Sintering Mechanism in Mixed Powder Compacts of the Fe–Cu–C Ternary System*

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Using mixed powder compacts of the Fe–8.0%Cu–C ternary system containing up to 1.5% graphite, and Fe–Cu–1.0%C ternary system containing up to 12.0%Cu, a study of the effect of graphite content on the elimination of the abnormal expansion during the heating process of the Fe–Cu binary mixed powder compacts was carried out mainly by the differential dilatometric method and thermal analysis.

The results obtained were as follows: In both of the mixed powder compacts of the Fe–8.0%Cu–C ternary system with more than 8% graphite, and of the Fe–Cu–1.0%C ternary system with more than 4.0%Cu, a maximum expansion was observed at a temperature slightly higher than 1090°C during heating and then shrank at higher temperatures, and thermal analysis confirmed that the above-mentioned phenomenon is caused by the liquid phase sintering due to the Fe–Cu–C ternary monotecto-eutectic reaction at 1095°C.

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I. Introduction

The sintered Fe–Cu binary alloys containing 3~25%Cu are widely used as the mechanical parts, and many papers(1)~(10) have been reported on the sintering mechanism of Fe–Cu binary mixed powder compacts and sintering methods for the improvement of the mechanical properties.

According to these papers, it has been confirmed that the Fe–Cu binary mixed powder compacts expand abruptly from about 1083°C of Cu melting, and this expansion (swelling) becomes an obstacle to the sintering of the compacts to be followed.

In order to eliminate this expansion, graphite is added to the Fe–Cu binary mixed powder compacts. Many papers(11)~(16) have been reported about the sintering characteristics of Fe–Cu–C ternary mixed powder compacts, while the elimination mechanism of the expansion by the graphite addition has not yet been clarified.

Therefore, in this experiment, the sintering characteristics of the Fe–Cu–C ternary mixed powder compacts were investigated by means of the differential dilatometric method and the differential thermal analysis method, and the considerations on the elimination mechanism of the abnormal expansion by graphite addition are presented from the viewpoint of the Fe–Cu–C ternary equilibrium.

II. Experimental Procedure

The characteristics of the electrolytic iron powder, electrolytic copper powder, and graphite powder are listed in Table 1. These powders were well mixed at a given proportion, with the addition of 0.3% glycerin as the lubricant and compacted at a pressure of 588 MPa.

The compacts obtained (5 mm × 5 mm × 20 mm) were used as specimens, and the 18–8 stainless steel rods of the same dimensions were used as the neutral.

In order to make clear the sintering behavior, the dimensional changes were measured by the differential dilatometer during heating up to 1150°C at a heating rate of 10°C/min and cooling down to room temperature at about 30°C/min after isothermal sintering for 60 min in a vacuum of 1.3332 × 10⁻³ Pa.

Furthermore, in order to examine the thermal changes related to phase transformations during sintering, differential thermal analysis was carried out for the Fe–8.0% Cu–C and Fe–Cu–1.0%C ternary systems.
Table 1  Characteristics of powders used in this experiment.

<table>
<thead>
<tr>
<th>Powder</th>
<th>Electrolytic Fe</th>
<th>Electrolytic Cu</th>
<th>Graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purity (%)</td>
<td>99.7</td>
<td>99.6</td>
<td>Carbon 99.5%</td>
</tr>
<tr>
<td>App. density (kg/m³)</td>
<td>2.68x10³</td>
<td>1.80x10³</td>
<td>Ash 0.5%</td>
</tr>
<tr>
<td>Flow rate (g/50g)</td>
<td>26.2</td>
<td>40.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particle size in mesh (%)</td>
<td>100~150</td>
<td>23.8</td>
<td>13.5</td>
</tr>
<tr>
<td></td>
<td>150~200</td>
<td>29.5</td>
<td>15.8</td>
</tr>
<tr>
<td></td>
<td>200~250</td>
<td>16.5</td>
<td>27.2</td>
</tr>
<tr>
<td></td>
<td>250~325</td>
<td>17.4</td>
<td>24.5</td>
</tr>
<tr>
<td></td>
<td>325~</td>
<td>12.8</td>
<td>19.0</td>
</tr>
</tbody>
</table>

1.0% C ternary mixed powder compacts using a pure Ni as a neutral during heating up to 1150°C at a constant heating rate of 5°C/min and cooling down to room temperature at a cooling rate of 5°C/min after isothermal sintering for 10 min in a vacuum of 1.3332x10⁻³ Pa.

III. Experimental Results

The differential dilatometric curves of the Fe–Cu binary mixed powder compacts containing up to 20%Cu are shown in Fig. 1. As indicated by the dotted line in Fig. 1, the pure Fe specimen, does not show any prominent characteristics except for the remarkable contraction due to the α→γ transformation during the heating process. Even the specimens with Cu show nearly the same characteristics as the pure iron specimen up to 650°C, while above 650°C, the contraction becomes slightly larger than the pure iron specimen owing to the sintering of copper powders. Since, the α→γ transformation begins at 910°C, it is assumed that Cu has scarcely diffused into iron during sintering in the α-region. From about 1020°C after the α→γ transformation during the heating process, all of the specimens with Cu begin to expand, and especially from the Cu melting point of 1083°C, an abrupt expansion is observed, where the amount of expansion in-
creases nearly in proportion to the Cu content up to 8.0% and then remains constant.

Subsequently, in order to examine how the added graphite eliminates the abnormal expansion of the Fe–Cu binary mixed powder compacts, the sintering characteristics of the Fe–8.0% Cu–C ternary mixed powder compacts containing various amounts of graphite were investigated by the dilatometric method, and the results on the specimens containing up to 0.8% C and more than 1.0% C are shown in Fig. 2 and Fig. 3, respectively.

Even the specimens containing graphite show nearly the same characteristics as that of Fe–8.0% Cu binary mixed powder compacts during heating up to 700°C, while above 700°C, part of carbon diffuses into α-Fe, and a sub-

Fig. 3. Differential dilatometric curves of Fe–8.0% Cu–C ternary mixed powder compacts containing more than 1.0% C, during heating up to 1150°C and isothermal holding at 1150°C for 1 h.

Photo. 1 Microstructure of Fe–8.0% Cu–C ternary mixed powder compacts sintered at 1150°C for 60 min in vacuum: (A) Fe–8.0% Cu, (B) Fe–8.0% Cu–0.2% C, (C) Fe–8.0% Cu–1.0% C, (D) Fe–8.0% Cu–1.5% C.
stalltial contraction due to the $\alpha \rightarrow \gamma$ transformation lasts till 900$^\circ$C.

Immediately after the $\alpha \rightarrow \gamma$ transformation is terminated at about 900$^\circ$C, all of the specimens begin to expand, while during sintering in the $\gamma$ region above 1083$^\circ$C, the melting point of Cu, the elimination of the abnormal expansion by the graphite addition becomes remarkable. In particular, where the added graphite is less than 0.6%, the expansion (swelling) continues throughout the sintering in the $\gamma$ region. On the other hand, all of the specimens with more than 0.8%C contract abruptly from a temperature slightly higher than 1090$^\circ$C.

The microstructure of Fe–8.0%Cu binary sintered compacts is shown in Photo. 1(A), where almost all of the added copper has diffused into iron, while in the Fe–8.0%Cu–0.2%C ternary sintered structure of Photo. 1(B), the non-diffused copper has remained. With respect to the Fe–8.0%Cu–1.0%C ternary sintered structure of Photo. 1(C), a homogeneous eutectoid structure is observed, where the amount of non-diffused copper has increased, and in the Fe–8.0%Cu–1.5%C ternary sintered structure of Photo. 1(D), the precipitated Fe$_3$C develops into grain boundaries like a network.

All of the above-mentioned microstructures correspond fairly well to the differential dilatometric curves in Fig. 2 and Fig. 3.

The line analysis profiles of Cu along the arrows shown in Photo. 1(A) and Photo. 1(C) are presented in Fig. 4. As to the Fe–8.0%Cu binary system, a gentle slope of the Cu concentration from 10%Cu at the circumference to 6.0%Cu at the inner area is observed. The maximum Cu concentration of 96% was observed in the Fe–8.0%Cu–1.0%C ternary sintered compacts, while inside the iron powder particle, the concentration of Cu was uniformly 6.0%, which suggests that the good quality of sintered Cu steel was obtained.

For the purpose of investigating the reason why all of the specimens with more than 0.8%C show abrupt shrinkage from a temperature slightly higher than 1090$^\circ$C. The differential thermal analysis was carried out, and the results are shown in Fig. 5.

The Fe–8.0%Cu binary mixed powder compacts shows an endothermic peak due to Cu melting at 1083°C during heating, while during the cooling process, it shows only one exothermic peak at 820°C due to eutectoid reaction, which means that all of added Cu has diffused into iron during heating up to 1150°C and isothermal holding.

Among the specimens with graphite, the two specimens with 0.2% and 0.6%C show only one endothermic peak at 1083°C during
heating due to Cu melting as that of the Fe–8.0%Cu binary mixed powder compacts, while during the cooling process, both of them show the exothermic peak at 1083°C due to Cu solidification, where the height of the exothermic peak for the former is lower than that for the latter.

Furthermore, as to the specimens with more than 0.8%C, another endothermic peak at 1095°C during heating is observed, besides the above-mentioned endothermic peak due to Cu melting, which suggests the appearance of a new liquid due to the non-variant reaction. During the cooling process, these specimens show the exothermic peak at 1095°C, which means that the newly produced liquid has remained throughout the sintering process in the γ region.

Subsequently, in order to examine the endothermic reaction at 1095°C during heating for the specimens with more than 0.8%C, the secondary electron images and the line analysis of Fe, Cu, and C were carried out with respect to the two specimens with 0.6% or 1.0%C and quenched into ice-water from 1080 and 1100°C during heating. The results are presented in Photo. 2 and Fig. 6.

Quenched from 1080°C, the added Cu retains its original form in both specimens, as shown in Photo. 2(A) of the specimen with 0.6%C and Photo. 2(B) of the specimen with 1.0%C. As to the specimen with 0.6%C quenched from
1100°C, only the remaining Cu decreases, as shown in Photo. 2(C), while the specimen with 1.0% C shows mixed phases, as shown in Photo. 2(D). According to the line analysis by EPMA, corresponding to the above-mentioned secondary electron images of Fig. 7(A), (B) and (C), scarcely any Fe and C are not contained in the remaining Cu, and it is shown that carbon is distributed in the Fe matrix fairly well, and Cu diffuses into Fe slightly. However, in the mixed phase of Photo. 5(D) composed of Fe, Cu, and C, the irregularity of the concentration is observed, so it seems that the composite phase due to the ternary non-variant reaction is produced.

Subsequently, the dimensional changes for the Fe–Cu–1.0% C ternary mixed powder compacts were examined by the differential dilatometric method, and the results are presented in Fig. 7 and Fig. 8.

All of the specimens show nearly the same characteristics up to 900°C during heating, while they begin to expand abruptly from 1020°C in the γ region, where the amount of expansion increases nearly in proportion to the Cu content up to 6.0%, and then remains constant.

After this expansion, the specimen with 1.0% Cu begins to contract from 1080°C, and the specimen with 2.0~3.0% Cu begin to contract from a temperature slightly higher than 1083°C, the Cu melting point. Furthermore, all of the specimens containing more than 4.0% Cu show the maximum expansion
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Fig. 7 Differential dilatometric curves of Fe–Cu–1.0%C ternary mixed powder compacts containing up to 5.0%Cu during heating up to 1150°C and isothermal holding at 1150°C for 1 h.

Fig. 8 Differential dilatometric curves of Fe–Cu–1.0%C ternary mixed powder compacts containing more than 6.0%Cu, during heating up to 1150°C and isothermal holding at 1150°C for 1 h.

at a temperature slightly higher than 1090°C and then begin to contract. The remarkable characteristics during isothermal holding, appears in the specimens with more than 6.0%Cu, where the amount of shrinkage increases in proportion to the addition of Cu. During the cooling process any prominent changes is not observed except for the expansion due to the eutectoid reaction.

Figure 9 shows the total amount of expansion observed in the γ-region during the heating process, and the dimensional changes at room temperature after sintering with addition of Cu.

The total amount of the abnormal expansion increases with increasing Cu content up to 6.0%, beyond which the value becomes con-
thermic peak due to the Cu melting at 1083°C during heating, while in the γ-region higher than this temperature, no thermal changes were observed, and during cooling, only one exothermic peak at 710°C due to the eutectoid reaction was noticed.

However, the specimens with more than 4.0%Cu show the same endothermic peak at 1095°C as observed in the Fe–8.0%Cu–C ternary mixed powder compacts with more than 0.8%C, besides the above-mentioned endothermic peak due to Cu melting. During the cooling process, the specimens containing up to 4.0%Cu, show only one exothermic peak due to the eutectoid reaction, while it is noted that in the case of the specimens with more than 6.0%Cu, the exothermic reaction due to the solidification of liquid appears at 1095°C, which means that the liquid produced by the non-variant reaction during heating for the specimens with more than 6.0%Cu has remained throughout the sintering process in the γ-region.

IV. Discussion

The Fe–Cu–Fe₃C pseudoternary phase-diagram reported by Hamazumi and Ohira(17) is shown in Fig. 11. According to this phase diagram, the discussion on the sintering mechanism of the Fe–Cu–C ternary mixed powder compacts was carried out from the viewpoint of Fe–Cu–C ternary equilibrium.

All of the Fe–8.0%Cu–C ternary mixed powder compacts containing up to 0.6%C in Fig. 6 show only one endothermic peak due to Cu melting at 1083°C during heating, while the specimens with 0.8% or 1.0%C show another endothermic peak at a temperature slightly higher than 1090°C during heating, besides the above-mentioned one due to Cu melting. This second endothermic peak must be related to the non-variant reactivity of the peritectoeutectic reaction at 1092°C shown by (1), or that of monotecto-eutectic reaction at 1095°C shown by (2).

\[ M(\gamma) + Fe_3C \xrightarrow{\text{heating}} L(\gamma-Fe) + K(\text{melt}), \quad (1) \]

\[ H(\gamma-Fe) + I(\text{melt}) + Fe_3C \xrightarrow{\text{cooling}} E(\text{melt}). \quad (2) \]

In the first place, we consider the possibility of the production of a new liquid by ternary peritecto-eutectic reaction.

Fig. 11 The qualitative diagram of the ternary system Fe–Cu–Fe₃C.
In order to produce liquid \((K)\) by reaction (1), the existence of \(\varepsilon\) phase \((M)\) and Fe\(_3\)C at 1092°C is necessary. However, even if the non-diffused graphite coexists where graphite diffuses into iron during heating for the Fe–8.0% Cu–C ternary mixed powder compacts containing 0.8 or 1.0% C, the generation of Fe\(_3\)C is impossible, and even if the already molten Cu diffuses into iron at 1092°C, the production of solid \(\varepsilon\) is also impossible. In this way, the existence of Fe\(_3\)C and \(\varepsilon\) is impossible at 1092°C. It is thus unnecessary to consider the peritecto-eutectic reaction shown by (1). Therefore, it is concluded that the new liquid is preferentially produced by the ternary monotecto-eutectic reaction at 1095°C during heating.

During the cooling of the Fe–8.0% Cu binary mixed powder compacts, only one exothermic reaction due to the eutectoid reaction is observed, from which it is considered that all of the added Cu has diffused into iron during heating and isothermal holding in the \(\gamma\)-region. In the specimens containing 0.2% C or 0.6% C, the exothermic peak due to Cu melting at 1083°C during cooling is observed, which proves that the super-saturated Cu remains non-diffused. In this case, the phenomenon that the amount of exothermic reaction for the specimen with 0.6% C is larger than that for the specimen with 0.2% C may be attributed to two reasons. One reason is that the solubility of Cu into Fe decreases in proportion to the carbon content in iron as shown in Fig. 11, and the other is that the decrement of the diffusion velocity of Cu into \(\gamma\)-iron with increasing C content in \(\gamma\)-iron, though it needs to be examined further.

The specimens with 0.8, and 1.0% C show the exothermic peak due to the monotecto-eutectic reaction at 1095°C during the cooling process, where the eutectoid temperature is lowered depending upon the amount of the additional graphite, and it becomes 698°C for the specimen with 1.0% C, which is slightly supercooled from 702°C, the Fe–Cu–C ternary eutectoid temperature.

Subsequently, it is evident from Fig. 10 that the specimen with 3.0% Cu among the Fe–Cu–1.0% C ternary mixed powder compacts shows only one endothermic peak due to Cu melting at 1083°C, while the specimens with more than 4.0% Cu show another endothermic peak due to a monotecto-eutectic reaction at 1095°C in addition to the one due to Cu melting, and it is confirmed that this peak enlarges with increasing addition of Cu.

During the cooling process for the specimen with 4.0% Cu, the exothermic reaction due to solidification is not observed, which proves that the liquid produced by the monotecto-eutectic reaction at 1095°C has diffused into \(\gamma\)-Fe during heating in the \(\gamma\)-region higher than 1095°C, while the specimens containing more than 6.0% Cu show the exothermic peak due to the monotecto-eutectic reaction at 1095°C. Therefore, for the specimens with more than 6.0% Cu, the liquid produced by the monotecto-eutectic reaction during heating has remained throughout the sintering process at temperatures higher than 1095°C.

From the above-mentioned consideration, we can make clear the sintering behavior of the Fe–Cu–C ternary system.

First of all, the phenomenon that the Fe–8.0% Cu–C ternary mixed powder compacts with more than 0.8% C contracts from a definite temperature slightly higher than 1090°C during heating, is explained by the liquid phase sintering due to the newly produced liquid by a ternary monotecto-eutectic reaction at 1095°C.

Subsequently, the thermal analysis of the Fe–Cu–1.0% C system in Fig. 10 verifies that, in the case of the specimens with more than 6.0% Cu, the liquid phase sintering due to the newly produced liquid by the monotecto-eutectic reaction at 1095°C plays an important role, while in the case of the specimen with 4.0% Cu, it is considered that the same liquid produced by the monotecto-eutectic reaction has diffused into \(\gamma\)-Fe and disappeared during sintering in the \(\gamma\)-region higher than 1095°C. It is to be noted that the newly produced liquid composed of the complicated monotecto-eutectic structure containing Cu, Fe, and C, as shown in Fig. 6, is different from the pure Cu liquid.

From the above-mentioned consideration, the phenomenon that the amount of expansion observed during sintering becomes constant for the Fe–Cu binary system with more than
8.0%Cu, and the Fe–Cu–1.0%C ternary system with more than 6.0%Cu is considered to be due to the liquid phase sintering, and the phenomenon that the amount of expansion for the former surpasses that for the latter in the case of the same amount of added Cu, is explained by the difference between the components of the two liquids.

V. Conclusion

As the result of thermal analysis, the Fe–8.0%Cu–C ternary mixed powder compacts with more than 0.8%C, and the Fe–Cu–1.0%C ternary mixed powder compacts with more than 6.0%Cu showed the second endothermic peak at 1095°C due to the Fe–Cu–C ternary monotecto-eutectic reaction at 1095°C during heating, besides the first endothermic peak at 1083°C due to Cu melting, and it was clarified that the newly produced monotecto-eutectic liquid has remained throughout the sintering process at temperatures higher than 1095°C in both specimens.

Therefore it was confirmed that the liquid phase sintering due to the above-mentioned monotecto-eutectic liquid plays an important role in both cases.

REFERENCES

(10) T. Watanabe and M. Kawaguchi: Transactions of the Castings Research Ravoratory, No. 27 (1973), 65.
(13) P. U. Gummeson und L. Forss: Planseeberichte fur P/M, 5 (1957), 94.