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Heats of formation of $(U,Mo)Al_3$ and $U(Al,Si)_3$ ☆

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Abstract

The heats of formation of $(U,Mo)Al_3$ intermetallic compounds were obtained by measuring the reaction heats of U–Mo/Al dispersion samples by differential scanning calorimetry. Based on literature data for the reaction heats of U_3Si/Al and U_3Si_2/Al dispersion samples, the heats of formation of $U(Al,Si)_3$ as a function of the Si content were calculated. The heat of formation of $(U,Mo)Al_3$ becomes less negative as the Mo content increases. Conversely, the heat of formation of $U(Al,Si)_3$ becomes more negative with increasing Si content.

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1. Introduction

U–Mo/Al dispersion fuel with low enrichment (<20 wt%) in U-235 has been under development for advanced research reactors because of its high uranium density compared to U_3Si_2/Al and UAl_x/Al (UAl_x means a mixture of UAl_2, UAl_3 and UAl_4) [1]. A typical as-fabricated microstructure of U–Mo/Al dispersion fuel is shown in Fig. 1(a). U–Mo alloy particles tend to form an interaction layer with an Al matrix through a diffusion reaction process during irradiation or thermal annealing of the dispersion fuel sample. U–Mo/Al dispersion fuel revealed unacceptable pore development in the interaction layers that formed between U–Mo fuel and Al matrix at high fission rates during the irradiation as shown in Fig. 1(b) [2]. Because UAl_x/Al dispersion fuel is free of such a phenomenon [3], it is Mo that decreases the irradiation stability of the interaction layer. In order to counteract this adverse effect of Mo, the addition of Si to the Al matrix was proposed [4]. Irradiation tests of U–Mo/Al–Si with various Si contents have been underway in the RERTR (Reduced Enrichment for Research and

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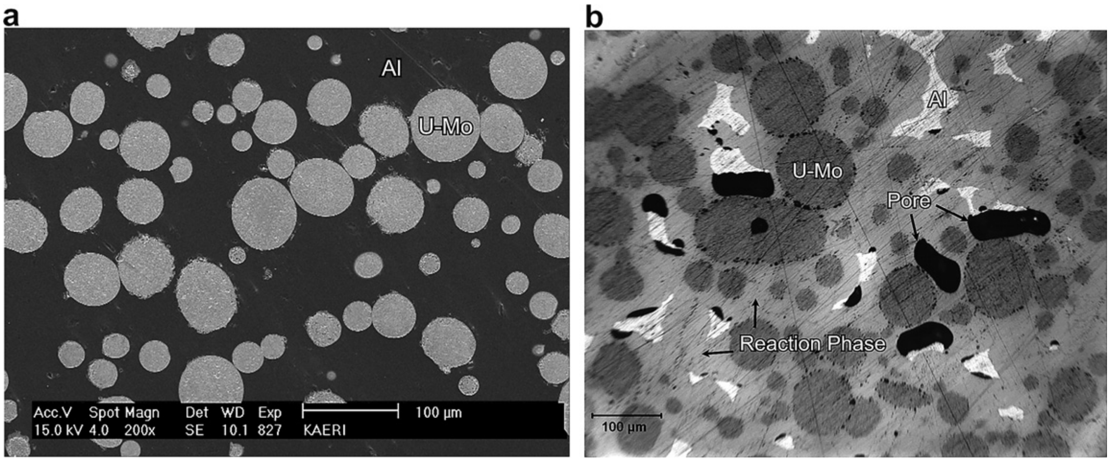

Fig. 1. Microstructures of U–Mo/Al dispersion fuel: (a) a scanning electron micrograph (SEM) of an as-fabricated sample, (b) an optical micrograph of an as-irradiated sample.

Test Reactors) programs in countries including the US, France, Russia and South Korea to verify the efficacy of Si addition [5].

The unstable pore development in U–Mo/Al dispersion fuel resembles the pore development behavior of radiation-induced amorphized uranium compounds such as U_3Si or U_6Fe during irradiation of U_3Si/Al or U_6Fe/Al dispersion fuel [6]. On the other hand, high Si content dispersions of U_3Si_2/Al and USi/Al did not show such unstable pore development. This may imply that Si has a beneficial effect on irradiation stability of interaction product.

Analyses using Miedema's theory have shown that Si addition decreases the formation enthalpies (i.e., to more negative values) of the interaction compounds [5]. The objective of this paper is to obtain the heats of formation of uranium aluminides with minor amounts of Mo or Si addition.

Reaction heats of U–Mo/Al dispersion samples were measured calorimetrically. Although other phases have been reported, $(U,Mo)Al_3$ is the prominent reaction product in the U–Mo/Al dispersion samples when observed by X-ray diffractometry and differential scanning calorimetry (DSC) [7]. For uranium silicide/Al dispersion fuel, however, $U(Al,Si)_3$ is the only reaction phase [8]. The formation reactions of $(U,Mo)Al_3$ and $U(Al,Si)_3$ are given as follows:

$$(1-v)\mathrm{U} + v\mathrm{Mo} + 3\mathrm{Al} = (\mathrm{U}_{1-v}\mathrm{Mo}_v)\mathrm{Al}_3 \qquad (1)$$

$$\mathrm{U} + 3(1-w)\mathrm{Al} + 3w\mathrm{Si} = \mathrm{U}(\mathrm{Al}_{1-w}\mathrm{Si}_w)_3 \qquad (2)$$

Table 1
Heats of formation at 298 K ($\Delta_f H^0_{298}$) of U_3Si, U_3Si_2, USi_3, and UAl_3 [9]

Compounds	U_3Si	U_3Si_2	USi_3	UAl_3
$\Delta_f H^0_{298}$ (kJ/mol)	−134.0	−170.7	−132.2	−104.6

The heats of formation of $(U,Mo)Al_3$ were calculated from the measured data in this study, while the heat of formation of $U(Al,Si)_3$ was calculated by using the relevant measured data available in the literature. Table 1 contains the heats of formation of U_3Si, U_3Si_2, UAl_3 and USi_3 available in the literature [9].

2. Experimental procedures

Centrifugally-atomized U–6 wt%Mo and U–10 wt%Mo alloy powders of 75 µm in average diameter and a pure Al powder of 20 µm in average diameter were mixed and extruded into U–Mo/Al dispersion samples at 673 K. Throughout this paper, the number in front of Mo in U–Mo alloy stands for the Mo content in wt%. Volume fractions were measured by image analysis of scanning electron micrographs of U–Mo/Al dispersion samples. The measured volume fractions were 33 and 37 vol.% for U–6Mo, and 30 and 37 vol.% for U–10Mo.

The thermal analyses were carried out on 30 mg of U–Mo dispersion samples with a high temperature differential scanning calorimeter (Netzsch DSC). Dispersion samples were heated in a Pt crucible in a flowing high purity (99.999%) Ar atmosphere from room temperature to 973 K at a heating rate of 10 K/min. The time-resolved power changes (in W) under the controlled temperature program were measured during the heating cycle.

3. Results

Two examples of the power changes recorded during the heating cycle of DSC are shown in Fig. 2. The negative spike of the power change (in Watts) resulting from the spontaneous reaction between U–Mo and Al was integrated with respect to time (in seconds) to obtain the exothermic heat (in Joules) of the reaction. The durations for the power spikes measured in the tests were in the range of 20–30 s. Once obtained the mole number of the reaction product per gram of the reacted dispersion sample, we converted the heat generation measured per gram of sample to the heat per mole of the reaction product. These results are given in Table 2. We confirmed the completion of the reaction by microstructural analyses after the test. An example of the reacted sample is shown in Fig. 3, where we can see no Al left after the test. The black phase shown in the figure is the polyester resin impregnated during SEM sample preparation. The same procedure was used for the U–10Mo/Al cases, and the results are also included in Table 2.

Because the mole number of reaction product per gram of the reacted dispersion sample for the 33 vol.% sample is greater than that of the 37 vol.% sample, the heats of reaction per mole of reaction product from samples with different U–Mo vol.% became similar to each other. The measured heats of formation (i.e., the heats of reaction for this case) at reaction temperatures ($\Delta_f H_T^0$ in Table 2) were transferred to 298 K for comparison with literature data in Fig. 4 by using the following equation:

$$\Delta_f H_{298}^0 = \Delta_f H_T^0 - \int_{298}^{T} \Delta C_p \, dT. \tag{3}$$

The molar heat capacity of (U,Mo)Al_3 was estimated using that of UAl_3 in the literature [9] as follows:

$$C_p^{(U,Mo)Al_3} = \frac{(1 - v_{Mo})C_p^{U} + v_{Mo}C_p^{Mo}}{C_p^{U}} C_p^{UAl_3} \tag{4}$$

where v_{Mo} is the molar ratio of Mo/(U+Mo). Eq. (4) is valid only for cases with $v_{Mo} \ll 1$ as U–6Mo and U–10Mo in the present study. We had to use

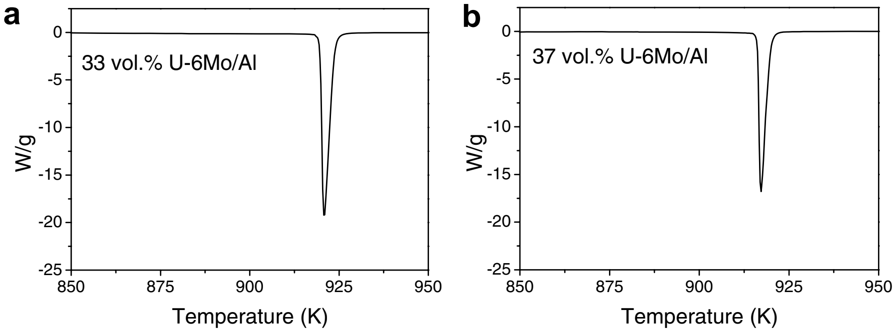

Fig. 2. Thermal analysis graphs of DSC tests of U–6Mo/Al dispersion samples: (a) 33 vol.% U–6Mo, (b) 37 vol.% U–6Mo.

Table 2
Heats of formation of (U,Mo)Al_3 formed in U–6Mo/Al and U–10Mo/Al dispersion samples

Dispersion sample	U–6Mo/Al		U–10Mo/Al	
U–Mo vol.%	33	37	30	37
Exothermic heat of reaction per gram of sample at reaction temperature (J/g)	233	201	238	178
Mole of reaction product per gram of dispersion sample	2.95×10^{-3}	2.57×10^{-3}	3.37×10^{-3}	2.66×10^{-3}
Reaction temperature (K)	921	917	923	922
$\Delta_f H_T^0$ (kJ/mol)	−79.0	−78.1	−70.5	−66.9
$\Delta_f H_{298}^0$ (kJ/mol)	−67.5	−66.8	−58.0	−54.5

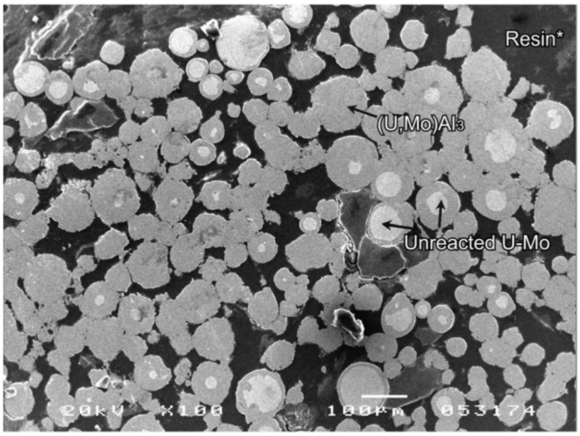

Fig. 3. SEM of the cross section of the U–Mo/Al dispersion sample with 37 vol.% U–Mo after differential scanning calorimetry test [7]. (∗ The black phase is the polyester resin impregnated as-reacted pores during SEM sample preparation. No unreacted Al is left.)

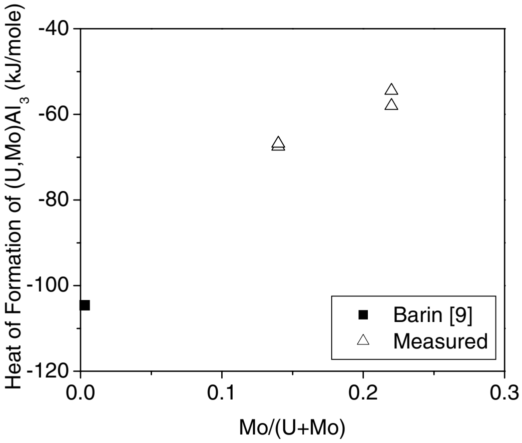

Fig. 4. Heat of formation ($\Delta_f H^0_{298}$) of (U,Mo)Al_3 versus Mo/(U + Mo) molar ratio.

this approximation since the molar heat capacity of $MoAl_3$ is not known and, furthermore, the existence of $MoAl_3$ is still in controversy.

As shown in Fig. 4, (U,Mo)Al_3 has a less negative heat of formation ($\Delta_f H^0_{298}$) than UAl_3, and the heat of formation of (U,Mo)Al_3 becomes less negative as the Mo content increases.

4. Discussion

Table 3
Experimental data reported by Domagala et al. [10]

Dispersion sample	U_3Si/Al	U_3Si_2/Al
U_3Si_n fraction (vol.%)	32.0	32.0
Mass of U_3Si_n (mg)	30.9 ± 1.9	24.0 ± 1.0
Exothermic heat of reaction (J)	9.0 ± 1.6	6.1 ± 2.2
Reaction temperature (K)	866	855

Table 4
Heats of reaction of the U_3Si/Al and U_3Si_2/Al dispersion samples calculated based on the measured data by Domagala et al. [10]

Dispersion sample	U_3Si/Al	U_3Si_2/Al
Reaction product mass per gram of U_3Si_n (g)	1.29	1.25
Mole of reaction product per gram of U_3Si_n	4.04×10^{-3}	3.90×10^{-3}
$\Delta_r H^0_T$ (kJ/mol)	−72.8	−64.7
$\Delta_r H^0_{298}$ (kJ/mol)	−65.7	−58.2
$\Delta_f H^0_{298}$ (kJ/mol)	−110.6 ± 15.3	−115.1 ± 21.5

Domagala et al. [10] measured the heat released during heating of U_3Si/Al and U_3Si_2/Al dispersion samples as given in Table 3. For both, the uranium silicide volume fraction was 0.32. Domagala et al. did not obtain the heats of formation for the reaction compounds. Using their experimental data, we calculated the heats of formation of U(Al,Si)$_3$. Table 4 shows the calculated masses of the reaction compound produced after the reaction of 32 vol.% U_3Si/Al and U_3Si_2/Al dispersion samples per gram of U_3Si or U_3Si_2 consumed. By using this result and the DSC data, the heats of reaction per mole of U(Al,Si)$_3$ ($\Delta_r H^0_{298}$) were calculated by the similar method described in Section 3. Since those of UAl_3 and USi_3 are known, the molar heat capacity of U(Al,Si)$_3$ was estimated by the rule-of-mixtures as follows:

$$C_p^{U(Al,Si)_3} = v_{UAl_3} C_p^{UAl_3} + (1 - v_{UAl_3}) C_p^{USi_3} \tag{5}$$

where v_{UAl_3} is the UAl_3 mole fraction.

The heat of formation of U(Al,Si)$_3$ can be obtained from the heat of reaction by considering the heat of formation of pre-existing U_3Si or U_3Si_2 as listed in Table 1. The reaction products from U_3Si–Al and U_3Si_2–Al reactions were calculated as $U(Al_{0.89}Si_{0.11})_3$ and $U(Al_{0.78}Si_{0.22})_3$, respectively, according to the following mass balance equations:

$$U_3Si + 8Al = 3U(Al_{8/9}Si_{1/9})_3 \tag{6}$$

$$U_3Si_2 + 7Al = 3U(Al_{7/9}Si_{2/9})_3 \tag{7}$$

As a result, the heats of formation of $U(Al_{0.89}Si_{0.11})_3$ and $U(Al_{0.78}Si_{0.22})_3$ were obtained and given in Table 4.

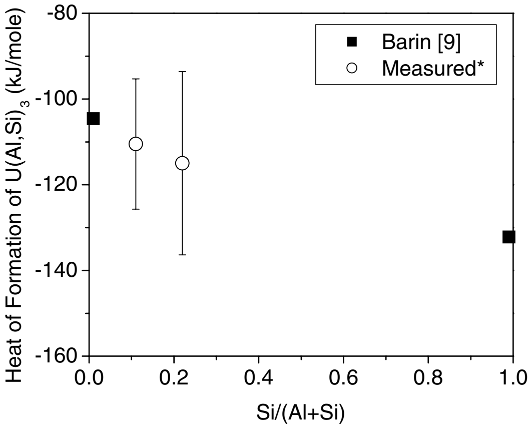

Fig. 5. Heat of formation ($\Delta_f H^0_{298}$) of $U(Al,Si)_3$ versus Si/(Al + Si) molar ratio. (* Calculated based on the measured data by Domagala et al. [10].)

The results together with the heats of formation of UAl_3 and USi_3 are compared in Fig. 5. As the Si content increases in $U(Al,Si)_3$, the heat of formation becomes more negative. The present results are in accord with the theoretical work by the Miedema model reported in Ref. [5].

5. Conclusions

The heats of formation of $(U,Mo)Al_3$ and $U(Al,Si)_3$ were calculated based on experimental data for several Mo and Si contents. An increase in the Mo content yields a less negative heat of formation of $(U,Mo)Al_3$, whereas an increase in the Si content yields a more negative heat of formation of $U(Al,Si)_3$.

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