DESIGN OF HIGH DENSITY GAMMA-PHASE URANIUM ALLOYS FOR LEU DISPERSION FUEL APPLICATIONS[*]

by

Gerard L. Hofman and Mitchell K. Meyer
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

and

Allison E. Ray
Purdue University
West Lafayette, Indiana

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Abstract

Uranium alloys are candidates for the fuel phase in aluminum matrix dispersion fuels requiring high uranium loading. Certain uranium alloys have been shown to have good irradiation performance at intermediate burnup. Previous studies have shown that acceptable fission gas swelling behavior and fuel-aluminum interaction is possible only if the fuel alloy can be maintained in the high temperature body-centered-cubic γ-phase during fabrication and irradiation, i.e., at temperatures at which α-U is the equilibrium phase. Transition metals in Groups V through VIII are known to allow metastable retention of the gamma phase below the equilibrium isotherm. These metals have varying degrees of effectiveness in stabilizing the gamma phase. Certain alloys are metastable for very long times at the relatively low fuel temperatures seen in research reactor operation. In this paper, the existing data on the gamma stability of binary and ternary uranium alloys is analyzed. The mechanism and kinetics of decomposition of the gamma phase are assessed with the help of metal alloy theory. Alloys with the highest possible uranium content, good gamma-phase stability, and good neutronic performance are identified for further metallurgical studies and irradiation tests. Results from theory will be compared with experimentally generated data.

I. INTRODUCTION

Several uranium-based fuels were analyzed in this study in order to determine an appropriate uranium alloy which could best meet the objectives of the Reduced Enrichment for Research and Test Reactors (RERTR) program. The main objective of this project is to develop a high-uranium density fuel that remains stable in the body-centered-cubic gamma structure during fabrication and irradiation. It has been experimentally determined that uranium alloys that can be retained in the cubic phase are most likely to exhibit good irradiation behavior.

Several transition metals, particularly 4d and 5d elements in Group IV, through VIII, form solid solutions with γ-U, and this cubic phase can be retained in its metastable state upon cooling. The γ stabilizing power of these elements increases with atomic number as d-electrons participate in bonding through hybridization with s and p atomic orbitals. However, their solubility decreases as the size difference with uranium atoms becomes larger, and the increased bond strength promotes intermetallic compound formation. For example, the first two elements in the 4d series, Zr and Nb, form complete solid solutions with γ-U, but U-Zr cannot be retained in the γ phase and U-Nb can be retained in the γ phase only at rather large concentrations. On the other extreme, Pd and Pt have only ~2 at% solubility and form many very-stable compounds with uranium.

It was early recognized that Mo, which has substantial solubility in U (~35%) presents a good compromise between the amount needed to stabilize γ-U and acceptable U density so achieved. Results of these early studies[1] are shown in time-temperature-transformation (TTT) diagrams in Fig. 1. In order to allow sufficient time to fabricate a dispersion fuel at a working temperature of ~500°C, approximately 20 at% of Mo is required. Also at this concentration the alloy should not decompose into α-U and the only existing U-Mo compound, U_2Mo, during reactor operation, where fuel temperatures which are typically below 250°C.

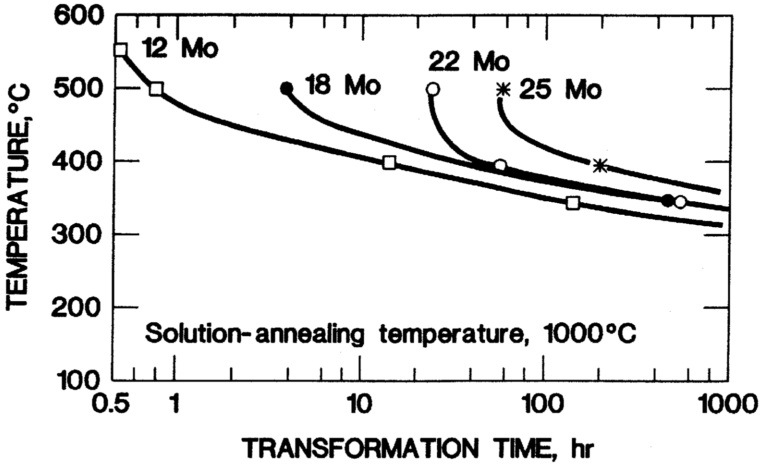

Fig. 1. Effect of Mo Concentration on the Start of Metastable γ-Phase Decomposition. (Mo Concentration in at.%)

It was further found[2] that small amounts of elements to the right of Mo in the periodic table had a powerful stabilizing effect when added to U-Mo alloys. This effect is illustrated for Pt in Fig. 2. It appears that for this case of 18 at% Mo, ~1 at% Pt has the same stabilizing effect as an additional 7 at% Mo without Pt. This observation and some other work involving Re and Ru[3] form the impetus of the present study. which attempts to quantify the relative γ-stabilizing effects of the whole range of 4d and 5d transition metals.

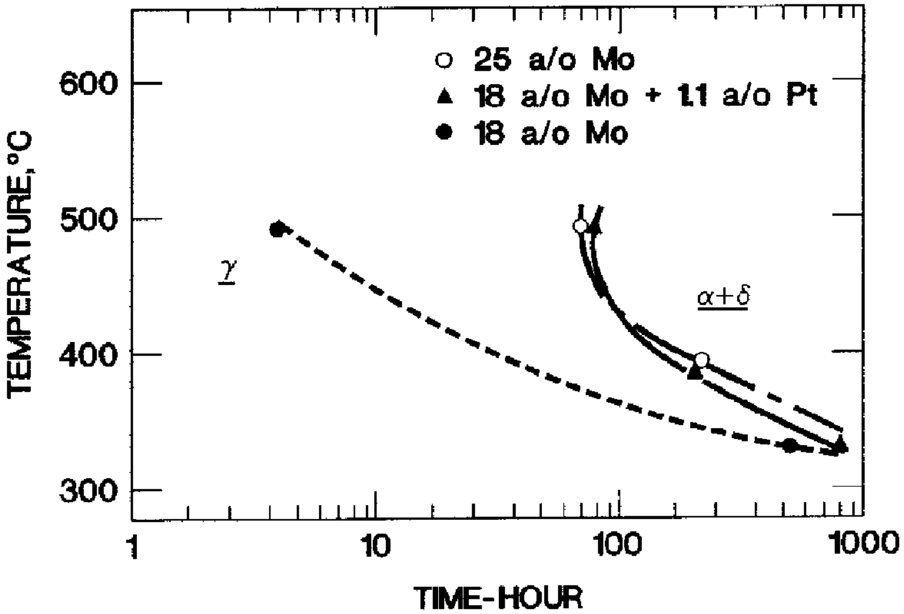

Fig. 2. Comparison of Additional Mo and Pt on Start of Metastable γ-Phase Decomposition in 18 at.% Mo-U Alloys

II. NUCLEATION OF DECOMPOSITON PHASES IN U-Mo AND U-Nb ALLOYS

The start of decomposition of a metastable γ-phase requires the formation of nuclei of the equilibration phases, α-U and for U-Mo, U_2Mo. The nuclei form heterogeneously at γ grain boundaries in colonies or cells, hence the name cellular decomposition. Nucleation processes are thermodynamically driven. Thermal motion of atoms takes place to a greater or lesser extent depending on temperature. During this motion, clusters of atoms may form that are compositionally different than the average composition of the matrix. If the matrix phase in which the motion is occurring is the phase with the lowest free energy of formation in the system, then the clusters represent a high energy region, and are short lived. If, however, the matrix phase is existing in a metastable state, then clusters provide potential nucleation sites.

In order for a cluster to survive and become a nucleus for a new phase, there must be a reduction in the net-free energy for growth of the cluster to a nucleus. Growth of the cluster into a nucleus involves creation of a new interface between the matrix and the nucleus and may involve introduction of lattice and elastic strains into the matrix. If the strain energies are assumed to be small, relative to the interface energy, then the net-free energy of formation of a (homogeneous) nucleus is a summation of the reduction in free energy brought about by formation of a volume of a less energetic new phase and the increase in energy from the formation of a new interface.

$$\Delta G_{net} = 4/3\pi r^3 \Delta G_v + 4\pi r^2 \gamma_s \tag{1}$$

where, γ_s in the surface energy

At some critical value of $r=r_c$, further increases in r causes ΔG_{net} to decrease due to the stronger r dependence of ΔG_{net} on energy reduction ΔG_v brought about by the growth of a volume of new phase. Under conditions far from equilibrium, ΔG_v may be very large and r_c may be very small.

In alloys, nucleation most often occurs at imperfections in the microstructure. Typically, during cellular decomposition of γ-U alloys, nucleation occurs at grain boundaries and is heterogeneous in nature.

Following the Volmer-Weber[4] theory with modifications for heterogeneous nucleation, the rate of nucleation, *I*, may be written as:

$$I = \sum_{j=o}^{i=max} \frac{N_j}{V} A_j \exp - \left[\frac{U_I + U_j^*}{RT} \right] \tag{4}$$

where: $\frac{Nj}{V}$ is the number of nucleation sites per unit volume. A_j is the frequency factor, U_I is the activation energy for atomic motion (diffusion) and U_j^* the activation energy to form a critical nucleus (a surviving cluster capable of growth).

If we consider well-annealed alloys only, having similar grain size and no grain boundary segregation, $\left(\frac{N_j}{V}\right)$in constant and we may assume an average value $\overset{-*}{U}$ for U_j^*.

An analytical form of $\overset{-*}{U}$ is obtained by differentiating ΔG_{net} with respect to r and setting the result equal to zero.

$$\overset{-*}{U} = 16\pi\gamma^3 / 3(\Delta G_v)^2 \tag{5}$$

ΔG_v is roughly proportional to ΔT, the amount of undercoating below the equilibrium isotherm. Thus, at low temperatures $\bar{U}^*$ becomes small and nucleation is controlled by U_I. At temperatures close to the equilibrium, $\bar{U}^*$ becomes more important. This gives rise to the familiar "C" shape of the TTT curves.

Time-temperature-transformation diagrams present a tool for determining the values of $\bar{U}^*$ and U_I for a material. Assuming that the time (t_i) to the onset of detectable transformation is proportional to the nucleation rate (I), an equation describing the dependence of t_i on $\bar{U}^*$ and U_I can be written by taking the logarithm of the nucleation rate equation and differentiating with respect to 1/T.

$$\ln(t_i) = \ln A - (U_I + \bar{U}^*)/RT - \ln A \qquad (6)$$

$$R[d/(\ln(t_i))/d(I/T)] = -U_I + \bar{U}^* + 1/T[dW/d(1/T)] \qquad (7)$$

At lower temperatures, both $\bar{U}^*$ and $d\bar{U}^*/d(1/T)$ approach zero as $(\Delta G_v)^2$ becomes large.

$$D(\ln(t_i))/d(1/T) = -U_I/R \qquad (8)$$

On a plot of 1/T versus $\ln(t_i)$, the slope of the lower temperature region is $-U_I/R$. One might expect this activation energy (U_I) to be similar to the activation energy (Q_D) of diffusion, since both processes involve correlated atomic jumps.

The procedure described above was first used to extract the activation energy of nucleation (U_I) over the composition range 12-25 at% molybdenum below 425°C. Several sets of TTT curves are available in the literature for this class of alloys. The results are plotted in Fig. 3 for some of the available data. Activation energies for transformation data plotted here are restricted to data taken from well-annealed bulk samples for which actual data points were plotted on published TTT curves.[1,6,7} Time-temperature-transformation curves determined using hardness and skewing detection of the onset of transformation or determined using powder samples[9] were not used.

Two sets of diffusion data are also available from the literature, and they are markedly different. Data from Adda[5] is well referenced and was presented over a number of years in different publications, and was taken at temperatures of 850 an 1050°C. Data by Federov is presented, unreferenced, in a monograph and perhaps not as reliable.

If one compares the Q taken from diffusion data of Adda to the U_I values taken from the TTT curves (Fig. 3), reasonable agreement is found between the values, outside of the anomalous data point from Van Thyne. These data suggest that there is a link between the activation energies and that diffusion is predominant in controlling the nucleation of decomposition phases in U-Mo alloys. If this is the case, a possible strategy for delaying the onset of decomposition from the gamma phase is to identify elements that slow the rate of interdiffusion in alloy systems.

For dispersion fuels, the most important temperature range, however, lies between 425 and 500°C, a range in which fuel plates are fabricated and where the uranium alloys should not commence nucleation. As can be seen in Fig. 4, the slope of the $\ln(t_i)$ vs 1/T plot decreases drastically at these higher temperatures, when presumably $\bar{U}^*$ (see Eq. 6) is no longer negligible. Analysis of the above-mentioned U-Mo alloys as well as some U-Nb alloys for which both TTT curves[14] and diffusion data[10] are available show that the "effective" activation energy for nucleation is approximately 0.5 that for diffusion in the higher temperature range (see Fig. 5). This indicates that diffusivity is indeed not the sole factor in controlling nucleation at higher temperatures, increasing the activation energy of diffusion by alloying would still decrease t_i in the important (for fabrication) higher-temperature range in these two binary alloys. This can only be achieved through higher Mo and Nb content, indeed so high for Nb as to eliminate this alloy as a high-density fuel candidate.

There are, however, a few examples where small additions of a third element have been shown to significantly retard phase decompositions, such as shown in Fig. 2 for Pt in U-Mo.

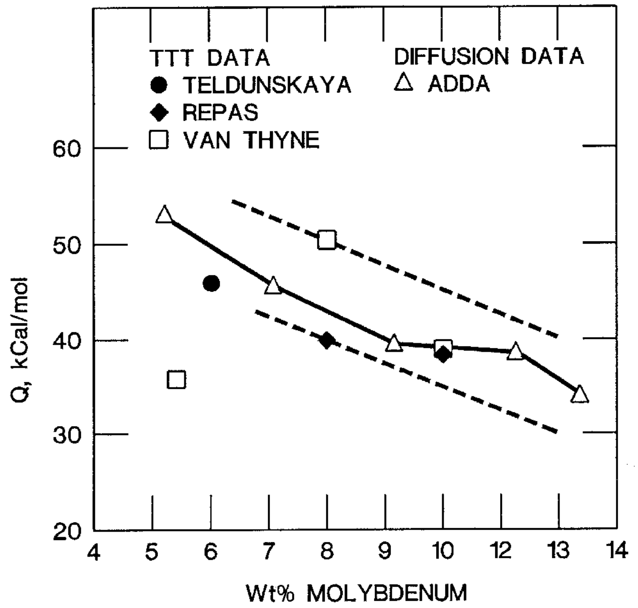

Fig. 3. Comparison of Activation Energy of Start of Decomposition and Interdiffusion of γ U-Mo Alloys.

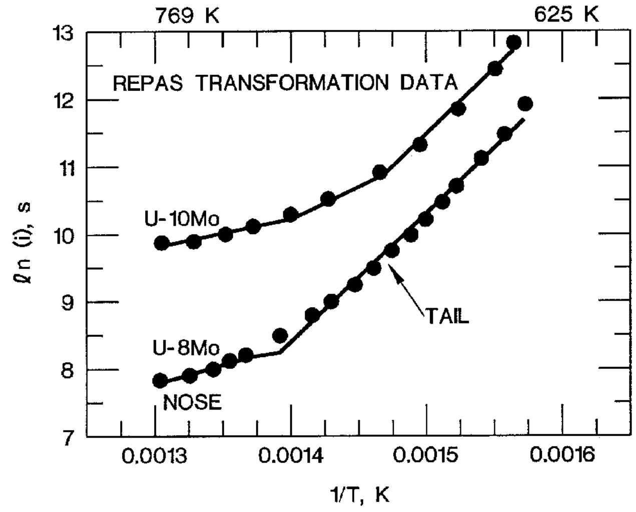

Fig. 4. Start of Metastable U-Mo γ-Phase Decomposition as a Function of Temperature. (Mo Concentration in wt.%)

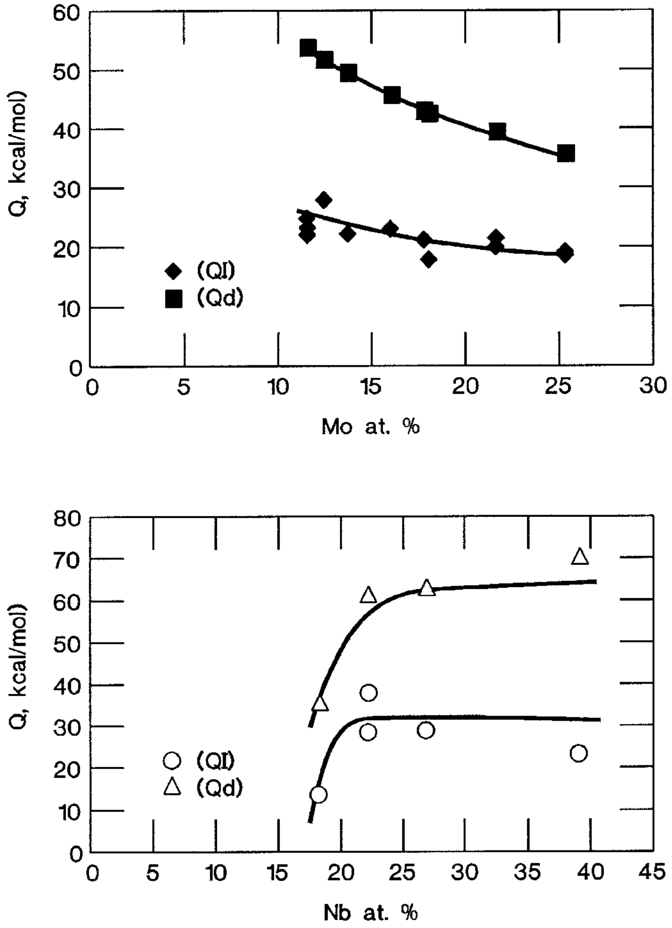

Fig. 5. Activation Energy of Start of Metastable γ-Phase Decomposition, Q_I, compared with the Activation Energy for Interdiffusion, Q_d, for U-Mo and U-Nb Alloys.

III. ANALYSIS OF TERNARY ALLOYS

In the preceding discussion it has been shown that diffusivity (the mobility) of the alloy constituents appears to be an important property controlling the nucleation of phase decomposition. Unfortunately very few experimental diffusion data exist for binary uranium alloys of interest, and practically none exist for ternary alloys. We have, therefore, made use of the idea that the activation energy of diffusion and nucleation are fundamentally related to the metallic bond strength between the atoms in the solid solution alloys at issue. The same may be said for $\bar{U}^*$ as this energy is calculated to the difference in bond character of the phases involved in the transformation. Thus, the entire activation energy term in Eq. 2 $\left(U_I + \bar{U}^*\right)$ is related so the bond strength between the alloy constituents. Although there have been recent developments in solid-state physics methods for the calculation of the bond character in alloys, we have chosen the established semi-emperical method by Miedema et al. [11,12,13] by which the enthalpy of mixing, a measure of bond strength, can be calculated for alloys of uranium and 4d and 5d transition metals. Since all these alloys are of the same crystal structure (bcc, γ-U) structure effects need not be considered. The difference in atomic diameter of the various solvent atoms does affect the activation energy, but these differences will be small for potentially useful elements because of solubility requirements.

Using the following semi-empirical equation from Miedema for a mixture of two transition metals (the parameters for the elements of interest are given in Table I),

$$\Delta H_m = \left[-Pe\left(\Delta \overset{*}{\Phi}\right)^2 + Q\left(\Delta n_{ws}^{1/3}\right)^2 \right] f(c^S) \tag{9}$$

where:

$f(c^s)$ = a function of atomic concentrations

ϕ^* = electronegativity parameter

n_{ws} = electron density at the boundary of a Wigner-Seitz atomic cell

e = electron charge

Q_o and P are emperical constants, P = 14.1, and Q_o/P = 9.4

Table I. Parameters Specified in Miedema for the Calculation of the Enthalpy of Solution in an A-B Mixture of Two Transition Metals

	Element	ϕ^*	$n_{ws}^{1/3}$(d.u.$^{1/3}$)
5f	U	3.939	1.57493
4d	Zr	3.45	14.4
	Nb	4.05	1.64
	Mo	4.65	1.77
	Tc	5.3	1.81
	Ru	5.55	1.87
	Rh	5.4	1.76
	Pd	5.6	1.65
5d	Hf	3.6	1.45
	Ta	4.05	1.63
	W	4.8	1.81
	Re	5.2	1.85
	Os	5.55	1.89
	Ir	5.55	1.83
	Pt	5.65	1.78

We may test the hypothesis of a relation between the enthalpy of mixing, and the activation energy of nucleation by calculating -ΔH_m for a series of U-Mo alloys for which TTT diagram are available. Figure 6 shows that a plot of the nucleation time, t_i, at 500°C (the position of the "nose") versus ΔH_m has an exponential form as does the aforementioned Volmer-Weber expression; (see Eq. 4)

From this plot, it appears that the activation energy term in Eq. 4 is indeed proportional to ΔH_m. Based on this observation ΔH_m was calculated for several binary alloys for which phase transformation data have been published. The results are shown in Fig. 7 for 4d and 5d additions to a base alloy of 16 at%

Mo. Both Zr and Nb decrease the nucleation time relative to Mo whereas Re, Ru, and Pt progressively substantially increase it. The correlation with calculated values of ΔH_m for these elements in uranium is shown in Fig. 8 for 1 at% additions to 16 at% Mo. Since there is a significant fraction of bonds with Mo in this alloy, which are weaker than bonds with U, an estimate of this reduction in ΔH_{mix} was made, as indicated by arrows in Fig. 10. If this is taken into account, a linear relation between the relative increase in nucleation times, t_i/t_i (Mo^{16}), and $-\Delta H_m$ (X) is obtained.

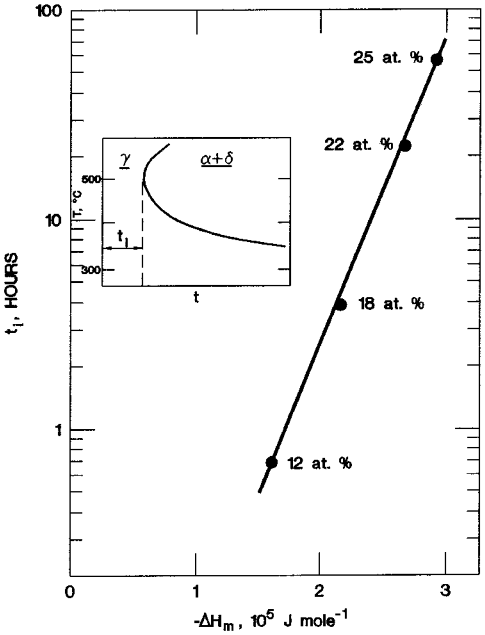

Fig. 6. Nucleation Time of Metastable γ-Phase Decomposition Versus Calculated Heat of Mixing of U-Mo Alloys.

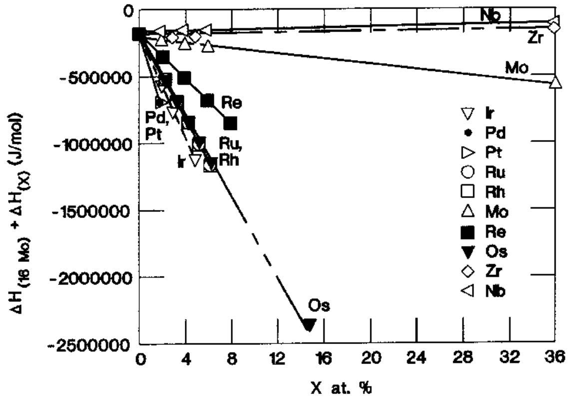

Fig. 7a. Enthalpy of Mixing of Transition metals in γ-U up to their Solubility Limit

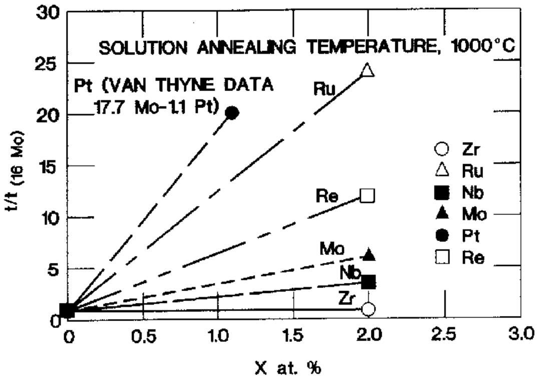

Fig. 7b. Effect of Certain Transition Metals on Experimentally Determined Nucleation Time of Decomposition in U-16 at.% Mo

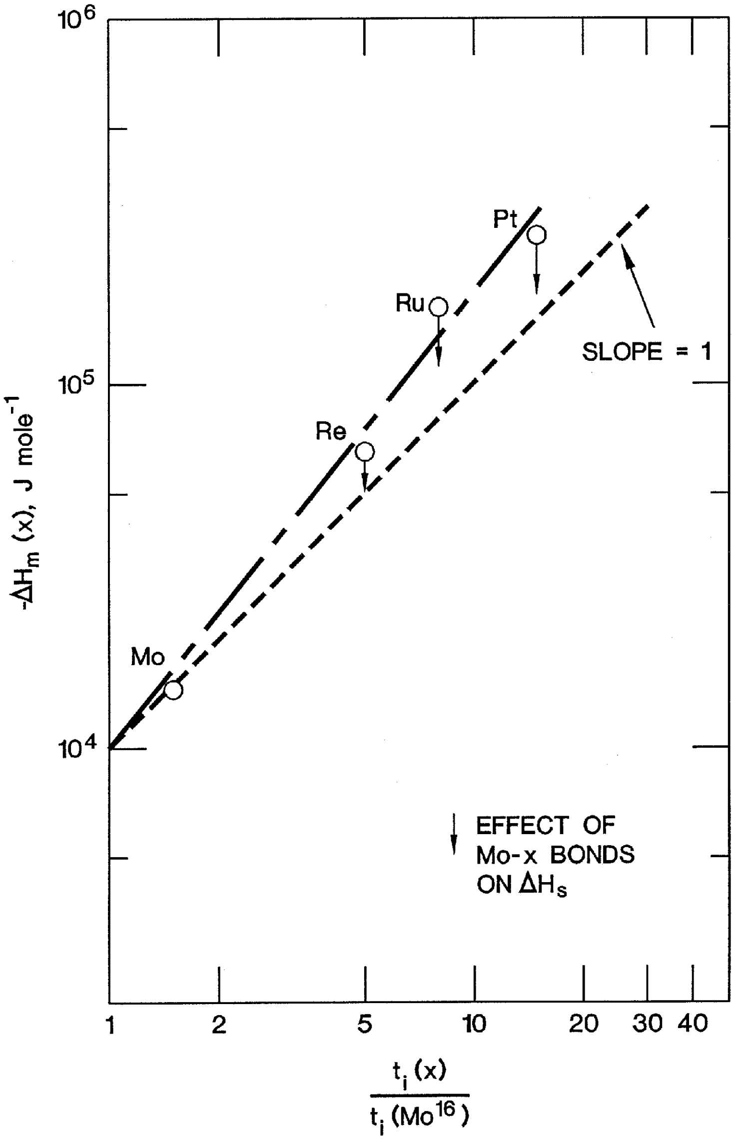

Fig. 8. Increase in Nucleation Time of Metastable γ-Phase Decomposition Relative To U-16 at.% Mo as a Function of Heat of Mixing

Using this correlation, the relative nucleation times for the other 4d and 5d elements were determined, as shown in Table II. The power of γ stabilization increases on proceeding to the right in the periodic table for both groups. There are, however, other factors to be considered, namely neutron capture, cross-sections of the elements and their extent of solubility. The neutronic penalty associated with one percent of each of the added elements expressed as percent of reactor cycle length decreases (ΔCL) for a hypothetical research reactor[15] is also shown in Table II. A relative figure-of-merit may than be derived by dividing the relative nucleation time increase by the percentage of cycle length decrease. This figure shown in Table II indicates that Ru, Pd, Os, and Pt have a positive effect relative to Mo.

However, the ultimate effectiveness of these substitutions depends on how much of each of these elements can be kept in solid solution in the U-Mo alloy.

The last row in Table II shows the solubility limit of the elements in U at 900°C. The limits for a U-Mo alloy are likely to be smaller. Taking all the factors into account, only small amounts (~1 at%) of Pd and Pt are expected to be effective, but these two elements should nevertheless have a powerful stabilizing effect at these low concentrations. The two other elements Ru and Os, on the other hand, have a much larger potential for replacing Mo because of their greater solubility.

Table II. Effect of 1 at% Additions on U-16 at% Mo

Element 1 at%	Mo	Tc	Ru	Rh	Pd	W	Re	Os	Ir	Pt
Δt_i	1.0	-	4.7	4.7	11.3	3.3	3.3	4.0	5.3	11.7
$\Delta t_i/\Delta t_i$ (16 Mo)	1.5	-	7	7	17	5	5	6	8	17.5
ΔCL, - %	2.28	-	2.48	25.71	3.47	8.23	19.11	6.00	67.6	5.48
ΔCL/ΔCL (16 Mo)	1.0		1.09	11.26	1.52	3.61	8.38	2.63	29.6	2.40
$\Delta t_i/\Delta$CL Relative to Mo	1.0	-	4.38	0.42	7.4	0.9	0.39	1.5	0.18	4.8
Max-Solubility in U at 900°C	36	-	6	6	<2	~1	8	15	5	<2

IV. CONCLUSION

Examination of available experimental data on the transformation of metastable γ-U alloys leads us to conclude that the nucleation kinetics of the equilibrium two-phase structures found in these alloys is primarily controlled by diffusion. A emperical correlation has been established between the calculated heat of mixing and the "activation energy" of nucleation of γ-phase decomposition. This correlation allows an assessment of the relative power of γ-phase stabilization of all suitable transition elements. Taking into account their solubility limits in the γ-phase as well as their neutron absorption characteristics, allows a ranking of their suitability as fuel alloy constituents.

The method described here will be used to select an optimum set of high density U alloys for further metallurgical studies. The data from these studies will be used to further improve the method described in this paper with the ultimate goal of selecting optimum high density alloys for irradiation testing.

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