Calculations of the Stability of U-Mo-Al Mixtures and Compounds

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1. Introduction

Since the demonstration of high-power-density dispersion fuel of U-Mo/Al, a number of researches for the application of U-Mo/Al fuel have been investigated [1]. Recently, Hofman et al. reported that high porosity formation that has occurred in the U-Mo/Al interaction phase, and proposed a way of increasing the stability of the interaction phase by the addition of a fourth element [2]. In order to find appropriate additional element, the calculation of the thermodynamic stability of the U-Mo-Al mixtures and compounds should be investigated.

The change in Gibbs free energy is the measure of the stability of an alloy mixture. Enthalpy change is the dominant part of Gibbs free energy at low temperatures compared to the entropy change in dispersion fuel. Knowing the enthalpy of formation provides an approximate measure of the stability of mixtures.

In this study, calculations of the enthalpy of formation were provided for the binary mixtures using the Miedema model [3]. An extension method to ternary and quaternary systems is also demonstrated.

2. Methods and Results

2.1 Miedema Model

This method is partly based on the Wigner-Seitz atomic cell theory for pure metals [4]. Miedema et al. [3] assume that the change in the density of electrons at the boundary of the Wigner-Seitz cell, Δn_{ws}, contributes a positive term to enthalpy in alloy mixing, and change in the electronegativity of elements, φ, contributes a negative term to enthalpy. This electronegativity potential of electrons in metals is lowered upon alloying and consequently ΔH is lowered.

The interfacial enthalpy for solution of one mole of A atoms is given by

$$\Delta H^{\text{inter}}(A\,in\,B) = \frac{2V_A^{2/3}}{n_{wsA}^{-1/3} + n_{wsB}^{-1/3}}(-P(\Delta\varphi)^2 + Q(\Delta n_{ws}^{1/3})^2 - R)$$

where ΔH^{inter} is the interfacial enthalpy for solution of one mole of A atoms in B, in which the A atom is contacted by the B atoms only, V is the atomic volume, n_{ws} the electron density, φ the electronic charge. P, Q and R are constants in various conditions [5]. The equation for the formation enthalpy of an AB binary is given by

$$\Delta H^{form} = c_A f_B^A \Delta H^{\text{inter}}(A\,in\,B)$$

The variables and constants are described in reference [5].

2.2 Calculation of Binary Mixtures

The interfacial enthalpies of U in Mo based on basic values [5] were +9 kJ/mol, and that of U in Al were –184 kJ/mol. The positive enthalpy suggests that Mo does not spontaneously dissolve into U. Contrary, Al can dissolve into U and form intermetallic compounds.

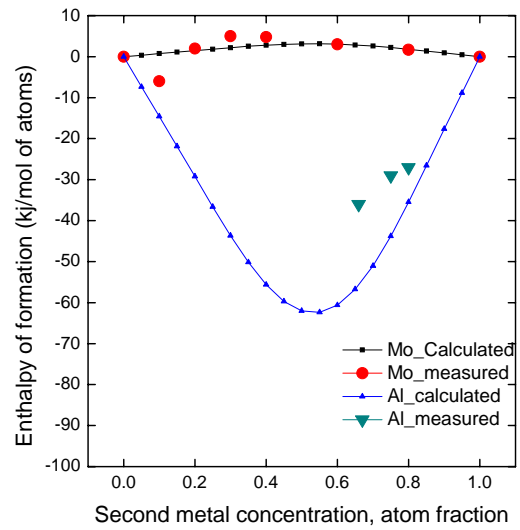Figure 1 shows the calculated enthalpy of formation.

Fig.1. Enthalpies of formation of U-Mo, U-al alloys

The calculated values fit relatively well to the experimental data for alloys with Mo contents higher than ~60 at% but the calculation is inaccurate for low Mo contents. Below the 20 at% Mo, the calculated data was positive but the experimental data showed negative value. The deviation is attributed to the complex phase changes of the U-Mo alloy system. The enthalpies of UAl$_2$, UAl$_3$, and UAl$_4$ are calculated as –55, –44, and –35 kJ/mol, respectively. The measured enthalpies of formation for UAl$_2$, UAl$_3$, and UAl$_4$ compounds are –36, –29, and –27 kJ/mol, respectively [6]. The reasons for the consistent deviations are attributed to the negligence of heat content difference between 0 and 298 K, effect of volume change, and elastic enthalpy due to mismatch between atoms and structural enthalpy.

2.3 Calculation of Ternary System

For a A-B-C ternary system, the formation enthalpy is given by

$$\Delta H^{form} = c_A f_B^A \Delta H^{\text{inter}}(A\,in\,B) + c_A f_C^A \Delta H^{\text{inter}}(A\,in\,C)$$
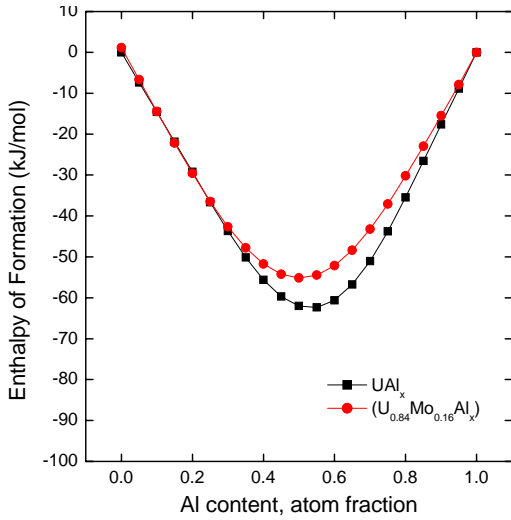$$+ c_B f_C^B \Delta H^{\text{inter}}(B\,in\,C)$$

Fig. 2. Enthalpy of formation of $(U_{0.84}Mo_{0.16})Al_x$ and UAl_x

In U-7wt% Mo system, ΔH^{form} of $(U_{0.84}Mo_{0.16})Al_x$ is calculated and compared to that of UAl_x in Fig. 2. It is noticed that the enthalpy of formation of $(U_{0.84}Mo_{0.16})Al_x$ is less negative than that of UAl_x because of the positive interfacial enthalpy of Mo in U. It suggests that UAl_x is more stable than $(U_{0.84}Mo_{0.16})Al_x$ and U-7wt% Mo should be decomposed in Al Matrix.

2.4 Effect of fourth element

The Miedema method was extended to be applicable to a quaternary system. For a quaternary, the formation enthalpy is given by

$$\Delta H^{form} = c_A f_B^A \Delta H^{inter}(A\,in\,B) + c_A f_C^A \Delta H^{inter}(A\,in\,C)$$
$$+ c_A f_D^A \Delta H^{inter}(A\,in\,D) + c_B f_C^B \Delta H^{inter}(B\,in\,C)$$
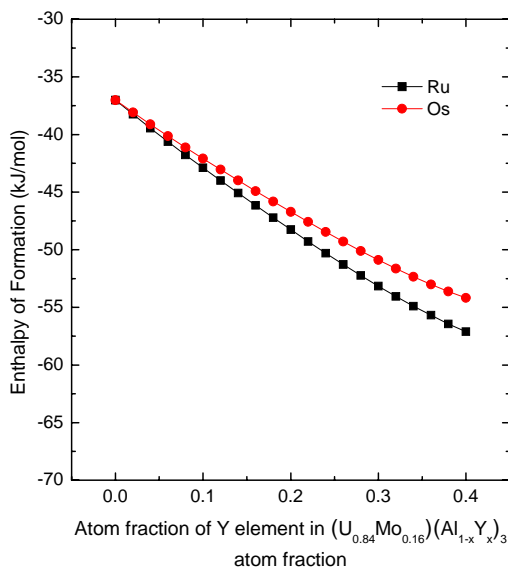$$+ c_B f_D^B \Delta H^{inter}(B\,in\,D) + c_C f_D^C \Delta H^{inter}(C\,in\,D)$$

Fig. 3. Enthalpy of formation of $(U_{0.84}Mo_{0.16})(Al_{1-x}\,Y_x)_3$

The effect of Ru and Os on the stability of intermetallic compound in U-7wt% Mo/Al dispersion fuel was calculated. Figure 3 shows the effect of element on the enthalpy of formation of an assumed interaction phase composition. This result means that the addition of Ru or Os increases the stability of the compound. Preliminary experiments showed that U-Mo-Os alloy showed good stability with Al matrix, but U-Mo-Ru alloy reacted with Al matrix. For accurate predictions, another investigation is needed.

3. Conclusion

In the present investigation, the calculation of the enthalpies of the U-Mo/Al system was provided using the Miedema Model. The calculation showed that UAl_x compounds are more stable than U-Mo/Al_x compounds. The binary model was extended to the ternary and quaternary to calculate the enthalpies. It has been shows that it is possible to increase the stability of the U-Mo/Al by addition of appropriate element.

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