

FIRST PRINCIPLES CALCULATIONS OF LATTICE PARAMETER AND ELASTIC CONSTANTS OF BCC γ (U,Mo) DISORDERED PHASE.

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ABSTRACT

IRRADIATION TESTS HAVE SHOWN THAT U-MO DISPERSION FUEL SUFFERS FROM INTERACTION BETWEEN THE FUEL AND THE ALUMINUM MATRIX AT HIGHER TEMPERATURE. A POTENTIAL SOLUTION TO MITIGATE THESE PHENOMENA IS TO USE A FUEL ALLOY FOIL IN PLACE OF THE FUEL-ALUMINUM DISPERSION. THIS MONOLITHIC FUEL PROVIDES A LOWER FUEL-MATRIX INTERFACIAL SURFACE AREA AND A MUCH HIGHER URANIUM DENSITY THAN DISPERSION TYPE FUEL. INTERNAL STRESSES WILL ARISE, DURING FABRICATION AND OPERATING CONDITIONS, IN THE INTERFACE BETWEEN FUEL AND CLADDING MATERIALS DUE TO THE DIFFERENCE IN THERMAL EXPANSION COEFFICIENTS AND ELASTIC CONSTANTS. OUR AIM IS TO ASCERTAIN THESE PROPERTIES FOR THE GAMMA PHASE IN THE U-MO ALLOY FROM THE KNOWLEDGE OF ITS INTERNAL ENERGY AS A FUNCTION OF DEFORMATION. INTERNAL ENERGY OF THE DISORDERED PHASE IS OBTAINED AS A CLUSTER EXPANSION FROM AB INITIO CALCULATED INTERACTION PARAMETERS IN EACH OF THREE DEFORMATION MODES: HYDROSTATIC, TETRAGONAL AND TRIGONAL. PRELIMINARY RESULTS ARE PRESENTED THAT HAVE SERVED AS A PROOF OF METHOD SUITABILITY.

1. Introduction

Low enrichment reactor fuel program is greatly based in the development of a dispersion fuel with density between 8 and 9 gU/cm³. Actual elements consist in a dispersion of U(Mo) bcc powder (20 at. % approx) in an Al matrix. The resultant compact material is placed between Al cladding and laminated. Though it seemed a promising device, post irradiation examination exhibit problems related to interdiffusion between Al and UMo alloy [1].

An alternative for fixing this problem has been proposed by the use of monolithic fuel, this is, by placing a thin sheet of monolithic fuel between Al cladding and thus reducing U alloy–Al interaction surface. The whole set is friction welded [2]. In this case

problems arise from internal stresses produced by temperature changes during fabrication and later use inside reactor, due to differences in elastic constants and thermal expansion coefficients. If elastic constants are known, element behaviour can be evaluated a priori. Although elastic constants can be experimentally measured, we have not found that information in literature for U(Mo) alloys.

The present work is an effort to obtain estimations of these quantities from first principles thermodynamics. Results are shown for lattice parameter (a_0) and the three independent elastic constants of the cubic solid solution U(Mo) as a function of uranium concentration.

Interactions energies of a set of basic clusters are obtained from ordered compounds total energy first principles calculations via an inversion method. Afterwards, a calculation model is used to reproduce elastic energy that is based in a cluster expansion of internal energy of the binary alloy.

2. Model

Internal energy of a multicomponent crystalline structure G can be written as a lineal expansion in known binding energies of clusters taken as a basis set [3]:

$$E_G(\underline{x}, \underline{z}) = \sum_{i=0}^N \zeta_i^G(\underline{x}) e_i(\underline{z}) \quad (1)$$

where, G is a crystalline structure characterized by geometry and site occupation; \underline{z} is the matrix containing the base vectors describing the lattice; \underline{x} is the composition vector; $\zeta_i^G(\underline{x})$ is the Structure Correlation Function (SCF) containing geometry information and cluster configuration for structure G ; $e_i(\underline{z})$ is the Energy Cluster Interaction (ECI) depending on the alloy and cluster, and not on the other G characteristics. Sum is extended over the $(N+1)$ clusters in the selected approach.

To establish the $(N+1)$ values $e_i(\underline{z})$, at least $(N+1)$ known internal energies $E_{G_i}(\underline{z})$ are needed. These energies can be experimental measured or, as in our case, theoretically calculated. We have chosen to use a first principles method based in the Local Density Approximation (LDA) [4].

The present approach for bcc U(Mo) substitutional solution includes the empty cluster, the point and one pair of first neighbours ($N=2$). Calculated structures are the pure bcc solutions U and Mo (A2, cI2, W type) and the intermetallic compound with B2 structure (cP2, CsCl type).

SCFs from Eq 2 corresponding to U (A2), Mo (A2) and UMo (B2), and structures energies $E_{A2,U}(\underline{z})$, $E_{A2,Mo}(\underline{z})$ and $E_{B2,UMo}(\underline{z})$, can be introduced in either sides of Eq 1 to obtain the ECIs by inversion.

$$\zeta^{U,A2} = [1 \quad 2 \quad 1] \quad ; \quad \zeta^{Mo,A2} = [1 \quad -2 \quad 1] \quad ; \quad \zeta^{UMo,B2} = [1 \quad 0 \quad -1] \quad (2)$$

The SCF corresponding to U(Mo) A2 solid solution is:

$$\zeta^{A2}(\underline{x}) = [1 \quad 2(2x-1) \quad (2x-1)^2], \quad (3)$$

then we can write the internal energy of the disordered bcc solid solution U(Mo) in terms of ECIs and structure corresponding SCF:

$$E_{A_2,UMo}(\underline{x},\underline{z})=2x(1-x)E_{B_2,UMo}(\underline{z})+x^2E_{A_2,U}(\underline{z})+(1-x)^2E_{A_2,Mo}(\underline{z}) \quad (4)$$

If dependence of $E_{A_2,U}(\underline{z})$, $E_{A_2,Mo}(\underline{z})$ and $E_{B_2,UMo}(\underline{z})$ with \underline{z} base vectors is known, then we have a description of variation of internal energy with orientation and magnitude of those vectors, this is to say, we can describe variation of internal energy with lattice deformation.

From elasticity theory it is known that change in energy due a small deformation $\underline{\varepsilon}$ in the harmonic approximation can be written as a function of the elastic constants tensor \underline{C} . For cubic symmetry only three constants are needed:

$$\begin{aligned} \Delta E_{el} &= \frac{1}{2}V_0 \sum_{i,j,k,l=1}^3 C_{ijkl} \varepsilon_{ij} \varepsilon_{kl} = \\ &= \frac{1}{2}V_0 \left[(\varepsilon_{11}^2 + \varepsilon_{22}^2 + \varepsilon_{33}^2) C_{11} + 2(\varepsilon_{11}\varepsilon_{22} + \varepsilon_{11}\varepsilon_{33} + \varepsilon_{22}\varepsilon_{33}) C_{12} + 4(\varepsilon_{12}^2 + \varepsilon_{13}^2 + \varepsilon_{23}^2) C_{44} \right] \end{aligned} \quad (5)$$

We need three sets of independent calculations to determine C_{11} , C_{12} and C_{44} .

Deformations can be considered that change the primitive equilibrium lattice vectors \underline{z}_0 as $\underline{z} = (\underline{1} + \underline{\varepsilon}) \cdot \underline{z}_0$, with $\underline{z}_0 = a_0 \underline{1}$ for the cubic structure, where $\underline{1}$ is the unity tensor and a_0 is the equilibrium lattice parameter.

Finally, if we consider an equivalence between variation in elastic energy due to macroscopic deformation (Eq (5)) and variation in internal energy due to deformation in structure base vectors (Eq (4)), we have a tool to calculate elastic constants for the bcc solid solution U(Mo) from first principles thermodynamics. This hypothesis has been previously used by other authors and applied to pure elements and intermetallic compounds [5-7]. We want to emphasize that it has not been previously used for solid solutions.

Next we can focus on the particular choice of deformations we have employed.

Applying an hydrostatic deformation (Fig 1) to the crystal gives us the Bulk modulus (B_0) value and the first relation between C_{11} and C_{12} :

$$B_0 = V_0 \left[\frac{\partial^2 E}{\partial V^2} \right]_{V_0} = (C_{11} + 2 C_{12}) / 3 \quad (6)$$

The remaining elastic moduli can be obtained by applying tetragonal and trigonal distorsions (Fig 1).

A tetragonal distorsion can be obtained with a deformation tensor defined as:

$$\underline{\varepsilon}_{tetra} = \begin{bmatrix} -\delta/2 & 0 & 0 \\ 0 & -\delta/2 & 0 \\ 0 & 0 & \delta \end{bmatrix}$$

Applying the tensor for several values of δ , and calculating energy density $U=E/V$, another relation between elastic constants and energy can be obtained:

$$\frac{1}{3} \left[\frac{\partial^2 U}{\partial \delta_{tetra}^2} \right]_{\delta=0} = \frac{1}{2} (C_{11} - C_{12}) = \frac{1}{2} C', \quad (7)$$

The remaining C_{44} modulus can be calculated from variation in energy after applying a trigonal deformation:

$$\underline{\varepsilon}_{trig} = \begin{bmatrix} \delta^2 & \delta & \delta \\ \delta & \delta^2 & \delta \\ \delta & \delta & \delta^2 \end{bmatrix}, \text{ being } C_{44} = \frac{1}{12} \left[\frac{\partial^2 U}{\partial \delta^2} \right]_{\delta=0}, \quad (8).$$

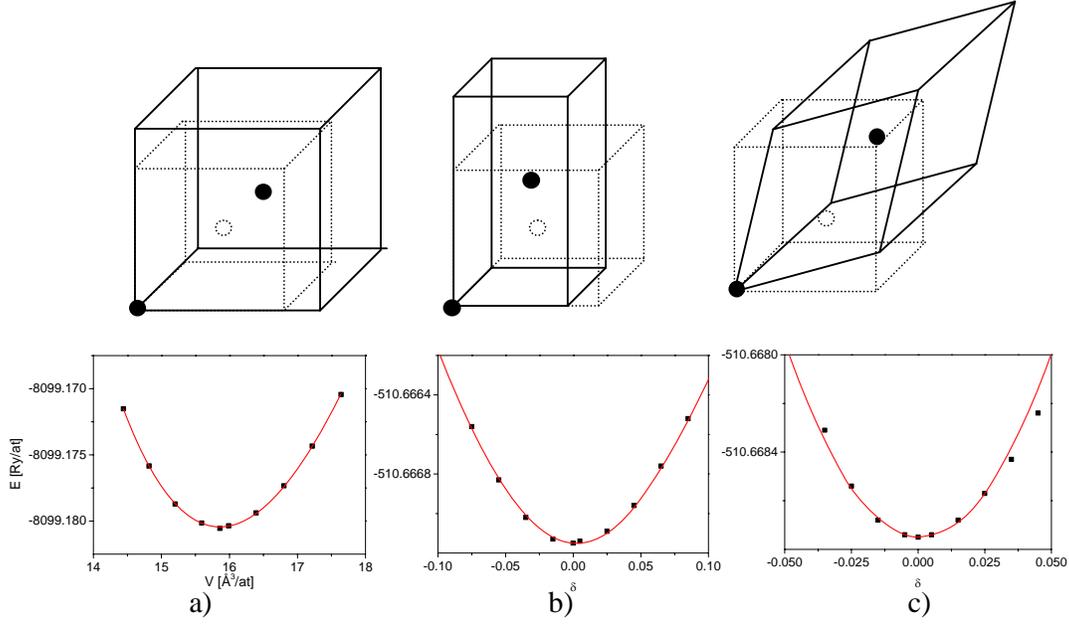


Figure 1. Schematic representation of deformations: a) hydrostatic; b) tetragonal; c) trigonal. Dashed lines in schemes represent original cubic cell, while solid lines represent cell after the corresponding deformation. Plots show Mo Total Energy vs volume for hydrostatic deformation, and Mo Total Energy vs deformation parameter δ in the other two cases.

The procedure is as follows: deformations in the three modes are applied to the three base structures, U, Mo and UMo B2. For each mode Eq (4) is written, thus obtaining the dependence of internal energy of the disordered bcc phase with volume, for hydrostatic deformation, and with deformation parameter of the bcc solid solution δ in the other two cases. Through equations (6) to (8), the corresponding modulus or elastic constants are calculated.

3. Results and discussion

Total energy (internal energy) calculations have been performed for the pure U and Mo crystals and the ordered compound with equiatomic composition B2 UMo *via* the Full Potential Linearized Augmented-Plane-Wave (FP-LAPW) method implemented in the WIN 97.8 code [5]. k mesh consisted in 286 k points in the Brillouin irreducible zone for hydrostatic deformations, 792 k points for tetragonal deformations and 2820 k points for trigonal deformations. Convergence in energy could be obtained for 0.01 mRy/atom in hydrostatic and tetragonal deformations, and 0.1 for trigonal deformations.

Validation of calculations can be found in a previous work [6] (determination of U-Mo phase equilibrium diagram) while validation of method was performed through its

application to Mo experimental parameters. The reported experimental values for Mo lattice parameter and bulk modulus are respectively 3.15 Å [7] and 268 GPa [8], whose differences with the calculated in this work (Table I) are within 0.4% and 2%, respectively. Thus, the agreement is excellent since typical LDA lattice parameter 1%-2% smaller than experimental ones [7].

Results of our calculations for ordered structures are summarized in Table I. As our results come from first principles calculations, uncertainties mostly arise from the fitting process. They are in all cases between 2 and 6 GPa for elastic constants, and between 2 and 5 10^{-4} Å for lattice parameter.

Structure	a_0 (Å)	B_0 (GPa)	C' (GPa)	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)
Mo(A2) exp. [7, 8]	3.15	268	302	469	167	107
Mo(A2)	3.1655	262	299	461	162	112
U(A2)	3.4520	93	-85	37	122	71
UMo(B2)	3.3980	147	68	192	124	3

Table 1. Results for equilibrium lattice parameter a_0 , Bulk modulus B_0 , C' , and elastic constants C_{11} , C_{12} and C_{44} .

3.1 Lattice parameter, Bulk modulus and elastic constants of the disordered phase.

As a first result, volume dependence (hidrostatic deformation) of disordered bcc phase energy was calculated. In order to determine equilibrium value of volume or lattice parameter, we used a second order fit of internal energy to the atomic volume as proposed by Birch [8]:

$$E^G(x, V) = E_0^G(x) + \frac{9}{8} B_0^G(x) V_0^G(x) \left[\left(\frac{V_0^G(x)}{V} \right)^{2/3} - 1 \right]^2 \quad (9)$$

where $E_0^G(x)$, $V_0^G(x)$ and $B_0^G(x)$ are respectively the equilibrium values of internal energy, atomic volume and Bulk modulus, for an ordered intermetallic structure G with concentration x of a given atomic species. The function was then minimize and derived to obtain equilibrium values of lattice parameter and bulk modulus. Predictions as a function of composition are shown in Fig 2 together with experimental values [9]. Reported lattice parameter values were measured at room temperature in samples quenched from high temperature where U(Mo) disordered bcc phase is stable. The good agreement encourages us to rely on bulk modulus calculations.

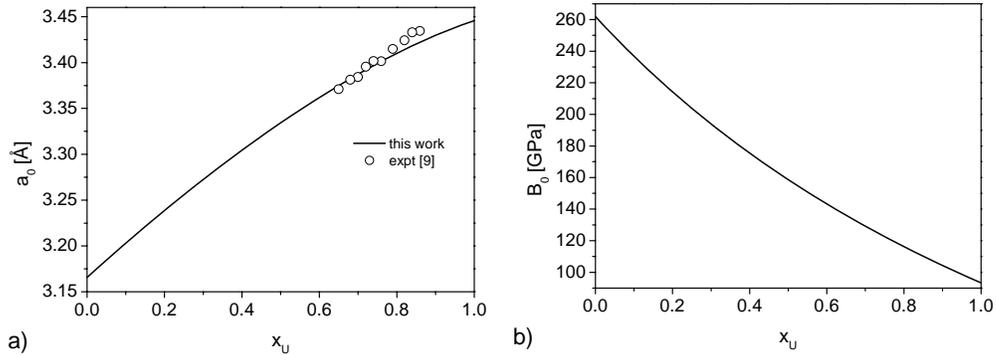


Figure 2. Lattice parameter (a) and bulk modulus (b) as a function of U content x_U for U(Mo) phase.

As an expansion based in tetragonal and trigonal deformations of the basic clusters, we obtained dependence of disordered bcc phase internal energy with deformation. Therefore, constant elastic values for C' , C_{11} , C_{12} and C_{44} could be derived as a function of composition as shown in equations (6), (7) and (8) and plotted in Figure 3.

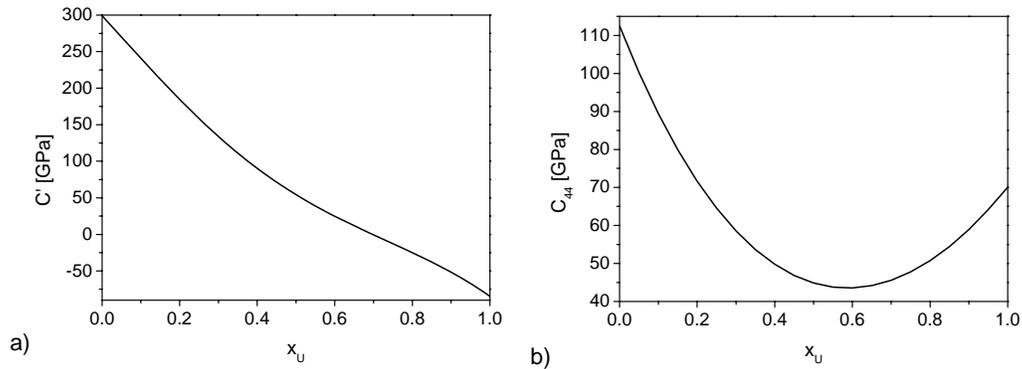


Figure 3. Calculated values of a) C' , and b) C_{44} , for the bcc disordered phase as a function of U content.

Our first principles calculations predict a negative value for C' of U cubic phase. This result agrees with experimental knowledge of equilibrium orthorrombic phase at low temperatures, reflecting the instability of γ phase with respect to tetragonal distortions. This instability is extended in the binary U-Mo system to γ U(Mo) phase, giving also place to a negative value of C' for high values of U content in the disordered solution. For smaller values, closer to Mo phase, bcc phase is predicted as stable and positive values are obtained. The result implies that a deformation of a retained γ U(Mo) phase at low temperature can produce a phase transformation to a more stable structure.

3.2 Finite element analysis.

We can now profit from our calculations to evaluate other thermal and mechanical properties. Work is being devoted to estimate mechanical stresses due to differences in volume changes between meat and cladding. A Finite Elements Simulation (FES) model has been tested for estimation of stresses related to deformation (Fig. 4).

A diffusion pair was considered under the conditions that there was perfect contact between Al surface and U(Mo) surface and that there were no previous residual stresses nor diffusion products remaining from the fabrication process. A two dimensional rectangle of Al was considered with a hole of were U(Mo) meat was placed. Stresses between U(Mo) meat and Al cladding at 530°C are shown in Fig 4 as obtained by FES. As it can be seen that in this model, stress are greater along hardest material for stresses parallel (x axis) or perpendicular (y axis) to meat, and concentrate mainly in the extremes of the rectangle simulating the U(Mo) foil.

We are now able to calculate Young (Y) and Poisson (ν) modulus based in our more accurate values of elastic constants and obtain a more reliable depict of stresses.

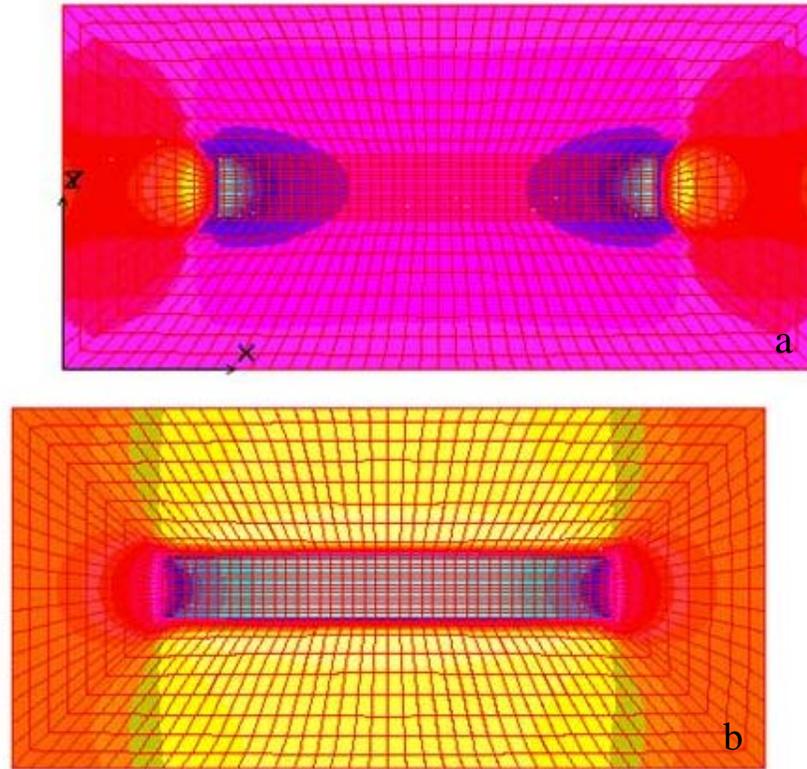


Figure 4. Scheme from Finite Elements Simulation of stresses between meat and Al cladding under thermal expansion: a) s_y , b) s_x .

4. Conclusions

We have implemented a method to accurately calculate elastic constants from first principles methods. The method can be used to predict mechanical properties even in unstable phases, such as U(Mo) bcc phase at low temperature. In combination with finite element simulation it can be extended to predict stresses in fuel elements.

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