Microstructure and Mechanical Properties of Consolidated Rapidly Solidified Fe-30Cr-5Al Alloy Powder[†]

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Rapidly solidified Fe-30Cr-5Al alloy powders containing Ce up to 0.69 mass% produced by the Rotating-Water-Atomization Process were sintered and sheath-rolled. Rapidly solidified powders without Ce could be well sintered at temperatures more than 1673 K for time more than 3.6 ks. The grain size grew from 20 to 30 μm after annealing at 1673 K for 14.4 ks. The tensile strength of compacted Fe-30Cr-5Al powder was in the range from 350 to 450 MPa, and the elongation was in the range from 2 to 3%. The surface oxidation of particle was increased with the addition of Ce. However, it was suppressed in the Rotating-Water-Atomization under Ar atmosphere. The tensile strength of sheath-rolled Fe-30Cr-5Al-0.69Ce powder was 210 MPa. The tensile strength of compacted powders was superior to that of the as-cast material.

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I. Introduction

Because Fe-Cr-Al stainless steels have good heat resistance properties, they have been studied by many researchers⁽¹⁾⁻⁽⁴⁾. With the development of chemical industry, high temperature corrosion has been an important problem. We⁽⁵⁾⁽⁶⁾ found that the R_2M_{17} type intermetallic compound formed in an Fe-30Cr-5Al alloy containing Ce improves the high temperature corrosion resistance against 80% Na_2SO_4 -20% NaCl molten salt. The improvement mechanism is the following: In the earlier stage of the corrosion period, Al_2O_3 acting as the protective layer to the corrosion is formed with help of the R_2M_{17} intermetallic compound. The Al_2O_3 layer prevents the diffusion of oxygen, chlorine and sulfur from the environment to the alloy and alloying elements to the environment. On the other hand, the addition of Ce decreases the elongation of the alloy, resulting in difficulty in hot working and machining. Even for the case without Ce additions, this alloy must be rolled with very low reduction to improve mechanical properties⁽⁷⁾ and conventional hot rolling could not be applied for this alloy even at 1673 K. It has been reported⁽⁸⁾⁻⁽¹⁰⁾ that a rapid quenching can suppress the generation of coarse crystal and improve ductility. Therefore, in the previous paper⁽¹¹⁾, the Rotating-Water-Atomization Process⁽¹²⁾ was applied to the alloys and the properties of rapidly solidified particles were examined in detail. In the present

work, rapidly solidified powders^{††} produced by the Rotating-Water-Atomization Process were sintered or sheath-rolled⁽¹³⁾. Microstructure and mechanical properties of the consolidated powder were investigated.

II. Experimental Procedures

The preparation of sample powder was described in the previous paper⁽¹¹⁾. Particles under 300 μm in size of the atomized powder (its amount was about 90% of total mass and the mean diameter was about 100 μm) were used for sintering and sheath-rolling. After these particles were well mixed, those weighing about 2.5 g were cold-compacted to a plate of 50 mm in length, 5 mm in width and 1.5 mm in thickness at 1500 MPa for 60 s. The porosity of the cold-compacted sample was about 10%. The cold-compacted sample was sintered in H_2 atmosphere of 1.01×10^5 Pa at sintering temperatures between 1223 and 1773 K. For comparison, rapidly solidified particles weighing about 5 g were inserted in a SUS304 stainless steel pipe of 8 mm and 6 mm in outside and internal diameters and cold-compacted to a cylindrical shape at 1500 MPa for 60 s. The porosity was between 30 and 40%. Both ends of the pipe were spot-welded in vacuum of 0.1 Pa. The pipe was sheath-rolled to 5 mm in thickness (the inserted powder in the pipe was about 3 mm in thickness) at the room temperature, followed by heating in the same manner as sintered samples. After heating, the sample was immediately sheath-rolled to 3.5 mm in thickness (the powder was

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^{††} It seems that the surface oxidation of particles atomized in water is heavier than that atomized in inactive gas. However, in the present experiment, we applied the Rotating-Water-Atomization Process which is economical for small lot production.

about 1.5 mm in thickness). After sheath-rolling, the outside of the SUS304 pipe was removed from sheath-rolled sample. Optical and scanning electron microscope observation and tensile testing were carried out for both sintered and sheath-rolled powders.

III. Experimental Results and Discussion

1. Consolidating conditions of powders

To determine the consolidating conditions of powders,

Fig. 1 Structure of Fe-30Cr-5Al alloy as-sintered at various temperatures for 3.6 ks. (a) 1223 K (b) 1523 K (c) 1623 K (d) 1673 K (3) 1723 K (f) 1773 K

Fig. 2 Structure of Fe-30Cr-5Al alloy as-sintered at 1673 K. (a) for 1.8 ks (b) for 3.6 ks (c) for 7.2 ks (d) for 14.4 ks

Fig. 3 Structure of Fe-30Cr-5Al-Ce alloy as-sintered at 1673 K for 3.6 ks. (a) without Ce (b) 0.69 mass% Ce (c) without Ce (d) 0.68 mass%Ce. Powder of (a) and (b) has been atomized in water under air atmosphere. Powder of (c) and (d) has been atomized in water under Ar atmosphere.

sintered powders were subjected to optical microscope observation. Figure 1 shows the change in the microstructure of the Fe-30Cr-5Al alloy powder atomized in water under air atmosphere with sintering temperature. At the sintering temperatures less than 1623 K, interfaces between particles were distinguishable clearly (see Fig. 1(a)–(c)). On the other hand, at the sintering temperatures higher than 1673 K, interfaces were not clear and bonding of particles was observed (see Fig. 1(d)–(f)). Figure 2 shows micro structure of powder as-sintered at 1673 K for 1.8–14.4 ks. At the sintering times longer than 3.6 ks, bonding of particles was observed (see Fig. 2(b)–(d)). From these results, consolidation of the powder was carried out at 1673 K for 3.6 ks in the following experiments.

2. Change in the microstructure with Ce additions and ejection atmosphere

Figure 3 shows the change in the microstructure of sintered powder with Ce additions and the atmosphere of water-atomization. By comparison of Fig. 3(a) and (b), it was confirmed that particles containing Ce could not well be sintered. However, particles atomized under Ar atmosphere were better sintered than those atomized under air as shown in Fig. 3(c) and (d). We⁽¹¹⁾ reported that particle surface oxidation increased with Ce addition. Therefore, increasing surface oxidation of particles with Ce addition is expected to be one of main factors

Fig. 4 Oxygen content of Fe-30Cr-5Al-Ce powders produced by the Rotating-Water-Atomization process. (Particle diameter is in the range from 100 to 150 μ m)

● : as-atomized in water under air atmosphere
○ : as-atomized in water under Ar atmosphere

causing difficulty in bonding of particles. Figure 4 shows the effect of Ce additions on the oxygen content of the particles in the size ranging from 100 to 150 μ m. The oxygen content of the particles atomized under air increased drastically with Ce content and that of the powder containing 0.69 mass%Ce was about 0.4 mass%. However, when the atomization atmosphere was Ar, the

oxygen content of the particles containing 0.68 mass%Ce was about 0.2 mass%. Hence, when the atomization atmosphere was Ar, it was expected that the surface oxidation of particles was suppressed and the bonded area of the interface between particles increased. The microstructure of the sheath-rolled powders qualitatively agreed with the results of the sintered powders.

3. EPMA analysis of interface between particles

To examine the bonding of particles in more detail, interface between particles was subjected to scanning electron microscope observation and EPMA analysis, as shown in Fig. 5. Particles could be bonded at the sintering temperatures higher than 1673 K. This was almost the same tendency as the result of Fig. 1. However, even at 1773 K, a few parts of interface were not bonded. Figure 4(g) and (h) shows the result of EPMA analysis on the interfaces between particles in Fig. 4(d). Figure 4(g) and (h) clearly reveal the high concentration of Al and O at the unbonded interface. Al_2O_3 presumably exists at the unbonded interface. These Al_2O_3 were expected to be formed during atomization rather than sintering, because sintering was carried out under H_2 atmosphere.

To clarify this fact, EPMA analysis on the interface of cold compacted powder before sintering was carried out, as shown in Fig. 6. Surface oxide films of particles were formed before sintering. The amount of Al_2O_3 at the interface increased with Ce additions (see Fig. 6(b)) and decreased when atmosphere of atomization was Ar (see Fig. 6(c) and (d)). These facts were qualitatively agreed with the experimental results in the previous paper⁽¹¹⁾ and in Fig. 4 of this paper. To examine the ability of consolidation of powder containing Ce, Fig. 6(b) was compared with Fig. 6(d). The Al_2O_3 oxide film at the interface between cold-compacted particles atomized under Ar was broken to some pieces by compression. Therefore, the powders containing Ce were also expected to be able to be consolidated, when atomization was performed under Ar. Figure 7 shows the vicinity of the interface between sintered particles. Interface between sintered particles qualitatively agreed with that between cold-compacted particles in Fig. 6. Namely, to consolidated the powder produced by the Rotating-Water-Atomization Process, particles surface oxidation should be suppressed so slight that the particle surface oxide film could be broken to some pieces by compression.

Fig. 5 Microstructure and X-ray distribution of images of as-sintered Fe-30Cr-5Al alloy sintered at various temperatures for 3.6 ks. (a) 1223 K (b) 1523 K (c) 1623 K (d) 1673 K (e) 1723 K (f) 1773 K (g) and (h) X-ray distribution of images of (d).

Fig. 6 Microstructure and X-ray distribution of images of Fe-30Cr-5Al-Ce alloy as-compressed at R. T.
 (a) without Ce (b) 0.69 mass%Ce (c) without Ce (d) 0.68 mass%Ce. Powder of (a) and (b) has been atomized in water under air atmosphere. Powder of (c) and (d) has been atomized in water under Ar atmosphere.

Fig. 7 Microstructure and X-ray distribution of images of Fe-30Cr-5Al-Ce alloy as-sintered at 1673 K for 3.6 ks.
 (a) as-sintered Fe-30Cr-5Al alloy powder atomized in water under air atmosphere
 (b) as-sintered Fe-30Cr-5Al-0.69Ce alloy powder atomized in water under air atmosphere
 (c) as-sintered Fe-30Cr-5Al-0.68Ce alloy powder atomized in water under Ar atmosphere

4. Change in the microstructure of particles with sintering

To clarify the change in the microstructure of particles with sintering, cold-compacted powders were sintered at various sintering temperatures and times. Sintered powders were etched electrolytically by oxalic acid aqueous solution and observed by optical microscopy. Figure 8 shows the change in the grain size of sintered particles with sintering temperature and time. The grain size of the particles as-atomized was about $10\text{ }\mu\text{m}$ and that of particles annealed at 1673 K was about $30\text{ }\mu\text{m}^{(11)}$. Although the grain size also grew with sintering, the grain size of the particles sintered at 1773 K for 3.6 ks was kept in the range from 20 to $30\text{ }\mu\text{m}$ (see Fig. 8(b)). The grain size of the particles sintered at 1673 K for 14.4 ks was also kept in the range from 20 to $30\text{ }\mu\text{m}$ (see Fig. 8(c)). In the previous paper⁽⁷⁾, we reported that the metal

Fig. 8 Change in the grain size of Fe-30Cr-5Al sintered alloy with sintering temperature and time.

Fig. 9 Relative density of Fe-30Cr-5Al compacted powder.
○: as-sintered □: as-sheath-rolled

mold cast rod rolled with low reduction resulted in its grain size from 20 to $30\text{ }\mu\text{m}$, tensile strength of about 600 MPa and elongation from 15 to 20% . Namely, when the powder consolidated at 1673 K for 3.6 ks are bonded completely and contain no porosity, the consolidated powder is expected to have almost the same mechanical properties as the rolled cast rod.

5. Density of consolidated powder

Figure 9 shows the density of the powders sintered and sheath-rolled at 1673 K . The apparent density of sintered powder was about $6.5 \times 10^3\text{ kg}\cdot\text{m}^{-3}$; hence, the porosity was about 10% . The porosity decreased with sintering and that value attained about 5% at the sintering time of 3.6 ks . However, the porosity was about 5% even after sintering for 14.4 ks . On the other hand, the porosity of the sheath-rolled powder after sintering for 1.8 ks was about 0% . It suggests that compaction at high temperatures is important in the consolidation of the powder of brittle alloy such as Fe-30Cr-5Al alloy.

6. Mechanical properties

Figure 10 shows the change in the tensile strength of sintered powders with sintering temperature and time. The tensile strength of the sintered powder not containing Ce and atomized under air atmosphere increased with increasing sintering temperature. This value was saturated at the sintering temperature higher than 1673 K and at the sintering time longer than 3.6 ks . These results were qualitatively consistent with the results in Fig. 1 and Fig. 5. Figure 11 shows the change in the tensile strength of the consolidated powders with Ce content. In the case without Ce, the tensile strength of sintered powder was in the range from 350 to 400 MPa and that of sheath-rolled powder was in the range from 400 to 450 MPa . These values were lower than that of the rod subjected to the low reduction rolling⁽⁷⁾ but much higher than that of the cast rod⁽⁷⁾. However, the tensile strength of the cast rod decreases drastically with increasing Ce content and this

Fig. 10 Change in the tensile strength of Fe-30Cr-5Al sintered alloy with sintering temperature and time.

alloy containing Ce more than 0.2 mass% cannot be rolled even by the low reduction rolling⁽⁷⁾. The tensile strength of the consolidated powder produced by the Rotating-Water-Atomization Process also decreased with increasing Ce content. However, the tensile strength of sheath-rolled Fe-30Cr-5Al-0.68Ce alloy powder atomized under Ar was 210 MPa and this value was almost the same value as that of the as-cast rod not containing Ce. Although the elongation of the as-cast rod is about 0%, the elongations of the sintered powder and the sheath-rolled powder were about 2 and 3%, respectively. It suggests that both the tensile strength and elongation of this alloy not containing Ce could be improved by means of consolidation of the rapidly solidified powder. However, the elongation of the consolidated powder containing Ce was about 0%. Both the oxygen content of the Fe-30Cr-5Al alloy powder atomized in water under air and that of the Fe-30Cr-5Al-0.68Ce alloy powder atomized in water under Ar were about 0.2 mass%. When the thickness, physical properties and adherence of the surface oxide films of the particles containing Ce were the same as those of the particles not containing Ce, the tensile strength and elongation of the consolidated Fe-30Cr-5Al-0.68Ce powder atomized in water under Ar would be about 400 MPa and 2%, respectively. However, these values were 210 MPa and about 0%, respectively. In the previous paper⁽¹¹⁾, we reported that particle shape became spherical and particle surface became smooth with Ce additions. These results suggest that specific surface area decreases with Ce additions. Hence, even if the amount of surface oxidation of particles containing Ce is equal to that of particles not containing Ce, the surface oxide film of particles containing Ce would be thicker than that of the particles not containing Ce. Therefore, the existence of particle surface oxide films preventing particles from bonding might be the primary factor for the decreasing tensile strength and elongation of consolidated powder

Fig. 11 Change in the tensile strength of Fe-30Cr-5Al-Ce alloy with cerium content.

●: as cast, ○ and ○: as sintered, □ and □: as sheath-rolled
Powder of ○ and □ has been atomized under air atmosphere.
Powder of ○ and □ has been atomized under Ar atmosphere.

Fig. 12 SEM fractography of fracture of Fe-30Cr-5Al-Ce alloy as sheath-rolled at 1673 K.

(a) without Ce (b) 0.69 mass%Ce (c) without Ce (d) 0.68 mass%Ce
Powder of (a) and (b) has been atomized under air atmosphere.
Powder of (c) and (d) has been atomized under Ar atmosphere.

containing Ce. However, more detailed researches should be performed. SEM micrographs of fractured specimens are shown in Fig. 12(a)-(d). Dimples were observed on the fracture surfaces of all specimens. Namely, the particles of sheath-rolled powder are expected to be ductile similar to particles as-atomized. Primary particle boundaries as well as transgranular cracks were observed on the fracture surface. However, increasing strength of interfaces between particles by means of increasing reduction of sheath-rolling or using hot extrusion was expected to improve the mechanical properties of consolidated powder.

IV. Conclusion

Rapidly solidified Fe-30Cr-5Al alloy powders containing Ce up to 0.69 mass% produced by the Rotating-Water-Atomization Process were sintered and sheath-rolled. The following results are obtained.

- (1) Rapidly solidified powders without Ce could be well sintered at temperatures higher than 1673 K for times longer than 3.6 ks.
- (2) The grain size grew from 20 to 30 μm after sintering at 1673 K for 14.4 ks.
- (3) The surface oxidation of particles was increased with the addition of Ce. However, it was suppressed in Rotating-Water-Atomization under Ar atmosphere.

(4) The tensile strength of consolidated Fe-30Cr-5Al powder was in the range from 350 to 450 MPa, and the elongation was in the range from 2 to 3%. The tensile strength of sheath-rolled Fe-30Cr-5Al-0.68Ce powder was 210 MPa. The tensile strength of consolidated powders was superior to that of the as-cast material.

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