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<tr>
<th>Title</th>
<th>Study on the Sintering of Metallic Powder of the Iron Family. IV: Study on the Sintered M. K. Type Magnet</th>
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Studies on the Sintering of the Metallic Powder of the Iron Family. IV
Studies on the Sintered M.K. Type Magnet

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Synopsis

Although the Alnico-type permanent magnet has been manufactured by powder-metallurgical method in foreign countries, good results have not yet been obtained in Japan. To sinter successfully the magnet of this type, the author studied the sintering atmosphere and furnace-materials together with effects of size and kind of powder particles. Good magnetic properties were obtained by using mechanically pulverized powders and sintering in the atmosphere of thoroughly purified hydrogen.

I. Introduction

The M.K. steel has very superior property as a permanent magnet. But the product manufactured by the casting method is very hard and brittle; its machinability is low and the precise machining is almost impossible. When melted, it is liable to contain its oxide and to react with a crucible; its magnetic property lacks in uniformity.

However, powder products have no such drawbacks, and the following merits may be mentioned:\(^1\):
(1) As the product is directly made by molding, the product having complex form is manufactured and its minute machining is possible.
(2) The product having better properties is manufactured and its coercive force and tensile strength are superior to the cast one.
(3) Owing to its small grains and uniform construction, uniform flux density is obtained.
(4) As no wastage is produced, minimum material is needed per piece.

By adopting the powder metallurgical method, products having superior properties mentioned above are manufactured. As nickel and cobalt to be used for the manufacture of the magnet in large amount are imported materials in Japan, a study on the sintered M.K. type magnet is the pressing need of the hour, because the adoption of the method saves not only the material, but also gives the maximum amount of the magnet with a given amount of nickel and cobalt. However, the manufacturing method by the powder process has technically difficult points and has not yet succeeded in our country. The object of this study is to put the sintered magnet to practical use in consideration of the facts stated above.

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(1) C.G. Goetzel, Treatise on Powder Metallurgy, Chapter XXIV.
In foreign countries, many attempts have also been made for the manufacturing of sintered magnets. A glance at these results will be given. The sintering method is applied to other magnets except the M. K. magnet. As the machinability of the other magnet is comparatively good, there is no special advantage in using the powder method. There are two methods for manufacturing the powder M. K. magnet. One is to diffuse each component in molten state; the homogeneous alloy thus produced is pulverized and the powder is molded into magnet. But, as the powder is very hard, its molding is very difficult and the product having high density is not produced. Then the powder is mixed with synthetic resin and the mixture is molded at the polymerizing temperature of the resin, by which a magnet having proper magnetic property has first been obtained. But the method widely adopted is the other, viz., a method to diffuse each component at the same time with sintering. In the latter method, virgin aluminium powder is not used as the aluminium source. As aluminium has strong affinity for oxygen, it forms an oxide film combining with a minute amount of oxygen or water contained in the sintering atmosphere, which completely prevents the diffusion of the components. By using powder of aluminium-iron or aluminium-nickel alloy, the above obstacle is overcome to a certain extent, and a sintering product having proper magnetic property has been obtained by using thoroughly purified hydrogen. But it was impossible to avoid minimal oxidation of aluminium during pulverization and in storage, which prevented the diffusion of the component. The oxidized film of aluminium could not be reduced with hydrogen, but scarcely with nascent hydrogen produced by thermal decomposition of metallic hydrides. After all, using thoroughly purified hydrogen as the atmosphere, powdered alloy of iron-aluminium or nickel-aluminium as the aluminium source and 1~2 per cent of titanium or zirconium hydride, the M. K. sintered magnet was first obtained, which was sufficient for practical use.

Thus we can know the outline of the method manufacturing Alnico type magnets, there are some unknown details. In the present study, the work was performed in the similar manner as in the above example. Many difficulties occurred and the problem has not yet been completely dissolved, but the sintered product having magnetic property of a certain degree has been obtained. So the result obtained so far is reported here.

II. Powders used for the Experiment

The components of the M. K. magnet are nickel, aluminium, cobalt, copper and iron, of which the main ones are nickel, aluminium and iron. Alnico-III is composed of main three components; Nos. I and IV contain cobalt in addition to the above, and Nos. II and V contain copper besides the above four.

The powder used for the experiment was shown in Table 1. As the aluminium

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source, ferro-aluminium powder containing 50 per cent aluminium and nickel-
aluminium powder containing 36 per cent aluminium were used, being easily
crushed. FA-I powder was prepared by ordinary crushing method, while FA-II
with special attention to prevent it from mixing with impurities and from oxida-
tion. N-I nickel powder is a commercial product. Although its history is not
clear, it will be the product crushed by a stamp mill, because it contained fairly
large amount of flat powder. When compared with N-II of the author's making,
the packing density of N-I powder was low. Co-I powder contained about 0.2 per
cent impurity insoluble in nitric acid, but Co-II contained no such impurity.
Co-I powder did not solidified after reduction and blackish in color, but Co-II
powder shrunk and slightly solidified by reduction at lower temperature than that
of Co-I powder. Co-III was prepared by mechanically pulverizing the cube cobalt.

<table>
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<tr>
<th>Mark</th>
<th>Composition</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA-I</td>
<td>Fe-Al (52% Al)</td>
<td>Crushed by a stamp mill. -300 mesh.</td>
</tr>
<tr>
<td>FA-II</td>
<td>Fe-Al (50% Al)</td>
<td>Carefully crushed in an iron mortar.</td>
</tr>
<tr>
<td>NA</td>
<td>Ni-Al (36% Al)</td>
<td>Crushed by a stamp mill. -300 mesh.</td>
</tr>
<tr>
<td>F</td>
<td>Electrolytic iron</td>
<td>Crushed by a stamp mill. After reducing in hydrogen at 600°C for 1 hr, recrushed in a mortar.</td>
</tr>
<tr>
<td>N-I</td>
<td>Nickel</td>
<td>Commercial product. After reducing in hydrogen at 600°C for 1 hr, crushed again in a mortar.</td>
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<tr>
<td>N-II</td>
<td>Nickel</td>
<td>Cast nickel, crushed by a stamp mill. After reducing crushed again in a mortar.</td>
</tr>
<tr>
<td>N-III</td>
<td>Reduced nickel</td>
<td>Nickel nitrate, roasted to nickel oxide and reduced in hydrogen at 700°C for 5 hrs, then crushed again in a mortar.</td>
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<tr>
<td>Co-I</td>
<td>Reduced cobalt</td>
<td>Commercial cobalt nitrate, roasted to cobalt oxide and reduced in hydrogen at 750-800°C.</td>
</tr>
<tr>
<td>Co-II</td>
<td>Reduced cobalt</td>
<td>Recrystallized cobalt nitrate, roasted to cobalt oxide and reduced in hydrogen at 650-700, for 3 hrs.</td>
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<tr>
<td>Co-III</td>
<td>Cobalt</td>
<td>Crushed by a stamp mill.</td>
</tr>
</tbody>
</table>

III. Preliminary Experiments

Until a sintered product having fairly large magnetic property was obtained,
the author met with difficulties in having hydrogen of high purity, and in keeping
its high purity even at high temperature. Owing to a strong affinity of aluminium
for oxygen, the compact remarkably expanded through the combination of alumi-
nium with a trace of oxygen in hydrogen. In early experiments, iron-aluminium
compact containing 50 per cent FA-I powder and sintered at 1,200°C sometimes
expanded by scores of per cent. The compact composed of iron, nickel and cobalt
was sintered smoothly and its shrinkage was large. When FA-I powder was
added to the above compact, it expanded and its shrinkage was hardly caused by
highly purified hydrogen, which shows that the oxidation of aluminium gave a
definite effect. The success in manufacturing the M.K. sintered magnet may be
said to depend on this point. The components to be expelled are oxygen and
water. In the experiment, as electrolytic hydrogen was used, there was no chance containing other gas. It is necessary that the amount of water contained is to be dew point at below -50°C, or less than 0.006 per cent by volume. The amount of oxygen should be in the same degree calculating as water. Phosphorous pentoxide is a powerful dehydrating agent and good for removing water. For removing oxygen, the usual hot copper is not sufficient. It is not simple to measure such a minute component and its fitness is only determined by sintering F.A. powder. And for sintering the powder, the sintering furnace was the problem.

(a) Sintering furnace

The above compact containing 50 per cent FA-I powder was sintered in a quartz tube in the current of hydrogen at 1,250°C for 1 hour, by which the tube was contaminated with aluminium vapour and destroyed. As fire-proof materials, alundum and alumina tubes may be mentioned. When alundum tube was used, it was found that oxygen or vapour penetrated into the tube at high temperature. To examine the effect, an apparatus shown in Fig. 1 was used. Electrolytic hydrogen was introduced into the sintering furnace through a tube containing hot copper and drying tubes. Hydrogen, on passing the furnace, was introduced into a P₂O₅-tube and then into a water bottle, in which the water pressure of 10~15 cm was given to the gas. The furnace was first empty. When oxygen or water vapour penetrated into the tube by an unknown cause, the weight of \( u_4 \) tube increased, from which the amount of water in 1 lit. of hydrogen was calculated. The flow amount of hydrogen was calculated from the electrolytic current. The amount of absorbed water in \( u_3 \) tube in the experiment was 0.00~0.06 mg/lit. Water of 0.06 mg/lit, roughly corresponds to the dew point at -50°C. When the furnace was kept at room temperature, the absorbing amount of \( u_4 \) was 0.2 mg/lit, while 7.6 mg/lit at 1,250°C. This fact shows that, although the inside pressure of the furnace is kept greater than the outside one, oxygen or water diffuses into the furnace through the alundum tube at high temperature. When a quartz tube was used instead of the alundum tube, the increased amount was 1.1 mg/lit. at 1200°C. The increase of the weight must have been due to oxygen which was not removed even with hot copper. From the experiment, it became clear that the alundum tube was not suitable for the purpose.

Then came an alumina tube for the purpose. Ordinarily, the alumina tube is porous and unfit for the purpose. But a high alumina tube is very compact. In this case, the absorbed amount of \( u_4 \) at 1,200°C, was 1.5 mg/lit. However, the high alumina tube was weak for thermal shock and unfit for the use for a long time.

(4) C.G. Goetzel, “Treatise on Powder Metallurgy”, Chapter XVII.
After using ten times minute cracks were found in the boundary between the high and the low temperature parts. In this case, the absorbing amount at 1,200°C was 11.6 mg/lit., although the inside pressure of the furnace was kept higher than the outside one. For the connection of the U-tubes, an ordinary rubber tube was used which was coated with paraffin. The error at the above measurement would be less than 0.2 mg/lit. No fire proof material suitable for sintering of the M.K. magnet has been found. Howe\(^3\) used an iron tube as the Alnico sintering furnace instead of the fire proof material for the same reason as mentioned above. Following his idea, a sintering furnace was constructed as shown in Fig. 2. As a furnace core, an iron tube was used and molybdenum wire as a heating element. It was an furnace for laboratory scale not a continuous one.

An ordinary thermocouple was not suitable for measuring the temperature of the furnace. When Pt-Pt-Rh is used, an iron tube should be used as a protection. But, as the tube is easily oxidized, it should be further protected with a quartz tube and a reducing or neutral gas should be introduced between the two tubes. Such a tube becomes large in size and inconvenient for use. It seems that Howe\(^3\) used a pyrometer for the purpose. The author used Mo-Ni thermo-couple. Its thermo-electromotive force was rather large, reaching about 49 mV at 1,300°C. But, it should be noticed that the relation between the temperature and the electromotive force was not linear. Both the elements were fairly stable in hydrogen and used for a long time, so long as mechanical shock and tension were not given. But, as they were attacked by aluminium vapor, the high temperature part had to be protected with an iron tube. Iron used for the core and the protection of the thermocouple combines with aluminium vapor and becomes hard but stands for a long time.

For laboratory scale, an iron pipe was used, inserting into a quartz tube, by which the quartz was protected from aluminium vapor, which was used for a fairly long duration.

(b) Purification of hydrogen

Hydrogen used in the experiment had to be of high purity. Electrolytic hydrogen generally contains 0.2 per cent oxygen and saturated water vapor.\(^4\) The latter was sufficiently removed with phosphorous pentoxide, but the former was not perfectly removed with a heated copper. Completely dried hydrogen through \(\nu_1\) tube (Fig. 1) was passed through a heated copper and the produced water was absorbed by \(\nu_2\) tube, from which the amount of water was calculated and shown in Table 2, showing the mean value of 2 or 3 measurements, the experimental error being about 0.2 mg per lit. The optimum temperature of the
copper was about 700°C. But, when an iron compact containing 50 per cent FA-I was sintered, using hydrogen purified with the copper heated at 700°C, it showed growth. In other words, the mixed powder was molded with pressure of 5 ton cm² and sintered at 1,250°C for 1 hour using a high alumina tube in the apparatus shown in Fig. 1, and the growth of 10~20 per cent was found.

<table>
<thead>
<tr>
<th>Temperature of copper °C</th>
<th>Amount of water produced by hot copper mg/litr</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>0.62</td>
</tr>
<tr>
<td>600</td>
<td>0.40</td>
</tr>
<tr>
<td>700</td>
<td>0.98</td>
</tr>
<tr>
<td>800</td>
<td>0.85</td>
</tr>
</tbody>
</table>

But pure hydrogen causing shrinkage of the compact was obtained by treating hydrogen with heated silicon powder. After passing through a tube (Fig. 1), hydrogen was passed through a silicon furnace, heated at 800°C and dried with phosphorous pentoxide and then introduced into a high alumina sintering furnace. The fineness of the silicon powder was minus 150 mesh. When hydrogen, residual oxygen of which was removed with silicon, was used, the above compact caused the shrinkage of 0~9 per cent by sintering at 1,210°C for 1 hour and of 4~17 per cent at 1,280°C for 1 hour. The shape of the sample after the sintering was the so-called hour-glass type, the exact volume of which was, therefore, not measured. When the silicon powder was repeatedly used, the degree of shrinkage of the compact decreased. The used silicon was tinged with black or blue color and oxidized to a certain degree. So, such a method is not suitable for long continuous experiments.

To use palladium asbestos for removing oxygen is the most effective method. By using palladium asbestos instead of the silicon furnace and absorbing the produced water with phosphorous pentoxide, the above compact caused the same shrinkage with the case of the fresh silicon powder in the sintering. Moreover, as palladium asbestos reacts catalitically, it may be used semipermanently.

As a purifying apparatus, the author has devised the use of fused magnesium or aluminium, which will be described later.

As stated above, to purify hydrogen, palladium asbestos and phosphorous pentoxide were used. The furnace shown in Fig. 2 or a quartz tube protected with an iron tube was used as sintering furnace and powder containing aluminium was sintered in the degree to cause shrinkage. Also special attention was paid to the reserve of purified hydrogen. As oxygen or water may diffuse through an ordinary rubber tube though the inside pressure is greater than the outside one, heavy tube should be used.

Samples composed of the above components and the third element attained magnetic property of some degree by the above sintering method. Then the effect of sintering and powder conditions on the magnetic property was to be studied.
IV. The Preparation of the Sample and the Measuring Method of Magnetism

The sample was prepared by molding the powder into a rod of 6 mm in width, 150 mm in length and a few mm in height with the pressure of about 5 ton/cm², and it was used in the experiment by dividing it into two or threes. In the sintering, as stated above, the special attention was paid to the purification of hydrogen and its reserving. The sintering temperature was kept at 1,280~1,310°C. After the completion of the sintering, the sample was quickly taken out from the place heated at 1,220~1,230°C to the water-cooled place for quick cooling but not annealed.

After the sintering, the shrinkage, the density and the magnetism of the sample were measured. For the measurement of magnetism, the ballistic galvanometer method was adopted and a solenoid coil was used as the magnetizing coil. Generally, in the measurement of magnetism of Alnico magnet, its external field is required to be 2,000~3,000 Oersted. However, in the experiment, the external field was 800 Oersted owing to the capacity of the magnetizing coil, and the sample was not saturated. So the described demagnetizing curve, coercive force and residual magnetism were lower than the real numerical valuer.

V. The Relation between the Particle Size and the Sintering Time

The sintered magnet is made in a homogeneous structure by mutual diffusion of each element in the sintering treatment. It is the problem of prime importance to clarify the relation between the magnitude of particles and the time necessary for sintering. Kalischer stated that it should be sintered at 1,200°C for 24 hours or at 1,300°C for 1~6 hours, but made no reference to the subject.\(^{(1)}\) Before clarifying this relation, a consideration should be made on mutual diffusion of binary system. The diffusion velocity of aluminum and nickel in iron is shown in Table 3.\(^{(5)}\) As shown in the table, the diffusion velocity of nickel in iron is very slow. The author refrains from giving a conclusion but gives an important suggestion, because in the sintering of M.K. steel, virgin aluminum is not used, the composition consists of ternary elements, and it is also necessary to consider the diffusion velocity of iron or nickel in ferro-aluminum alloy. Iron, nickel and cobalt consist of same group elements in the periodic table and their lattice-

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1. Kalischer stated that it should be sintered at 1,200°C for 24 hours or at 1,300°C for 1~6 hours, but made no reference to the subject.
constants are almost the same, so the diffusion velocity of iron in nickel or in cobalt will also be slow. And so the diffusion velocity of sintered magnet is controlled by that of iron-nickel system. In this system, para-magnetic property is obtained with 25～30 per cent nickel. A compact with 27 per cent nickel consisting of -250 mesh powders was selected for the purpose of clarifying the diffusion of the binary alloy. The sintered specimens was placed in a search coil in an external field of 500 Oersted. The deflection of galvanometer when the field was reversed is shown in Fig. 3. Detailed discussions on Fig. 3 are omitted, but it is clear that it is in need of high temperature and long time to obtain homogeneous structure. In the case of ternary system, the diffusion velocity will be much larger because an atom having the lattice constant with great difference will diffuse. The necessary sintering time in ternary system was determined by the magnetic properties of specimens.

Components of the magnet used for clarifying the relation were those of the Alnico III, composed of 14-28-58 Al-Ni-Fe. As the powder, FA-I powder, N-I powder and Fe powder were used. As a coarse powder, minus 110 mesh iron and minus 200 mesh nickel were combined, and as a fine one, minus 250 mesh iron and minus 250 mesh nickel were used. As an aluminum source, minus 300 mesh FA-I powder was used in the both cases. And the sintering temperature was 1,300°C.

As the magnetic properties of the samples obtained by the same condition were not same, many samples were prepared under the same condition and the effect of time on the magnetic properties produced by repeated sintering of each sample was examined. The results are shown in Figs. 4–7.
When minus 110 mesh iron powder and 200 mesh nickel powder were used (Figs. 4 and 5), coercive force increased with the progress of sintering time, almost reaching saturation in 3~5 hours, but the residual magnetism was in the opposite tendency. According to Kalischer (2) the relation between the sintering time and the magnetic property was in the same inclination, but Br increased again at the end. When the coercive force became almost constant, the sintering was assumed to be completed, for which 3~5 hours were needed. But, when the powder of minus 250 mesh was used in both cases (Figs. 6 and 7. Sample Nos. 35 and 36), it was completed within 2~3 hours. Moreover, although the same kind of powder was used, the finer powder gave the last product having larger coercive force. Also in the case of Nos. 35 and 36, Br decreased with the progress of time. When coarse powder was used, it took long time for the completion of the sintering, as diffusion delayed and the metals were oxidized with a very minute amount of oxygen remaining in hydrogen and the process of the sintering was prolonged. When the material of −250 mesh was used, coercive force of a certain degree was attained in 1 hour and was almost saturated in 2~3 hours, but Br decreased and its energy product was almost same even in 1 hour or 2. In some cases, their energy products decreased by sintering of long hours, which must have been due to the oxidation by the minute amount of oxygen.

VI. On the Repressed Sample

The apparent densities of the samples Nos. 27~36 were 5.8~6.1 and generally small. As a matter of course, there was a certain relation between the apparent density and the shrinkage. The time changes of shrinkage of these samples are shown in Fig. 8. The form of the sample after the sintering became hour-glass form to a certain extent, and the measurement
of the shrinkage was, therefore, not accurately conducted. The numerical values of the shrinkage are shown roughly on the figure; they were 10~12 per cent in the former period, while 12~16 per cent in the latter. High molding pressure could not be obtained because the small capacity of our molding machine. For getting high density, they were repressed. But, the sample in which sintering-diffusion occurred was hard and brittle, so the repressing was impossible. When the compact was annealed before the componental elements mutually diffused, they were capable of being repressed. But, when the annealing temperature was too high, the compact expanded and was hardened, it was, therefore, broken by repressing. The volume change of the compact, composed of 14-28-56 Al-Ni-Fe and pressed with the power of 5 ton/cm² and kept for 30 min, at each temperature is shown in Fig. 9. It expanded at above 700°C, it became maximum at about 900°C and shrunk at above the melting temperature (about 1150°C) of Fe-Al. The cause of expansion has not yet been clarified. It was possible to repress the samples annealed at 700~800°C expanded by less than 5 per cent (Fig. 9). The samples Nos. 39~41 were sintered after being repressed. The repressing power was 10 ton/cm². As the shrinkage of such samples at the sintering was generally small, the last density was not elevated so much as expected and it was 5.9~6.2. But, their magnetic properties were remarkably improved. It was a remarkable point that the repressed sample in Figs. 10 and 11 had large residual magnetism. With the progress of sintering time, the residual magnetism increased in the repressed sample, but not in the non-repressed one. The coercive force decreased by the repressing, but increased with the lapse of sintering time. The above complex phenomena must have been due to the following causes, but not yet clear at present: (1) By the increase in con-
tacting area of the powder, the atom-moving amount of the component element increases, according to the Fick's 1st equation by which the uniformity of the structure is completed within short time. (2), by the slight oxidation due to the repressing, the sintering is checked. In addition to the terms (1) and (2) which are due to the repressing operation, the effects of the mutual diffusion and atmosphere should be considered, that is (3), in the case of low sintering temperature, only aluminum will diffuse and hardly with nickel. Then the compact will have the composition similar to M.T. steel, and so the coercive force will be small. (4). In the case where the diffusion of nickel is easy (high temperature), but that of aluminum is difficult (purity of hydrogen is low), the compact will have the component similar to the para-magnetic steel, and the residual magnetism will be small.

The increase of energy product according to the progress of sintering time (Fig. 11) will show that the improvement of magnetic property due to diffusion will be greater than the lowering by oxidation. When repressed, the magnetic property of the samples of the other components were improved (Table 4). The repressed sample had an advantage in not going out of shape after sintering.

VII. The Effect of Atmosphere

It was stated that the purity of hydrogen plays an important role in the sintering of Alnico-type magnet. In order to eliminate the trace of oxygen, palladium asbestos is much effective, but there is some individual difference in its removing capacity which is probably due to particle size of palladium. It is considered that the size of palladium used in the previous sections was comparatively large. When the quality of asbestos is good the magnetic properties of sintered specimens are still more improved although they may be of the same compositions (Nos. 116, 122 and 123 in Table 4), and the typical demagnetizing and energy product-curves are shown in Fig. 12. Favourable magnetic properties having Br, 5,100 gauss and Hc, 460 oersted, were obtained by the sintering at 1,300°C for 2 hr, and the resultant density was 6.2. Thus the density was improved, but not sufficiently. The low density must be due to the irregular shape of particles owing to the mechanical pulverization and to the low compacting pressure.

![Fig. 12. Typical magnetic properties of sintered magnets. "a" belongs to Alnico I and "b" to Alnico III.](image-url)
Furthermore, it was convenient that such fine asbestos showed its capacity at room temperature.

In addition to the cleaning methods mentioned above, the author has devised a molten-magnesium method. Magnesium (or aluminum) has a big affinity for oxygen, and forms MgO (or Al₂O₃) by combining with oxygen of trace in hydrogen. Magnesium chips are frequently used for washing hydrogen, but the method is to pass hydrogen through molten magnesium (or aluminum). A fairly great effect was obtained by merely passing the gas over the molten metal. The vapor pressure of molten magnesium (or aluminum) was high, and the neighboring atmosphere of the molten metal was saturated with magnesium vapor. By passing hydrogen over the molten metal, magnesium oxide in minute form was formed by quickly and perfectly combining with oxygen or water in the gas. In using the method, there was a limit in the crucible or a furnace material; moreover, magnesium vapor condensed in the cooling part of the furnace, causing many obstacles. So the author has not yet succeeded in the construction of a furnace, which might be used safely for continuous operations. Generally, good results were obtained by using an experimental apparatus. The sinterings of Nos. 27, (Fig. 5) 39 (Fig. 11) and Nos. 54 and 55 in Table 4 were conducted by using hydrogen purified with molten magnesium. The adoption of the method generally yielded the good results, but not always.

This method is not only applicable for magnesium, but also aluminum. Any metal having a great affinity for oxygen and high vapour pressure may be applicable to the method, which seems to be one of the so called getter process. The details of the method require further study and will be reported in next report.

Table 4. The composition, the kind of the powder and the magnetic property.

The sintering conditions: 1,300°C for 2 hr. The samples were quickly cooled from 1,230°C. The fineness of iron and nickel powders was —250 mesh.

<table>
<thead>
<tr>
<th>No.</th>
<th>Composition (%)</th>
<th>Repressing ton/cm²</th>
<th>Magnetic property</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td>H₀ Oersted</td>
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<tr>
<td>54*</td>
<td>Al 14 Ni 28 Co</td>
<td>FA-I N-I</td>
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<td>Al 12 Ni 20 Co</td>
<td>NA N-I</td>
<td>10</td>
</tr>
</tbody>
</table>

* Mg-process was adopted.
† Particle size of palladium was fine.
VIII. The Effect of the Kind of the Powder and Composition

It has been stated that the special attention should be paid to the nature of the sintering atmosphere in preparing the sintered Alnico-magnet, and it is true of the perfect reduction of the powder itself. Though kept in a desiccator, the powders of iron, nickel and cobalt are slightly oxidized after a long time. They have, therefore, to be promptly molded after reduction and to be sintered. In the experiment, mixed powder of iron and nickel (or cobalt) was reduced at 650°C for 30 min, to which Fe-Al powder was added, molded quickly and sintered.

From the above standpoint, in the case of using reducing powder of an oxide, special attention should be paid to its purity. In the course of reduction, the oxide is reduced from the surface and a small amount of the oxide is liable to remain in the inner part. The powder containing the oxide remarkably prevents the diffusion and the magnetic property does not develop. In Table 4, the magnetic property of the sample No. 64 used the reduced powder did not develop. Its residual magnetism was slightly elevated, but \( H_e \) was very small, compared with samples of N-I or N-II powder (Nos. 54, 55 and 78). That \( H_e \) was small and Br large showed the imperfection of diffusion. The result of the experiment using cobalt was the same. In No. 62, its \( H_e \) was small, but the magnetic property was elevated by using Co-II powder (No. 88) manufactured with special attention. The best result was obtained by using Co-III powder in No. 116. Co-III powder was pulverized mechanically.

The samples, Nos. 80-83 are representatives of Alnico III. FA-II powder was used in Nos. 80 and 82, while FA-I powder in Nos. 85 and 86. \( H_e \) of the latter was smaller than that of the former, which must have been due to the presence of the oxide, because FA-I powder was prepared without special attention to the prevention of oxidation, and was perhaps oxidized during powdering as the powder was fairly fine. When Fe-Al powder was too coarse, another bad influence was perceived. When Fe-Al melted at high temperature, it penetrated into the skeleton of Fe-Ni and caused holes remained on the surface. From these points, the most adequate fineness of the powder would be about ~250 mesh.

In Nos. 80 and 82, the difference between N-I and N-II powders were tested. No big difference was found, but N-I powder seemed to be slightly superior, although the cause of it was not clear.

In No. 103, NA powder was used as aluminum source, and the results were almost the same as in the case of FA powder. FA powder melts at 1,150°C and NA above 1,600°C. This shows that aluminum diffuses in the form of gas, not liquid.

Although no metal hydride was used in the experiment, the product could have fairly improved magnetic property.

Summary

(1) As a preliminary study to sinter Alnico magnet, a discussion was given
on the sintering furnace.

(2) Considering the former washing method of hydrogen, the comparison was made of purity of the gas by the hot copper, hot silicon and palladium asbestos.

(3) The relation between the sintering time and the magnetic property was examined in connection with the particle size of the powder.

(4) By annealing and repressing the compact, a magnet having extremely superior quality was obtained.

(5) When reduced powder is used as the material powder, the powder having the highest purity should be used.

(6) It was found that a kind of the powder gave an effect on the magnetic property to a certain degree.

(7) The optimum particle size of Fe–Al powder was about −250 mesh.

(8) The purifying method of hydrogen by molten magnesium was very effective.

(9) Without using a metal hydride, the magnetic property of the compact was attained in a certain degree.