Application of Neutron Radiography to Measuring Hydrogen Contents in Hydrogen Containing Solid Solutions I. Solid Solubility of CaH_2 into CaF_2

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1. Introduction

Several kinds of high temperature protonic conductors have been investigated by many workers¹⁻³⁾, because they are expected to work as solid electrolytes of fuel cells or hydrogen sensors. Although hydride ion conductors might also work as such, almost no work exists on them. This is because hydrides composed by ionic bond, such as LiH and CaH_2 , are easily oxidized. But hydride ion conductors are still suitable for measuring hydrogen concentration in liquid metal such as lithium or sodium which are to be used in the field of nuclear engineering⁴⁾.

In order to get stable hydride ion conductors, it would be worthwhile to form some solid solution based on oxide or halide. Here, CaF_2 based materials are known to be fluoride ion conductors and the ionic radius of fluoride ion is almost equal to that of hydride ion ($r_{\text{F}^-}=1.36$, $r_{\text{H}^-}=1.5\text{\AA}$)⁵⁾. If the solid solution of fluorite structure is obtained in the CaF_2 - CaH_2 system, hydride ion conduction is expected. From such a viewpoint, phase relations and electrochemical properties of this system have been investigated in our laboratory. In the course of this investigation, it was needed to measure the accurate amount of hydride ion in prepared

samples because CaH_2 is unstable and the amount of hydride ion in prepared samples may not coincide with that in starting materials. But very few techniques are available for this purpose.

Although neutron radiography (NRG) technique was used to measure hydrogen contents in palladium or niobium by some workers before^{6,7,8)}, the systems investigated were very limited. In this work, this technique was applied to measuring hydrogen amount in the CaF_2 - CaH_2 system and the superiority of this method was confirmed. The results as well as the principle of neutron radiography will be explained in detail below.

2. Experimental

Samples prepared are listed in Table 1. As for SMP1~SMP5 in that, powders of CaF_2 (Wako Pure Chemicals 99.5%) and CaH_2 (Wako Pure Chemicals) were mixed in a mill according to the ratios noted. Thereafter, these were calcined at 700°C for 8 hours in airtight copper capsules. The volume of the capsule is 0.2cm³ and the weight of the reagent in one capsule is between 0.3 and 0.5g. STD1,2,3 are the standard samples prepared for NRG. They have the same compositions as SMP2,3,4 but they were not calcined. Therefore, the compositions of standard samples remain unchanged from those listed in Table 1. Since hydride compounds are easily oxidized by water vapor in air, weighing, mixing and capsulizing were carried out in a glove box purged by N_2 gas.

X-ray powder diffraction analyses of the SMP1~SMP5 were carried out by using a Rigaku

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Table 1 Samples prepared

sample	CaF ₂ :CaH ₂	
SMP1	0.9 : 0.1	calcined at 700°C for 8h
SMP2	0.75 : 0.25	calcined at 700°C for 8h
SMP3	0.5 : 0.5	calcined at 700°C for 8h
SMP4	0.25 : 0.75	calcined at 700°C for 8h
SMP5	0.9 : 0.1	calcined at 700°C for 8h
STD1	0.75 : 0.25	
STD2	0.5 : 0.5	
STD3	0.25 : 0.75	

diffractometer with a Cu X-ray tube and a Ni filter. The diffraction patterns were taken over the range of $20^\circ < 2\theta < 80^\circ$ with a scan rate of $2^\circ/\text{min}$. For comparison, the same analyses were carried out with respect to pure CaF₂ and pure CaH₂. All samples that contain CaH₂ were kept dry in an airtight holder during the measurement.

The sample holder used in NRG measurement is presented in Fig.1. Powdered sample ($2.56 \times 10^{-3} \text{ mol}$) is packed in airtight aluminum capsules and 8 capsules are set in front of X-ray film (Kodak SR for industrial use). The converter (Konishiroku Photo. Industries, KO500) is placed behind the X-ray film. The cylindrical case is revolved slowly on wheels by a small electric motor so that every capsule is irradiated equally.

After SMP1~SMP4, STD1~STD3 and CaF₂ were packed in aluminum capsules in a glove box and set in the holder, they were irradiated in the NRG facility for 3.5 minutes. After the irradiation, the film was developed and its optical

density was measured with a densitometer (Sakura PDA-15).

3. Principles and facilities of NRG

The principle of NRG is similar to that of normal absorption spectroscopies. As illustrated in Fig.2, when a sample is placed across the neutron beam n_0 (/cm²s), part of neutrons are scattered or absorbed in the sample and remaining neutrons n (/cm²s) penetrate through the sample, which are converted into visible light by the converter and recorded on the X-ray film. The relation between n_0 and n is expressed as;

$$\log(n/n_0) = -\mu L \quad (1),$$

where L (cm) denotes the thickness of the sample and μ (/cm) corresponds to the absorption coefficient. This coefficient is expressed as;

$$\mu = \sum_i \sigma_i N_i \quad (2)$$

by using a cross section σ_i (cm²) and concentration N_i (atoms/cm³) of component i in the sample. Cross section σ_i presents the magnitude of interaction between neutron and component i . As shown in Table 2⁹⁾, large difference exists among cross sections of different substances. Since the cross section of hydrogen is far larger than those of calcium and fluorine, the logarithm of penetration ratio n/n_0 largely depends on the hydrogen content in the sample, and eqs(1) and (2) indicate that this dependency is linear. Besides, there exists another linear relation between the film density and the logarithm of neutron exposure in case the film density is not far from 2 as shown in Fig.3. Therefore, the amount of hydrogen in the sample must be expressed as a linear function of the film density and this function can be easily determined by measuring standard samples whose hydrogen contents are known beforehand.

Although there exist more complicated problems on the uniformity of neutron beam or the effect of scattered neutrons to the film density¹⁰⁾, many of them can be eliminated if geometry and irradiation condition of all samples, including standard samples, are made equal.

Fig.1 Experimental apparatus

Fig.2 Schematic illustration of neutron radiography

Fig.3 Relation between film density and neutron fluence

Table 2 Cross section of several substances

substances	cross section τ ($\times 10^{-24} \text{ cm}^2$)
hydrogen	82.0
fluorine	4.0
aluminum	1.7
calcium	3.5
gadolinium	49000

The NRG facility used in this work is installed in the E-2 exposure tube of KUR (Kyoto University Reactor) as shown in Fig.4. Since the exposure tube E-2 is not directed to the core but to the D_2O tank, where energy of fast neutron generated in the core is reduced, the fast neutrons and the gamma ray that come out through this tube

are limited. This condition is ideal for NRG. The detail characteristic of the facility is presented in Table 3. Although real time NRG TV is available in this facility as illustrated in Fig.5, it was not used in this work and the samples were irradiated in front of the TV camera unit.

Fig.4 Horizontal cross section of KUR (Kyoto University Reactor)

Table 3 Characteristics of the KUR neutron radiography facility

1. Reactor / Power	KUR / 5000 [kW]
2. Peak flux of thermal neutron in core	$6 \times 10^{13} \text{ [}/\text{cm}^2 \text{ s]}$
3. Range of L	500 [cm]
4. Standard L/D	100
5. Flux of thermal neutron at film	$1.2 \times 10^6 \text{ [}/\text{cm}^2 \text{ s]}$
6. Gamma dose rate	4.2 [R/h]
7. Cadmium ratio	400
8. Neutron/gamma ray ratio	$1.1 \times 10^6 \text{ [}/\text{cm}^2 \text{ mR]}$
9. Film size available	16 [cm in dia.]
10. Beam Uniformity	+3.5 [%]

Fig.5 Vertical cross section of the NRG facility

4. Results and discussion

The diffraction patterns obtained are presented in Fig.6. The peaks of CaH_2 can not be recognized until the molar ratio of CaH_2 exceeds 0.75, while the peaks of CaF_2 are still recognizable even when molar ratio of CaF_2 is 0.1. This indicates the tendency that a large amount of hydride ions can be dissolved into CaF_2 and the solubility of CaF_2 into CaH_2 is poor. Although further study is necessary to identify all unknown peaks observed in SMP3,4,5, it is reasonable to conclude that SMP1 and SMP2 are made of one phase.

The recorded NRG image on the film is presented in Fig.7. Film densities of five points near the center of each circular image were measured and averaged. The measured film densities of standard samples (STD1~STD3) and pure CaF_2 were plotted against their hydrogen concentrations as shown in Fig.8. In this way the relation

Fig.6 Results of X-ray diffraction

between film density and hydrogen concentration was obtained and this relation was used to determine the hydrogen concentrations of SMP1~SMP4 from their film densities. From Fig.8, the minimum detectable amount is estimated to be 5%.

However, it should be noted here that the converter consists of eight small trapezoidal pieces and the sensitivity of each piece is slightly different. This difference was compensated by adding or subtracting some values to or from measured values so that the film densities of directly exposed areas became equal.

Fig.7 Results of NRG

Fig.8 Relation between film density and hydrogen content

The hydrogen contents of SMP1–SMP4 determined in this way are listed in Table 4. Although partial decomposition and oxidization were believed to occur, most of hydrogen remained in solid phase except SMP4. From these results, it was concluded that

1)NRG technique was confirmed to be valid in measuring hydrogen contents in the CaF_2 – CaH_2 system, and that

2)large solubility of CaH_2 into CaF_2 phase was made clear from the results of X-ray diffraction and NRG.

Table 4 Hydrogen contents measured with NRG

sample	molar ratio of CaH_2 in starting materials	molar ratio of CaH_2 measured with NRG
SMP1	0.1	0.099
SMP2	0.25	0.234
SMP3	0.5	0.425
SMP4	0.75	0.592

More advantages of NRG are as follows.

1)Since NRG is nondestructive and remote sensitive method, NRG can be applied to samples in any chemical form or in any physical state. For example, samples being heated in a furnace or those under high pressure can also be measured.

2)Cross section of hydrogen to cold (or low energy) neutron is far larger than that listed in Table 2. This means more accurate measurement is possible if cold neutron is used.

3)By using real time NRG TV method, changing phenomena can also be investigated.

Improvement of NRG technique by using these advantages is now under study and the results will be reported in near future.

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