Enhancement of Sintering of Injection Molded Ferrous Mixed Powder Compacts by Silane Treatment

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In the metal injection molding process, it is very important to sinter the debound compact of very low density to a high dense compact while keeping its initial shape.

The effects of silane treatment on the sinterability of injection molded Fe, Fe-Si and Fe-Co powder compacts were investigated. The treatment was done in such methods as to coat the powder particles with a silane coupling agent, or to add it directly to the organic binder in hot mixing.

The results obtained were as follows:

It was shown that the densification of the injection molded Fe and Fe-Si compacts during sintering was markedly accelerated by the silane treatment. The sintering enhancement was pronounced especially at relatively low temperatures of 1373 to 1453 K, and the effect of silane was only realized in the case of the injection molded compacts. The optimum quantity of the silane as an enhancer for the injection molded compacts was estimated to be about 0.2 mass%. It was also shown that the linear shrinkage of the silane coated powder compacts during sintering occurred more isotropically than that of the compacts with silane directly mixed or without silane.

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I. Introduction

Various techniques of metal injection molding (MIM) processes are being developed, but there are still required a more detailed knowledge and improvements for each of the unit processes from the binder selection to the sintering⁽¹⁾⁻⁽³⁾.

In the conventional powder metallurgy (P/M) process high density is achieved mainly by compaction, whereas in the MIM process it is achieved mostly by sintering. The injection pressure in the MIM process is considerably low (about 50~100 MPa) compared to the compacting pressure in the P/M process (500~1000 MPa). Besides the binder prevents the direct compressive stress transmit to the metal powder particles. Thus, the density level of the green compacts in MIM is as low as the tap density of the starting powder. For this reason, it is very important to find the most suitable means for sintering the debound compacts to high dense compacts keeping their initial shapes. The sintering behavior of the injection molded compacts are influenced by the characteristics of metal powders, the binder components⁽⁴⁾, the debinding⁽⁵⁾ and sintering conditions (atmosphere⁽⁶⁾, heat profile⁽⁷⁾, etc.).

In general, the elements like B (boron)⁽⁸⁾, Sn (tin)⁽⁹⁾, C (carbon)⁽¹⁰⁾ and P (phosphorus)⁽¹¹⁾⁻⁽¹³⁾ are known as the sintering enhancement additives for ferrous powders. In this study, the silane coupling agent which is one of the surface-active agents is used to improve the sinterability of injection molded ferrous compacts. The silane coupling agent has been typically used to enhance the

adhesiveness between ceramics or glass powders and plastics in the composite materials⁽¹⁴⁾. The same effect will be expected in the hot mixing of metal powders and the binder. Besides if Si in the agent remains as a fine layer on the surface of Fe particles and Si content become higher at that portion after debinding, the densification of ferrous powder compacts will be also expected by the α -phase sintering because Si has a strong ferrite stabilization effect.

This paper dealt with the effects of the silane treatment on the sintering enhancement and the isotropic shrinkage during sintering of MIM compacts using Fe, Fe-Si and Fe-Co powders. The variation in sintering behavior with the method of silane treatment was also discussed.

II. Experimental

The experiments were performed according to the procedure shown in Fig. 1. The silane coupling agent was added by two methods. One was previously coating the surface of metal powder with the agent, and the other was to add the agent directly into the binder during hot mixing (kneading). In the following, the former is described as "silane coating" and the latter as "silane addition". The amount of silane agent using in this work was usually 0.3 mass% in both methods. Carbonyl Fe powder around 4.5 μm , Si powder under 37 μm and Co powder around 1.4 μm were used. The binder was composed of EVA (Co-polymer of ethylene and vinyl acetate), HDPE (high density polyethylene) and wax (micro-crystalline, paraffin and carnauba wax). At first, the metal powder was hot mixed with the binder in air at 453

Fig. 1 Flow chart of experimental procedure.

K and the mixture was granulated into the feedstock pellet. The pellet was then injection molded into the cylindrical compacts 14 mm in diameter and 10 mm in length. These compacts were debound in air at 553 K and sintered at 1373 ~ 1523 K for 7.2 ks in H_2 . The relative density and dimensional change were measured for the sintered compacts and their microstructures were also examined.

III. Experimental Results and Discussion

1. Effect of silane treatment on sintering enhancement

Table 1 shows the influence of the silane treatment on the green density of injection molded Fe and Fe-Si compacts. The density is slightly changed by the Si content, but the influence of the silane treatment on the green density is not seen.

Figures 2 ~ 4 show the relations between relative density and sintering temperature for Fe, Fe-1 mass%Si and Fe-3 mass%Si MIM compacts, respectively. Obviously the compacts with 0.3 mass% silane were sintered to

higher densities than the compacts without silane. The enhancing effect of the silane on the sinterability of MIM compacts was more pronounced even in the sintering at relatively low temperatures such as 1373 ~ 1453 K. The relative densities of the silane treated compacts were 3 ~ 8% higher than that of the compact without silane. The enhancing effect seems not dependent on the method of silane treatment. As shown in Fig. 4, the Fe-3 mass% Si compacts are sintered to higher densities compared

Fig. 2 Relation between relative density and sintering temperature for injection molded Fe compacts. (Sintered for 7.2 ks. in H_2) Fig. 3 Relation between relative density and sintering temperature for injection molded Fe-1 mass%Si mixed powder compacts. (Sintered for 7.2 ks. in H_2)

Table 1 Green densities of injection molded compacts.

Powder	Density of green compact (Mg/m ³)
Fe	4.66
Fe (s.c.)	4.67
Fe (s.a.)	4.66
Fe-1 mass%Si	4.57
Fe-1 mass%Si (s.c.)	4.61
Fe-1 mass%Si (s.a.)	4.60
Fe-3 mass%Si	4.45
Fe-3 mass%Si (s.c.)	4.43
Fe-3 mass%Si (s.a.)	4.45

s.c.; silane coating
s.a.; silane addition

Fig. 4 Relation between relative density and sintering temperature for injection molded Fe-3 mass%Si mixed powder compacts. (Sintered for 7.7 ks. in H_2)

with the Fe-1 mass%Si or Fe compacts. This may be due to the following reason. In the phase diagram of Fe-Si⁽¹⁵⁾, Fe containing 3 mass%Si is outside of the γ -loop at which the α phase is stable, whereas Fe containing 1 mass% or less Si is in the range of the γ phase at about 1373 to 1523 K. Since the self-diffusion coefficient of α -Fe is $2.0 \text{ cm}^2/\text{s}$ which is much higher than that of γ -Fe ($0.49 \text{ cm}^2/\text{s}$)⁽¹⁶⁾, sintering is greatly accelerated in the Fe-3 mass%Si compacts.

Figure 5 shows the microstructures of the Fe compacts sintered at 1423 K, which shows a pronounced enhancing

effects of silane treatment on the sinterability. Without silane a large number of irregular shaped pores remain in the compact, whereas the size and number of pores are reduced and most of the pores show the rounded shape in the silane treated compacts.

Figure 6 shows the microstructures of the Fe-3 mass% Si compacts sintered at 1523 K. All compacts were sintered to the densities over 95% of theoretical. Therefore, the differences in the shape and number of pores are scarcely distinguished. However, significant grain growth are observed in the compacts made from the silane coated powder, which suggests that the sintering proceeds more rapidly.

The enhancing effect of silane treatment on the sinterability of MIM compacts of Fe and Fe-Si powders is considered to be owing to the formation of thin films of Si on the surface of Fe particles. The silane coupling agent has been usually used to strengthen the adhesion between plastics and inorganic materials such as glass or oxide powders in the field of composite materials, and the agent is considered to make bridges between plastics and inorganic powders by bonding with oxygen on the surface of powder particles. In the case of Fe powder for MIM, the particle surfaces are always more or less oxidized, and the effect of the silane as the adhesive is also considered to be useful. In addition, after the complete binder removal by both debinding and initial sintering, thin films of Si (or ultra fine Si particles) may be left on the surface of Fe particles. Furthermore, the α -Fe phase may be formed in the surface layer of Fe particle by those Si films as shown in Fig. 7 schematically, then the sintering will be activated in the early stage of sintering, at which the surface diffusion is dominant. If all amounts of Si in the 0.3 mass% silane remain after sintering, the Si content of the compact is estimated to increase by 0.034 mass%. In fact, by means of the absorption spectro-photometry with Mo-blue line (quantitative analysis), Si content in the silane treated compact sintered at 1423

Fig. 5 Microstructures of Fe injection molded compacts, sintered at 1423 K. (a) Without silane, (b) Silane addition, (c) Silane coating. The sintering enhancing effect of silane is shown evidently in this case.

Fig. 6 Microstructures of Fe-3 mass% injection molded compacts sintered at 1523 K. (a) Without silane, (b) Silane addition, (c) Silane coating. The sintering enhancing effect of silane is not so pronounced in this case.

Fig. 7 Expected silane (Si) distribution during sintering.

K was 0.037 mass%, while that of the compact without silane was 0.003 mass%. From this, it seems reasonable to assume that the Si is concentrated in the surface of Fe particles as shown in Fig. 7 to explain the enhancing effect of such a small amount of Si on the sinterability.

Figure 8 shows the relation between relative density and sintering temperature for the die-pressed compacts without binder. In this case, the enhancing effect of silane on the sinterability of compacts is much less than that of MIM compacts. The silane films on the surface of individual particles are broken by the direct contacts between the particles which are strongly rubbed each other by the frictional force in the rearrangement stage of cold pressing of powder. On the other hand, for the case of MIM compacts the direct contacts between the particles can be avoided by the binder. Thus the silane will remain between particles to be a thin film of Si, which enhance sintering.

Figure 9 shows the effect of silane content on the sintering enhancement of MIM compacts. The sintered density increases rapidly with increasing in silane content up to 0.15 mass%. When the silane content exceeded over 0.3

Fig. 8 Relation between relative density and sintering temperature for die-pressed compacts without binder. (Compacted at 300 MPa and sintered for 7.2 ks. in H_2)

mass%, the moldability of the feedstock became worse due to the decrease in viscosity. Therefore the optimum silane content is considered to be around 0.2 mass%. The minimum coating area with silane and the specific surface area of carbonyl Fe powder used in this work are 314 and $0.35 \text{ m}^2/\text{g}$, respectively, according to the inspection certificate. Then the required content of the silane agent for coating uniformly all the surface of powder particles is calculated to be 0.11 mass%. Accordingly, the optimum silane content is about double the content calculated to coat all the powder surface.

For reference, Fig. 10 shows the relation between relative density and sintering temperature for injection mold-

Fig. 9 Effect of silane content on the sintered density of injection molded Fe compacts.

Fig. 10 Relation between relative density and sintering temperature for injection molded Fe-50 mass%Co mixed powder compacts.

ed Fe-50 mass% Co (permendur) mixed powder compacts with and without silane. In this case the addition of silane has much effect on the sinterability; silane coating has a detrimental effect. This is considered to be due to the oxidation of Co powder. The particle size of Co powder used here is around $1.4 \mu\text{m}$, and Co powder will be easily oxidized. Therefore, Co powder might have been oxidized during the dipping in the solution of silane. Thus, in this case it may be more effective to add the silane into the binder.

Fig. 11 Relation between linear shrinkage and sintering temperature for injection molded Fe compacts.

2. Effect of silane treatment on the isotropic shrinkage during the sintering

Figure 11 shows the relation between linear shrinkage and sintering temperature of injection molded Fe compacts. Large shrinkage of 12 to 16.5% took place in the temperature range of 1373 to 1523 K. Obviously the compacts of silane coated powder shrank more isotropically than the others during sintering. This reason is not clear but it is considered that the silane coated Fe powder disperse more uniformly in the binder, and the non uniform packing of powder particles in a compact is eliminated.

It is expected in the MIM process that the sintering shrinkage proceeds more isotropically than that in the conventional P/M process. Usually, about $\pm 0.3\%$ of shrinkage difference depending on the direction is often observed⁽¹⁷⁾. Therefore, it will be possible to manufacture more complex shaped MIM products with higher precision by the silane treatment.

IV. Conclusion

The effects of silane treatment ("coating" and "addition by mixing") on the sintering behavior of injection molded Fe, Fe-Si and Fe-Co powder compacts were investigated.

The main results obtained were as follows:

(1) The sintering of injection molded Fe and Fe-Si compacts was markedly enhanced by the silane treatment.

(2) Especially, the enhancing effect of silane was pronounced in the temperature range between 1373 to 1453 K.

(3) The optimum content of silane agent which enhance the sintering of injection molded Fe and Fe-Si com-

pacts was estimated to be about 0.2 mass%.

(4) The effect of silane treatment on the sintering enhancement was restricted only to the case of the injection molded compacts.

(5) The linear shrinkage of the silane coated powder compacts during sintering occurred more isotropically than the silane mixed compacts or without silane.

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