Corrosion Properties of the Fe-Cr-Based Soft Magnetic Alloys Fabricated by Metal Injection Molding*1

Yuki Hamataka1, Masahiko Hatakeyama2, Toshiko Osada3, Hideshi Miura3, Osamu Iwatsu4, Shigeo Tanaka4 and Satoshi Sunada2,*2

1Graduate School of Science and Engineering for Education, University of Toyama, Toyama 930–8555, Japan
2Graduate School of Science and Engineering for Research, University of Toyama, Toyama 930–8555, Japan
3Department of Mechanical Engineering, Kyushu University, Fukuoka 819–0395, Japan
4Taisei Kogyo Co, LTD, Neyagawa 572–0073, Japan

Fe-Cr based soft magnetic alloy, which has excellent soft magnetic properties and practical corrosion resistance is required. SUS430L is one of the candidate Fe-Cr based alloys with soft magnetic property in stainless steels. To improve soft magnetic properties, sintering process is useful to make low Cr alloy by adding the pure iron powder to SUS430L powder. While, reduction of Cr content expected to deteriorate corrosion resistance of the alloys. To evaluate the effect of Cr content on mechanical and electrochemical properties of the soft magnetic alloys, sintered SUS430L based alloys with different Cr content were prepared using metal injection molding process. We carried out slow strain rate tensile (SSRT) test and open circuit potential (OCP) to evaluate their mechanical properties and electrochemical properties. The results of SSRT and OCP suggest that Cr content enhance stress corrosion cracking. OCP value was affected formation of passive film on elastic deformation and collapse of it on plastic deformation during SSRT test. [doi:10.2320/matertrans.Y-M2016833]

(Received June 28, 2016; Accepted September 8, 2016; Published November 18, 2016)

Keywords: slow strain rate tensile, stress corrosion cracking, stainless steels, metal injection molding (MIM), soft magnetic properties, iron-chromium alloys

1. Introduction

Electronic controlling mechanisms are employed for various industrial equipment, consumer electronics and automobiles. Assembled parts with soft magnetic properties in these mechanisms are fabricated mainly by laminated magnetic steel sheets or press molded P/M magnetic alloys. Accompanied by increased demand for complicated shapes, fabrication methods with higher flexibility are required to correspond to the complexity. Metal Injection Molding method (MIM) can fabricate near net shape parts with three-dimensional complexity and expected to be a suitable method to realize production cost reduction of parts having complicated shapes and large-lot productions1).

Fe-Cr based soft magnetic alloys had been developed during 1960s to 1970s as the soft magnetic materials for use in high corrosive environment2–4); they have been widely used owing to their relative inexpensiveness compared to PB & Powder Co,.Ltd. FE-OM) prepared by the carbonyl reaction and dissolving of the passive film on a stainless steel9).

So far, investigations are ongoing based on the above composition of the base steel: improvement on the machinability5)

1This Paper was Originally Published in Japanese in J. Jpn. Soc. Powder Powder Metallurgy 63 (2016) 291–297.
*2Corresponding author, E-mail: suna@eng.u-toyama.ac.jp

and application in higher frequency ranges by adjusting contents of additional elements or modifying the heat treatment condition5/7). Further, sintered Fe-Cr alloy steels fabricated with P/M method using powder alloy having these compositions had been investigated and certain results were obtained for middle range frequency and low magnetic flux density applications5). On the other hand, it has been found that the higher Cr content decreases the maximum magnetic flux density7). In this study, a Cr content range lower than 12 mass% that had not been researched yet was noted; magnetic properties were measured for Cr content adjusted alloy fabricated by changing mixed proportion of SUS430L(Fe-17Cr) alloy powder and Fe powder, and the influence of lowered Cr content on the magnetic properties were evaluated in DC and AC magnetic fields5). Open Circuit Potential measurements (OCP hereafter) and Slow Strain Rate Tensile tests (SSRT hereafter) were combined to evaluate the influence of Cr content on the mechanical properties and further to confirm the formation and dissolving of the passive film on a stainless steel9).

2. Experimental Procedure

Table 1 shows chemical compositions of the raw powders and the referential wrought materials. Raw powders were comprised of SUS430L alloy powders (typical composition; Fe-17Cr, mean particle diameter; 18.6 μm, Epson Atmix Corporation) prepared by the water atomization process and iron powders (mean particle diameter; 3.6 μm, Fukuda Metal Foil & Powder Co.,LTD. FE-OM) prepared by the carbonyl reaction. SUS430L powders have relatively higher carbon content of 0.76 mass%. Therefore, carbon content in the mixed powders increases with the mixed proportion of iron powders. In this experiment, sintered alloys fabricated using SUS410L alloy powders alone (typical composition; Fe-13Cr, mean particle diameter 12.2 μm, Epson Atmix Corporation) were

Table 1 shows chemical compositions of the raw powders and the referential wrought materials. Raw powders were comprised of SUS430L alloy powders (typical composition; Fe-17Cr, mean particle diameter; 18.6 μm, Epson Atmix Corporation) prepared by the water atomization process and iron powders (mean particle diameter; 3.6 μm, Fukuda Metal Foil & Powder Co.,LTD. FE-OM) prepared by the carbonyl reaction. SUS430L powders have relatively higher carbon content of 0.76 mass%. Therefore, carbon content in the mixed powders increases with the mixed proportion of iron powders. In this experiment, sintered alloys fabricated using SUS410L alloy powders alone (typical composition; Fe-13Cr, mean particle diameter 12.2 μm, Epson Atmix Corporation) were

and application in higher frequency ranges by adjusting contents of additional elements or modifying the heat treatment condition5/7). Further, sintered Fe-Cr alloy steels fabricated with P/M method using powder alloy having these compositions had been investigated and certain results were obtained for middle range frequency and low magnetic flux density applications5). On the other hand, it has been found that the higher Cr content decreases the maximum magnetic flux density7). In this study, a Cr content range lower than 12 mass% that had not been researched yet was noted; magnetic properties were measured for Cr content adjusted alloy fabricated by changing mixed proportion of SUS430L(Fe-17Cr) alloy powder and Fe powder, and the influence of lowered Cr content on the magnetic properties were evaluated in DC and AC magnetic fields5). Open Circuit Potential measurements (OCP hereafter) and Slow Strain Rate Tensile tests (SSRT hereafter) were combined to evaluate the influence of Cr content on the mechanical properties and further to confirm the formation and dissolving of the passive film on a stainless steel9).

2. Experimental Procedure

Table 1 shows chemical compositions of the raw powders and the referential wrought materials. Raw powders were comprised of SUS430L alloy powders (typical composition; Fe-17Cr, mean particle diameter; 18.6 μm, Epson Atmix Corporation) prepared by the water atomization process and iron powders (mean particle diameter; 3.6 μm, Fukuda Metal Foil & Powder Co.,LTD. FE-OM) prepared by the carbonyl reaction. SUS430L powders have relatively higher carbon content of 0.76 mass%. Therefore, carbon content in the mixed powders increases with the mixed proportion of iron powders. In this experiment, sintered alloys fabricated using SUS410L alloy powders alone (typical composition; Fe-13Cr, mean particle diameter 12.2 μm, Epson Atmix Corporation) were

and application in higher frequency ranges by adjusting contents of additional elements or modifying the heat treatment condition5/7). Further, sintered Fe-Cr alloy steels fabricated with P/M method using powder alloy having these compositions had been investigated and certain results were obtained for middle range frequency and low magnetic flux density applications5). On the other hand, it has been found that the higher Cr content decreases the maximum magnetic flux density7). In this study, a Cr content range lower than 12 mass% that had not been researched yet was noted; magnetic properties were measured for Cr content adjusted alloy fabricated by changing mixed proportion of SUS430L(Fe-17Cr) alloy powder and Fe powder, and the influence of lowered Cr content on the magnetic properties were evaluated in DC and AC magnetic fields5). Open Circuit Potential measurements (OCP hereafter) and Slow Strain Rate Tensile tests (SSRT hereafter) were combined to evaluate the influence of Cr content on the mechanical properties and further to confirm the formation and dissolving of the passive film on a stainless steel9).

2. Experimental Procedure

Table 1 shows chemical compositions of the raw powders and the referential wrought materials. Raw powders were comprised of SUS430L alloy powders (typical composition; Fe-17Cr, mean particle diameter; 18.6 μm, Epson Atmix Corporation) prepared by the water atomization process and iron powders (mean particle diameter; 3.6 μm, Fukuda Metal Foil & Powder Co.,LTD. FE-OM) prepared by the carbonyl reaction. SUS430L powders have relatively higher carbon content of 0.76 mass%. Therefore, carbon content in the mixed powders increases with the mixed proportion of iron powders. In this experiment, sintered alloys fabricated using SUS410L alloy powders alone (typical composition; Fe-13Cr, mean particle diameter 12.2 μm, Epson Atmix Corporation) were
Table 1 Chemical composition of powders and the wrought material.

<table>
<thead>
<tr>
<th>Powder</th>
<th>Si</th>
<th>Mn</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Cu</th>
<th>Fe</th>
<th>O</th>
<th>C</th>
<th>P</th>
<th>S</th>
<th>Mean particle size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SUS430L</td>
<td>0.82</td>
<td>0.82</td>
<td>0.15</td>
<td>16.49</td>
<td>0.02</td>
<td>0.03</td>
<td>Bal.</td>
<td>0.33</td>
<td>0.030</td>
<td>0.014</td>
<td>0.008</td>
<td>18.6</td>
</tr>
<tr>
<td>Iron</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.6</td>
</tr>
<tr>
<td>SUS410L</td>
<td>0.45</td>
<td>0.49</td>
<td>0.10</td>
<td>12.45</td>
<td>0.01</td>
<td>0.01</td>
<td>Bal.</td>
<td>0.21</td>
<td>0.016</td>
<td>0.010</td>
<td>0.004</td>
<td>12.2</td>
</tr>
</tbody>
</table>

also prepared to evaluate the influence of non-presence of iron powders. Further, wrought materials Fe-13Cr-2Si (Tohoku Steel Co., Ltd) were also prepared as references.

SUS430L alloy powders and Fe powders were mixed, where Cr content was adjusted to 5 mass%, 8 mass% and 14 mass% (SUS430L alloy powder is referred as Fe-17%Cr, mixed powder with Cr content of 5 mass%, 8 mass%, 11 mass% and 14 mass% are referred as Fe-5Cr, Fe-8Cr, Fe-11Cr and Fe-14Cr respectively hereafter). After hot-mixing of prepared powders with the binder and cooling, pellets were formed by grinding. Compacts were formed using these pellets to evaluate soft magnetic properties by injection molding. The compact has an annular shape with dimensions of 45 mm in outer diameter, 30 mm in inner diameter and 1.1 mm in thickness. Wax component was extracted from the formed compacts in a heptane atmosphere, then the compacts were heated at 898 K during 3.6 ks (1 hr) to degrease, followed by sintering treatment of 10.8 ks (3 hr) at 1648 K to obtain test pieces. Hot degreas ing and sintering were carried out in a hydrogen atmosphere to reduce carbon content as low as possible.

A high frequency magnetic measurement apparatus (Yokogawa Electric Corporation) was used for measurements of DC magnetic properties. A sintered material attached with the primary and the secondary coils both having 100 turns was prepared. A magnetic field is generated by applying exciting current to the primary coil, which induces a magnetic flux density in the sintered material. It is detected by the secondary coil to obtain a magnetization curve. The intensity of the magnetic field applied was set to 796 A/m.

A B-H analyzer (Iwatsu test instruments corporation, SY-8219) was used for measurements of AC magnetic properties. A test pieces with the primary and the secondary coils both having 50 turns was prepared. AC magnetic field with a frequency between 100 Hz and 1000 Hz was generated by applying exciting current to the primary coil. Induced magnetic flux density in a sintered material was detected by the secondary coil to measure B-H loop for each frequency. The maximum magnetic flux density \( B_{m}(T) \) was measured by applying magnetic field of 796 A/m and 396 A/m to the primary coil.

Each specimen used for the SSRT test had the same plate-like shape having a parallel body with the dimension of 3.4 mm in thickness, 2.0 mm in width and 10 mm in length. As a pretreatment for the SSRT test, a parallel body of the specimen was polished sequentially using fine abrasive papers of 80 to 2000 grades followed by immersion in acetone for 0.3 ks ultrasonic cleaning. The surface of the specimen was coated with silicone rubber for isolation except a parallel body. Corrosive solution used in this experiment was 2.5 M \( \text{H}_2\text{SO}_4 \) + 0.2 M \( \text{NaCl} \) solution. The solution was kept at 298 K and fully degassed with pure nitrogen gas before measurements. SSRT was measured to obtain a stress-strain curve for comparison of mechanical characteristics of the specimen in the air and under a corrosive environment. Figure 1 shows the SSRT testing in the experiment schematically. SSRT measurements were carried out in the air and in a corrosive solution. The corrosive solution was deoxidized sufficiently with \( \text{N}_2 \) gas and kept at 298 K, then injected to the SSRT test cell. Strain rate was set at \( 1.75 \times 10^{-7} \) s\(^{-1}\). The SSRT test in a corrosive solution was accompanied with the natural immersion potential measurement to evaluate a formation of the passive film simultaneously. Potential and time were measured and recorded using a potentiostat. Each specimen was arranged as a working electrode and an \( \text{Ag}/\text{AgCl} \) (3.33 kmol. \( \text{m}^{-3}\text{KCl} \) electrode was referred. After the SSRT test, ruptured side surfaces were examined by means of low vacuum scanning electron microscopy (SEM).

3. Results and Discussions

The magnetic properties of iron-based soft magnetic materials are influenced by the carbon content or their fine structures. It is found that the magnetic properties such as the coercive force can be improved by decreasing carbon content and coarsening of crystal grain since impurities or grain boundaries suppress magnetic wall movement by pinning and degrade magnetic performance\(^{(10)}\). Figure 2 shows the carbon content of the specimen fabricated using MIM. Although variation was exhibited in the carbon content according to proportion of raw powder materials as mentioned above, the carbon content was reduced to extremely low level, less than 0.002 mass% for all the specimens. They were also densified, showing relative density of more than 98.5%. Figure 3 shows microstructures of the specimens under a microscope. As a
result of carbon reduction in a hydrogen atmosphere, every specimen has a ferrite single phase. Grain growth was enhanced with reduced Cr content. The proportion of fine iron powder becomes high under low Cr condition, which is considered to contribute to improvement of sintering performance.

Next, the experimental results of DC magnetic properties are examined. Figures 4 and 5 show initial magnetization curves and following magnetization curves in an applied magnetic flux of 796 m/A respectively. The lower the Cr content is, the higher the maximum magnetic flux density becomes. This is caused by increased magnetic momentum of the material with decreased Cr content. The initial magnetization curves indicate that the magnetic flux density raises earlier and permeability becomes higher by application of magnetic field as the Cr content becomes lower. Regarding the shape of magnetization curves, the loop becomes narrower with lower Cr content, showing lower coercive force. Fe-5Cr showed an excellent DC magnetic properties compared to other two Cr conditions in particular. It is assumed that decreased number of grain boundaries caused by grain growth may contribute in addition to the influence of decreased Cr
Figure 6 shows measurements of the maximum magnetic flux densities under an AC magnetic field. Improved density due to decreased Cr content was confirmed in the frequency range about 100 Hz to 500 Hz in an applied magnetic field of 796 m/A. The magnetic flux density became clearly higher as the frequency decreased and at 100 kHz, Fe-5Cr showed about 50% improvement at most in a magnetic property compared to Fe-17Cr. However, decline in the magnetic flux density with increase in frequency became pronounced as the Cr content became lower. At 1000 Hz, the same values were obtained regardless of test piece. When the applied magnetic field was lowered to 398 m, the test piece with higher Cr content showed lower density and the test piece with lower Cr maintained higher density in comparison with the results measured under 796 m/A. In a high frequency range however, the same values were obtained regardless of test piece as with the results under 796 A/m.

The stress-strain curves obtained by SSRT are shown in Fig. 7 a) Fe-17Cr, b) Fe-14Cr, c) Fe-11Cr, d) Fe-8Cr, e) Fe-5Cr. Both nominal stress and strain in solution significantly reduced in comparison with those in air. Stress-strain curves show little change in elastic range. While nominal stress and strain significantly reduced in plastic range, especially in Fe-17Cr and Fe-5Cr. Figure 8 shows the surface of the specimens after SSRT in solution. Many cracks along grain boundaries were observed in Fe-17Cr, Fe-14Cr and Fe-11Cr. In the cases of Fe-8Cr and Fe-5Cr, mechanical properties were degraded although cracks were not observed.

OCP obtained by SSRT are shown in Fig. 9. In the cases of without stress OCP was increased with the lapse of time in Fig. 9. a), b) and c). The phenomenon can be explained by using EVANS. It is thought that corrosion rate is decreased by increasing potential because cathodic reaction is almost constant. Thus, corrosion rate is controlled by only anodic reaction. Although it can’t be understood the reason, OCP was temporarily increased in the lensing from 0 to 20 ks under SSRT. On the other hand, OCP was gradually decreased from 20 ks. Since the formation of clacking was faster than that of passive, it is thought that the area of new surface is increased under SSRT.

In Fe-8Cr and Fe-5Cr, OCP was increased initial stage and then decreased gradually as observed in OCP of Fe-17Cr, Fe-14Cr and Fe-11Cr. However, the OCP indicate constant value in late stage. It is thought that the passive film of these alloys is not significant effect on prevention of dissolving reaction. According to the results of microstructure observation and OCP, the corrosion behavior is similar to SCC. Hence, we have carried out EPMA analysis to research the typical SCC factors of Cr depletion and carbide precipitation.

Figure 10 shows SEM images and elemental mapping of C, Cr, Fe. It shows the data of Fe-17Cr (alloyed powder) and Fe-8Cr (mixed powder) to research the reason of formation of preferentially dissolving along grain boundary in Fig. 8. The surfaces of specimens were slightly electro polished. However, a part of grain boundaries was preferentially dissolved in the treatment. Cr distribution around undissolved grain boundaries and matrix was homogeneous in all alloys used in this study. While, enrichment of C like white dot were seen in...
C mapping in both Fe-17Cr and Fe-8Cr. In the same positions of the white dots, many particles were recognized in SEM image. Therefore, the particle seemed to be carbide’s precipitates. The carbide’s precipitates were also distributed homogeneous. Hence, it is thought that the carbides have not significant role in corrosion behavior such as SCC. In the MIM process, metal powders grow large grains by mutual diffusion. Under the process, each grain boundary has various boundary energies. Therefore, the preferentially dissolving depends on mainly grain boundaries’ structure. In high energy boundaries, preferentially dissolving occurs. While, corrosion rate of surface of grains depend on the protection by passive film. It is well known that the corrosion rate of stainless steels follows concentration of Cr. Thus, in low Cr alloys, the surface dissolving is fast as preferentially dissolving of grain boundary, cracks along the grain boundary was not observed after SSRT. In high Cr alloys, the surface of the grain is protected by strong passive films. While many of grain boundaries dissolved under the harsh SCC environment in the study. Although, the corrosion behavior of this study is similar to SCC, it was thought that the effect of Cr concentration leads surface morphology.

4. Conclusion

Magnetic and mechanical characters of Fe-Cr alloys made by MIM in solution were summarized as follows.

(1) It is found that the magnetic properties such as magnetic flux density and the responsivity can be improved by decreasing Cr content under the applied DC magnetic field.

(2) In the AC applied magnetic field, magnetic flux density and the responsivity were imploded with decreasing Cr contents. While in the case of high frequency, magnetic properties were declined with decreasing Cr contents, because of the effect of over current.

(3) In high Cr alloys, mechanical properties were deteriorated by cracks along grain boundary. In low Cr alloy, since passive film does not prevent dissolving of surface, corrosion rate of surface is higher than that of grain boundary.

(4) Elemental mappings and SEM micrographs suggest that distribution of alloying elements is relatively homogeneous around grain boundary and matrix. Although, car-

Fig. 9 Corrosion potential for SSRT of specimens in corrosive solution, (a) Fe-a17Cr, (b) Fe-14Cr, (c) Fe-11Cr, (d) Fe-8Cr, (e) Fe-5Cr.
Bide precipitates were observed in all specimens, the effect of it on preferential dissolving seemed to be limited. It is thought that the preferential dissolving along grain boundary appears the protection ability of passive film under the harsh SCC environment.

REFERENCES


Fig. 10 EPMA elemental map for (a), (e) C, (b), (f) Cr, (c), (g) Fe and (d), (h) SEM images of Fe-17Cr and Fe-8Cr.