Formation of LaNi_5 by Reduction-Diffusion Process with CaH_2 [†]

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To clarify the mechanism of formation of La-Ni compounds by the reduction-diffusion (R-D) process, the reduction of La_2O_3 by CaH_2 and the R-D reaction to form La-Ni compounds were carried out at 1200, 1300 and 1400 K. In the reduction experiment, pellets of mixed La_2O_3 and CaH_2 powders were heated in a deoxygenated Ar gas stream and the reduction rate was estimated from the diffraction intensity measured by XRD. In the R-D experiment, La_2O_3 and CaH_2 were mixed with Ni powder or Ni wires and pressed into pellets, and the reacted samples were then examined by XRD, SEM and EPMA.

The reduction with CaH_2 of 1.7 times the chemical equivalent for the reduction of La_2O_3 showed that the reduction rate was considerably higher, and that the reaction was completed in about 1 ks from the start of the reaction at 1300 or 1400 K. In the R-D reaction, LaNi_5 , La_2Ni_7 and CaNi_5 were formed, and the amount of CaNi_5 at 1300 K and 1400 K diminished as the reaction proceeded. It was also shown in the R-D reaction for pellets containing Ni wires that a double-layer of CaNi_5 and LaNi_5 was formed on the surface of each Ni wire, and that La diffused into the CaNi_5 layer to form LaNi_5 . When the amount of CaH_2 mixed in a pellet was three times the chemical equivalent for reduction, Ni wires in the pellet were dissolved in Ca melt and their original shapes were not retained. However, with the amount of CaH_2 at the chemical equivalent required for reduction, the reaction rate was reduced and the reaction products were LaNi_5 and $\text{La}_7\text{Ni}_{16}$, although no formation of CaNi_5 was observed.

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I. Introduction

The authors have carried out previously fundamental studies⁽¹⁾⁻⁽⁴⁾ to determine the rate and mechanism of the production of rare earth-iron intermetallic compounds, which have attracted attention as promising magnetic materials, by the reduction-diffusion (R-D) process. In succession to these studies, we investigated in the present study the formation kinetics of rare earth-nickel compounds by the R-D process.

A few fundamental studies on the formation kinetics of La-Ni compounds by this process were reported previously by Itagaki *et al.*⁽⁵⁾⁽⁶⁾. Li *et al.*⁽⁵⁾ prepared pellets composed of misch-metal (Mm) oxides, Ni particles of about 100 μm in diameter and metallic Ca as a reducing reagent, and investigated the formation of various compounds in the R-D process. They reported that the reaction proceeded with a clear reaction interface in the interior of each Ni particle, and that CaNi_5 , formed between an unreacted Ni core and an outer Mm-Ni compound layer, almost disappeared in the last stage of the reaction. Moreover, Kim *et al.*⁽⁶⁾ presented an interesting result that the formation rate of LaNi_5 was enhanced when the Ni surface was coated with CaNi_5 prior to the

reaction.

The authors have shown through previous studies⁽¹⁾⁻⁽⁴⁾ on the formation kinetics of the rare earth-iron compounds that an appropriate balance is necessary between the reduction rate of rare earth oxides and the reaction diffusion rate to effectively produce these compounds by the R-D method. To clarify the formation mechanism of LaNi_5 by the R-D process, therefore, we carried out two kinds of experiments, that is, reduction of La_2O_3 by CaH_2 and formation of LaNi_5 by the R-D reaction.

II. Experimental Procedures

Calcium hydride, CaH_2 , was used as a reducing reagent; it decomposes at about 830 K to generate H_2 gas, which does not contribute to the reduction, and plays a similar role as metallic Ca in the reaction. Moreover, CaH_2 is easier to grind than metallic Ca, facilitating the preparation of pellets. Reagents of 99.9% purity, La_2O_3 powder, Ni particles 20–30 μm in size, and Ni wires 200 μm in diameter, were used.

In the reduction experiment, pellet samples were prepared as follows. Firstly, La_2O_3 powder and CaH_2 particles were weighed, ground in a motor and mixed. The amount of CaH_2 used was set at 1.7 times the chemical equivalent (C_{eq}) required for the reduction of the amount of La_2O_3 included. The mixture was pressed in an 11 mm ID die under 2×10^8 Pa (2 ton/ cm^2) to make a pellet approximately 2 mm thick. Pellets for the R-D experiment were prepared as follows. Ni powder or wires were added to a mixture of La_2O_3 and CaH_2 and pressed in the die.

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The amount of CaH₂ was varied from 1.0 to 1.7 times C_{eq} required for the reduction of La₂O₃, and the molar ratio of Ni to La was set as 5:1. These treatments were carried out in a box through which Ar gas was passed, and the pellets were prepared in a polyethylene bag filled with Ar gas.

Details of the experimental apparatus used have already been reported in a previous paper⁽¹⁾. The pellet was placed on a Mo stand fixed in a Mo crucible. After covering with a stainless steel plate, the crucible was hung in the upper part of a reaction tube. As much as possible of the O₂ gas in the reaction tube was removed by repeated degassing with a rotary pump and flushing with Ar gas. Thereafter, the crucible was brought down to a hot region of the furnace in an Ar gas flow, the rate of which was 5×10^{-6} m³/s, and the reaction was started. After the predetermined reaction time had elapsed, the crucible was lifted to a cold region in the upper part of the reaction tube. The reaction temperatures were selected as 1200, 1300 and 1400 K. Observation of the fractures of the reacted pellets, identification of the reaction products and analysis of the elements were performed using SEM, XRD and EPMA, respectively.

III. Results and Discussion

1. Reduction of La₂O₃ by CaH₂

Figure 1 shows XRD patterns of the samples heated at 1300 K for 60 s and 0.3 ks. From these patterns, the peaks of CaO were clearly observed after the reaction for only 60 s, although no peaks due to the formation of metallic La were ascertained. After the reaction for 0.3 ks, however, the diffraction intensities of La and La₂O₃ peaks were increased and decreased, respectively. Thus, the reduction proceeded according to the following reaction

Normal volumetric analysis could not be applied in

this experiment to determine the fraction of La₂O₃ reacted, due to the coexistence of Ca and CaO in the system. Since we could not find, at this stage, an appropriate method to separate Ca and CaO from the samples, we estimated the fraction reduced from intensities measured using XRD. Both types of La, hexagonal α -La and cubic β -La, were occasionally observed in the samples, and the highest peaks of Ca (111) and La₂O₃ (222) overlapped with each other around the bases of their peaks. It is difficult, therefore, to estimate the fraction reacted from the intensities of La and Ca peaks. Thus, we used the intensities of CaO (200) at 37.45° and La₂O₃ (440) at 45.43° which are not affected by the other peaks, to calculate roughly the fraction of La₂O₃ reduced in terms of the following equation:

$$X = I_{\text{CaO}} / (I_{\text{La}_2\text{O}_3} + I_{\text{CaO}}) \quad (2)$$

In this equation, $X=0$ before the reaction starts because $I_{\text{CaO}}=0$, and $I_{\text{La}_2\text{O}_3}=0$ and $X=1$ when the reaction is completed.

Figure 2 shows a plot of the fraction of La₂O₃ reduced, X , estimated from the intensities in XRD patterns of the samples reacted at 1200, 1300 and 1400 K. The starting time of the reaction was set as the sample pellet was lowered to the hot region in the reaction tube. As shown in this figure, the reaction rate increased as the temperature was elevated, although no differences were observed in the rates at 1300 and 1400 K. The reaction proceeded rapidly at all temperatures studied, and seemed to be completed after about 1 ks from the start of the reaction at 1300 and 1400 K.

In the temperature range of this experiment, Ca is in the liquid state, and the reduction proceeds when this Ca is in contact with the surfaces of La₂O₃ particles. Since La formed in the reduction is also in the liquid state, La and Ca would generate a melt together. However, CaO, one of the reaction products, is a solid at all temperatures used, and the reaction would cease to proceed when the surface of each La₂O₃ particle was covered with CaO, as already clarified from the R-D experiment for the Nd-Fe

Fig. 1 XRD patterns of samples reacted at 1300 K; (a) 0.06 ks and (b) 0.3 ks.

Fig. 2 Time variation of the fractions of La₂O₃ reduced estimated from the intensity ratios of CaO and La₂O₃ in pellets.

system⁽¹⁾. Thus, CaO would have to be removed from the surfaces of the La_2O_3 particles, when the reaction is required to be continued. CaO has excellent wettability to metallic Ca⁽⁷⁾ and may be removed from the La_2O_3 particles simultaneously with the dissolution of La into the Ca melt. Thus, the melt formed on the surfaces of La_2O_3 particles probably plays an important role in ensuring that the reaction proceeds continuously.

2. Formation of La-Ni intermetallic compounds

X-ray diffraction patterns of the samples formed in the R-D reactions at 1300 K for 0.3, 0.6 and 1.5 ks are shown in Figs. 3(a), (b) and (c), respectively. The reaction products containing La and Ni were identified as LaNi_5 and La_2Ni_7 . The intensities of La_2O_3 and Ni decreased and those of LaNi_5 and CaO increased with reaction time. As La_2Ni_7 identified in the pattern is a liquid at 1300 K, it may be precipitated during the cooling of the sample from La-Ni or La-Ni-Ca melts. As seen in the pattern shown in Fig. 3(b), each peak attributed to LaNi_5 was much broader than that of the other cases. This was due to the overlapping of LaNi_5 and CaNi_5 peaks, because both of the compounds have the same hexagonal crystal structure and similar lattice constants. Figure 4 shows XRD patterns obtained using a Philips PW7000-type high resolution X-ray diffractometer, of the samples reacted at 1200 K for 0.18 and 1.5 ks. The patterns clearly show the peaks of LaNi_5 , CaNi_5 and La_2Ni_7 appearing close to each other in the diffraction angle. Thus, CaNi_5 disappeared with time, although it was formed in the reaction at 1300 K.

Fig. 3 XRD patterns of samples reacted by the R-D process at 1300 K; (a) 0.3 ks, (b) 0.6 ks and (c) 1.5 ks.

Fig. 4 XRD patterns of samples reacted at 1200 K; (a) 0.18 ks and (b) 1.5 ks.

The peaks of La_2O_3 in the XRD patterns shown in Figs. 3 and 4 are different from those of cubic La_2O_3 shown in Fig. 1. Although hexagonal and monoclinic La_2O_3 were identified in the samples at 1300 K (Fig. 3), the formation of the cubic and hexagonal types were observed in samples reacted at 1200 K for 0.18 ks and 1.5 ks, as shown in Fig. 4. The reason for the changes in the crystal structure of unreacted La_2O_3 under the various conditions used remains unsolved.

Next, the diffraction intensities of the compounds containing Ni (LaNi_5 , La_2Ni_7 and CaNi_5) were measured from the XRD patterns of the samples reacted at temperatures from 1200 to 1400 K, and plotted in Fig. 5. We could not examine quantitatively the formation rate of each compound from this diagram but it shows a rough estimation of the tendency for their formation, because the lower parts of the peaks, as mentioned above, overlapped with each other. The formation rate of LaNi_5 was relatively high at every temperature, although it showed irregular behavior in the early stages of the reaction at 1200 and 1400 K. At higher temperatures, CaNi_5 was formed in the early stages of the reaction and faded as the reaction proceeded, which is similar to the result reported by Li *et al.*⁽⁵⁾. The formation rate of La_2Ni_7 was relatively high in the early stages of the reaction at 1400 K, and decreased with reaction time; at 1300 K, the rate was largely similar to that at 1400 K, although much higher than that at 1200 K.

As described in the Introduction, the authors have clarified in previous studies⁽¹⁾⁻⁽⁴⁾ on the formation of rare earth-Fe compounds by the R-D process, that dissolution of Fe in rare earth melts and compound formation by diffusion of rare earth metals in Fe compete with each other. Thus, in the system of the present study, it can be concluded that Ni dissolves into liquid La or La-Ca melt and that La_2Ni_7 is precipitated during the cooling of the melt, since La_2Ni_7 formation would not be stable at 1300 or 1400 K, as expected from the phase diagram⁽⁸⁾ shown

Fig. 5 Time variations of intensities of LaNi_5 , La_2Ni_7 and CaNi_5 .

in Fig. 6. Thus, formation of large amounts of La_2Ni_7 in the samples reacted at 1400 K indicates that a high dissolution rate of Ni generated a large amount of the melt. Conversely, at 1200 K the amount of La_2Ni_7 increased with time, as it would be stable at this temperature.

3. R-D reaction using Ni wires

To further clarify the feature of the reaction process, the R-D reaction was carried out with Ni wires in place of particles in pellets. SEM photographs of the cross-sections of the samples reacted at 1200, 1300 and 1400 K are shown in Figs. 7(a), (b) and (c), respectively. From these photographs, LaNi_5 and CaNi_5 layers were formed on the

Fig. 6 Binary phase diagram of the La-Ni system⁽⁸⁾.

surface of the Ni wire, indicating that Ca first reacted with Ni wires and then LaNi_5 formed, as already reported by Li *et al.*⁽⁵⁾. Figure 8 shows EPMA line analysis along the reaction product layers on a Ni wire in the sample reacted at 1300 K for 2.1 ks; La diffused into the interior of the CaNi_5 layer from the $\text{LaNi}_5/\text{CaNi}_5$ interface. Since a portion of the Ca sites in this CaNi_5 phase was replaced by La and may be transformed into LaNi_5 when the concentration of La exceeds a certain critical value, it would be reasonable to express the phase as $(\text{Ca}, \text{La})\text{Ni}_5$.

4. Effects of amount of CaH_2 on compound formation

Since CaNi_5 forms ahead of LaNi_5 , the amount of CaH_2 added to pellets may considerably affect compound formation. Taking this possibility into consideration, the R-D reaction was also carried out for pellets with $C_{\text{eq}} = 1.0$ and 1.3. X-ray diffraction patterns of the pellets reacted at 1300 K for 0.3 ks are shown in Fig. 9. In the case of $C_{\text{eq}} = 1.0$, most of the La_2O_3 in the pellets seemed to remain unreduced. In the sample with $C_{\text{eq}} = 1.3$, on the other hand, formation of La_2Ni_7 was similar to that in the case of $C_{\text{eq}} = 1.7$ shown in Fig. 5, although not La_2Ni_7 but $\text{LaNi}_{2.28}$ ($\text{La}_7\text{Ni}_{16}$) was formed in the samples with

Fig. 7 Cross-sections of Ni wires in pellets; (a) 1200 K, 3.6 ks, (b) 1300 K, 64.8 ks and (c) 1400 K, 2.2 ks.

Fig. 8 EPMA line analysis along the cross-section of a Ni wire in the pellet reacted at 1300 K for 2.1 ks.

Fig. 9 XRD patterns of samples reacted at 1300 K for 0.3 ks; (a) $C_{eq}=1.0$ and (b) $C_{eq}=1.3$.

$C_{eq}=1.0$. The LaNi_2 phase described in the phase diagrams was recently confirmed to be quasi-stable, and the $\text{La}_7\text{Ni}_{16}$ phase was shown to be stable⁽⁹⁾. These phases were precipitated from the melt during the cooling of samples. Hexagonal La_2O_3 was identified from the XRD pattern shown in Fig. 9(a), and this structure is different from the cubic or monoclinic ones shown in Fig. 1 or Fig. 3.

Diffraction intensities due to LaNi_5 (101) and CaNi_5 (201) in the samples reacted at 1300 K for 0.3 ks are shown in Fig. 10 against the amount of CaH_2 added. Formation of CaNi_5 was not confirmed at $C_{eq}=1.0$. In this diagram it is clear that CaNi_5 formed more easily and that the formation of LaNi_5 was suppressed as the amount of CaH_2 in the pellets increased. This tendency was, of

Fig. 10 Variations in the intensities of LaNi_5 (101) and CaNi_5 (201) with C_{eq} -values; 1300 K, 0.3 ks.

course, seen in the samples reacted for 0.3 ks, and the diminishing of CaNi_5 at the reaction finish has already been described.

These results show, as previously reported by Ogawa⁽⁷⁾, that Ca does not only play a role as a reducing reagent but also promotes the progression of the reaction by including itself into the Ca-La or Ca-La-Ni melts. As an extreme example, the results at $C_{eq}=3.0$ are shown in Fig. 11. The SEM photograph demonstrates a feature of the reaction at 1300 K for 2.4 ks; the cross-sections of the Ni wires 200 μm in diameter lost their original shape, and LaNi_5 was found throughout the pellet. This indicates, in the case of higher Ca content, that not only La but also Ni tended to dissolve in the Ca-melt to form a ternary Ca-La-Ni melt, and thus various kinds of compounds, according to the composition of the melt, would be precipitated during cooling.

Fig. 11 Cross-section of a pellet containing excess CaH_2 ($C_{\text{eq}}=3.0$) reacted at 1300 K for 2.4 ks.

5. Reaction mechanism

Based on the results described above, the mechanism of the formation of La-Ni compounds by the R-D process can be summarized as follows. Firstly, CaH_2 decomposes at about 830 K with the heating of samples to generate H_2 gas and produces La melts at 1110 K. Lanthanum oxide La_2O_3 is rapidly reduced to form liquid La and solid CaO . At the same time, Ni partly dissolves in liquid Ca, La or La-Ca melt and LaNi_5 would be precipitated from the melt when its composition reaches that of the Ni-side liquidus line. In samples containing excess Ca, as shown in Fig. 11, Ni only dissolves into the melt and LaNi_5 is not formed by diffusion but by precipitation during the cooling of the melt, which may cause difficulty in controlling the formation of LaNi_5 . In the Ni-RE systems, in contrast to the Fe-RE systems, Ni can react with not only La but also Ca. The result shown in Fig. 7 indicates that CaNi_5 forms more easily rather than LaNi_5 , at the initial stage of the reaction. One of the reasons why CaNi_5 forms ahead of LaNi_5 may be that La can react with Ni after it is formed by the reduction of La_2O_3 , although Ca is contained as a metallic state in the sample before the reaction and reacts easily with Ni. Once CaNi_5 is formed, La diffuses into the phase to form LaNi_5 by

substituting Ca sites with La. The EPMA analysis shown in Fig. 8 indicates that LaNi_5 is not changed directly to CaNi_5 but that the change proceeds gradually accompanying the formation of $(\text{Ca}, \text{La})\text{Ni}_5$ as a transition state. This may be a result of CaNi_5 and LaNi_5 having the same hexagonal crystal structure and that the ionic radii of Ca and La are not very different from each other.

IV. Summary

To clarify the mechanism of the formation of La-Ni compounds by the R-D process, two kinds of experiments, the reduction of La_2O_3 by CaH_2 and the formation of La-Ni compounds by the R-D method, were carried out at 1200, 1300 and 1400 K. The results obtained can be summarized as follows:

(1) In the reduction of samples containing CaH_2 at 1.7 times C_{eq} , their reduction rate was fairly high, and the reduction was completed in about 1 ks from the start of the reaction at both 1300 and 1400 K.

(2) In the R-D reaction for pellets containing Ni particles 20 to 30 μm in size, small amounts of La_2Ni_7 and CaNi_5 were also identified in addition to LaNi_5 . At 1300 and 1400 K, the formation of CaNi_5 seemed to diminish with reaction time.

(3) In the reaction using Ni wires 200 μm in diameter, LaNi_5 layers formed on the surfaces of the wires and CaNi_5 also formed between the Ni core and the outer LaNi_5 layer; LaNi_5 formed by diffusion of La into the CaNi_5 .

(4) When the quantity of CaH_2 in pellets was increased to 3 times the C_{eq} , the Ni wires dissolved considerably in melts. In the case of $C_{\text{eq}}=1$, the reduction rate was lowered and the formation of LaNi_5 and La_2Ni_7 was confirmed, although no CaNi_5 was formed.

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