Sulfurization of Rare-Earth Oxides Using H_2S and CS_2

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SUMMARY

Sulfurization of rare-earth oxides R2O3 (R=Nd, Eu) using sulfurizing reagents, such as H2S and CS2 was examined for the sulfide magnetic separation of spent fuel. Eu2O3 was found to react with H2S gas forming the mixture of Eu2O2S and EuS at 500 oC, while EuS was formed by CS2 at 800 oC. In the case of the mixture of R2O3 and UO2, EuS and Nd3S4 were formed as well as Eu2O2S and Nd2O2S at 500oC in H2S, though UO2 remained unreacted.

INTRODUCTION

Recent years, dry processes have potentials for the application in nuclear engineering field, since the crude separation and volume reduction of radioactive materials have become acceptable. The magnetic separation process would be a candidate for such dry processes. According to our previous study for magnetic separation of uranium and rare-earths, it was proved that the combination of uranium oxide and rare-earth sulfide is favorable for increasing the separation efficiency, since the sulfides have higher susceptibility than oxides [1].

In this paper, sulfurization behavior of rare-earth oxides R2O3 (R=Nd, Eu) in the presence of H2S or CS2 was studied as well as the thermodynamical consideration for the sulfuization of R2O3.

EXPERIMENTAL

Both Nd2O3 and Eu2O3 powders were obtained from Nippon Yttorium Co. Ltd., and used as received. Stoichiometric UO2 was prepared by the H2 reduction of U3O8 at 1000 oC, which was obtained by the oxidation of U metal turnings in air at 800 oC. Nitrogen and H2S gases of 99.99% purity (Nippon Sanso Co., Ltd.) were used as received. The mixed sample of UO2, Nd2O3 and Eu2O3 was prepared by grinding the equimolar amounts of each powders intimately in an agate mortar. The samples were set in a quartz reaction tube. The tube was evacuated by RP and refilled with N2. Then the sample was heated in a flow of H2S or CS2/N2 gas at an intended temperature for 1 hour. The X-ray powder diffraction analysis for the products was carried out with a Rigaku Type RAD-IC diffractometer using CuKa radiation(40kV, 20mA) monochromatized by curved pyrolytic graphite.

THERMODYNAMICAL CONSIDERATION

Figure 1 shows the potential diagrams of the Nd, Eu-S2-O2 systems at 500 oC constructed using the DATABASE MALT2. The SO2, H2S, H2O, CO2 and CS2 pressure of 1 atm are

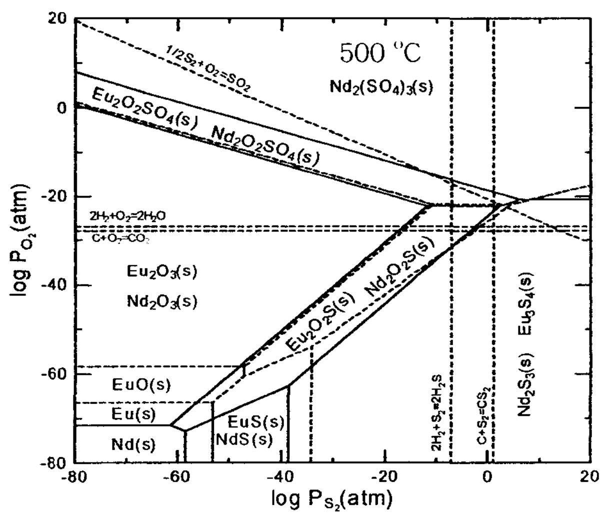


Fig. 1 Potential diagrams of the Nd, Eu-S_2-O_2 systems.

also given in the figure as dotted lines. The stable sulfides are NdS and Nd2S3 for Nd and EuS and Eu3S4 for Eu. As for the oxides, EuO and Eu2O3 are stable while only Nd2O3 appears. Oxysulfides and oxysulfate appears between the oxides and sulfides. If H2S is used, oxysulfides would be formed at this temperature, while sulfides seem to be formed by the reaction with CS2.

RESUTLS AND DISCUSSION

In our previous report [2], Nd2O2S, Nd3S4 and Nd2S3 were formed by the reaction of Nd2(SO3)4 with CS2. When Eu2O3 was reacted with CS2 at 800 oC, the XRD pattern of the product was shown in Fig. 2. It is seen that almost EuS is formed with a small amount of Eu3S4, while Eu2O2S was not obtained. On the other hand, the XRD pattern of the product obtained by the reaction of Eu2O3 with H2S at 500 oC for 3 hours showed that the product was a mixture of Eu2O2S and EuS as seen in Fig. 3. From the above results, selective sulfurization was found to be possible by the types of the sulfurizing agents.

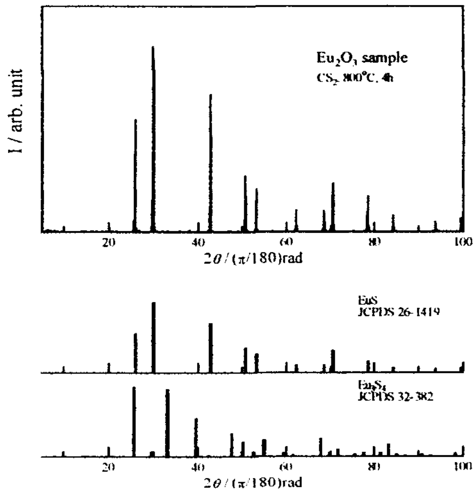
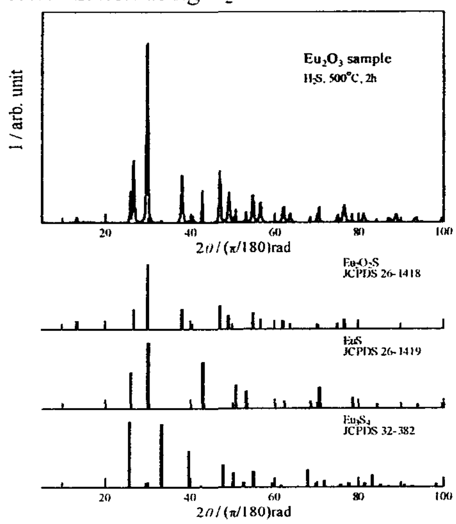


Fig.2 XRD pattern of the product obtained by sulfurization using H_2S at 800°C for 4 hs.



When the mixture of of UO2, Nd2O3 and Eu2O3 powders was heated in a flow of H2S with a rate of 30 ml/min at 500 °C for 1 hour, the XRD pattern for the product is shown in Fig.3 with the reported patterns of related compounds. It is seen that Eu_2O_3 and Nd_2O_3 are sulfurized forming Eu_2O_2S and EuS for europium and Nd_2O_2S and Eu_3S_4 for neodymium, while UO_2 remained without sulfurization.

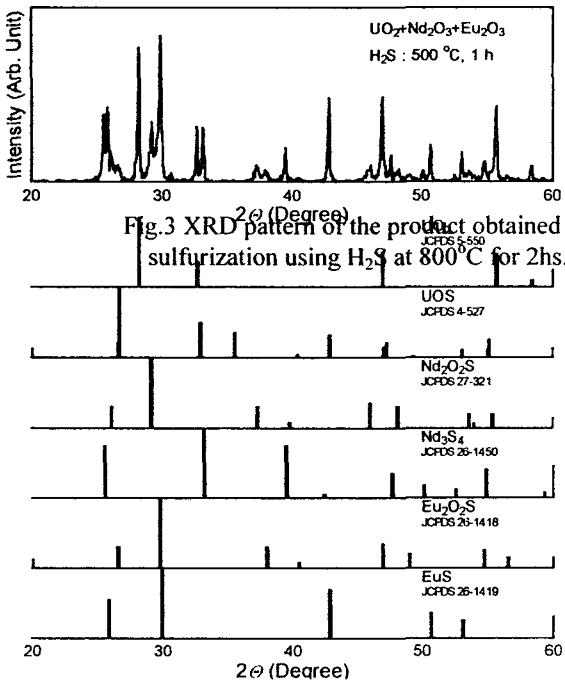


Fig.3 XRD pattern of the product obtained by sulfurization using H_2S at 800°C for 2hs.

Fig.4 XRD pattern of the product obtained by sulfurization using H_2S at 500°C for 1 hour.

SUMMARY

For the application of magnetic separation process to the spent fuel processing and waste treatment, sulfurization of R2O3 (R=Nd, Eu) using H2S and CS2 was examined. Eu2O3 was sulfurized by CS2 at 800oC forming EuS, while the mixture of Eu2O2S and EuS was obtained by H2S at 500oC. By the sulfurization of the mixture of UO2 and R2O3, the selective sulfurization of R2O3 by H2S or CS2 was found to occur at relatively low temperature.

REFERENCES

[1] S.Sato et al., Proc. of Fall Meeting of Atomic Energy Society of Japan, I13(2003).

[2] M. Skrobian et al., Thermochim. Acta, 249(1995)211.