Liquid Phase Sintering of Ni-Base Superalloy IN-100*

By Masao Morishita**, Hiroshi Nagai*** and Keiichiro Shoji***

The sintering behavior of prealloyed powder of Ni-base superalloy IN-100 was investigated by studying the solidification process of melted IN-100 powder through dilatometry, microstructural observations, DTA and EPMA.

Rapid densification of powder compacts occurred above 1513 K, while the sintering rate was very slow below 1493 K. This result suggested that the mechanism of sintering changed in the temperature range of 1493–1513 K. DTA during the sintering process of IN-100 powder compacts and during the solidification process of melted IN-100 powder detected five endothermic and five exothermic reactions, respectively. Microstructural observations revealed that three reactions (in the highest two temperature regions and the lowest temperature region) among the five reactions detected during the sintering process might be equivalent to those during the solidification process, that is, complete melting, γ'-eutectic and γ' solvus, respectively. The microstructures in the two intermediate temperature regions during sintering (1498–1523 and 1523–1548 K), where the mechanism of sintering changed, were greatly different from those during the solidification process, but approached those found during the solidification process after holding in the temperature regions for extended time. This result showed that the two reactions might correspond to non-equilibrium incipient melting which resulted from relatively rapid cooling from a melt in the powder production process (vacuum atomization).

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I. Introduction

The use of powder metallurgy is becoming increasingly important in the manufacture of superalloys. Superalloy powders are usually consolidated by either hot isostatic pressing (HIP) or hot extrusion, and by subsequent hot working(1); however, other methods are still under investigation. Among these methods, liquid phase sintering in a mould, followed by forging or hipping is attractive, since this method offers several advantages over the usual methods. For example, parts of a complex form could be obtained by sintering in a mould, and post-sintering hipping could be done without a sealed container. In order to obtain superalloy parts of high performance, an investigation of liquid phase sintering of superalloy powders is of great importance. Although there have been a few reports(2)–(7) on this subject, very little attention has been paid to the clarification of phase reaction, including melting.

In the present report, the sintering behavior of superalloy IN-100 powder was investigated by dilatometry. Phase reactions during sintering were detected by differential thermal analysis, and clarification of phase reactions was carried out in comparison with the phase reactions during the slow cooling of melted powder.

II. Experimental Procedure

The IN-100 powder was produced by vacuum atomization (Homogeneous Metals, Inc.). The chemical composition and particle size distribution of the powder are given in

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Tables 1 and 2, respectively. Figure 1 shows the microstructure of the powder. The powder was compacted at 392 MPa and sintered in a vacuum of $10^{-4}$ Pa. In order to study the sintering behavior, the dimensional change during sintering was measured by a dilatometer. DTA was used to detect the phase reactions during the sintering process of powder compacts and the slow cooling process of melted IN-100 powder. The heating and cooling rates were $8.3 \times 10^{-2}$ K/s. To examine the reactions detected by DTA, the microstructure of the specimens were observed by optical microscopy, SEM and EPMA. The composition of phases and distribution of alloying elements were determined by energy dispersive X-ray analysis (EDX). Mable's reagent was used as an etchant.

III. Results

1. Densification and phase reactions during sintering

Figure 2 shows dilatometric curves for powder compacts heated to various temperatures and held isothermally at these temperatures. In the case of sintering at 1473 and 1493 K (curve (a) and (b)), the densification rate was very slow; however, in the case of sintering at 1513 and 1533 K (curve (c) and (d)), rapid densification occurred. Figure 3(a), (b) and (c) show the microstructures of specimens sintered at 1493, 1513 and 1553 K for 3.6 ks, respectively. From these micrographs, the sintering was negligible at 1493 K but was significant at 1513 K. The sintering was more pronounced at 1553 K and a large amount of liquid phase was observed. It should be noted that the sintering temperature for the specimen in Fig. 3(b) was only 20 K higher than that for the specimen in Fig. 3(a). This result suggested that the mechanism of densification changed in the temperature range of 1493–1513 K.

In the sintering of superalloy powder, Westerman(2) found that the rapid densification was caused by a small amount of liquid phase. Later, in the sintering of Inconel 718 powder, Hajmrle and Angers(3) observed an...
abrupt change in the sintering rate at a temperature of approximately 1460 K which was considerably lower than the melting range of the alloy. It was interpreted that the fast sintering around 1460 K was due to incipient melting. The formation of liquid phase during the sintering of a superalloy powder, however, has not been examined in detail.

In the present investigation, DTA was performed to detect the formation of a liquid phase during sintering. Figure 4 shows a DTA thermogram of IN-100 powder during heating to 1623 K. Five endothermic reactions were detected, i.e., the reactions in the temperature range of 1397–1498 K (P_5), 1498–1523 K (1st), 1523–1548 K (2nd), 1548–1572 K (3rd) and above 1572 K (L), as shown in Fig. 4. To examine these reactions, microstructures were observed for the specimens sintered at the respective temperatures corresponding to the reactions detected by DTA, i.e. at 1513 K (1st), 1533 K (2nd) and 1553 K (3rd), for 3.6 ks and then cooled to room temperature. A SEM photograph of the specimen sintered at 1513 K (1st) is shown in Fig. 5(a). Blocky $\gamma'$ and $\gamma$ (white region) formed from the liquid phase were observed at the grain boundaries inside the particles. This result suggests that the 1st
reaction, which caused rapid desification, corresponds to incipient melting. A SEM photograph of the specimen sintered at 1533 K (2nd) is shown in Fig. 5(b). This structure is similar to that shown in Fig. 5(a), but a fraction of γ surrounding γ' is slightly larger than that in Fig. 5(a). A SEM photograph of the specimen sintered at 1553 K (3rd) is shown in Fig. 5(c). This is a typical γ-γ' eutectic structure which has been observed in many other superalloys. The reaction L (above 1572 K) corresponds to complete melting. The reaction P55 (1397–1498 K) has no relation to the liquid phase and is discussed later.

2. Phase reactions during solidification of melted powder

It is important to clarify whether or not the reactions detected by DTA during sintering are the reversal of reactions during the slow cooling of a melted powder. During sintering, metastable phases are likely to exist, because powder used in this investigation is produced by relatively rapid cooling (vacuum atomization). To clarify this problem, phase reactions during slow cooling of a melted powder were examined. Figure 6 shows a DTA thermogram during slow cooling of a melted powder. Five exothermic reactions were detected, i.e., the reactions in the temperature range of 1610–1583 K (P1), 1583–1546 K (P2), 1546–1528 K (P3), 1528–1483 K (P4) and 1483–1408 K (P5), as shown in Fig. 6. These reactions are summarized in Fig. 7 and compared with the reactions during sintering. To examine these reactions, microstructures were observed for the specimens slowly cooled from 1623 K to each completion temperature of the reactions and then cooled to room temperature. Figure 8 shows an optical micrograph of the specimen slowly cooled to 1583 K (P1). Dendritic γ and a small amount of blocky MC carbide are observed. Figure 9 shows a SEM photograph of the specimen slowly cooled to 1546 K (P2). This is a typical γ-γ' eutectic structure. These results indicate that primary γ and eutectic γ-γ' are formed by the reactions of P1 and P2, respectively. Figure 10(a), (b) and (c) show SEM photographs for different regions in the same specimen slowly cooled to 1528 K (P3). As shown in Fig. 10(a), a white phase (mark 3A) is surrounding eutectic γ-γ', and a gray phase and a black phase adjoin the white phase. The compositions of gray phase and black phase are shown in Table 3. It was found that the gray phase was enriched with Cr and Mo and the black phase was enriched with Zr.

Fig. 6 Differential thermal analysis thermogram of IN-100 during slow cooling from melt.

Fig. 7 Reactions during slow cooling of melted IN-100 powder and sintering process.

Fig. 8 Optical micrograph of specimens slowly (8.3 × 10⁻² K/s) cooled to 1583 K and rapidly cooled to room temperature.
The white phase (mark 3B) invading eutectic $\gamma-\gamma'$ is observed in Fig. 10(b), and isolated $\gamma'$ in eutectic $\gamma-\gamma'$ is formed through deeper invading as seen in Fig. 10(c). The composition shown in Table 3 suggests that the white phase is $\gamma$. It is concluded from the shape and composition that this $\gamma$ phase may be formed by the reaction between $\gamma'$ in eutectic $\gamma-\gamma'$ and the Cr and Mo enriched melt in the temperature range of $P_3$.

Figure 11(a) shows an SEM photograph of the specimen slowly cooled to 1483 K ($P_4$). Figure 11(b) and (c) are a magnified SEM photograph and a Zr-La image for the region (mark 4A) in Fig. 7(a), respectively. The Cr and Mo enriched phase observed in Fig. 10 disappeared, and the white and black phases appeared (mark 4B). The composition of these phases is shown in Table 4. These results suggest that the Zr enriched phase and $\gamma$ were formed in the temperature range of $P_4$ by the reaction between the Cr and Mo enriched melt and $\gamma'$ in eutectic $\gamma-\gamma'$.

### IV Discussion

It was found that various reactions took place during the sintering process of IN-100 powder and during the slow cooling process of melted IN-100 powder. Since the phase reactions during both processes occurred in approximately the same temperature range as seen in Fig. 7, it is of importance to clarify whether or not the phase reactions during sintering are reversed to those during slow cooling.

Comparing the microstructure in Fig. 5(c) with that in Fig. 9, the typical $\gamma-\gamma'$ eutectic

<table>
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<tr>
<th>Ni</th>
<th>Cr</th>
<th>Co</th>
<th>Ti</th>
<th>Al</th>
<th>Mo</th>
<th>Zr</th>
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<tr>
<td>20.5</td>
<td>39.4</td>
<td>21.1</td>
<td>2.4</td>
<td>0.5</td>
<td>15.9</td>
<td>0.2</td>
</tr>
<tr>
<td>18.2</td>
<td>13.4</td>
<td>19.3</td>
<td>18.8</td>
<td>—</td>
<td>4.7</td>
<td>25.8</td>
</tr>
<tr>
<td>45.9</td>
<td>14.6</td>
<td>21.0</td>
<td>8.2</td>
<td>7.5</td>
<td>2.8</td>
<td>—</td>
</tr>
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Fig. 10 SEM photographs of specimen slowly ($8.3 \times 10^{-2}$ K/s) cooled to 1528 K and rapidly cooled to room temperature.
structure was observed in both cases, and it is considered that the 3rd reaction during sintering is equivalent to the P2 reaction during slow cooling.

It is the most important purpose of this study, on the other hand, to clarify what is taking place in the 1st and 2nd reactions during the sintering process. As seen in Figs. 5(b), (c), 10 and 11, the phases formed by the 2nd and 1st reactions during sintering are very different from those formed by P3 and P4 reactions, although the temperature regions where these reactions occurred were very close, respectively. This difference seems to be reasonable. That is, since the powder used in this study was produced by means of vacuum atomization (relatively rapid cooling rate), the powder is considered to be in a non-equilibrium state and has not reached its equilibrium state in the temperature ranges of 1st and 2nd reactions during sintering. Then, it is considered that the difference would be diminished by increase in the sintering time. To confirm this, powder compacts were held at 1533 K (in the temperature range of the 1st reaction) for an extended time.

Figure 12 shows a SEM photograph of the powder compact held at 1533 K for 25.2 ks (7 h) and then cooled to room temperature. γ (mark 8A) and the Cr and Mo enriched phase (mark 8B) were observed at the grain boundary. This structure is equivalent to the structure formed by a P3 reaction during slow cooling (Fig. 10). Figure 13(a) and (b) show a SEM photograph and Zr-La X-ray image of the powder compact held at 1513 K for

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Cr</th>
<th>Co</th>
<th>Ti</th>
<th>Al</th>
<th>Mo</th>
<th>Zr</th>
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<tbody>
<tr>
<td>Zr rich phase</td>
<td>26.7</td>
<td>7.2</td>
<td>16.4</td>
<td>25.7</td>
<td>—</td>
<td>1.8</td>
<td>22.3</td>
</tr>
<tr>
<td>White phase (γ)</td>
<td>42.4</td>
<td>21.1</td>
<td>20.7</td>
<td>5.7</td>
<td>4.8</td>
<td>4.2</td>
<td>1.2</td>
</tr>
</tbody>
</table>

**Table 4** Result of EPMA for specimen slowly (8.3×10⁻² K/s) cooled to 1483 K and rapidly cooled to room temperature. (at%)
1.73 Ms (20 days) and then cooled to room temperature. This structure, containing Zr, is equivalent to the structure of Fig. 11 which was formed by a $P_4$ reaction during slow cooling.

These observations revealed that the liquid phases which appeared in the temperature ranges of the 1st and 2nd reactions during sintering were non-equilibrium phases. These might result from relatively rapid cooling during the preparation of powder.

Murata et al.\textsuperscript{(8)}, on the other hand, investigated the solidification behavior of IN-100 and the effect of alloying elements on it by means of DTA, microstructure observation, X-ray diffraction and EPMA analysis. They reported different temperatures and different explanations for the reactions from those of the present study. The difference is considered to result from the difference in the composition of raw material, especially in the carbon content, although the contents of other elements slightly differ between the two studies. That is, the IN-100 powder used in the present study is modified for powder metallurgical use and the carbon content is lowered to 0.068%, while IN-100 cast alloy used by Murata et al. contains 0.16% carbon. The solidification behavior must be greatly depended on the carbon content in the alloy, because formation of carbides at high temperatures should selectively consume the carbide forming elements (Ti, Mo, Zr, etc.) and change the composition of the remaining alloy, and as a result, change the amounts and compositions of phases in the following solidification process. This would lead to different results in DTA and microstructure.

Still more variation of the composition of alloy powder may affect the respective reaction temperatures during slow cooling and sintering. During sintering, in particular, the cooling rate in the powder production process may also affect the reaction temperatures, because the cooling rate in the powder production process changes the distribution of alloying elements in each powder particle. In addition, the faster the cooling rate is, the finer the particle size of powder is, and the particle size distribution may affect the reaction temperatures during sintering. To clarify these problems, further investigation of the effect of composition, cooling rate and particle size of powder on the reaction temperatures will be necessary.

The exothermic reaction $P_{65}$ (1483–1408 K) during slow cooling, on the other hand, may correspond to precipitation of $\gamma'$, as reported by Burton\textsuperscript{(9)}. To clarify this problem, the microstructure of the specimens slowly cooled...
from 1623 K to room temperature and then reheated at various temperatures were examined. Figure 14(a), (b) and (c) show SEM photographs of the specimens reheated at 1408, 1453 and 1483 K for 0.9 ks and then quenched in water, respectively. As shown in Fig. 14(a), coarse $\gamma'$ particles were retained in the specimen quenched from 1408 K; however, most of $\gamma'$ particles dissolved in the specimen quenched from 1453 K. Furthermore, $\gamma'$ particles, except for those in eutectic $\gamma$-$\gamma'$, entirely dissolved in the specimen quenched from 1483 K. As a result, it was ascertained that the exothermic reaction $P_{E5}$ during slow cooling precipitated $\gamma'$. The endothermic reaction $P_{S5}$ during sintering occurs in nearly the same temperature range as that for the exothermic reaction $P_{E5}$. It may be concluded that the reaction $P_{S5}$ would be the dissolution of $\gamma'$, although the determination of phases in powder was hard because of its very complex microstructure resulting from rapid cooling.

IV. Conclusion

The sintering behavior of the prealloyed powder of Ni-base superalloy IN-100 was investigated by studying the solidification behavior of melted IN-100 powder by dilatometry, DTA and EPMA. The results were as follows:

1. Rapid densification of powder compacts occurred above 1513 K, while the sintering rate was very slow below 1493 K. The rapid densification around 1513 K was caused by the presence of a small amount of liquid phase (incipient melting).

2. DTA during the sintering process of IN-100 powder and during the cooling process of melted IN-100 powder detected five endothermic and five exothermic reactions, respectively. Microstructure observations revealed that three reactions among the five reactions during sintering were equivalent to those during the solidification process. The reaction in the highest temperature region during sintering corresponds to complete melting and is a reversed reaction during solidification, i.e., formation of primary $\gamma$ from melt. The reaction in the 2nd highest temperature region during both processes corresponds to a $\gamma$-$\gamma'$ eutectic reaction. The reaction in the lowest temperature region corresponds to dissolution of $\gamma'$ during sintering and precipitation of $\gamma'$ during solidification.

3. Two reactions in the intermediate temperature regions during sintering correspond to incipient melting which caused the rapid densification of powder. The microstructure of powder compacts in these temperature regions during sintering approached those during solidification after maintaining the compacts in these temperature regions for extended time. Then, it can be concluded that these two reactions during sintering are not at equilibrium, which resulted from relatively rapid cooling of melt in powder production.

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