Effects of Ca and CaCl_2 Amounts in Preparation of Nd-Fe Alloys Using NdF_3 -Ca- CaCl_2 -Fe Reaction System*

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Effects of dimension of a cylindrical crucible (D/L), temperature, excess metallic Ca and salt ratio on the preparation of Nd-Fe alloys from NdF_3 -Ca- CaCl_2 -Fe reaction mixtures have been investigated. The alloy was formed on the bottom of the crucible as well as along the periphery due to creeping action of excess Ca metal on the inside wall of the mild steel crucible. In order to minimize the alloy formation along the periphery and to improve the process efficiency, the following condition was found to be optimum: (1) the ratio, D/L at 1.0, (2) at a temperature of around 860 °C, (3) with 5 mole % excess Ca, and (4) salt ratio, the amount of CaCl_2 per gram of the stoichiometric Nd in the NdF_3 , at 1.15. Under the above condition, the Nd recovery in the alloy formed on the crucible bottom was 98.5 % and composition by weight of the alloy was as follows: 17.2 % Fe, 0.42 % Ca, 0.02 % oxygen, 0.048 % C, < 0.01 % nitrogen and < 0.02 % chlorine. The small quantity of residual Ca was removed to a trace amount by vacuum arc melting.

KEY WORDS : Calciothermic Reduction, NdF_3 , CaCl_2 , Nd-Fe Alloy

1. Introduction

The authors described in earlier paper¹⁾ that as much as 98 % alloy recovery of low melting type of Nd-Fe alloys was attainable within five minutes by heating the NdF_3 -Ca- CaCl_2 -Fe reaction mixture to a temperature above the melting point of Ca (843 °C). When evaluating the alloy recovery, some difficulties were experienced since two kinds of Nd-Fe alloys were formed: one was formed on the bottom of the mild steel crucible (abbreviated as 'alloy B'), the other was that formed along the periphery of the exposed crucible (abbreviated as 'alloy A'). The shape of the former was a from of bottom and the latter was ring¹⁾. The ring type alloy mass was difficult to remove from the crucible by machining, and caused reduction of the yield of alloy. Besides this problem the dimension of the crucible is considered to be another important factor. Since the process considered here is a batch-type one, the volume ratio of the salt to alloy occupied become an important factor in determining the process efficiency. The increase of the ratio causes lower alloy productivity per unit volume of the crucible, because the ratio is governed by the amount of CaCl_2 added as a fluxing material.

In this paper effort was made to achieve the optimum process conditions and to minimize the problems by investigating the following variables: the variation of excess metallic Ca (Ca°) in the feed, temperature and amount of CaCl_2 added.

Since the ratio of the inner diameter to length of the crucible, D/L , is also observed to be influential to the mass of the alloy formed on the crucible bottom, effect of D/L on the Nd-Fe alloy recoveries have also been investigated.

2. Experimental Procedure

The most of the experimental procedures for the preparation of the Nd-Fe alloy were described in detail in the earlier paper¹⁾. In the NdF_3 -Ca- CaCl_2 -Fe reaction mixture, the Ca° content was controlled as excess mole percentages of Ca° over the stoichiometric amount. The amount of Fe was adjusted to form a Nd-Fe eutectic alloy with Nd from NdF_3 . The CaCl_2 content was controlled as a salt ratio, a weight ratio of the added amount of CaCl_2 to Nd of the NdF_3 . The salt ratio was varied from 1.15 to 3.65.

Effects of excess Ca° and the salt ratio in the feed on the alloy recovery and the Nd recovery in the 'alloy A' were primarily investigated. Effect of dimension of cylindrical crucible was also studied as a function of the ratio of D/L , in the range from 0.5 to 1.5. At this point, it was noted that D/L of a product increased two and a half times, because the packing density of the starting mixture was about 40 % of its theoretical density calculated under the assumption that each substance in the mixture is solid. The increase of the D/L of the product had already been observed in the earlier work¹⁾.

The alloy recovery represents the percentage of the amount of the whole alloy formed in the crucible to the theoretical amount of the alloy calculated from the starting materials. The method to determine the alloy recovery was also described in detail in the earlier paper¹⁾. The 'alloy A' formed along the periphery of the crucible and the 'alloy B' on the bottom were

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separated from the crucible by machining. The Nd contents in the alloys were analyzed by atomic absorption spectroscopy with acetylene- N_2O flame. Percentage of Nd amount in each alloy to the stoichiometric amount of Nd in the NdF_3 was designated as the Nd recoveries in each alloy. Core samples of the Nd alloy on the bottom of the crucible were chemically analyzed and the contents of impurities were determined.

3. Results and Discussion

3.1 Effects of crucible dimension and temperature on the formation of the Nd-Fe 'alloy A'

From the NdF_3 -Ca- CaCl_2 -Fe reaction mixtures with 30 % excess Ca° and the salt ratio of 2.03, the Nd-Fe alloys were prepared with separate crucibles whose dimensional ratio, D/L , was varied. In any of these tests the feed mixture was heated for 40 minutes in the furnace whose hot zone temperature was 860 °C. All reaction products were treated by the procedure described in the earlier paper¹⁾. XRD and EDS analysis of the salts insoluble in hydrochloric acid of pH = 2–3 indicated that the NdF_3 was completely reduced. The XRD pattern obtained under the condition of $D/L = 0.5$, is shown in Fig. 1.

Weight percentages of Nd-Fe alloy particles, which were not collected in the alloy A and alloy B, against the theoretically obtainable weight of alloy decreased with increasing ratio, D/L , as follows: 1.38 %, 1.25 %, 0.62 % and 0.61 % respectively in the cases of D/L of 0.5, 0.8, 1.0 and 1.5. Alloy recoveries over 98.5 % were achieved regardless of D/L . As shown in Fig. 2, however, the Nd recovery in 'alloy B' increased with increasing D/L up to 1.0 and approached 95 %. When $D/L > 1.0$, the Nd recovery in 'alloy A' decreased to a constant value of 4.3 %.

The amount of 'alloy A' formed on the wall of the crucible

Fig. 1 X-ray diffractogram of slag undissolved in hydrochloric acid of pH = 2–3, obtained under the condition of $D/L = 0.5$.

Fig. 2 Effect of D/L on the Nd recovery in the Nd-Fe alloys formed on the bottom and the periphery of the crucible.

Fig. 3 Effect of temperature on the Nd recovery in the alloy formed on the periphery of the crucible.

increased with increasing the wall area, i. e., decrease of D/L (Fig. 2). Two additional experiments were conducted in order to find the time dependence of the 'alloy A' formation. One test was conducted under a condition of 2 hours of heating at $D/L = 0.5$, and the other 4 hours at $D/L = 1.0$. The result of the former experiment showed that the increase in heating time from 40 minutes to 2 hours resulted in decrease of the Nd recovery from 40 % to 8.3 %. However, in the latter experiment the increase of heating further to 4 hours did not affect the Nd recovery. From this result, the crucible of $D/L = 1.0$ was selected and used for the experiments thereafter.

Effect of temperature on the Nd recovery in the 'alloy A' was also investigated and the results are shown in Fig. 3. Heating times at the hot zone temperatures of 810 °C, 860 °C, 915 °C and 1,070 °C were respectively 60, 40, 30 and 20 minutes. As shown in Fig. 3, the Nd recovery in the 'alloy A' increased with increasing temperature. This result indicated that the decrease of temperature was necessary in order to increase the Nd recovery in the 'alloy B' when using the same excess quantity of Ca. Considering the fact that the high alloy recovery over 98 % can be attainable above the melting point of $\text{Ca}^{1)}$, the most appropriate temperature is found to be 860 °C.

3.2 Effect of excess Ca

The variation of alloy recovery and Ca contents of the product as a function of excess Ca° are shown in Fig. 4. The result was obtained by heating the feed mixture positioned in the hot zone of 860 °C and 1,070 °C for a period of 40 minutes and 20 minutes at the respective temperature. The feed mixture was so adjusted to give a constant salt ratio of 2.03. As seen from the result, the alloy recovery gradually increases to give nearly 99 % with increasing excess Ca° , but using more than 10 % is unnecessary since the consumption of reductant is accordingly increased. When using 5 % excess Ca° , as much as 2.7 % and 3.1 % of the NdF_3 were observed not to be reduced at 860 °C and 1,070 °C, respectively, whereas complete reduction was achieved when using excess Ca° more than 10 %. This reason can be explained as follows.

The Ca metal is an essential ingredient but the most volatile among the feed mixture. Assuming that Ca metal had

Fig. 4 Effect of the excess quantity of Ca° on the recovery of alloy and residual Ca content in the alloy product.

vapourized before use as reductant, then some of the fluoride would have remained unreduced. If we examine Fig. 4 carefully, it is interesting to note that the alloy recoveries with the variation of excess Ca° are independent of temperature. Besides this fact other experimental observation revealed that the weight loss after reaction below 915 °C gave a nearly constant value regardless of temperature¹⁾ and excess Ca°. This constant weight loss was as much as 0.025 grams. From these facts it is interpreted that the reductant Ca° firstly reacts with the moisture contained in starting materials, especially in the anhydrous CaCl₂ which is not absolutely free from water, to form Ca(OH)₂. The Ca(OH)₂ is then decomposed into CaO and H₂O above 580 °C²⁾. Above 580 °C the gaseous H₂O disappears into the argon atmosphere. The Ca° loss calculated on the basis of the reaction, $\text{Ca} + 2\text{H}_2\text{O} = \text{Ca(OH)}_2 + \text{H}_2$, corresponds to 3.5 % excess Ca°. However, actual consumption of Ca° should exceed this quantity considering the reaction of H₂O which is supplied from decomposition. Thus, the actual Ca loss may reach greater than the calculated value and we can now understand the reason why incomplete reduction of the NdF₃ results when using as much as 5 % excess Ca°.

The variation of the Nd recovery in the alloy A with excess Ca° was also determined and the results are shown in Fig. 5, which shows that the Nd recovery in the alloy A increases with increasing excess Ca° while the Nd recovery in the alloy B reaches maximum at 10 % excess Ca°. Thus, the formation of the alloy A is strongly dependent on the excess Ca°. This dependency would result from the combination effects of creeping of Ca metal along the inside wall of the crucible³⁾ and also the high solubility of Nd into liquid Ca⁴⁾. Metallic Nd or Nd-Fe alloy produced on the crucible bottom can dissolve into the molten excess Ca° which can be brought up to the surface by convection. During the course the possibility of reaction with the crucible material itself should not be neglected. Since degree of creeping and Nd amount dissolved into liquid Ca° increase with increasing temperature and excess Ca°, the Nd recovery in the alloy A is raised naturally with temperature and excess Ca (see Fig. 3 and Fig. 5).

3 · 3 Sum of the effect of amount of Ca° and CaCl₂

Effects of excess Ca° and salt ratio on alloy recovery and

Fig. 5 Effect of excess Ca° in the feed mixture on the Nd recovery.

Ca content in the product are shown together in Fig. 6. When using 10 % and 20 % excess Ca°, alloy recovery and Ca content are nearly independent of the salt ratio. However, in the case of 5 % excess Ca°, alloy recovery and Ca content decreases with increasing the salt ratio. Since the increase of the salt ratio means the increase of water amount per gram of Ca°, Ca° loss by reaction with water increases with increasing the salt ratio and accordingly the NdF₃ can be insufficiently reduced due to the corresponding deficiency of the reductant. This is interpreted as the reason that the alloy recovery decreases with increasing the salt ratio when using as low as 5 % excess Ca.

In order to reduce the volume ratio of the salt to alloy B and also to obtain the high Nd recovery in a form of alloy B, it was important to adopt the condition of 5 % excess Ca and the salt ratio of 1.15. Under the condition, the Nd recovery in the alloy B was achievable as much as 98.5 %. Even though the volume ratio of the salt to the alloy B decreased to about 5, the ratio of the thickness of the alloy B to its diameter was as small as around 0.05. In order to increase the thickness, firstly formed CaCl₂-CaF₂ fused salt must be removed from the crucible and a second charge should be fed and reacted likewise. From the tests conducted it was found that the thickness increased twice without sacrifice of the Nd recovery. The compo-

Fig. 6 Effect of salt ratio on the alloy recovery and Ca content in the alloy product.

Fig. 7 Microstructure of Nd-Fe alloy produced and remelted by vacuum arc ($\times 200$).

sition of the alloy B prepared under these conditions gave assay value in wt. % as follows: 17.2 % Fe, 0.42 % Ca, 0.02 % oxygen, 0.048 % C, < 0.01 % nitrogen and < 0.02 % chlorine. This residual Ca in the alloy can be readily removed by vacuum melting. No Ca was detected when the alloy was melted twice by a vacuum arc melting equipment. The microstructure of the vacuum arc melted alloy is shown in Fig. 7. The eutectic structure and the white rectangular $\text{Nd}_2\text{Fe}_{17}$ intermetallic phases are clearly observed.

4. Conclusions

Effects of crucible dimension, temperature, excess Ca and salt ratio on the alloy recovery and the Nd recovery in the alloy formed on the bottom and along the periphery of the crucible have been investigated. The results are summarized as follows.

1. The formation of Nd-Fe alloy along the periphery of

the crucible was inevitable due to creeping of Ca metal along the inside wall of the mild steel crucible, however, this can be minimized by adjustment of reaction conditions.

2. In order to minimize the formation of the peripheral product and improve the process efficiency, it is recommended to adopt the following conditions: (1) ratio of the inner diameter to the inner length of crucible, D/L , at 1.0, (2) sample temperature of around 860 °C, (3) with 5 mole % excess Ca, and (4) salt ratio of 1.15.

3. Under the above conditions, the Nd recovery in the alloy formed on the crucible bottom was 98.5 % and the alloy composition was as follows: 17.2 % Fe, 0.42 % Ca, 0.02 % oxygen, 0.048 % C, < 0.01 % nitrogen and < 0.02 % chlorine. The residual Ca can be readily removable by vacuum arc melting.

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NdF₃-Ca-CaCl₂-Fe 反応系からの Nd-Fe 合金の製造における Ca および CaCl₂ の添加量の影響

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NdF₃-Ca-CaCl₂-Fe 反応系から Nd-Fe 合金を製造する場合について Ca および CaCl₂ の添加量, 反応温度, 円筒型軟鋼材をつば内部直径(D)対長さ(L)の比, D/L の変化が製造収率に与える影響を調べた。Nd-Fe 合金はスラグとの密度差のため, つばの底部に生成されるだけでなく, 雰囲気とスラグ界面の周囲にも生成することが観察された。その理由は液相の Ca への Nd の溶解度が大きいことと溶融塩内の Ca はつば内壁を這い上る (creep 現象) ことの 2 つの複合効果で説明された。このような雰囲気とスラグ界面の周囲に生成する合金の合金量は試料温度と Ca 使用量を減少させることで減少することができ, その合金量を最小化する工程条件は次のように得られた。(1) $D/L = 1.0$, (2) 試料温度 = 860

°C, (3) Ca 過剰量 = 5 モル %, および (4) CaCl₂ 使用量対使用された NdF₃ 中 Nd 量との重量比 = 1.15。このような条件で 98.5 % の合金がつばの底部で形成された。この合金は Ca = 0.42 wt. %, 酸素 = 0.02 wt. %, 炭素 = 0.048 wt. %, 窒素 < 0.01 wt. %, 塩素 < 0.02 wt. % の不純物を含有してある。この中で Ca は真空 arc 溶解により容易に除去することができた。

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キーワード: Ca 熱還元, NdF₃, CaCl₂, Nd-Fe 合金