

Recycling of Rare Earth Magnet Scraps: Part I Carbon Removal by High Temperature Oxidation

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In the recycling of the permanent Nd-Fe-B magnet, the carbon such as free carbon and carbides at the grain boundary segregation in the magnet scrap are elements that are harmful and which obstruct the magnet performance. The removal of the carbon is currently a major problem. Remelting of scraps should, therefore, be done on condition that the carbon content is lowered to an appropriate level prior to melting. The aim of this work was to open the route for decarburization of the Nd magnet powder scraps with high carbon, as well as of the sintered body scraps with moderate carbon concentration. Decarburization via oxidation in air allowed the removal of not only free carbon but also grain boundary carbides at temperatures higher than 1273 K down to 300 mass ppm. However, an increase in the oxygen content is inevitable with the high temperature oxidation. The next step was then to reduce the iron oxide by heating it in a hydrogen atmosphere at 1273 K and subsequently to eliminate the oxygen combined with the rare-earth constituent using calcium which has a strong affinity with oxygen. The basic technology for the recycling process of the permanent Nd-Fe-B magnet scraps was discussed.

(Received October 22, 2001; Accepted November 9, 2001)

Keywords: recycling of magnet, magnet scraps, decarburization, deoxidation

1. Introduction

The amount of production of the permanent Nd-Fe-B magnet invented in Japan in 1983 kept expanding rapidly, and reached about 10000 tons all over the world in 1999. About 55% of the total amount of production, that is, about 5500 tons, was manufactured in Japan.

The application of this kind of magnet is for very strong magnetism. 60% is used for the voice coil motor (VCM) of computer hard disk drives (HDDs), and the remaining application, is for small, precise motors, and MRIs (magnetic resonance image devices). In addition, in the future this type of magnet will be increasingly applied to the type of miniaturized and lightened motors needed for electric vehicles and home electric appliances, such as air conditioners, washing machines and refrigerators, as the amount of use increases. The domestic production forecast for these appliances is expected to reach about 15000 tons in 2005, three times the current figure.

On the other hand, scrap from about 2400 tons (bulky scrap and powdery scrap) has been generated in the production of 5500 tons in the manufacturing process of the permanent Nd-Fe-B magnet. In spite of the high content of the expensive rare earth metal in these scraps, about 30 mass%, the present recycling ratio is only slightly less than 10% and the majority of the scrap is discarded as industrial waste.

In addition, a great deal of Nd magnets being incorporated in the devices and machines provided for general use will also become waste in time, if some effective recycling process is not realized. It must also be noted that the boron in the magnets is toxic¹⁾ when it merges with underground water, so that both the manufacturing waste and the used magnets will prob-

ably be designated as toxic industrial waste.

Recycling the permanent Nd-Fe-B magnet scrap is therefore extremely important from the point of greatly decreasing industrial waste and thus saving resources as well as helping to preserve the environment.

Therefore, we have promoted a project to develop a new recycling process, as shown in Fig. 1. This process is aimed at providing an economical method of returning the scraps to the conventional induction melting. The scrap from the

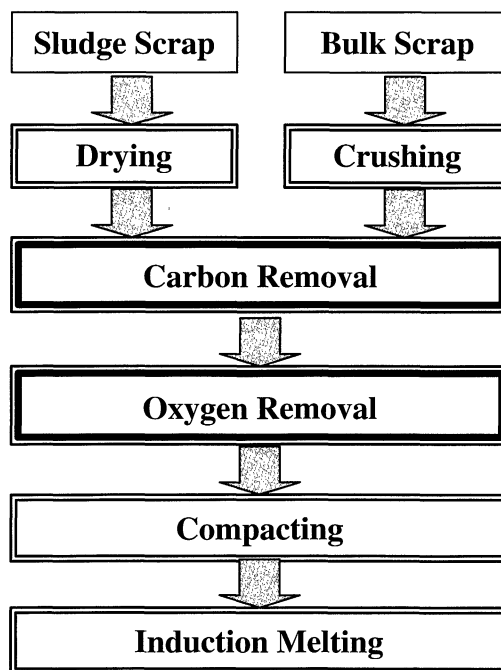


Fig. 1 Schematics of the process for recycling of Neodymium-Iron-Boron magnet scraps.

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permanent Nd-Fe-B magnet consists of two types: the one generated from the manufacturing process and the one collected from the market. The nature of the scraps is divided into two categories, powder and sintered body (bulk scraps). The powder scraps are formed mainly in grinding or machinery operations, and they have high contents of carbon and oxygen ($C > 1.5 \text{ mass\%}$, $O > 5 \text{ mass\%}$). The bulk scraps are compacts, sintered bodies, defectively plated magnets and the used magnets recovered from the market, and they have moderate content of carbon and high oxygen ($C = 0.07\text{--}0.1 \text{ mass\%}$, $O = 0.5\text{--}1.0 \text{ mass\%}$).

The surface of the powders is markedly oxidized, so that they cannot be remelted in the induction furnace. At present, they have to be discarded or treated with a very expensive wet process using acid.²⁾ It is expected that about 10% of all scraps can be recovered for recycling in this wet process. On the other hand, the solid scraps are covered with high-melting-point rare earth element (RE) oxides on their surface, which makes it difficult to remelt. If one insists on melting them, the crucible itself will corrode due to the high temperature. As a result, the RE recovery efficiency will be low because a large quantity of slag yields. The method of the addition of a small amount of bulk scraps at the induction melting to the seed melts is used, and the recycle ratio of a solid scrap is low. No discarding of the bulk scraps should be allowed as a matter of course, because of the high boron content ($B > 1 \text{ mass\%}$).

The problem involved in direct melting of the scraps with high oxygen is the remarkable slag loss of the RE, owing to its strong affinity with oxygen. What is more, the melting was not useful for removing the carbon. This is the reason why preliminary removal of both carbon and oxygen prior to melting is key for scrap recycling.

As for the oxygen elimination, we have noted the possibility of achieving this, based on the calcium-halide flux de-oxidation method,^{3–6)} feasibility of which has already been known.^{7,8)} The application to the RE-magnet scraps will be given in Part II.⁹⁾ As a consequence, this work and Part III¹⁰⁾ are focused on the development of the decarburization process.

The intention of this study was to decrease the carbon content in the scraps down to the level of less than 300 mass ppm by using an oxygen source at high temperatures. The samples whose carbon content was to be reduced were (a) the powder scraps (grindings) with high carbon and oxygen as a by-product during of the fabrication of the Nd sintered body magnets, and (b) the bulk scraps (sintered body) with moderate carbon and oxygen concentrations.

2. Experimental Procedure

In the first step, we studied the effect of oxidation temperature, time, thickness of sample layer and particle size on the decarburization efficiency. The sample of the grinding sludge scrap was dried at 353 K for 86.4 ks in air. The sample of the sintered body scrap was ground in nitrogen gas atmosphere with a stainless steel bowl and rod, and classified by the sieves into six size categories of +4 mm, 2–4 mm, 1–2 mm, 0.5–1 mm, 0.1–0.5 mm and –0.1 mm. The chemical

composition is represented in Table 1.

The grinding sludge powders were loosely packed in a stainless steel ($\square 150 \text{ mm} \times 150 \text{ mm}$) or an alumina crucible ($\phi 150 \text{ mm}$) at layers of 10, 15 or 30 mm in thickness, heated at the rate of 0.17 K/s in air, held for 3.6–43.2 ks at 873–1473 K, and then cooled in the furnace. The entire sample was lightly ground and mixed in a stainless steel bowl and subjected to analysis. The sample was analyzed for carbon and oxygen by using an LECO TC-336 and LECO CS-444 analyzer, for mean particle size measurements by the air permeability method (so-called FSS particle size). X-ray diffraction (XRD) analysis and metallographic observations were also conducted.

In the second step, the particle size suitable for decarburization treatment was investigated. The granular samples prepared from the sintered body scraps were packed in a stainless steel ($\square 150 \text{ mm} \times 150 \text{ mm}$) or alumina crucible ($\phi 150 \text{ mm}$) at a layer of 10 mm in thickness, heated at rising temperature rate of 0.17 K/s, held at 1373 K for 10.8 ks in air and cooled to room temperature. The entire sample was then lightly ground and mixed in a stainless steel bowl and subjected to the analysis. Some portions of this sample were subsequently heated in the hydrogen atmosphere of 1.07 kPa with a heating rate of 0.08 K/s, and kept at 1273 K for 10.8 ks.

3. Results and Discussions

3.1 Characterization of the sintered body scraps and the grinding sludge scraps

The sintered body scraps basically do not differ in the composition of the product. That is, the composition consists of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ which is the main phase, and the Nd-rich phase, which contains the RE oxide and the RE carbide.¹¹⁾ All the carbons and the oxygens of the sintered body scraps derive from the RE carbide and the RE oxide in the Nd rich phase respectively.

On the other hand, the grinding sludge scrap contains various carbons during the manufacturing process. The main sources are (1) the carbides from the RE-Fe-B alloy magnets, (2) the carbon powders issued from the carbon plate when cut together with the magnets, (3) the powders of whetstone consisting of the diamond and the resin as binder, and (4) the grinding oil.

As the grinding oil was removed by using butanol, the amount of the decrease of the carbon concentration in the grinding sludge scrap was 0.1–0.15 mass%. The existing form of the carbon in the grinding sludge scrap was considered as follows: carbon of 0.05–0.08 mass% was from RE carbide and carbon of 0.1–0.15 mass% was from the grinding oil and remainder was from carbon powder.

The mean particle size of the dry grinding sludge powders was 1.1 μm on average, and the particles had sharpened edges as seen in Fig. 2. The oxygen concentration of those powders was determined to be 5.6 mass%. This value is higher than the amount of oxygen concentration assumed to be oxidation of all the RE elements. Nevertheless, the compound identified by X-ray diffraction was neither such oxide nor hydroxide, but mainly $\text{Nd}_2\text{Fe}_{14}\text{B}$.

Table 1 Chemical composition of the Neodymium–Iron–Boron magnet scraps.

	(mass%)								
	Nd	Pr	Dy	B	Co	Al	Fe	C	O
Grinding sludge	19.5	4.86	2.36	0.84	0.87	0.23	Bal.	1.3	5.6
Sintered body	23.0	6.97	1.31	0.99	0.89	0.25	Bal.	0.07	0.54

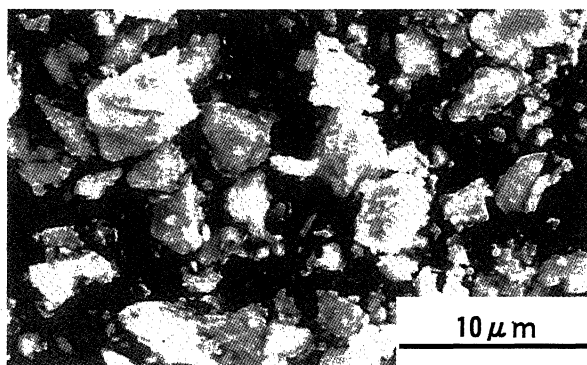


Fig. 2 Scanning electron micrograph of the dried grinding sludge powders.

3.2 The effect of heat treatment temperature, time and layer thickness on the efficiency of decarburization

The results obtained are shown in Fig. 3 for the sample with the layer of 10 mm in thickness. Residual carbon was made lower as treated at a higher temperature and for a longer time. The target carbon content, less than 300 mass ppm, was attained when treated at 1273 K for 10.8 ks. At temperatures higher than 1373 K, extra-low carbon, less than 100 mass ppm, was clearly realized.

Figure 4 shows the results obtained under various conditions of temperature over 1273 K and at various powder layer thicknesses. In order to decrease carbon below 300 mass ppm, longer than 10.8 ks was required below 1348 K, and 3.6 ks was sufficient at 1373 K. The decarburization reaction could not be completed at temperatures below 1373 K and needed to be treated for longer than 10.8 ks. Longer than 43.2 ks was needed at 1273 K as shown in Fig. 3. The residual carbon concentration did not differ from the stacking parts of the packed powder layer even in the case of oxidation at 1273 K for 3.6 ks. This may be due to one of two reasons or both: the first is the entire penetration of atmospheric oxygen into the layer, and the second is the initial content of oxygen enabled oxidation of the carbon, 5.6 mass% being unnecessary to accept the oxygen from the exterior. In Part III,¹⁰⁾ we confirmed that the decarburization of the sludge powders was made possible even under vacuum (0.13 Pa). This may then suggest that the oxygen source for decarburization exists, for the most part, inside the powder itself.

The morphology of the sample after the oxidation treatment was observed and shown in Fig. 5. In the treatment at lower temperatures, agglomerations like soot of the carbon existed, probably resulting from a cracking reaction, but with an increase in the treatment temperature, this occurrence tended to disappear and was never seen at 1373 K. This may be attributed to the fact that the substances that burnt easily, such as the particles of graphite and diamond, and the emulsion of water-oil and resin, would begin to be oxidized at lower tem-

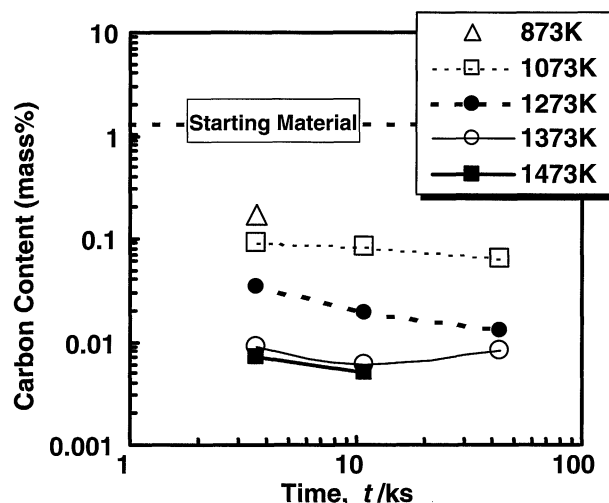


Fig. 3 Residual carbon concentrations in the samples obtained after decarburization in air with various temperatures and holding time. The samples were obtained in the grindings of packed layer of 10 mm in thickness.

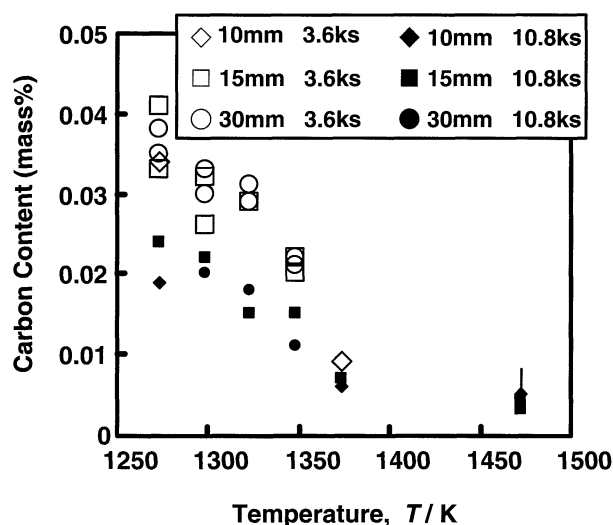


Fig. 4 Residual carbon concentrations of the grindings after decarburization with various temperatures, times and layer thicknesses.

peratures, but some portion of the organic substances (resin and emulsion) would be carburized and left in the form of carbides. The RE carbides may have been easily oxidized at 1073 K, emitting CO and CO₂ gases.

We measured the oxygen concentration with respect to the decarburization treatment. It was almost saturated at 873 K with an oxygen concentration of 22–24 mass%. When the sludge powders are completely oxidized, the oxygen concentration must be 27 mass% when calculated according to the values listed in Table 1. Considering the analytical error of oxygen, it may be said that the sludge powders had been fully

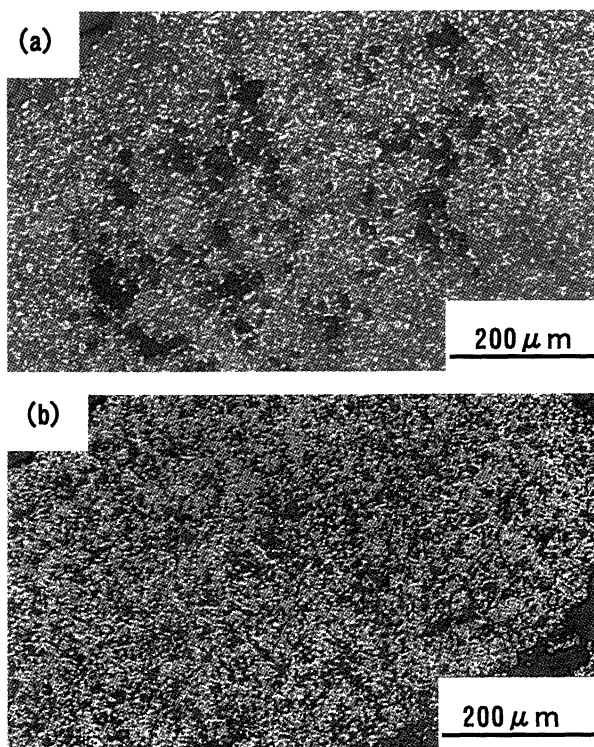


Fig. 5 Micrographs of the grindings after decarburization heating in air for 10.8 ks: (a) at 1073 K, (b) at 1373 K.

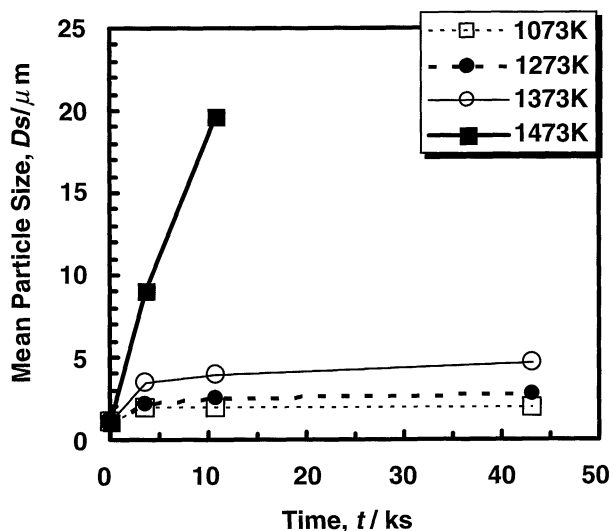


Fig. 6 Particle size of the grindings decarburized in air.

oxidized, even at 873 K. At this temperature, NdFeO_3 and Fe_2O_3 were identified by XRD measurements. With the oxidation treatment at higher temperatures, no other oxide was formed, and their XRD peaks became sharper due to better crystalline states.

Since the mean particle size after the decarburization treatment has an important role on the subsequent deoxidation treatment, the growth of the particles was examined. Remarkable growth was observed as shown in Fig. 6 when the sludge powders were heated over 1473 K.

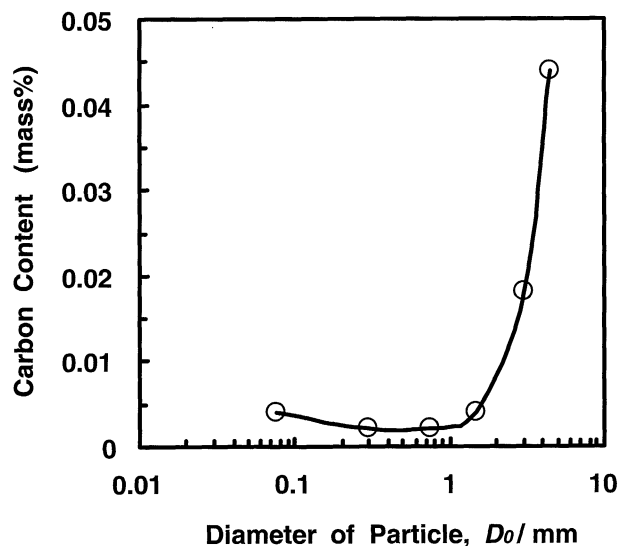


Fig. 7 Residual carbon contents of the crushed sintered body scraps after heating in air at 1373 K for 10.8 ks.

3.3 The effect of the particle size on the efficiency of decarburization of the sintered body scraps

The sintered body scraps were ground before decarburization. Figure 7 shows the effect of the particle size on the residual carbon content after the decarburization treatment. Even with an initial particle size as large as 4 mm, it was possible to reduce the carbon content to 300 mass ppm. The particle size with which residual carbon content could be reduced to below 100 mass ppm was less than 1 mm.

Figure 8 represents the cross sectional view of the grains after the decarburization treatment, exhibiting the trace of melting and separation into two phases. The sintered body scraps after the decarburization treatment was constituted of NdFeO_3 and Fe_2O_3 and the oxygen concentration was about 20 mass% in each phase.

3.4 Reduction and melting of the decarburized scraps

The granular scraps after decarburization (finer than 1 mm) were heated in a hydrogen atmosphere at 1273 K for 3.6 ks. By this heating, the granular scraps changed to porous powders like the reduced iron powders¹²⁾ as shown in Fig. 8. The scrap was consisted mainly of NdFeO_3 at the interior and α -Fe at the exterior of the granule, and the oxygen concentration was 7–8 mass%.

To completely remove oxygen from these powders, the sample was mixed with Ca by 1.5 times the amount needed to form CaO, and also with CaCl_2 by 5 mass% of the sample, as described details with Part II.⁹⁾ This mixture was heated at 1173 K for 3.6 ks in an Ar atmosphere. The reduced sample was washed in pure water, dried and pressed to make a compact for the induction melting. The carbon and oxygen concentrations in the melted ingot were 100 mass ppm and 300 mass ppm, respectively. These analytical values were equivalent to those in an ordinary commercial ingot.

On the other hand, yields of the alloy in this process gave the following results. In the decarburization and the hydrogen reduction process, a remarkable increase in the weight of the alloy by the oxidation was observed. The weight increase

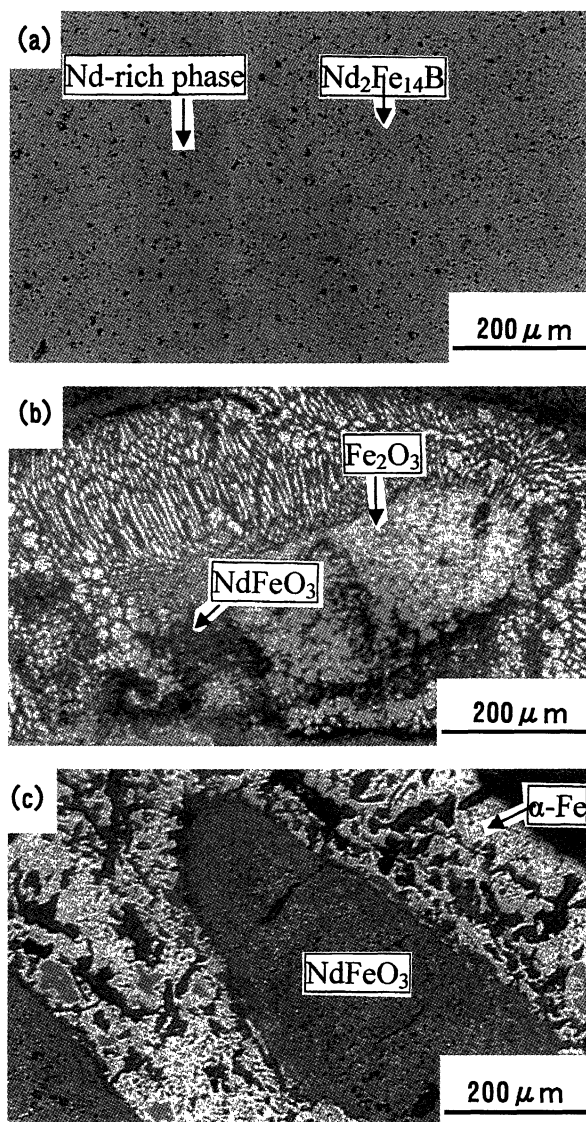


Fig. 8 Change in microstructure of the crushed sintered body scraps after decarburization: (a) as crushed, (b) 1273 K \times 10.8 ks in air, (c) 1273 K \times 10.8 ks in hydrogen.

was about 15 mass%, 20 mass% of the grinding sludge scrap and sintering scrap respectively, and the RE yield was almost 100 mass%. However, the yield of the weight of the alloy in the deoxidization by the Ca and washing process was low, about 60 mass% because of the outflow of the magnet powder under washing. This presents a major problem for future industrial use.

4. Conclusions

A new process for recycling Nd magnet scraps by the decarburization heat treatment at high temperature oxidation has

been examined. The results obtained are as follows.

(1) The samples were oxidized in air at 1273 K for 10.8 ks, and the residual carbon was below 300 mass ppm. When oxidized at 1373 K for 3.6 ks, the carbon content was reduced down to an extra-low level of less than 100 mass ppm.

(2) The decarburization reaction proceeded homogeneously in the powder layer loosely packed at 30 mm in thickness.

(3) The carbon level of the granules of 4 mm in size was in the order of 300 mass ppm by the oxidation in air at 1373 K for 10.8 ks. In the case of the particle size of less than 1 mm, the residual carbon content was below 100 mass ppm.

(4) After decarburizing, the powders are to be heated in the hydrogen atmosphere at 1273 K, subsequently deoxidized by Ca, washed in water, dried, compacted and melted in an induction furnace to meet a commercial quality.

Acknowledgements

This work was supported in part by a "Research Development Program of University and Industry Alliance-A Matching Funds Approach" both from the New Energy and Industrial Technology Development Organization (NEDO) and from the Japan Society for the Promotion of Science (JSPS) under Contact No. 99Y06-098-2. The authors thank Sumikin MolyCorp Inc. for technical information.

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