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DSC studies on reactions of the elements with sulfur

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Abstract

The sulfidation reaction of the elements in sealed silica tubes methods has been studied by differential scanning calorimetry (DSC) with a heating rate of 10 °C min^{-1} at temperatures between 25 and 800 °C. The reaction pathways were investigated by thermoanalytical and X-ray methods. The elements tested were as follows: Ag, Al, B, Bi, Cd, Co, Cr, Cu, Fe, Ga, Ge, Hf, In, Mg, Mn, Mo, Nb, Ni, P, Pb, Pt, Si, Sn, Ta, Ti, V, W, Zn and Zr. The sulfidation temperature of the elements has been determined from DSC data.

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Keywords: Sulfidation reactions; Differential scanning calorimetry; Elements; Sulfidation temperature

1. Introduction

The sealed silica tube method is known as the most convenient and simplest way to prepare sulfide compounds from the mixture of an element and sulfur. There is a lot of information available about the syntheses of sulfides by that method in the literature [1–3]. However, it is still lacking in knowledge on kinetics of the sulfidation of elements to sulfide compounds. Especially not much data have been reported about the sulfidation initiation point where the reaction starts remarkably. Differential scanning calorimetry (DSC) is one of the most effective methods for studying such phenomena and reaction pathways. In order to understand the reactivity of an element on sulfidation, systematic and comprehensive thermochemical studies are required. In this research, the mixing ratio of the starting materials was fixed to 1:1 because most of the reaction of sulfide formation could be expressed typically as either $M+S \rightarrow MS$ or $M+S \rightarrow 1/2MS_2 + 1/2M$. This paper concerns with thermochemical behavior of the mixture of M and S in the heating process and its sulfidation temperature.

2. Experimental

Reagents used are generally of high purity grade powders, mainly from Rare Metallic: Ag (3N, 325 mesh), Al (4N, 325 mesh), B (2N, 100 mesh), Bi (3N, 100 mesh), Cd (3N, 325 mesh), Co (3N, 325 mesh), Cr (3N, 200 mesh), Cu (3N, 325 mesh), Fe (4N, 200 mesh), Ga (4N, shot), Ge (4N, 100 mesh), Hf (2N6, 325 mesh), In (3N, 325 mesh), Mg (3N, 50 mesh), Mn (3N, 200 mesh), Mo (3N, 100 mesh), Nb (3N6, 200 mesh), Ni (3N, 200 mesh), P (3N), Pb (5N, 200 mesh), Pt (3N, wire 0.2 mm), S (6N, >100 mesh), Si (4N, 150 mesh), Sn (4N, 200 mesh), Ta (3N, 325 mesh), Ti (3N, 100 mesh), V (2N7, 325 mesh), W (3N, 3μ), Zn (3N, 300 mesh) and Zr (3N, 300 mesh).

Differential thermal analysis was carried out with SETARAM DSC-111 instruments at a heating rate of 10 °C min^{-1} in the temperature range of 25–800 °C. Mixtures of one element and sulfur were put into small silica glass ampoule (diameter 5 mm, length 15 mm) and sealed in vacuum below 10^{-3} Torr. The closed ampoule was set horizontally in the center of the furnace together with the empty identical one arranged on the reference side. A total of 10 mg S and equimolar amount of the selected element was used for each run. The DSC experiments were made repeatedly twice by using the same sample in order to determine the baseline.

The final products were characterized by X-ray powder diffraction using a Rint 2200HF + ULTIMA diffractometer

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(Rigaku) with Cu Kα radiation. Compositions of binary sulfide were analyzed by the weight-loss method on oxidation.

3. Results and discussion

3.1. General aspects of sulfidation reaction of the elements

When a mixture of an element and sulfur is heated, the reaction starts in most cases at high temperatures. Generally, the sulfidation reaction proceeds heterogeneously including gas, liquid and solid phases, so that the events happened in the heating process are not simple. However, it is possible for us to clarify such phenomena to some extent from the thermochemical view point. For example, the differential scanning calorimetry thermal effects of sulfidation generally appears as exothermic peaks on its thermogramme. On the contrary, the thermal effects due to fusion, phase transition, and evaporation of materials appear as endothermic peaks. The DSC curves of the mixture Fe + S are shown in Fig. 1(a) as representative for sulfidation reaction. The first small endothermic peak (1) of first run at ca. 119 °C is assigned to the melting of source sulfur. This is followed by two stages of intense exothermic events, (2) and (4), due to the sulfidation reaction above 250 °C. However, in the case of second run of the same sample, there appear no exothermic peaks. This suggests that the reaction $Fe + S \rightarrow FeS$ completed perfectly during first run. In order to clarify the reaction pathways, the products at (3) and (4) were characterized by X-ray powder diffraction. As shown in Fig. 1b, only Fe exists as crystalline phase according to XRD at (3), so that the sulfide formed at 250–280 °C is considered to be X-ray-amorphous. However, the final product after (4) is assigned as crystalline hexagonal FeS (troilite) with a = 5.9732(4) Å, c = 11.4832(7) Å [4]. This indicates that the sulfidation reaction of Fe is largely affected by the 3rd thermal event (320–425 °C). The enthalpy of formation of FeS calculated from the integration of areas of exothermic peaks becomes 18.8 kcal/mol, which is close to the value, 22 kcal/mol, reported in literature [5]. Similar works on the other elements were carried out through this study.

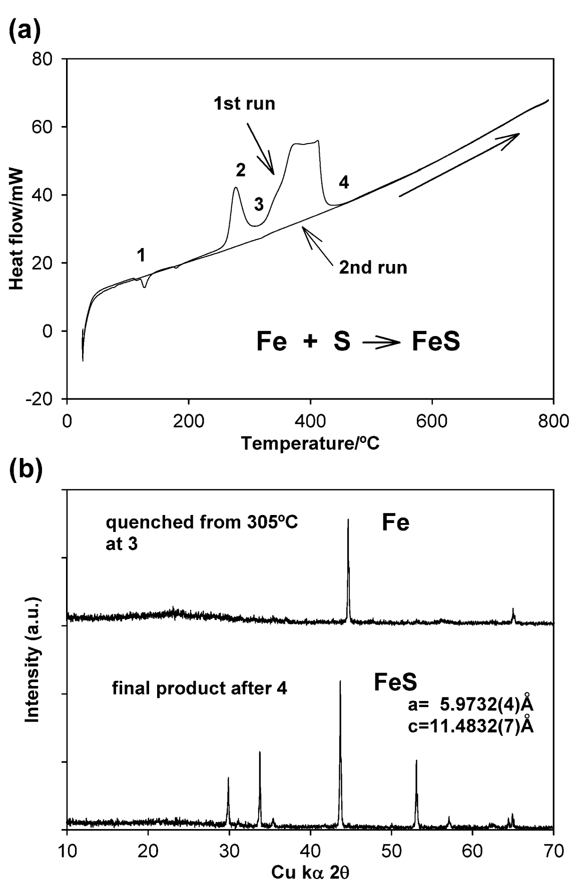

Fig. 1. (a) DSC curves of the mixture of Fe + S. Thermogrames are drawn duplicated for first and second runs. (b) XRD patterns of products at 3 (upper) and after 4 (lower).

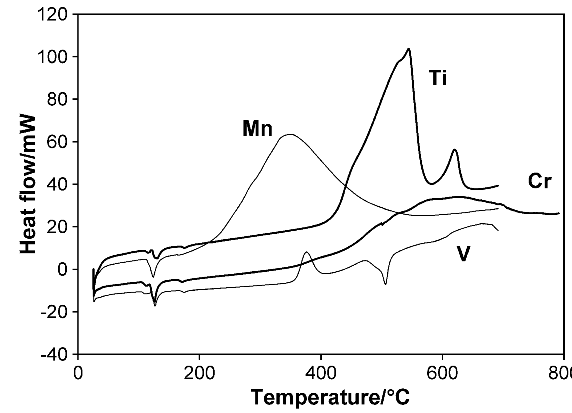

Fig. 2. DSC curves of mixtures of Ti–S, V–S, Cr–S and Mn–S.

3.2. Sulfidation reaction of the transition metals (3d, 4d and 5d series)

DSC curves of M + S with M = Ti, V, Mn and Cr are shown in Fig. 2. Sulfidation of Mn, Ti, Cr, V starts at 170, 410, 400 and 350 °C, respectively. Exothermic peaks of Mn at 350 °C and Cr at 600 °C are relatively broad. In the case

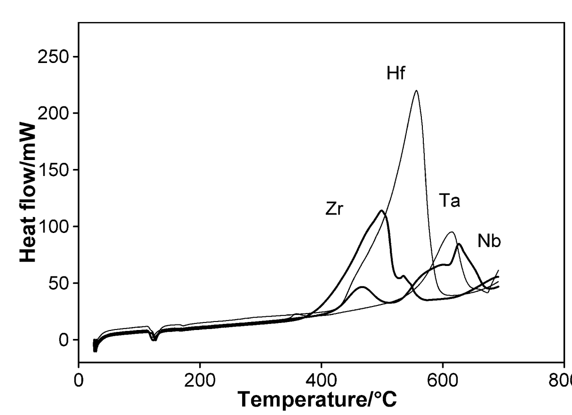

Fig. 3. DSC curves of mixtures of Zr–S, Nb–S, Hf–S and Ta–S.

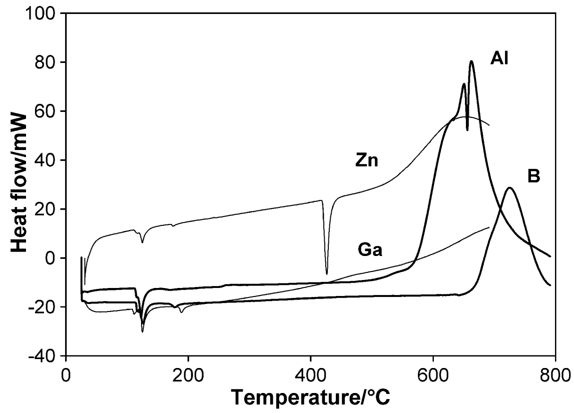

Fig. 4. DSC curves of mixtures of B–S, Al–S, Zn–S and Ga–S.

of V the reaction seems to be rather complicated because the phase transition from orthorhombic MnP to hexagonal NiAs-type VS_y [6,7] is observed at 505 °C in the intermediate stages of heating. DSC curves of M+S with M=Zr, Nb, Hf, Ta are shown in Fig. 3. The beginning temperatures of sulfidation reaction are 360 °C for Zr, 415 °C for Nb, 425 °C for Hf and 540 °C for Ta, respectively. As for thermogrammes of 4A elements, Ti, Zr and Hf show very similar profiles. As for those of 5A elements, Nb and Ta also behave similarly. In the cases of 4A and 5A transition metals, the sulfidation reactions seem to be completed in the process of heating to 800 °C. Enthalpies of formation of MnS and NiS from this work are 36.4 and 18.2 kcal/mol, respectively. The corresponding values in literature [5,8] are 44.0 and 22.2 kcal/mol. Enthalpies of formation of TiS_2, HfS_2 and MoS_2 are 103, 119 and 54.6 kcal/mol, respectively. These values are in relatively good agreement with the reported ones, 102, 140 and 60.4 kcal/mol although there is some difference between them.

3.3. Sulfidation reaction of the non-transition elements

DSC curves of M+S with M=3B elements, B, Al and Ga, are shown in Fig. 4 together with that of 2B transition metal Zn. Boron takes place to react with S at 658 °C.

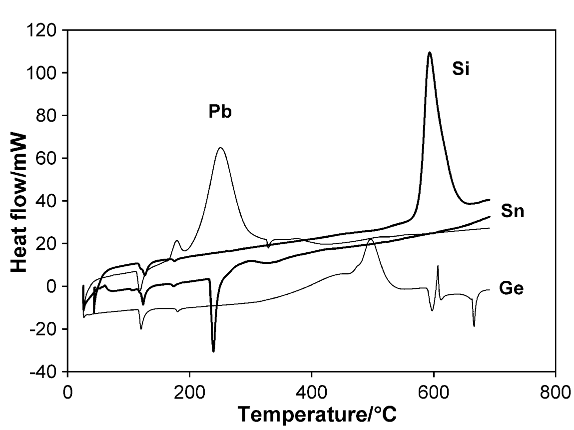

Fig. 5. DSC curves of mixtures of Si–S, Ge–S, Sn–S and Pb–S.

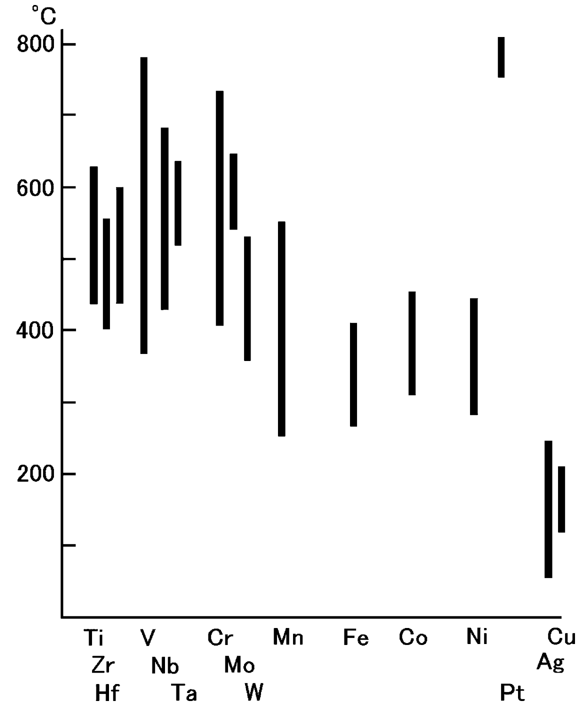

Fig. 6. Sulfidation temperatures of the elements Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zr, Nb, Mo, Ag, Hf, Ta, W and Pt.

Sulfidation of Al starts at 565 °C and ends around 800 °C. In the case of Ga, the reaction does not proceed even at 700 °C. After the run, we confirmed a lot of non reacted

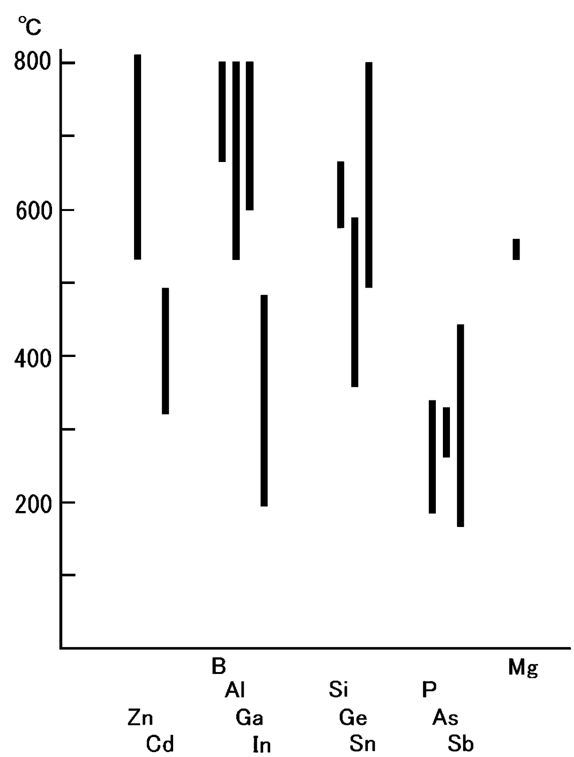

Fig. 7. Sulfidation temperatures of the elements B, Mg, Al, Si, P, Zn, Ga, Ge, As, Cd, In, Sn and Sb.

sulfur left in the ampoule. Similar result was obtained for Zn. In both cases, the exothermic reactions seem to be rather broad and sluggish. DSC curves of M + S with M = 4B elements, Si, Ge, Sn and Pb, are shown in Fig. 5. Sulfidation of Si, Ge and Pb starts at 568, 350 and 166 °C, respectively. In the case of Sn, however, the reaction doesn't proceed even at higher temperatures than its melting point (232 °C).

3.4. Sulfidation temperature of the elements

Thermochemical data on sulfidation of elements is very useful for preparation of sulfides. DSC method gives us correct information about the temperature at which sulfidation reaction start. Such a database is very convenient for sulfide chemistry if we can use it as graphical representation. For this purpose, we introduce here the concept of "sulfidation temperature", which implies the temperature range from the beginning to the finishing of thermal effects of reaction. Sulfidation temperatures of the elements obtained in this study are graphically shown in Figs. 6 and 7. Within our data, Ag and Cu metals exhibit relatively lower sulfidation temperatures of 110–220 and 60–250 °C, respectively. On the contrary, elements such as Zn, Ga and Sn show rather higher sulfidation temperatures of 530–800, 600–800 and 500–800 °C, respectively. Clearly the reactivity of sulfur to element is different with species of elements in the periodic table. Probably, the sulfidation reaction is closely related to the inherent nature of chemical bond between an element and sulfur. Now further detailed studies are in progress.

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