THERMODYNAMIC AND METALLURGICAL CONSIDERATIONS TO STABILIZING THE INTERACTION LAYERS OF U-MO/AL DISPERSION FUEL

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Argonne National Laboratory's work was supported by the U.S. Department of Energy, Office of International Policy and Analysis (NA-212), national Nuclear Security Administration, under contract W-31-109-ENG-38.

THERMODYNAMIC AND METALLURGICAL CONSIDERATIONS TO STABILIZING THE INTERACTION LAYERS OF U-MO/AL DISPERSION FUEL

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ABSTRACT

Maintaining the interaction layer of U-Mo/Al dispersion fuel as a stable compound appears to be the key to avoiding massive pore formation. The stability of the interaction layer can be improved if it stays as a low-Al content compound such as $(U\text{-}Mo)Al_3$ by adding alloying elements in the Al matrix and the U-Mo alloy. The Miedema semi-empirical model was used to estimate the stability of the interaction layer when Si is added to the Al matrix and transition metal elements such as Zr, Ti, V, and Nb to the U-Mo fuel. The minimum Si concentration for stabilization was estimated. A small amount of Zr, Ti, V, and Nb addition can reduce the necessary Si amount.

1. Introduction

At the 2004 RERTR meeting in Vienna, we presented our evaluation of high porosity formation that has occurred in the U-Mo/Al interaction phase of high-power-density dispersion fuel. We also proposed a way of increasing the alloy stability of the interaction phase through the addition of a fourth element. Earlier work on U-Al alloys had shown that elements of group IV B promoted the formation of $U(AlX)_3$ – a relatively stable cubic-compound. Of the elements in this group, Si appeared to be more suitable, and it was therefore selected for testing in the RERTR-6 irradiation test. In order for Si to readily diffuse into the interaction phase, it may be either coated on the fuel particles, or added in the matrix Al. We have chosen the latter. The key consideration is that the stabilizing element should have a tendency of forming a relatively weak bonding with Al and a strong bonding with both U and Mo. Diffusion tests with U-Mo/Al-Si couples confirmed that Si is depleted from the Al-Si alloy and concentrated in the interdiffusion zone as part of the compound; $(U\text{-}Mo)\ (Al\text{-}Si)_3$ [1,2].

The opposite is true if one seeks a stabilizing element to add to the fuel alloy: the bonding of element X should be weak with U and Mo, but stronger with Al in the interaction phase. This principal argument was neatly demonstrated by our colleagues at KAERI [2]. They proceeded to alloy U-8Mo with 1 wt% Si and performed an interdiffusion test. The results revealed that all Si ended up in very stable (U-Mo) Si precipitates in the fuel alloy, and no Si whatsoever in the U-Mo/Al was found in the interaction layer (IL). This clearly shows that Si only works on the Al side of the interdiffusion arrangement.

We have looked into which elements may work when added to the U-Mo side. Transition elements just to the left of Mo in the periodic table are the most likely candidates from a metallurgical standpoint. Elements such as Nb, Ti and Zr form, at most, one weak compound with U, but strong compounds with Al. A detailed thermodynamic analysis was performed to evaluate the stabilizing effect of the candidate elements.

In this paper, we present the thermodynamic and metallurgical analyses as to how to further improve the stability of the IL in (U-Mo)/Al dispersion fuel. Ex-reactor diffusion tests showed some positive results and irradiation tests are scheduled to further examine the full scope of the effectiveness of the remedy.

2. Thermodynamic analysis method

Gibbs free energy formation of a compound ($\Delta G = \Delta H - T\Delta S$) is the measure of the stability of a compound and spontaneity of a reaction. Although non-equilibrium conditions prevail during irradiation, current thermodynamic analysis is still a reliable method to predict the real situations. Since enthalpy is the dominant part of Gibbs free energy, knowing enthalpy of formation of a compound provides an approximate measure of how stable the compound is relative to other comparable compounds.

The Miedema model analytically assesses the enthalpy change during mixing of two elements by using an empirical correlation. The correlation for the formation enthalpy of an AB binary is given by

$$\Delta H^{f} = c_A \, f_B^A \frac{2V_A^{2/3}}{\left(n_{ws\,A}^{-1/3} + n_{ws\,B}^{-1/3}\right)} \left\{ -P(\Delta\varphi)^2 + Q\left(\Delta n_{ws}^{1/3}\right)^2 - R \right\} \qquad (1)$$

where ΔH^{f} is given in kJ/mol of atoms of A and B with concentrations in the mixture, and c_A the concentration of A. f_B^A is the degree to which A atoms are in contact with B atoms. V is the atomic volume, n_{ws} is the electron density, φ is the electronic charge. P, Q and R are constants fitted to experimental data (see Ref. 3 for more details).

3. Effect of Mo in interaction layers

We know from the past experience that UAl_x/Al system never developed pores in the interaction layers (ILs). This leads us to believe that, if Mo is included the interaction product behaves differently from that of the UAl_x/Al system; specifically, Mo facilitates higher-Al content ILs, such as $(U,Mo)Al_7$ that is not observed in the UAl_x/Al system. As can be seen in Fig. 1, except for the U_2Mo compound and low-Mo content solutions, the U-Mo system has positive ΔH^{f}, suggesting that it is thermodynamically unstable.

The stability of ILs that contain Mo will be discussed in the next section.

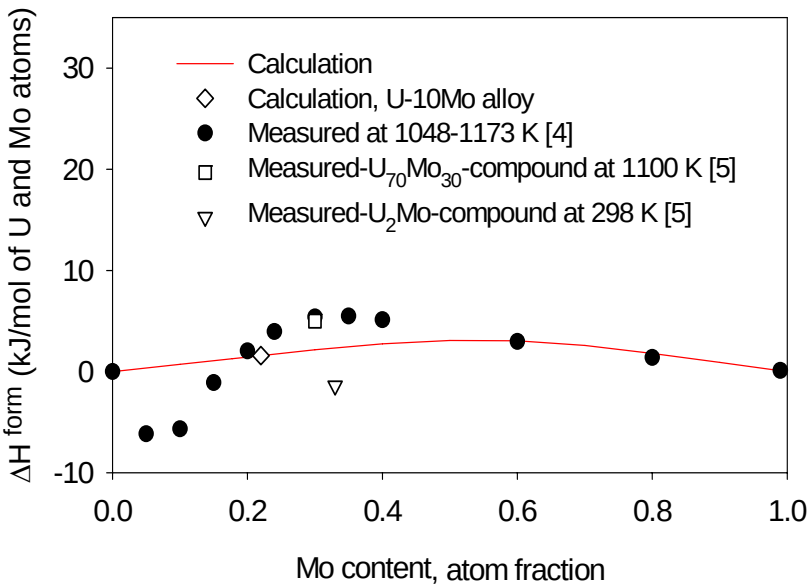

Fig. 1. Effect of Mo content in U-Mo alloy.

4. Stability of Interaction Layers

The data for enthalpy of formation of compounds at 298 K were collected and reviewed. Because the Miedema model predicts at 0 K, the literature data were to be revised to apply at 0 K. However, the difference between 0 K and 298 K is around 1 kJ/mole of atoms in compound so that the data at 298 K can be also applicable to 0 K.

Figure 2 provides a collection of measured data and the prediction results of the Miedema method. The U-Si and U-Al data generally follow the trend calculated with the Miedema model. The However, it predicts more negative values, meaning that the Miedema model over predicts the data. As seen in the figure, the compound stabilities increase from (U-Mo)Al_3 to UAl_3, and from UAl_3 toUSi_3. The $U(Al,Si)_3$ data fall between UAl_3 and USi_3.

The stability of the ILs with Mo inclusion can be estimated in Fig. 3 (the dashed line). The more Mo that is added to the UAl_x, the less negative enthalpy of formation the compound becomes, meaning that it becomes less stable. From these analyses, Mo in the IL appears to play an important role in degrading the IL. However, as also shown in Fig. 3, the addition of a proper amount is added, Si stabilizes the (U-Mo)Al_3 compound (shown by the dash-dot line). The effect of Si in $U(Al\text{-}Si)_3$ compound is increasing the stability of the compound (prediction in the solid line and measured in the symbol and line)

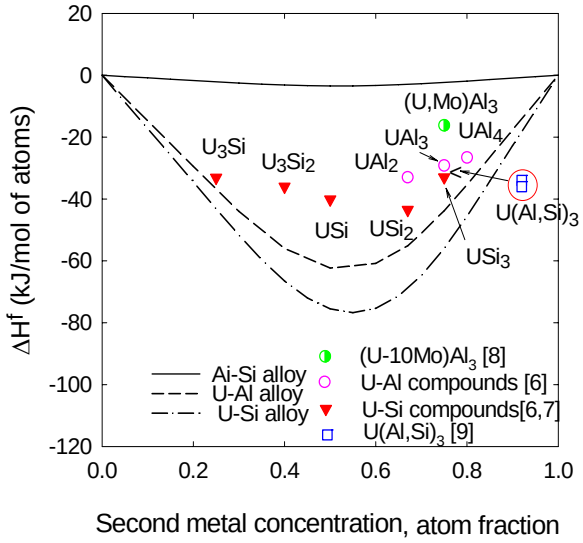

Fig. 2. Enthalpies of formation of compounds and alloys: predictions by the Miedema model (lines), measured data (symbols).

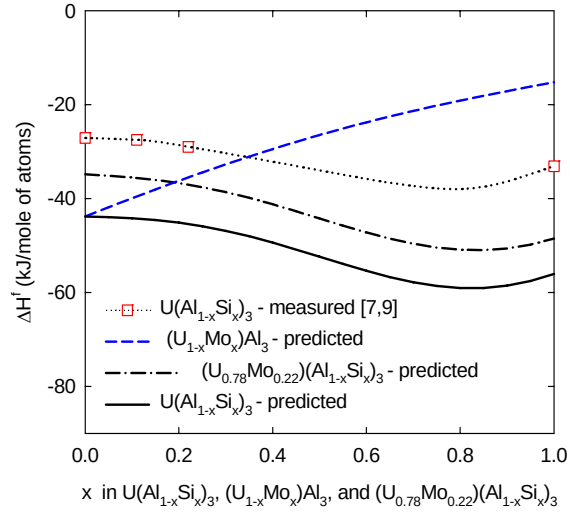

Fig. 3. Miedema model predictions of formation enthalpies.

5. Minimum Si content

From the literature [10,11] the amount of Si necessary to stabilize UAl_3 during extensive thermal treatments at 605°C is such that it forms compounds in the range $U(Al_{0.86}Si_{0.14})_3$ - $U(Al_{0.75}Si_{0.25})_3$.

From the above data, we can conclude:

- the minimum Si content in the reaction layer ranges $U(Al_{0.86}Si_{0.14})_3$ - $U(Al_{0.75}Si_{0.25})_3$.
- Si diffusion at this high temperature regime is fast and the affinity of Si by the reaction product is large. Therefore, as long as the Si supply is continued, the Si content in the reaction layer can be maintained above the minimum Si content.

The minimum Si content is calculated by

$$C_{Si}^{Min} = \frac{\rho_r V_r f_{Si}}{\rho_r V_r f_{Si} + \rho_r V_r f_{Al} + \rho_{Al} V_{Al}} \qquad (2)$$

where f_{Si} = mass fraction of Si in $(U\text{-}10Mo)(Al,Si)_3$, f_{Al} = mass fraction of Al in $(U\text{-}10Mo)(Al,Si)_3$, ρ_r = density of $(U\text{-}10Mo)(Al,Si)_3$ = 5.8 g/cm^3, ρ_{Al} = density of aluminum = 2.7 g/cm^3, V_r = volume fraction of reaction product in the fuel meat, and V_{Al} = volume of unreacted aluminum in the fuel meat.

The volume fractions of the reaction product and unreacted Al are also a function of reaction layer thickness. These can be obtained by fitting the PIE results of RERTR-4 and 5. In Fig.4, the measured volume fractions for RERTR-4 and 5 plates are shown by the symbols, and the corresponding fitting curves are also superimposed.

As a result, the correlations for the volume fractions are given by

$$V_r = 5.27\times10^{-2}\,y - 7.334\times10^{-4}\,y^2 - 1.0534\times10^{-5}\,y^3 \quad (3)$$

$$V_{Al} = 0.6128 - 5.24\times10^{-2}\,y + 1.7167\times10^{-3}\,y^2 - 2.1261\times10^{-5}\,y^3 \quad (4)$$

where V is the volume fraction and y is the IL thickness in μm.

The calculated results are shown in Fig. 5 for the two limiting cases: (U-10Mo)$(Al_{0.86}Si_{0.14})_3$ and (U-10Mo)$(Al_{0.75}Si_{0.25})_3$. We assume that the effect of the existence of Mo is negligible in the calculations. The Si content for (U-10Mo)$(Al_{0.75}Si_{0.25})_3$ is approximately double of (U-10Mo)$(Al_{0.86}Si_{0.14})_3$. The Si content for (U-10Mo)$(Al_{0.75}Si_{0.25})_3$ is too large but that of (U-10Mo)$(Al_{0.86}Si_{0.14})_3$ may be acceptable from the perspective of reprocessing. The primary source of uncertainty in the analysis originates from the assumption that all the Si is consumed in the reaction product, because some of Si can be consumed by precipitation in the matrix and reaction with U. In addition, the simulated irradiation effects require experimental verification.

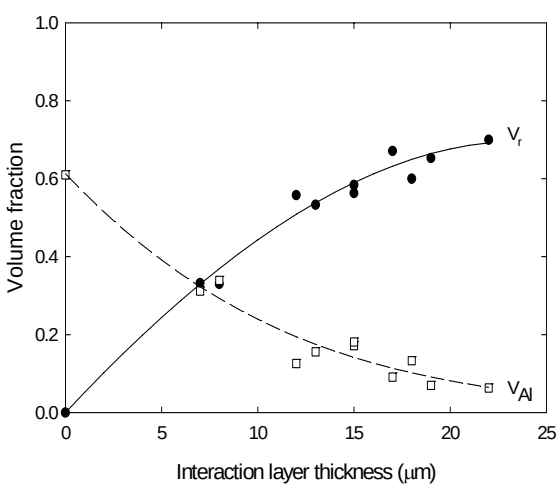

Fig. 4. Volume fractions of interaction layer (V_r) and unreacted Al (V_{Al}) measured for RERTR-4 and 5.

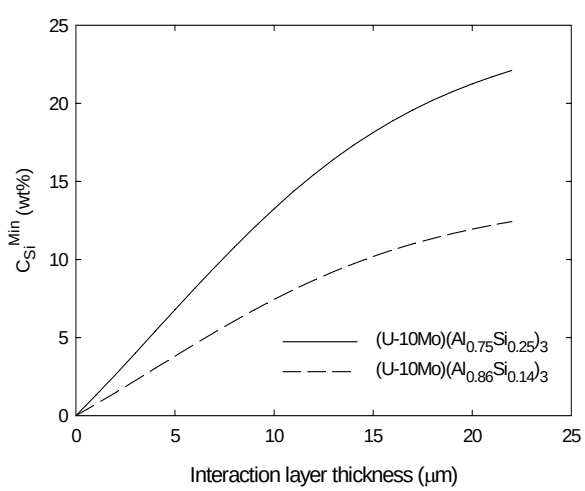

Fig. 5. Minimum Si contents to stabilize the IL of U-Mo/Al dispersion fuel.

6. Third element addition in U-Mo

To alleviate the burden of too much Si addition, we propose a third element addition in the fuel side. The candidates are Zr, V, Ti and Nb. Zr seems to have the strongest effect and

the next is Ti. However, Zr reduces the γ-phase stabilizing power of Mo by forming Mo_2Zr as shown in Fig. 6. As seen in the figure, a small amount of Zr, say 1 wt%, reduces the time of γ-to-α phase transformation almost one order of magnitude. Although it is not shown here, Nb and V have a similar effect. Ti apparently has the least harmful effect: if the amount is 1 wt%, the effect is negligible. Considering the neutron absorption cross sections, V and Ti are unfavorable. In order not to deleteriously reduce fuel loading, the amount of third element addition to the fuel is obviously restricted below approximately 3 wt%. By using a generalized Eq. (2), calculations for the minimum Si concentration in the case of a third element addition in U-Mo were made assuming all the third element in U-Mo is preferentially collected in the IL and Zr replaces Si with the same stabilizing power in a $(U\text{-}10Mo)(Al,Si,Zr)_3$ type compound. An example of the calculations is shown in Fig. 7. When ~3 wt% Zr is added in U-Mo, the reduction in the Si concentration is ~40% for a 22-μm IL. The reduction is most pronounced when Ti is used reducing the required Si concentration by 47%.

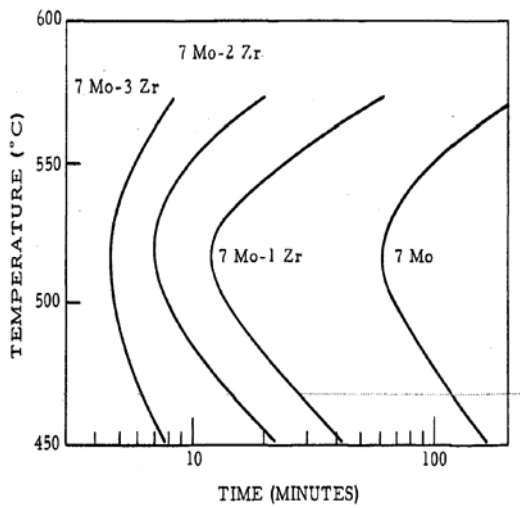

Fig. 6. TTT diagram of U-7Mo with addition of Zr [13].

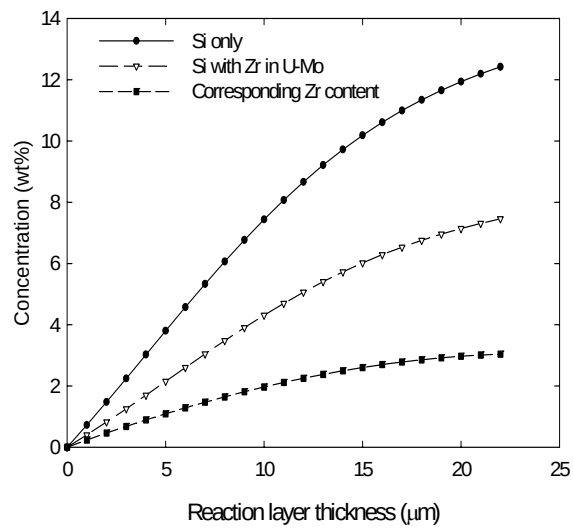

Fig. 7. Minimum Si concentration necessary in matrix Al with Zr in U-Mo.

7. Alloy modification scheme

In order to examine the effect of the additional alloying elements to U and Mo, the enthalpies of formation of binary alloys were estimated by the Miedema method. Figure 8 (a) shows that in contrast to Si the transition elements will not form precipitates with U. Conversely, in Fig. 8 (b) all of the candidate transition elements form compounds with Al, whereas Si does not. The ability of the candidate elements to stabilize the desirable interaction phase is also shown in the figure: in order from weakest to strongest is Si, V, Nb, Ti and Zr.

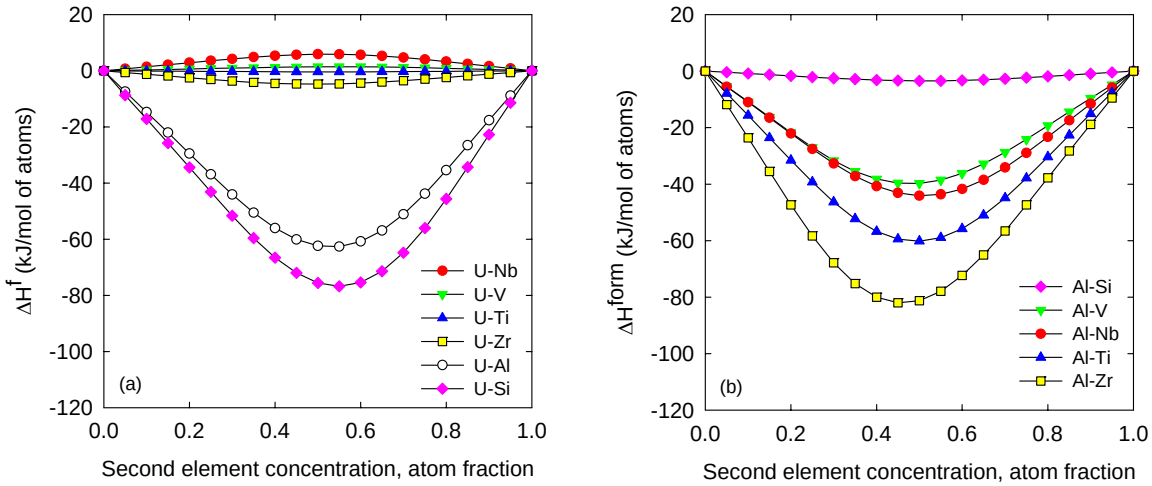

Fig. 8. Enthalpies of formation of binary alloys of (a) U with Nb, V, Ti, Zr and Si, (b) Al with Si, V, Nb, Ti and Zr. The larger the negative enthalpy of formation ($-\Delta H^f$), the stronger is the bond in the alloy.

From this analysis, a positive effect is indicated if transition elements are added to U-Mo, and if Si is added to the Al matrix. Figure 9 illustrates a schematic of the likely stabilizing action for the case with Si in the Al matrix and Zr in the U-Mo. Si is pulled to the U-Mo side because of its affinity for U and repulsion by Al. The Zr affinity for Al is slightly greater than that of U. This implies that Zr in U will be attracted to the Al side more than U but the driving force should be small.

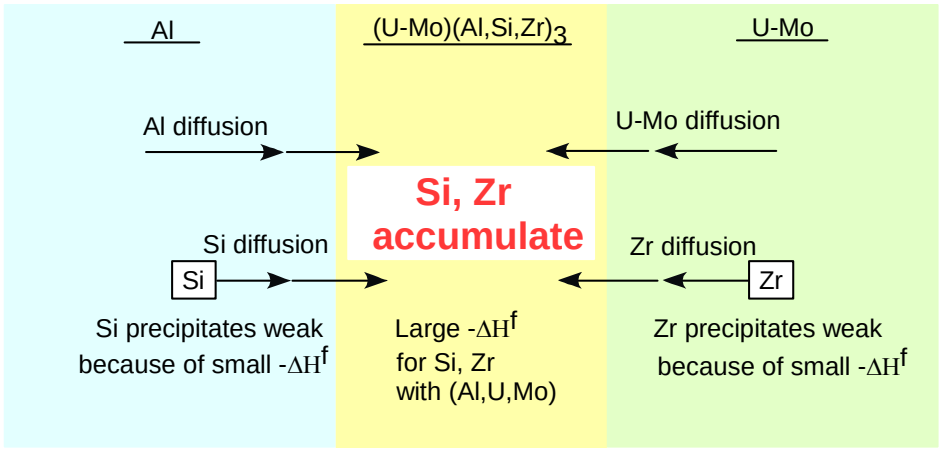

Fig. 9. Schematic of interdiffusion of U-Mo-Zr/Al-Si.

Experimental evidence to support these thermodynamic predictions was sought at CNEA and KAERI. Figure 10 shows the cross section of CNEA diffusion couple specimen annealed at 550°C for two (2) hours. The as-fabricated Si content in Al4043 alloy was 5.2 wt%. A thick (~50 μm) Si-depleted zone in fuel on the IL was observed, and a high-Si content IL such as $(U,Mo)(Al_{0.67}Si_{0.33})_3$ was also observed. The Si, originally in the form of

precipitates in this zone, was believed to have diffused to the IL to form the preferred UAl_3 type compound. The significance of this result is that Si preferentially diffuses to the IL to form a high-Al content IL and stabilizes the IL.

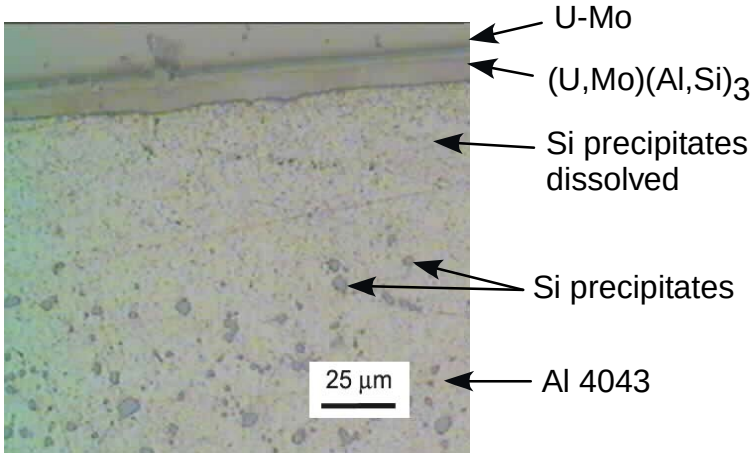

Fig.10. CNEA diffusion couple test result with U-Mo/Al-Si [1].

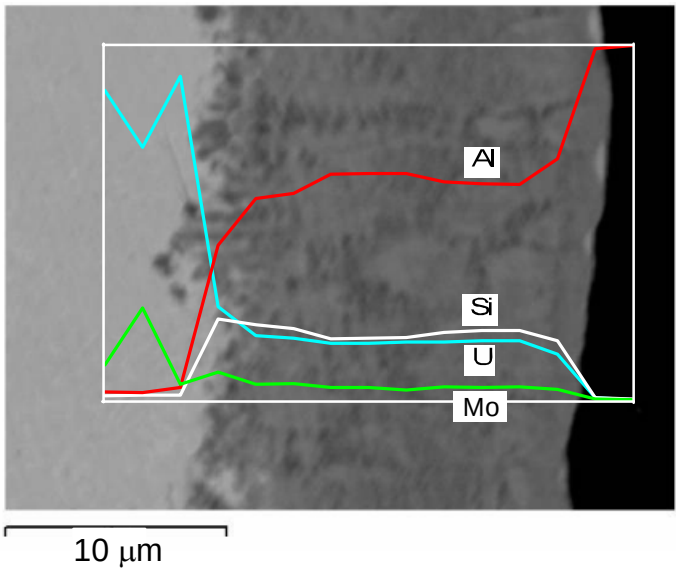

Fig. 11. KAERI annealing test of U-7Mo/Ai-2Si dispersion fuel. Composition of the IL in atom fraction is superimposed. [2].

Figure 11 shows a result from the KAERI U-7Mo/Ai-2Si dispersion fuel annealed at 550°C for 25 hours. Si was accumulated in the IL. The EMPA composition analysis result of the IL gives the compound type such as stable $(U,Mo)(Al,Si)_3$. These test results confirm the trend of the thermodynamic predictions.

In Fig. 12, the IL compositions with modified matrix Al as well as those with pure Al are plotted in a ternary diagram. The CNEA and KAERI results differ significantly from the

high-Al compounds from irradiation tests that populate at the Al-rich corner. All of the irradiation data show some porosity development, and their IL is believed to be unstable.

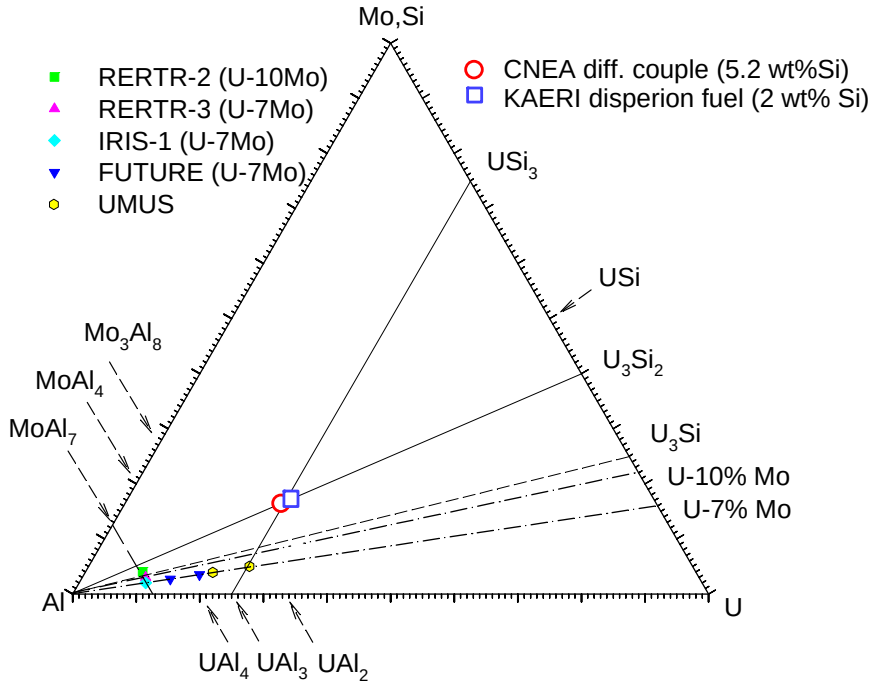

Fig. 12 Interaction product compositions and Si effect

The preliminary results of the diffusion-couple tests of U-Mo-1Zr/Al [2] revealed that Zr diffusion to the IL was not preferential compared to U and Mo. No test with the combination of a Si-added matrix and a Zr-added U-Mo has yet been performed. In RERTR-7 test, the modifications for both fuel and matrix Al are scheduled to be implemented. On the basis of U-7Mo up to 2 wt% Zr, Ti and V are to be added and/or up to 5 wt% Si is to be included to the matrix.

8. Conclusions

Maintaining the interaction layer of U-Mo/Al dispersion fuel as a stable compound appears to be the key to avoiding massive pore formation. Mo inclusion in the interaction layer of U-Mo/Al reduces the stability of the interaction zone. This can be compensated by adding Si in the Al matrix and the transition metals such as Zr, Ti, V, and Nb to the U-Mo fuel. The minimum Si concentration for stabilization was estimated. A small amount (~3 wt%) of Zr, Ti, V, and Nb addition can reduce up to about 40% of the required Si.

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