies according to Rault's Law⁽⁹⁾. Here, the reason why the carbon content of the starting powder was used instead of the carbon content of the sintered compact is that the isolation of pores is supposed to occur locally even in the initial stage of sintering and the amount of CO gas which escapes from the closed pores is assumed to be negligible.

Then, P_{co} at $a_c = 1.73 \times 10^{-2}$ was calculated to be 2.58 MPa (This was obtained by multiplying the P_{co} value at $a_c = 1$ by 1.73×10^{-2}). On the other hand, the surface stress (σ), i.e., the driving force for pore shrinkage was calculated to be 1.25 MPa (γ and r in the formula described before are 1.87 N/m and $3 \mu m$, respectively). Therefore, the P_{co} is larger than σ , suggesting that the cause for the incomplete densification of the carbonyl iron sintered compact is the higher equilibrium pressure of CO gas in closed pores over the surface stress.

If this idea is correct, a complete densification of an iron sintered compact could be expected when the powder with very low carbon content is used. In fact, the sintered compact of a special iron powder of $25 \mu m$ with carbon content of only 0.0059 mass%, the D_g of which was made to be 87% in order to promote the densification by making pore size smaller, surely showed complete densification. The optical microstructure is shown in Fig. 5, indicating that the pore does not exist although oxide particles clearly do. The d of the sintered compact was nearly equal to that of the above carbonyl iron sintered compact. Therefore, the above idea that the high equilibrium pressure of CO gas formed by the reduction reaction is the cause for the incomplete densification of the carbonyl iron sintered compacts is considered to be reasonable.

Fig. 4 Relationship between D_s and crystal grain size of sintered compact.

Fig. 5 Optical microstructure of sintered compact of very low carbon iron powder (0.0059 mass%), showing that the compact is free from pores. Dark particles are iron oxide. ($\times 600$)

Table 2 Contents of oxygen and carbon in compacts sintered at 1673 K.

	Fe	Fe+4% Cr	Fe+4% Mn	Fe+4% Mo	Fe+4% Si
Oxygen (mass%)	0.39	0.49	0.37	0.37	0.39
Carbon (mass%)	0.006	0.004	0.005	0.012	0.006
	Fe+4% W	Fe+4% Al	Fe+4% Nb	Fe+4% Ti	Fe+4% V
Oxygen (mass%)	0.36	0.34	0.41	0.52	0.50
Carbon (mass%)	0.010	0.007	0.014	0.013	0.010

Thus, the results of the effect of additives on the densification was considered from the same point of view, i.e., P_{co} . The oxides formed in each Fe-metal-O system⁽¹⁰⁾⁽¹¹⁾ are shown in Table 1. It is a notable characteristic that the oxides of the elements which were ineffective for the complete densification are FeO, complex oxide of both Fe and an added element or FeO + complex oxide, and on the other hand the oxides of the elements which were effective for the complete densification are mono-oxides of the element. Figure 6 shows a relation between D_s and ΔG_f° in each sintered compact. In the figure, the ΔG_f° of the mono-oxide was used because the ΔG_f° of the complex oxides are not known. There is a distinct correlation between them. This distinct correlation does not change, even if the ΔG_f° of the complex oxide is the average value of $\Delta G_{f,FeO}^\circ$ and ΔG_f° of the mono-oxide of the added element. This suggests that the results of the effects of these additives on D_s can be explained from the viewpoint of P_{co} .

Then, P_{co} for each alloy system was calculated for $a_c=1$ by using these ΔG_f° values of the mono-oxide and ΔG_f° values of CO ($\Delta G_{f,co}^\circ$). The results are shown in Fig. 7. The logarithm of the P_{co} is naturally proportional to ΔG_f° in accordance with the equation: $\log P_{co} = -(1/2.303 \times 2 \times RT)(\Delta G_{f,co}^\circ - \Delta G_f^\circ)$. It is obvious that the

Fig. 6 Relationship between D_s and standard free energy of formation of mono-oxide (ΔG_f°). The oxides in Fe-O, Fe-Cr-O and Fe-Si-O systems are all FeO.

Fig. 7 Relationship between calculated value of equilibrium pressure of CO gas in closed pores and ΔG_f° or $-(\Delta G_{f,co}^\circ - \Delta G_f^\circ)$. Surface stress (σ) of pore of $\phi 6 \mu\text{m}$ is shown in the figure.

D_s was 100% for the alloy systems where the P_{co} is below σ , and the D_s was less than 100% for the system where the P_{co} is above σ . Although the actual carbon activity is less than one, this relationship would hold for $a_c < 1$ in the same way as the iron sintered compact mentioned above. Therefore, it could be concluded that the equilibrium pressure of CO gas in the reduction reaction of the oxide with the carbon impurity determines whether the densification becomes incomplete or complete for these alloyed sintered compacts as well as for the carbonyl iron sintered compact.

The above idea of the equilibrium pressure is naturally thought to be applicable to the other coarse powders such as reduced or alloyed powders, because in general they have a carbon content of more than 0.01 mass%⁽¹²⁾ ($P_{co}=1.2 \text{ MPa}$) and the σ of pores in those powder compacts is small (0.37 MPa for $r=10 \mu\text{m}$). The application of the pressure larger than P_{co} on the compact during sintering is thought to be effective for the shrinkage of closed pores, i.e., the complete densification. These are now under investigation.

IV. Summary

The phenomenon that the densification of the vacuum sintered compact of carbonyl iron fine powder (5.3 μm ; 0.40 mass% O; 0.03 mass% C) peaked at about 94% and did not become complete was studied, mainly by examining the effect of the addition of Al, Cr, Mn, Mo, Nb, Si, Ti, V and W on the densification or the relative density of the sintered compact (D_s).

(1) The addition of Al, Nb, Ti and V resulted in the complete densification of the iron sintered compact, although the addition of Cr, Mn, Mo, Si and W did not substantially change the D_s .

(2) The above results on D_s could not be explained by well-known theories, such as the separation of grain boundaries from pores, liquid formation and diffusion rate of atoms.

(3) The result on D_s had a significant correlation with the standard free energy of the formation of oxides (ΔG_f°) for each added element, and the calculated value of the equilibrium pressure of CO gas (P_{co}), which is formed by the reduction reaction of the oxide with the carbon impurity and trapped in closed pores, was larger than the surface stress of the closed pores for the compacts with $D_s < 100\%$, and smaller for the compacts with $D_s = 100\%$. The D_s of iron compact became 100% for a special iron powder with a very low carbon content (0.0059 mass%) or a very low P_{co} .

(4) Therefore, it was concluded that the P_{co} in the reduction reaction of oxide is very important for incomplete or complete densification for the sintered compact of carbonyl iron fine powder having carbon impurity, in the same way as P_{H_2O} in the H_2 gas sintering of Cu base powders.

(5) The complete densification can be attained by the addition of the elements having low ΔG_f° or the use of iron powder with a very low carbon content.

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