Corrosion- and Wear-Resistant Alloys for Cylinders of Fluoroplastic Shaping Machines

By Masao Morishita*, Hiroshi Kawatani*, Akira Shimamoto*, Nobuyasu Kawai* and Toshiyuki Minamide**

Corrosion- and wear-resistant alloys for the cylinders of fluoroplastic shaping machines were developed by the HIP (Hot Isostatic Pressing) process. To determine the optimum alloy composition, corrosion resistance of Ar arc melted alloys of various compositions was initially investigated. After the optimum alloy composition was found, the new corrosion- and wear-resistant alloys were produced by the HIP process.

The arc melted alloy to which only B and Si were added to improve the wear resistance of Hastelloy C, was rapidly corroded in hydrofluoric acid. On the other hand, the alloy with not only B and Si but also Cu added, showed the same high corrosion resistance as Hastelloy C. It was found that the addition of Cu significantly affected the corrosion resistance of Ni-Cr-Mo-B-Si alloys. The compositions of the new alloys for the cylinders of fluoroplastic shaping machines was determined. The compositions of the new alloys were Ni-15.0 mass% Cr-15.0Mo-2.5B-3.0Si-1.0Cu (named C-700) and Ni-17.5Cr-24.0Mo-3.6B-2.9Si-1.0Cu (C-703). The prealloyed C-700 alloy powder was sintered by the HIP process. In the case of the C-703 alloy, the Ni-Mo-Si-Cu alloy powder and the CrB powder were reaction sintered by the HIP method. The CrB particles were transformed into M3B2 particles during the HIP process. The corrosion resistance of C-700 and C-703 to HF were slightly superior to that of Hastelloy C. The wear resistance of C-700 was 70 times better than that of Hastelloy C. Furthermore, the wear resistance of C-703 was 150 times better than that of Hastelloy C. It was found that C-700 and C-703 alloys have high performance for the cylinders of fluoroplastic shaping machines.

(Received July 26, 1988)

Keywords: corrosion- and wear-resistant alloy, cylinder of fluoroplastic shaping machine, powder metallurgy, hot isostatic pressing, rapid solidification, reaction sintering

I. Introduction

The highly corrosion resistant Hastelloy C alloy has been conventionally used for the cylinders of fluoroplastic shaping machines, because a corrosive HF gas is generated during the injection or extrusion molding of fluoroplastics. However, fluoroplastics become reinforced by hard materials (glass, carbon fiber, etc.). It is vital that the alloys of the cylinders have wear resistance as well as corrosion resistance. Recently, the high performance bimetallic cylinders of plastic shaping machines have been produced by the HIP process(1). In this method corrosion- and wear-resistant alloy powders are sintered and bonded to the inner surface of the steel cylinder body by the HIP process. The object of the present work was to develop super corrosion- and wear-resistant alloys for the cylinders of fluoroplastic shaping machines by the HIP process.

II. Experimental Procedure

1. Alloy design

To determine the optimum alloy composition, the corrosion resistance of Ar arc melting alloys of various compositions was investigated.

Initially the effect of B, Si and Cu on the corrosion resistance of the alloys was studied. The corrosion resistance of specimens 1 and 2 shown in Table 1 was examined in comparison with Hastelloy C. Specimen 1 had additions of 3%B and 3%Si to improve the wear resistance.* Materials Research Laboratories, Kobe Steel LTD., Chuo-ku, Kobe 651, Japan.
** Machinery Division, Kobe Steel LTD., Arai, Takasago 676, Japan.

* Materials Research Laboratories, Kobe Steel LTD., Chuo-ku, Kobe 651, Japan.
** Machinery Division, Kobe Steel LTD., Arai, Takasago 676, Japan.
of Hastelloy C. In the case of specimen 2, not only 3% B and 3% Si but also 1% Cu were added. The conventional method for producing cylinders of various plastic shaping machines is centrifugal casting. In this method, corrosion- and wear-resistant alloys were coated on the inner surface of a cylinder body by centrifugal casting. The corrosion resistance of the most widely used centrifugally cast alloy included in Table 1 was compared with that of specimens 1 and 2.

To determine the optimum Cu content, the effect of the Cu content on the corrosion resistance of Ni-15Cr-15Mo-3Si-3B alloys was investigated.

The effects of Cr and Mo contents on the corrosion resistance were investigated. Figure 1 shows the Cr and Mo contents of the Ni-xCr-yMo-3Si-3B-1Cu arc melted alloys examined. Three types of alloys, i.e. the ratio of Mo/Cr>1.0, Mo/Cr=1.0, Mo/Cr<1.0 were melted. In addition, the effect of the Co content on corrosion resistance was studied.

2. Production method of HIP-processed alloy

The optimum alloy compositions for HIP-processing for the cylinders of fluoroplastic shaping machine were determined after corrosion tests. Table 2 shows the compositions of the HIP-processed alloys named C-700 and C-703.

The following production methods were used for these alloys: In the case of the C-700 alloy, initially the alloy powder was produced by the vacuum melting-Ar gas atomization method. This C-700 alloy powder was vacuum sealed in a stainless steel container and treated with HIP in Ar at 1223 K. The pressure during the HIP process was 98 MPa.

In the case of C-703 alloy, the reaction sintering method was applied. It was difficult to prepare directly the alloy powder with the composition of C-703 by atomization, because the higher the content of Mo, the higher the melting point and viscosity of the melt. Initially, the Ni-31.0Mo-3.8Si-1.1Cu alloy powder was produced by the vacuum melting-Ar gas atomization method, as described above for C-700. Next, this Ni-31.0Mo-3.8Si-1.1Cu alloy powder and the CrB powder were mixed for 25.2 ks in Ar by using an Attriter. The ratio of alloy powder to the CrB was 79.0/21.0. Then this mixed powder was processed by HIP as described for C-700. The CrB particles were transformed into NbB particles during the HIP processing.

3. Corrosion and wear resistance test

The corrosion and wear resistance test pieces were cut from arc melted alloys and HIP-processed alloys. The size (mm) of the corrosion test pieces were ø6.5 x 10. The mass loss of test pieces were measured after corrosion tests. Corrosion solutions used were 10% HF, 15%
HCl, 15% H₂SO₄ and 6% HNO₃. The corrosion test temperature was 323 K and the time was 360 ks (100 h).

The wear resistance of the alloys was evaluated by the Ohgoshi type contact wear test. Figure 2 shows the shape of the specimen. After the rotor was brought into contact with the specimen, it was rotated. The sliding conditions are also shown in Fig. 2. The width of the friction trace was measured and converted into wear loss\(^3\). The wear loss value indicates specific wear (\(m³/m·N\))\(^4\).

After the above described corrosion and wear resistance tests, the powders of the new high corrosion- and wear-resistant alloys were sintered and bonded to the inner surface of the steel cylinder body by the HIP process.

### III. Results and Discussion

1. **The effects of B, Si and Cu on the corrosion resistance of the alloys**

   Figure 3 shows the mass loss of alloys (Table 1) in 10% HF at 323 K. Hastelloy C has a significantly higher corrosion resistance than the others. Although specimen 1 had additions of 3% B and 3% Si to improve the wear resistance of Hastelloy C, the corrosion resistance of specimen 1 was very low. However, specimen 2, to which 3% B, 3% Si and 1% Cu were added, shows almost the same high corrosion resistance as Hastelloy C.

   The corrosion resistance of the centrifugal cast alloy is very low. Mo is an important alloying element for improving corrosion resistance when halogen is present\(^5\)(\(^6\)) (hydrofluoric acid, hydrochloric acid, etc.). Mo cannot be added to the centrifugal cast alloys, because Mo makes the melting point and viscosity of the melt high. It has been concluded that the low corrosion resistance of the centrifugal cast alloy is caused by the absence of Mo, and that it is impossible to remedy this situation.

   To clarify why the corrosion resistance of specimen 2 was significantly superior to that of specimen 1, the cross section microstructures of the specimens were observed. Figure 4 shows the cross section microstructures of specimens 1 and 2 after the corrosion test in 10% HF. A primary and eutectic boride phase was observed in both specimens 1 and 2. It was identified by X-ray diffraction that this boride was \(M₃B₂\) (M: Ni, Cr, Mo)\(^7\)-(\(^11\)). In the case of specimen 1 (Fig. 4(a)) to which only B and Si were added, it seems that \(M₃B₂\) becomes the cathode and the matrix becomes the anode. As
a result, the matrix (anode) was preferentially corroded. However, in the case of specimen 2 (Fig. 4(b)) to which not only B and Si but also Cu were added, the preferential corrosion of the matrix that appears in specimen 1 (Fig. 4(a)) is not seen. It may be concluded that Cu makes the matrix (anode) noble, and that the potential difference between the matrix (anode) and M₃B₂ phase (cathode) becomes small. As a result, the mass loss of specimen 2 was very small.

To determine the optimum Cu content, the effect of the Cu content on the corrosion resistance of Ni-15Cr-15Mo-3Si-3B alloys was investigated. In the case of Hastelloy C, W has the solid solution hardening effect. Fe was, therefore, added to improve cold workability. W and Fe were eliminated in the following study, because the object of this study was to develop a sintered wear-resistant hard alloy. Figure 5 shows the effect of the Cu content on the corrosion resistance of Ni-15Cr-15Mo-3Si-3B alloys in 10% HF and 15% HCl. It was found that the addition of 1% Cu was enough to cause saturation.

2. The effects of Cr, Mo and Co on the corrosion resistance of the alloys

The optimum contents of Cr and Mo were investigated. In addition, the effect of the Co content on corrosion resistance was studied. As shown in Fig. 1, three types of the Ni-xCr-yMo-3Si-3B-1Cu alloys, i.e. the ratio of Mo/Cr > 1.0, Mo/Cr = 1.0, Mo/Cr < 1.0 were melted.

![Fig. 5 Effect of Cu content on mass loss of Ni-15Cr-15Mo-3Si-3B alloys in 10% HF and 15% HCl.](Image)

Figure 6 shows the result of the corrosion test in halogen agents (10% HF, 15% HCl) and an oxidizing agent (6% HNO₃). In the case of the Mo/Cr ≥ 1.0 alloys, excellent corrosion resistance was observed to the halogen agents. In the case of the Mo/Cr < 1.0 alloys, excellent corrosion resistance to the oxidizing agent was observed.

Figure 7 shows the effect of the Co content on the corrosion resistance of the Ni-15Cr-15Mo-3Si-3B-1Cu alloys. The corrosion resistance of Co-containing alloys to H₂SO₄ was slightly better than that of the Ni-15Cr-15Mo-3Si-3B-1Cu alloy. However, the alloys containing more than 50% Co showed very low corrosion resistance to HF. The alloys containing more than 13% Co also showed low...
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3. The properties of the HIP-processed alloys

(1) The microstructures of the HIP-processed alloys

After the above described corrosion tests, the compositions of the HIP-processed alloys for the cylinders of fluoroplastic shaping machines were determined. Table 2 shows the compositions of the HIP-processed alloys. The Mo/Cr ratio of the alloy named C-700 in Table 2 was 1.0, and the Mo/Cr ratio of the one called C-703 was 1.4.

Figure 8(a) shows the microstructure of the C-700 alloy. The fine particles of the M$_3$B$_2$ boride phase were dispersed.

Figure 8(b) shows the microstructures of the C-703 alloy. The fine homogeneous boride particles were dispersed.

Figure 8 shows the reaction sintering process of the C-703 alloy in detail. Stage I consists of the Ni-31.0Mo-3.8Si-1.1Cu alloy powder and the CrB powder after mixing. In this alloy, the CrB was the non-equilibrium phase and M$_3$B$_2$ was the equilibrium phase. As can be seen in Stage II, during the HIP process, the CrB particles were decomposed at the interface of the Ni-Mo-Si-Cu alloy powder. The decomposed Cr and B were diffused into the alloy powder and reacted with Ni and Mo in the alloy powder. As a result, the fine M$_3$B$_2$ boride particles reprecipitated in the alloy powder. At the same time, sintering of the alloy powder particles occurred. Finally, the microstructure seen in stage III (Fig. 8(b)) was obtained.

(2) The corrosion resistance of the HIP-processed alloys

Figure 10 shows the corrosion resistance of C-700 and C-703 in 10% HF. The corrosion resistance of C-700 and C-703 was slightly superior to that of Hastelloy C in Fig. 2. It was found that C-700 and C-703 satisfied the corrosion resistance for the cylinders of fluoroplastic shaping machines.

It is important to clarify whether C-700 and C-703 alloys can be applied to cylinders of various engineering plastics shaping machines. ABS (Acrylonitric Butadiene Styrene Copolymer), PES (Polyethersulfone), PPS (Polyphenylenesulfide), etc., are important plastics. SO$_2$ gas is generated during the injection molding of PES and PPS. NO$_x$ gas is generated during the injection molding of ABS. To clarify this problem, the corrosion resistance of C-700 and C-703 to H$_2$SO$_4$ and HNO$_3$ was investigated. Figure 11 shows the results of corrosion test in 15% H$_2$SO$_4$. C-700 and C-703 were clearly superior in corrosion resistance to the conventional centrifugal cast alloy and specimen 1 (Table 1). Figure 12 shows the results of the corrosion test in 6%HNO$_3$. C-700 and C-703 were clearly superior in corrosion resistance to
the conventional centrifugal cast alloy and specimen 1. It was found that C-700 and C-703 satisfied the corrosion resistance requirements for cylinders of other various engineering plastics.

(3) The wear resistance and mechanical properties of the HIP-processed alloys

Figure 13 shows the results of the Ohgoshi type\(^{(4)}\) contact wear test. The Vickers hardness of the HIP-processed C-700 (P/M C-700: powder metallurgy making) was 535. The Vickers hardness of the melting alloy (I/M C-700: ingot making), which has the same composition as P/M C-700, was 373. The rapid solidification during the powder atomization makes the dispersion of \(M_3B_2\) boride in the alloy significantly fine (Fig. 8(a)). As a result, the hardness of P/M C-700 was higher than that of I/M C-700. P/M C-703 (Fig. 8(b)) has a large amount of fine \(M_3B_2\) particles. The Vickers hardness of P/M C-703 was 786. The wear resistance of P/M C-700 was 70 times better than that of Hastelloy C, particularly under the condition of low friction speed. Although the composition of P/M C-700 was the same as that of I/M C-700, the wear resistance of P/M C-700 superior to that of I/M C-700. This wear resistance difference might be caused by the difference of the hardness between P/M C-700 (Hv 535) and I/M C-700 (Hv 373). Further, the wear resistance of P/M C-703 was 150 times better than that of Hastelloy C, particularly under the condition of low friction.
speed. Low friction speed (0.3 m/s) is the real operation condition of plastic shaping machines. It was found that the wear resistance of P/M C-700 and P/M C-703 was excellent.

Table 3 shows the mechanical properties of P/M C-700 and C-703. P/M C-700 and C-703 have high tensile and compression strengths. The thermal expansion coefficients of C-700 and C-703 were $13.2 \times 10^{-6} \text{ K}^{-1}$ and $12.1 \times 10^{-6} \text{ K}^{-1}$ (293-873 K), respectively, and nearly the same as that of steel. It is obvious that C-700 and C-703 might be easily bonded to steel.

Figure 14 shows the C-700 bimetallic cylinder. The alloy powder of the C-700 was sintered and bonded to the steel cylinder body by the HIP method. It is possible that C-703 is reaction sintered and bonded to the steel cylinder body by the same method.

### IV. Conclusion

The corrosion- and wear-resistant alloys for the cylinders of fluoroplastic shaping machines were developed by the HIP process. Initially, the corrosion resistances of various Ar arc melted alloys were investigated. After the optimum alloy composition was found, the new corrosion- and wear-resistant alloys were produced by the HIP process. The results were as follows:

1. In the case of the alloy with only B and Si added to improve the wear resistance of Hastelloy C, the matrix was preferentially corroded in HF. On the other hand, the alloy to which not only B and Si but also Cu were added, showed almost the same high corrosion resistance as Hastelloy C. It was found that the addition of Cu significantly affected the corrosion resistance of the Ni-Cr-Mo-B-Si alloys.

2. The optimum contents of Cr and Mo were investigated. In the case of the Mo/Cr $>1.0$ type alloy, excellent corrosion resistance to halogen agents (HF, HCl) was observed. In the case of the Mo/Cr $<1.0$ type alloy, excellent corrosion resistance was observed toward oxidizing agent (HNO$_3$).

3. The compositions of the new alloys for the cylinders of fluoroplastic shaping machines were determined. The composition of C-700 alloy is Ni-15.0Cr-15.0Mo-2.5B-3.0Si-1.0Cu.

| Table 3 Mechanical properties of C-700 and C-703. |
|-----------------------------------------------|
| **Alloy** | C-700 | C-703 |
| Tensile strength(MPa) | 1294 | 1401 |
| Compression strength(MPa) | 2440 | 2109 |
| Elastic modulus(MPa) | 256000 | 282000 |
| Poisson’s ratio | 0.27 | 0.28 |
C-703 alloy is Ni-17.5Cr-24.0Mo-3.6B-2.9Si-1.0Cu. In the case of C-700 alloy, Ar-gas atomized alloy powder was HIP-sintered. In the case of the C-703 alloy, the Ni-Mo-Si-Cu alloy powder and the CrB powder were reaction sintered by the HIP process. The CrB particles were transformed into M$_3$B$_2$ particles during the HIP process.

(4) The corrosion resistance of C-700 and C-703 to HF were slightly superior to that of Hastelloy C. The wear resistance of C-700 was 70 times better than that of Hastelloy C. Furthermore, the wear resistance of C-703 was 150 times better than that of Hastelloy C.

It was found that C-700 and C-703 have high performance for the cylinders of fluoroplastic shaping machines.

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