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Analysis of Dewaxing Behavior of Iron Powder Compacts Based on a Direct Observation of Decomposing Lubricant During Sintering in a Furnace†

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Abstract:

Dewaxing behavior of iron powder compacts containing zinc stearate (ZnSt) or ethylene-bisstearamide (EBS) was directly observed during sintering. First, small droplets of lubricant melt appeared scattered on the surface. Then, they gradually formed large pools, and finally vaporized. In addition, melt of ZnSt more remarkably bubbled than that of EBS during vaporization. After sintering the compact containing ZnSt in nitrogen, spot stains of rough surface and concentrated zinc with the diameter of 1 mm were found on the top of their surface. It is believed that the lubricant melt inhomogeneously flew out through the easier paths in the compacts to the surface accompanied by the exhausting gas of the decomposed lubricants.

1. Introduction

In the iron powder compacting process, it is general practice to add an organic lubricant powder such as zinc stearate (ZnSt) or ethylene-bisstearamide (EBS) in order to improve the flowability of the powder, increase green density, and reduce ejection force. Although the larger part of such organic lubricants is removed in the sintering process, in some cases, the lubricant remains on the surface of the sintered compact in the form of soot or stain, which reduces the quality and yield of sintered products.

The decomposition behaviors of simple ZnSt and EBS have been clarified previously in a number of studies[1–3]. The decomposition behavior of organic materials contained in metal powders had also been studied by German, particularly as it pertains to injection molded metal parts[4]. Nayar et al. reported on the causes of typical defects in the sintering of metal powder compacts and the related countermeasures[5], and Kameoka et al. analyzed the mechanism of rough surfaces of sintered compacts in an endothermic gas atmosphere[6]. In order to eliminate surface defects and improve the product quality of sintered compacts, a theoretical analysis of the controlling factors in the mechanism of dewaxing of the lubricants (i.e., decomposition and removal of the lubricant) and their interrelations is important. However, in addition to the fact that powder metallurgy treats substances which comprise multiple elements, consist of a large number of particles, and are porous, manufacturing conditions also change constantly in commercial operation. This complexity makes it difficult to analyze the mechanism of dewaxing.

Visualization of the actual behavior of the powder and green compact in the case described above, under conditions simulating commercial operation, is considered useful for understanding the phenomena involved. For example, Kondoh et al. developed a uniform filling technique by a direct understanding and visualization of the flow behavior of iron powder into the die cavity[7].

At JFE Steel, dewaxing behavior of iron powder compacts placed in a heating furnace was observed directly, and the generation mechanism of staining of the sintered compacts has been analyzed[8–10]. This paper summarizes the results of those researches and recommends essential points for avoiding staining of sintered compacts.

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2. Experimental Method

2.1 Raw Materials and Blending Method

The raw materials used were water-atomized iron powder (JIP®300A), electrolytic copper powder, and graphite powder. These materials were weighed to obtain a mass ratio of 97.2 : 2 : 0.8. As lubricants, 1 mass% of either zinc stearate (hereinafter, ZnSt) powder or ethylene-bisstearamide (EBS) powder was added to the raw material powder. These powders were then mixed using a V blender in order to prepare mixed powders. A segregation-free treated mixed powder (ZnSt-CMX) was also prepared by adding 1 mass% of ZnSt. The lubricant compositions and mixing methods used in preparing the experimental materials are shown in **Table 1**.

2.2 Experimental Conditions

The mixed powders described above were compacted in cylindrical shapes with a diameter of 25 mm and thickness of 5 mm or 25 mm so as to obtain a green density of 7.0 or 7.2 Mg/m^3. As shown in **Fig. 1**(a), these green compacts were dewaxed for 20 min at 700°C, followed by sintering with a holding time of 20 min at 1 130°C. As the atmospheric gas, endothermic gas produced from propane gas (RX gas), a mixed gas of 80%N_2-20%H_2 (N_2-H_2) gas, or N_2 gas was used. After sintering, the stains on the surface of the sintered compacts were observed.

The dewaxing behavior of the lubricants from the green compacts was observed directly through a quartz glass window installed in the heating furnace. In order to minimize the decomposition of the lubricant in these observations, N_2 was used as the atmospheric gas, and as shown in Fig. 1(b), the specimens were heated directly to 1 130°C at a heating rate of 25°C/min without holding time for dewaxing.

2.3 Evaluation Method

The melting and decomposition temperatures of the lubricants were measured using a differential thermobalance. The morphology of staining which occurred on the surface of the sintered compacts was observed using an optical microscope and scanning electron microscope (SEM). In order to identify the crystal structure of the stains, an X-ray diffraction device (XRD) with a beam diameter of 100 μm was used. The elemental distribution of the stains on the sintered compacts and their surrounding areas were analyzed using an electron probe microanalyzer (EPMA).

3. Experimental Results

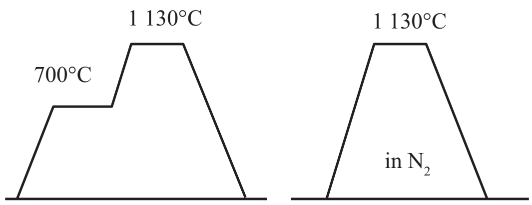
3.1 Effect of Atmospheric Gas on Stains

Green compacts with a thickness of 25 mm and density of 7.0 Mg/m^3 using mixed powders containing either ZnSt or EBS were sintered in the three species of atmospheric gases mentioned in “2.2 Experimental Conditions.” Photographs of the surfaces of the sintered compacts are shown in **Photo 1**. No staining was observed on the surface of the EBS-added sintered compact regardless of the sintering atmosphere. On the other hand, with the ZnSt-added compacts, a small amount of black spot stains was observed when sintering was performed under the RX gas or N_2-H_2 gas atmosphere. When sintering was performed in N_2 gas, numerous black stains consisting of adhering fine powdery soot formed.

Table 1 Added lubricant and mixing method of experimental materials

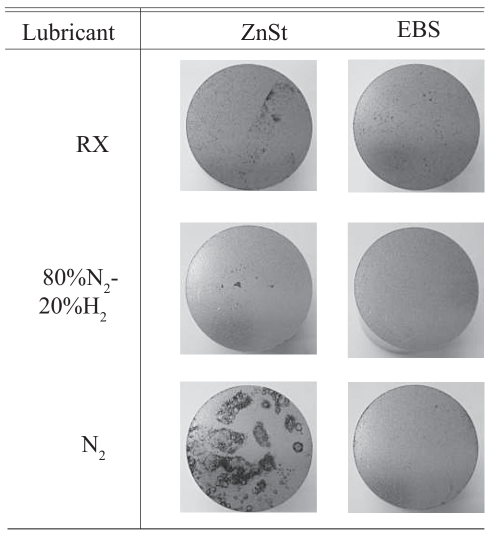
Sample name	Added lubricant	Treatment
ZnSt-Mix	ZnSt 1%	Mixing with V-shaped mixer
EBS-Mix	EBS 1%	Mixing with V-shaped mixer
ZnSt-CMX	ZnSt 1%	Segregation-free treatment

ZnSt: Zinc stearate
EBS: Ethylene-bisstearamide



(a) Simulating stains on the sintered bodies
(b) Observing dewaxing behavior by suppressing decomposition of lubricants

Fig. 1 Sintering pattern



RX: Endothermic gas

Photo 1 Sintered compacts' surface dependent on the sintering atmosphere and mixed lubricant

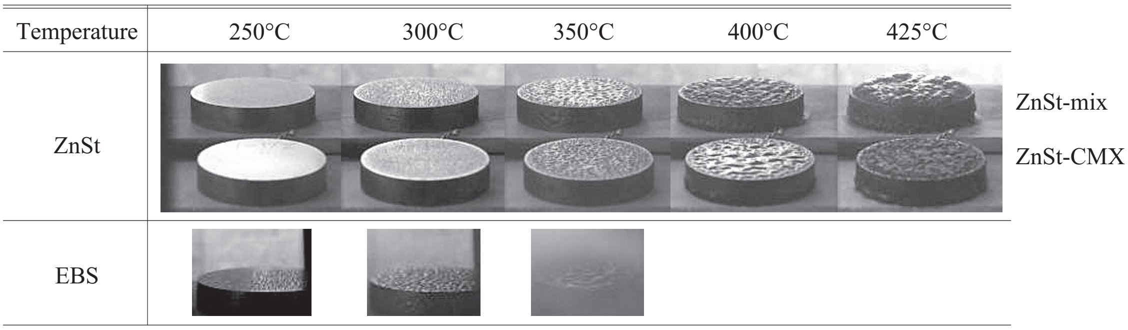


Photo 2 Directly observed dewaxing behavior of the compacts containing zinc stearate (ZnSt) or ethylene-bisstearamide (EBS)

3.2 Effect of Type of Lubricant on Dewaxing Behavior

Photographs obtained by direct observation of the dewaxing behavior of the green compacts with a thickness of 5 mm and density of 7.0 Mg/m^3 are shown in **Photo 2**. When using the mixed powder containing ZnSt, a melt of the lubricant leached out on the surface of the green compact when the temperature exceeded 300°C. The melt gradually coalesced and grew into large droplets. When the temperature exceeded 350°C, large droplets with a diameter of several millimeters flowed down the side of the compact. At temperatures over 400°C, bubbling of the lubricant melt occurred. This bubbling was observed on the top surface of the green compact and the outer circumference where the green compact was in contact with the base plate, but was not observed on the side surface. Furthermore, the bubbling on the top surface occurred at only certain locations. Bubbling became weaker as the temperature rose, and the pools of liquid lubricant gradually disappeared at temperatures over 450°C.

Phenomena similar to those described above were also observed when the ZnSt-CMX powder was used. However, in comparison with the ZnSt mixed powder, the temperature at which the lubricant leached from the compact and the temperature at which bubbling started were both 20°C lower.

With the EBS mixed powder, the temperature at which leaching of the lubricant occurred and the temperature at which bubbling began were 50°C lower than that with the ZnSt mixed powder, and the degree of bubbling was also weaker.

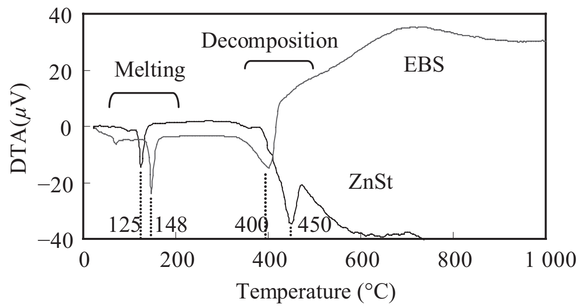


Fig. 2 Result of the differential thermal analysis in He gas for ZnSt and EBS

The results of differential thermal analysis of the ZnSt and EBS are shown in **Fig. 2**. The melting points of ZnSt and EBS were 125°C and 148°C, respectively. The decomposition temperature range was 400–450°C for ZnSt and 350–400°C for EBS, being 50°C lower in the case of EBS. The temperature at which bubbling of the lubricant melt started agreed with the decomposition temperature of the lubricant obtained in the results of these thermal analyses.

3.3 Effect of Green Compact Thickness and Green Density on Dewaxing Behavior

The results of direct observation of the dewaxing behavior of the green compacts with the thickness of 25 mm and density of 7.0 or 7.2 Mg/m^3 using the ZnSt mixed powder are shown in **Photo 3**. The temperatures of the start of leaching and start of bubbling of the lubricant were the same as when the green compact thickness was 5 mm. However, in comparison with the specimen having a green compact thickness of 5 mm, the pools of

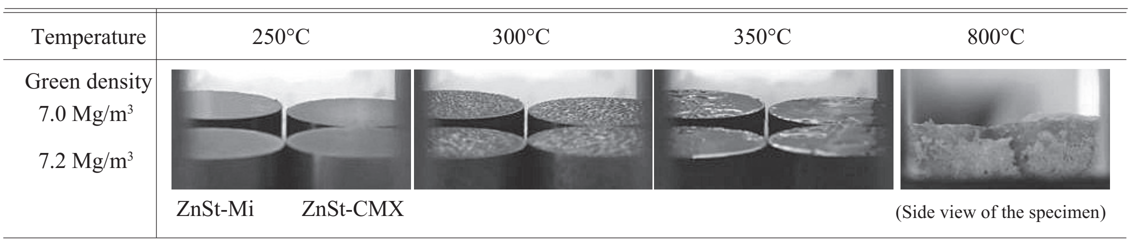


Photo 3 Effect of the density of green compacts with 25 mm thickness on the dewaxing behavior of zinc stearate (ZnSt)

molten lubricant on the top surface of the green compact were larger and the degree of bubbling was more remarkable. At 800°C, grayish-white ash adhered to the top and side surfaces of the specimens. This ash became smaller as the temperature increased and disappeared at 1 130°C. Because this phenomenon was not observed with the EBS mixed powder, the above-mentioned ash is considered to be the residue left after the decomposition and vaporization of ZnSt. When specimens having green densities of 7.0 and 7.2 Mg/m^3 were compared, no differences were observed in the lubricant decomposition behavior of the two specimens.

3.4 Analysis of Stains on Specimens Sintered in N_2 Gas

Green compacts were prepared by compacting ZnSt mixed powder and EBS mixed powder to a green density of 7.0 Mg/m^3, followed by sintered in N_2 gas. The appearance of the sintered specimens is shown in **Photo 4**. With the EBS added specimen, no stains were observed on the specimen surface. On the other hand, with the ZnSt-added specimen, gray or black stains had firmly adhered to the top and side surfaces of the specimen. A gray scale-like substance had also adhered to the top surface of the specimen, but this scaly substance could be peeled off easily. Discolored concentric stains with a diameter of approximately 1 mm were observed on the specimen surface under this scale. A photograph of this stain is shown in **Photo 5**.

An SEM image of the concentric stain in Photo 5 is shown in **Photo 6**. From the center to the outside of this concentric pattern, the pattern displays sponge form, fine needle, triangular pyramid, and rectangular morphologies. The width of all of these structures is roughly 50–100 μm. The results of identification of the crystal structures by XRD are shown in **Fig. 3**. In the sponge form structure which can be seen in the center of the stain, only iron oxides were detected. In the rectangular structure corresponding to the outer side of the stain, the

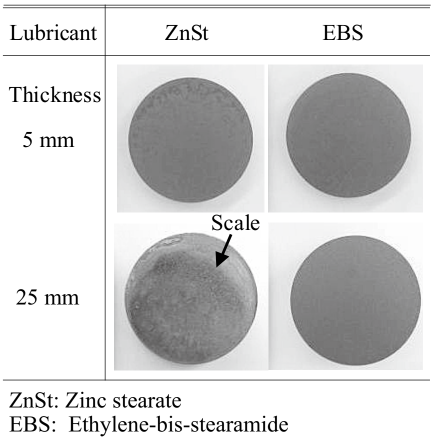


Photo 4 Effect of thickness and lubricant on the stains on the top surface of the compact sintered with the condition shown in Fig.1(b)

Photo 5 Concentric stains found adhered on the top surface of the sintered compact under a scale shown in Photo 4

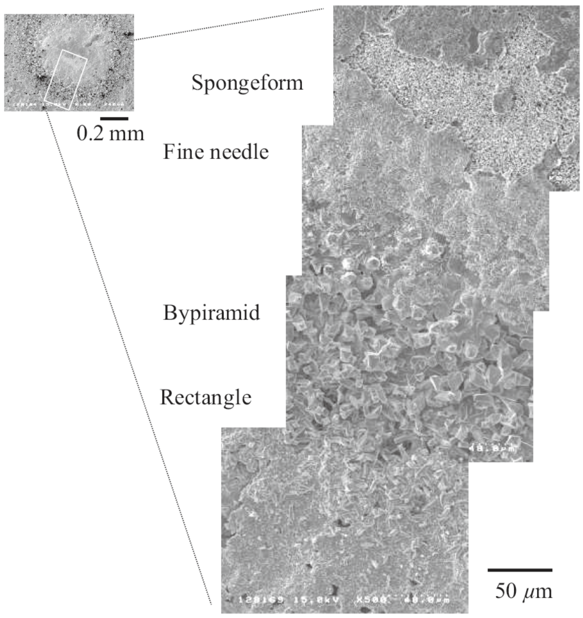


Photo 6 Scanning electron microscope photographs of the morphological shape of the stain shown in Photo 5

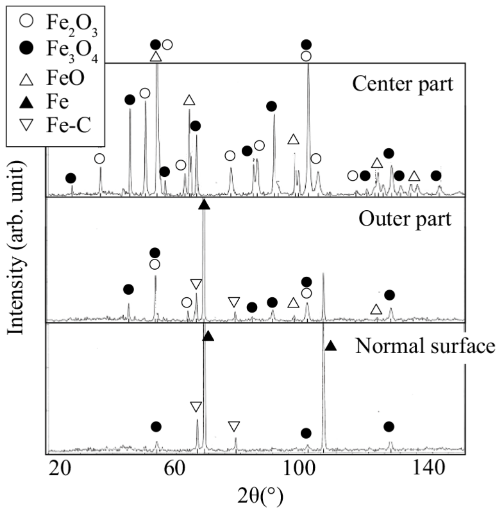


Fig. 3 X-ray diffraction pattern of the stain shown in Photo 6

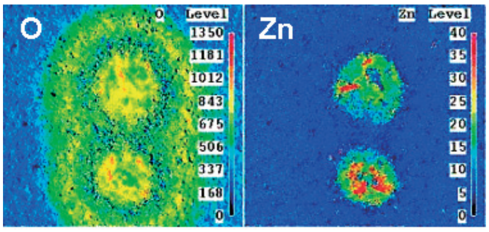


Photo 7 Distribution of Zn and O at the stain shown in Photo 5

peak intensity of iron oxides decreased, and accompanying this, the intensity of the Fe diffraction line increased. At the stain-free position 2 mm from the center of the stain, only Fe and FeC were detected. As shown in **Photo 7**, these changes in the degree of oxidation were also clear in the analysis of the elemental distribution using EPMA. The oxygen concentration was high at the center of the stain and decreased with distance toward the outer edge of the stain. Based on the fact that a Zn-rich area was detected in the central part, it is estimated that the ZnSt melt flowed out preferentially in this part.

4. Discussion

4.1 Model of Dewaxing and Stain Formation Process

A schematic diagram of the process of decomposition of the lubricant in an iron powder compact containing ZnSt and the process of formation of stains on the sintered compact is shown in **Fig. 4**. In the initial stage of dewaxing, the lubricant is heated to above its melting point and transforms from a solid into a liquid. As heating proceeds, the lubricant melt swells and begins to leach from the surface of the green compact. When the lubricant is heated to above its decomposition temperature, it is forced out by the pressure of the vaporized lubricant at the surface of the green compact via the routes (open pores) through which the lubricant melt can pass most easily. The lubricant melt which is forced out together with the decomposition gas bubbles

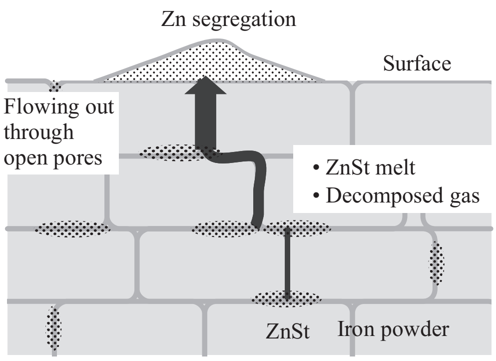


Fig. 4 Model of dewaxing and stain formation for the compact of the iron powder mixed with the lubricant, Zinc stearate (ZnSt)

at this egress point. With further heating of the lubricant melt, the organic component decomposes and vaporizes, leaving the inorganic components, including metals and metallic oxides, around the egress point. These residual inorganic substances react at high temperature with the green compact[6]. It is considered that the roughness of the sintered compact surface is increased and stains which cannot be removed are formed as a result of this reaction.

4.2 Controlling Factors of Dewaxing and Stain Formation

Based on the dewaxing model proposed in the previous section, it is considered important to focus on the following three element processes in dewaxing in order to avoid stains on the surface of sintered compacts.

First, the properties of the starting materials, including the lubricant, iron powder, and other additives are important. The lubricant must be completely decomposed and vaporized before stains can form by reaction of the iron powder and inorganic substances originating from the lubricant. This means that the decomposition temperature of the lubricant should be as low as possible. It is also necessary to minimize the contents of inorganic substances in the iron powder and lubricant.

Next, it is important to focus on the process by which the lubricant migrates to the surface by way of open pores. To ensure that migration of the lubricant melt is completed at a low temperature, it is desirable that the green compact have a thin thickness and high porosity. In order to avoid concentration of the lubricant melt at certain positions on the green compact surface, higher open pore ratios are desirable. Although this research did not show the effect of the green density on dewaxing behavior, if it is possible to increase the open pore ratio by setting the green density at <7.0 Mg/m^3, it is thought that localized segregation of inorganic substances such as Zn originating in the ZnSt can be mitigated.

Finally, though this could not be verified in the present paper, it is considered necessary to focus on the reaction in which stains are ultimately formed, in other words, the 3-way reaction of the lubricant, the green compact, and the atmospheric gas.

5. Conclusion

The dewaxing process of Fe-based green compacts containing ZnSt or EBS was directly observed during heating to 1 130°C. Based on these observations and the results of an analysis of the morphology and composition of the stains which formed on the sintered compacts, a model of the dewaxing process was proposed, and key perspectives for avoiding stains on sintered compacts were recommended. The main conclusions of this research are as follows.

(1) When green compacts containing ZnSt were sintered in N_2 gas, staining of the sintered compacts was remarkable; however, stains were not observed with EBS added green compacts.
(2) The temperature at which leaching of the lubricant melt began was 50°C higher with the ZnSt-added compacts than with EBS addition.
(3) With ZnSt-added segregation-free treated iron powder, the starting temperature of leaching of the lubricant and the starting temperature of bubbling were approximately 20°C lower than with the ZnSt mixed powder.
(4) In tests of specimens with green densities of 7.0 and 7.2 Mg/m^3, no differences in dewaxing behavior related to the green density were observed.
(5) The leaching temperature of the lubricant and thickness of the green compact were unrelated. However, the size of the lubricant melt pools became larger as the thickness of the green compacts increased.
(6) In the stains on sintered compacts of the ZnSt-added material, the surface morphology and degree of oxidation changed in a concentric manner, in which Zn had segregated to the central part of the stain. This was considered to show that the ZnSt melt leached out from the central part of the stain.
(7) In order to avoid stains on sintered compacts, it is important to control the properties of the raw materials, including the lubricant and iron powder, the process of migration of the lubricant melt, and the 3-way reaction of the lubricant, green compact, and atmospheric gas.

References

1) Legzdins, C. F.; Samarasekera, I. V.; Troczinski, T. Proc. 1998 PM World Congress. 1998, p. 266.
2) Dwyer, J.; Nayar, H.; Gerristead, W.; Wasicziko, B. Adv. Powder Metall. & Particul. Mater. 1992, p. 3–183.
3) White, G.; Nayar, H. Adv. Powder Metall. & Particul. Mater. 1996, vol. 3, p. 10–27.
4) German, R. M. Inter. J. Powder Met. 1987, vol. 23, no. 4, p. 237.
5) Nayar, H. S. Metals Handbook 9th Ed. vol. 7, compiled by Klar, E. American Society for Metals, Ohio, 1984, p. 339.
6) Kameoka, T.; Ishihara, K.; Hamamoto, H.; Obayashi, M. Abstracts of Jpn. Soc. Powder and Powder Metall. 1983, p. 78.
7) Kondoh, M.; Takemoto, S.; Urata, I. J. Jpn. Soc. Powder and Powder Metall. 1998, vol. 45, no. 5, p. 412.
8) Kawano, T.; Ono, T.; Ozaki, Y. Euro PM2009 Congress Proceedings (Sintering). 2009.
9) Kawano, T.; Ono, T.; Ozaki, Y. Abstracts of Spring Meeting of J. Jpn. Soc. Powder and Powder Metall. 2009, p. 132.
10) Kawano, T.; Ono, T.; Ozaki, Y. Curr. Adv. Mater. Process. 2009, vol. 22, no. 2, p. 1094.