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Mechanical and thermal properties of uranium intermetallic compounds

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Abstract

The structures and lattice constants of UFe_2, UNi_2, UPd_3, URh_3, URu_3 and UNi_5 were examined, and thermal expansion coefficients of the intermetallic compounds were evaluated from high-temperature X-ray diffraction data. The longitudinal and shear sound velocities of the intermetallic compounds were markedly different, which enabled us to estimate the elastic properties. The intermetallic compounds were found to have higher bulk moduli than uranium metal. The values of microhardness of the intermetallic compounds except UFe_2 were much higher than pure uranium. The physico–chemical properties of the intermetallic compounds such as Debye temperature and heat capacity were estimated from the sound velocities and the thermal expansion data, and the correlations between the properties were discussed. © 1998 Elsevier Science S.A.

Uranium; Intermetallic compounds; Thermal properties

1. Introduction

For improvement of the safety and economics of nuclear reactor systems, the industrial use of nuclear waste materials such as depleted uranium and noble metal fission products is attractive, which are inevitably produced through a nuclear fuel cycle. Several non-nuclear uses for depleted uranium and fission products have been proposed [1,2]. Uranium intermetallic compounds are exotic materials for practical applications such as hydrogen storage, catalyst, superconductors and radiation shields.

Uranium intermetallic compounds are also of technological importance for nuclear fuel chemistry, since these compounds are occasionally found to exist as metallic inclusions in irradiated fuel [3]. The predictions of compatibility of metallic uranium fuel with stainless steel cladding and behavior of insoluble residue in reprocessing of spent nuclear fuel may require the characteristics of the intermetallics.

It is therefore useful to understand the physico–chemical properties of the uranium intermetallic compounds. In the present study, UNi_2, UFe_2, UPd_3, URh_3, URu_3, and UNi_5 have been selected as the intermetallic compounds, and the mechanical properties of the compounds such as elastic moduli and hardness have been studied by means of ultrasonic pulse echo and hardness measurement. The lattice parameters and thermal expansion coefficient were also examined to estimate other physico–chemical properties such as Debye temperature and heat capacity. The present paper also describes the relationships between the physico–chemical properties of the uranium intermetallic compounds.

2. Experimental

2.1. Sample preparation

The samples of UNi_2, UFe_2, UPd_3, URh_3, URu_3, and UNi_5 in the form of button (about 20 mm in diameter and about 10 mm in height) were prepared by high vacuum induction melting. The purities of starting materials are above 99.9%. The prepared buttons were annealed at 1073 K for 10 h in a vacuum below 10^{-5} Pa.

2.2. X-ray diffraction analysis

The crystal structures of UNi_2, UFe_2, UPd_3, URh_3, URu_3, and UNi_5 were analyzed by a powder X-ray diffraction method using a Cu Kα radiation at room temperature. The high temperature X-ray diffraction analysis for UNi_2, UPd_3, URh_3, URu_3, and UNi_5 was carried out at temperatures between room temperature and 700 K

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to obtain the change in the lattice parameters with temperature and to estimate the thermal expansion coefficient.

2.3. Ultrasonic pulse-echo measurement

The longitudinal and shear sound velocities in UNi_2, UFe_2, UPd_3, URh_3, URu_3, and UNi_5 were measured by an ultrasonic pulse-echo method at room temperature to estimate their elastic properties. The changes in the longitudinal sound velocity with temperature were examined for URh_3 and URu_3 at temperatures up to 700 K.

2.4. Micro-hardness measurement

The hardness measurements were made for the uranium intermetallic compounds at room temperatures using a micro-Vickers hardness tester. Measurements were repeated ten times for a sample, and the applied load and loading time were chosen to be 4.905 N and 30 s.

3. Results and discussion

3.1. Lattice parameter and thermal expansion coefficient

The structure and the lattice parameters obtained at room temperature are listed in Table 1 for UFe_2, UNi_2, UPd_3, URh_3, URu_3, and UNi_5. The structures of UFe_2, URh_3, URu_3, and UNi_5 were cubic, the lattice parameters of which were 0.7063, 0.6679, 0.3992, and 0.3975 nm. Hexagonal UNi_2 and UPd_3 had the lattice parameters $a=0.4969$ nm, $c=0.8244$ nm and $a=0.5774$ nm, $c=0.9630$ nm. The results for crystallographic data for these compounds are in good agreement with the literature data [4].

Average thermal expansion coefficients from 298 to 700 K were estimated from the lattice parameters obtained by high-temperature X-ray diffraction. The volume thermal expansion coefficients α for UNi_2, UPd_3, URh_3, URu_3, and UNi_5 are shown in Table 1. As obvious from this table, the value of α ranges from 2×10^{-5} to 6×10^{-5} for the intermetallic compounds. The thermal expansion coefficients of UPd_3, URh_3, URu_3 were close to the α values expected from the data of U, Pd, Rh, and Ru, applying the rule of mixtures. The α values of UNi_2 and UNi_5 were much larger than the expected values from U and Ni. Relatively shallow potential energies in UNi_2 and UNi_5, which are expected from lower enthalpies of formation for UNi_2 and UNi_5 rather than for UPd_3, URh_3 and URu_3, appear to cause larger anharmonicity in the potential energy. This may brings about larger thermal expansion of UNi_2 and UNi_5.

For pure metals, the thermal expansion coefficient varies inversely as the melting temperature. The following relationship holds between the thermal expansion coefficient α at room temperature and the melting temperature T_m in K:

$$\alpha T_m = 0.077$$

which was derived by the present authors, using the literature data [5]. In Fig. 1, the variations in α with the decomposition temperature T_d (melting or peritectic temperature) of the uranium intermetallic compounds are shown. It is found from this figure that for the intermetallic compounds there holds the same correlation between thermal expansion coefficient and the decomposition temperature as for pure metals.

3.2. Elastic moduli

There are marked differences in longitudinal sound velocity V_l and shear sound velocity V_s obtained at room temperature among the compounds, as given in Table 1. The sound velocities for URu_3 are the largest and those for UFe_2 are the smallest.

For isotropic media, the shear modulus G, Young's modulus E, and bulk modulus K can be written in terms of the longitudinal sound velocity V_l and shear sound velocities V_s [6] by,

$$G = \rho V_s^2$$

$$E = G[(3V_l^2 - 4V_s^2)/(V_l^2 - V_s^2)]$$

Table 1
Physico–chemical properties of the uranium intermetallic compounds

Compounds (nm)	Prototype (K^{-1})	Lattice parameters ($m\ s^{-1}$)	Thermal expansion coefficient α ($m\ s^{-1}$)	Longitudinal sound velocity V_l (K)	Shear sound velocity V_s (GPa)	Debye temperature Θ_D (GPa)	Micro-hardness H_v (GPa)	Young's modulus E	Shear modulus G (GPa)	Poisson's ratio ν	Bulk modulus K
UNi_2	$MgZn_2$	$a=0.4970$ $c=0.8244$	5.53×10^{-5}	3773	1907	248	8.50	130	48.8	0.328	126
UFe_2	$MgCu_2$	$a=0.7063$		3518	1289	178	0.78	62.4	21.9	0.423	134
UPd_3	TiNi3	$a=0.5774$	3.97×10^{-5}	4309	2122	261	5.09	161	60.0	0.340	167
URu_3	$AuCu_3$	$a=0.3975$	2.60×10^{-5}	5217	2549	340	11.60	249	92.5	0.343	264
URh_3	$AuCu_3$	$a=0.3993$	2.78×10^{-5}	5068	2367	316	5.93	218	80.2	0.361	261
UNi_5	$AuBe_5$	$a=0.6787$	4.62×10^{-5}	4844	2342	333	5.88	167	62.0	0.347	182
U	αU			3286	1904	229	3.18	172	69.1	0.247	114

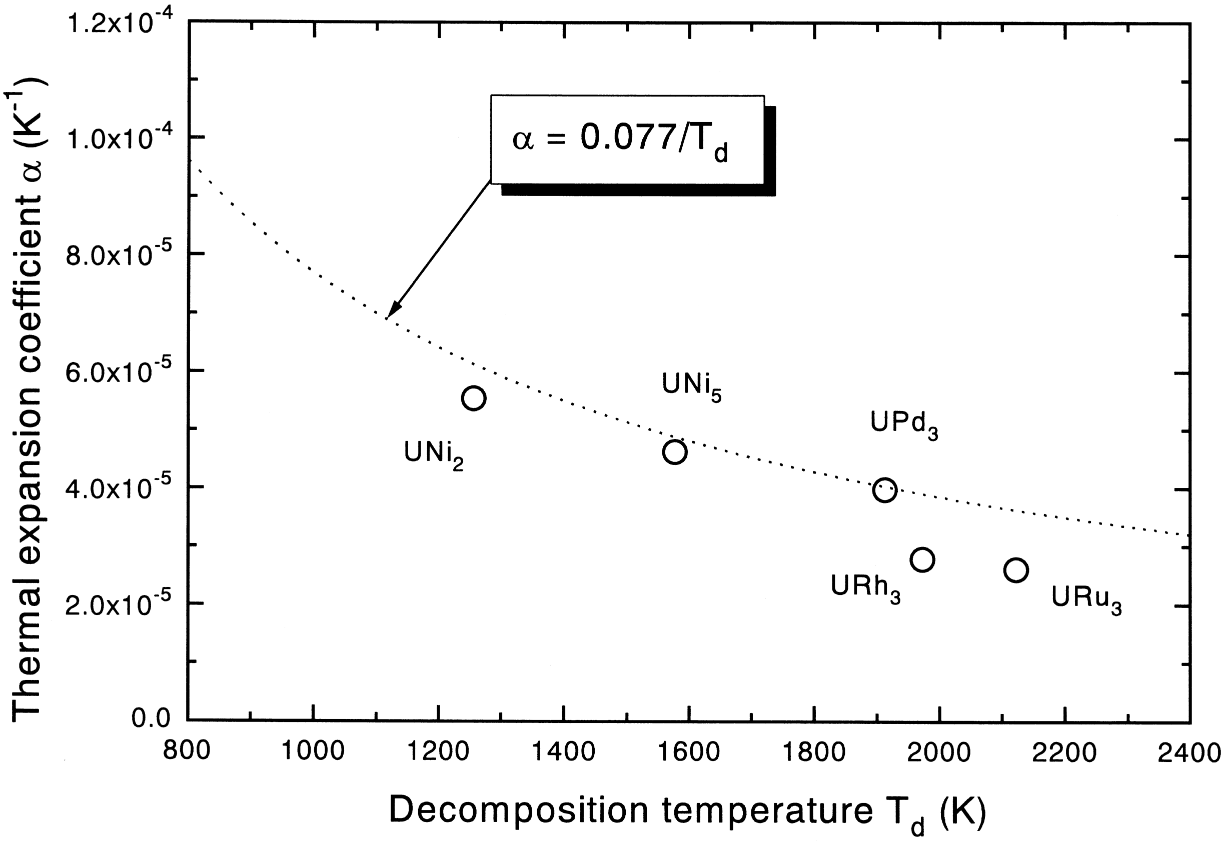

Fig. 1. Dependence of thermal expansion coefficient α on the decomposition (melting or peritectic) temperature T_d for the uranium intermetallic compounds.

$$K = \rho(3V_l^2 - 4V_s^2)/3$$

where ρ is the sample density. The Poisson's ratio ν can be expressed in terms of V_l and V_2 as,

$$\nu = (V_l^2 - 2V_s^2)/2(V_l^2 - V_s^2)\,.$$

The values of G, E, K and ν estimated from the sound velocities are shown for the uranium intermetallic compounds in Table 1. The elastic moduli estimated from sound velocities are adiabatic ones. Since the differences between adiabatic and isothermal moduli for the uranium intermetallic compounds were estimated to be below 5% around room temperature, the elastic moduli obtained in the present study are considered almost identical with isothermal ones.

For the intermetallic phases such as $MgCu_2$ and $MgZn_2$, their moduli can be expressed by the rule of mixtures [7]. The intermetallics of less metallic character observed in the Cu–Zn and Cu–Sn systems show the acute maxima on the modulus–composition curves. For URu_3 and URh_3 the values of E and G were larger than that of pure uranium and for UNi_2, UFe_2, UPd_3, and UNi_5 the values of E and G were smaller. For all the compounds, the bulk moduli were higher than pure uranium and smaller than those of constituent metals. For UNi_2, UPd_3, URh_3, URu_3, and UNi_5, no marked deviation from the rule of mixture was observed, but for UFe_2, small negative deviation was observed.

Since Young's modulus E is proportional to $(\mathrm{d}^2U/\mathrm{d}r^2)$ and $1/r$ where U is the potential energy and r is the atom distance, E is related to the cohesive energy U_0 and the equilibrium atom distance r_0. For pure metals, their Young's moduli are proportional to RT_m/V_a [8] where T_m is the melting temperature of pure metal and V_a is the volume of pure metal per gram atom. We obtained the relationship: $E = 97.9(RT_m/V_a)$ for pure metals, which is in good agreement with the results of Frost and Ashby [8]. A comparison of Young's modulus is made between the uranium intermetallic compounds and pure metals in Fig. 2, indicating that the magnitude of Young's modulus is not markedly different from the uranium intermetallic compounds and pure metals, when plotted as function of RT_m/V_a or kT_d/V_a, where T_d is the melting or peritectic temperature of the compounds and V_a is the volume of the compounds per gram atom. The same correlation was found to be applied to other intermetallics possessing the prototype structures of CsCl, Cu_2Mg, $TiAl_3$ and $AuCu_3$. Only the Young's modulus of UFe_2 is comparatibly smaller than the value expected by the correlation. Thus,

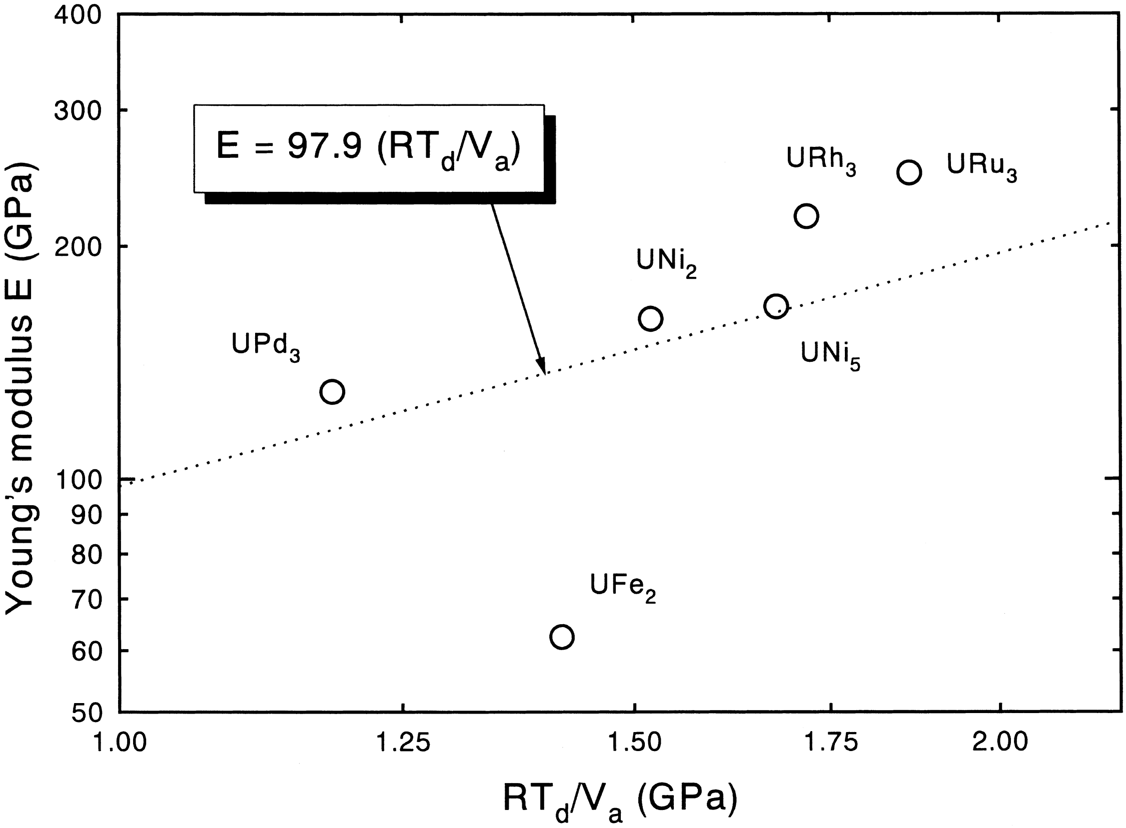

Fig. 2. Dependence of Young's modulus E on (RT_d/V_a) for the uranium intermetallic compounds.

these results suggest that in general the bond characters in the uranium intermetallics are metallic and their potential energies are almost the same in shape as that of pure metals.

3.3. Micro-hardness

The values of micro Vickers hardness obtained for the intermetallic compounds are given in Table 1. The hardness values for the intermetallic compounds are markedly higher than that of pure U or constituent metals, except for UFe_2. The hardness of URu_3 indicates the highest value among the intermetallic compounds.

The hardness provides the information of the resistance of a material to plastic deformation. For various materials, the Vickers hardness is also known to be associated with the Young's modulus E. For some oxide and carbide ceramics, the hardness H_v was found to be proportional to be Young's modulus E with the values of $H_v/E \doteqdot 0.05$ [9]. For pure metals, we estimated the H_v/E values using the literature data [10] and obtained the values of 0.006, 0.003 and 0.004 for bcc, fcc and hcp metals, respectively. The values of H_v for the uranium intermetallic compounds are plotted in Fig. 3 as a function of the Young's modulus E. As evidenced by this figure, the hardness values of UNi_2 and URu_3 show the characteristics of ceramics, however, UFe_2 appears to have metallic characters. The other uranium intermetallics indicate intermediate properties between ceramics and metals.

3.4. Debye temperature

Debye temperatures Θ_D for the intermetallic compounds of UFe_2, UNi_2, UPd_3, URh_3, URu_3, and UNi_5 can be estimated from the sound velocities and the lattice parameters. The Debye temperature Θ_D is related to the longitudinal and shear and velocities [11] as follows:

$$\Theta_D = (h/k)(9N/4\pi V_c)^{1/3}(1/V_l^3 + 2/V_s^3)^{-1/3}$$

where h is the Plank constant and k is the Boltzman constant, N is the number of atoms in a unit cell, and V_c is the unit cell volume. Table 1 shows the Debye temperatures for the intermetallic compounds obtained in the present study. Inaba and Yamamoto [11] have reported that Debye temperatures estimated from sound velocities or elastic moduli show less temperature dependence than those from X-ray diffraction or calorimetry. Therefore, we assumed that the Θ_D values obtained in the present study are not significantly different from Debye temperature at 0 K. The Debye temperature of 229 K obtained for pure uranium reasonably agrees with the literature data sets of 206–222 K [12]. Cordfunke et al. [13] have estimated that the Debye temperature at 0 K for UPd_3 are 273 K, which

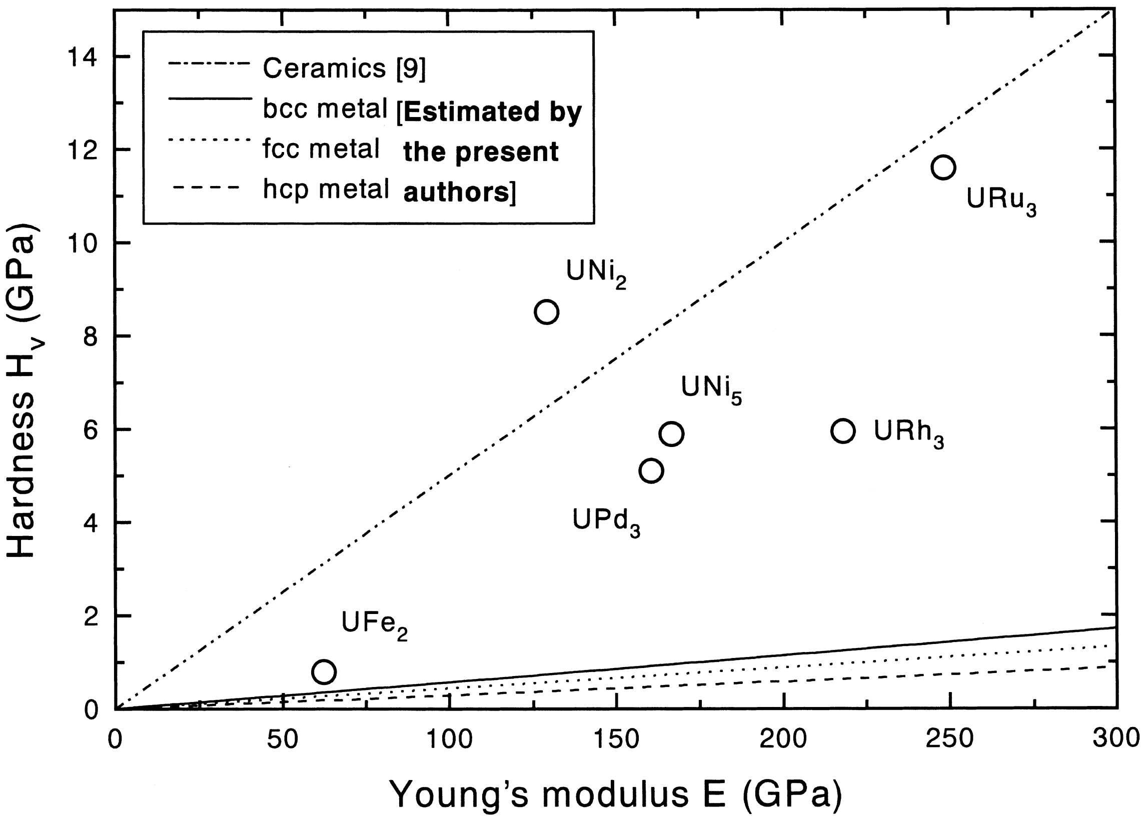

Fig. 3. Relationship between Young's modulus E and hardness H_v for the uranium intermetallic compounds.

is close to the value in the present study. The reported values of 297 and 299 K for URh_3 and URu_3 [13] are slightly smaller that those obtained in the present study.

According to the Kopp–Neumann rule, the Debye temperature Θ_D^{UM} for a compound of uranium and metal at a low temperature can be expressed as,$(1/\Theta_D^{UM})^3 = (1-x)(1/\Theta_D^U)^3 + x(1/\Theta_D^M)^3$where Θ_D^U is the Debye temperature of uranium, Θ_D^M is the Debye temperature of metal, x is the composition of the compound [11]. In Fig. 4, the Debye temperature estimated for each compound is compared with the values calculated from the above equation. For UPd_3, URh_3, URu_3 and UNi_5, the experimental Debye temperatures well agree with the calculated values. For UFe_2 and UNi_2, the experimental values are lower than those expected by the above equation. Their negative deviations from the Kopp–Neumann rule presumably result from high coordination number and dense packing in the structures of UFe_2 and UNi_2 [7].

It is known that the Debye temperatures of pure metals are associated with the melting temperatures T_m, the molar mass m, and the molar volumes V_a by the Lindemann relationship [14]. The relationships were reexamined for pure metals, and the ratios of Θ_D to $(T_m/m/V_a^{2/3})^{1/2}$ were estimated to be 1.42, 1.60, and 1.80 for bcc, fcc, and hcp metals. We assume likewise that for the uranium intermetallic compounds Θ_D is proportional to $(T_d/V_a^{2/3}/M)^{1/2}$ where T_d is the melting or peritectic temperature, V_a is the volume per gram of atom, and M is the average mass per gram atom. Fig. 5 represents the relation of the Debye temperature with the $(T_m/V_a^{2/3}/M)^{1/2}$ for the uranium intermetallic compounds obtained in the present study, together with other uranium compounds reported in the literature [13,15]. It is obvious from this figure that for uranium intermetallic compounds, a similar relationship appears to hold, in particular for the $AuCu_3$ type compounds such as URh_3, URu_3, UAl_3, and UGa_3 which show a good linearity. There is no remarkable difference in the relationships between pure metals and uranium intermetallics, except for UFe_2 which slightly departs from the general trend.

3.5. Heat capacity

The heat capacity C_p for the intermetallic compound can be approximately estimated from

$$C_p = C_h + C_d + C_{el}$$

where C_h is the harmonic term of the lattice vibration, C_d is the dilatational term and C_{el} is the electronic term. Strictly speaking, the anharmonic and other contributions such Schottky effect should be added to the sum. The harmonic term C_h is expressed as,

$$C_h = 3nRD(\Theta_D/T)\,.$$

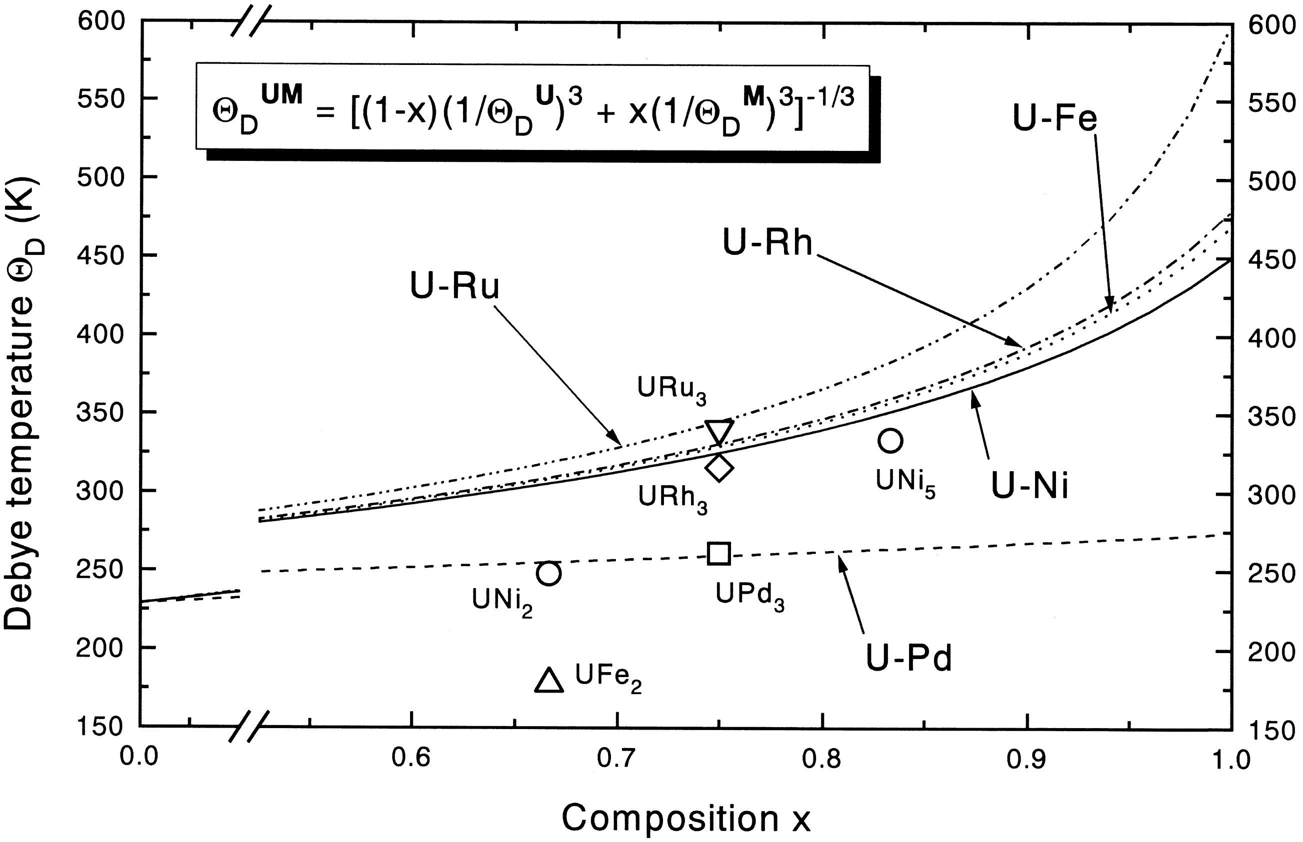

Fig. 4. Change in Debye temperature Θ_D with composition x for the uranium intermetallic compounds.

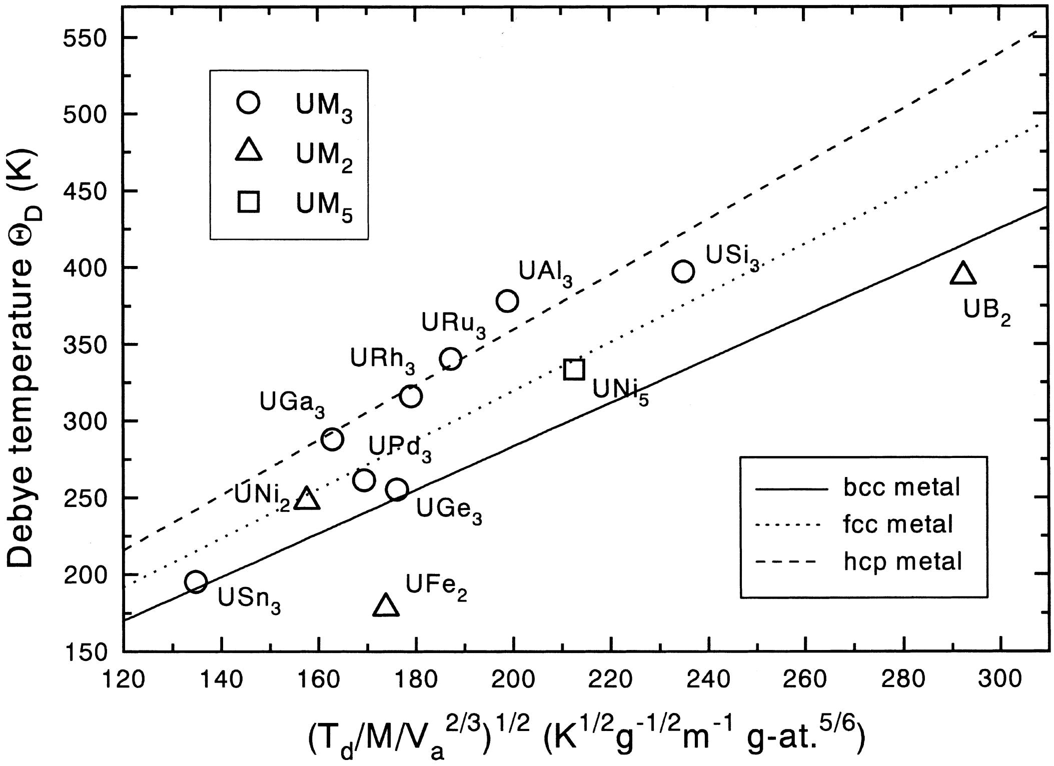

Fig. 5. Dependence of Debye temperature Θ_D on $(T_d/M/V_a^{2/3})^{1/2}$ for the uranium intermetallic compounds.

where $D(\Theta_D/T)$ is the Debye function and n is the number of atoms per molecule. The dilatational term C_d can be calculated by

$$C_d = \alpha^2 V_m T/\beta .$$

In this equation, V_m is the molar volume and $\beta(=1/K)$ is the compressibility. The electronic term is written by,

$$C_{el} = \gamma T$$

where γ is the coefficient of electronic heat capacity.

Using the experimental values of Θ_D, α and β obtained in the present study and the reported values of γ [13], we estimated the temperature dependence of heat capacity C_p for the intermetallic compounds. For UM_3 type compound, UPd_3, URh_3 and URu_3, the heat capacities estimated in the present study are compared in Fig. 6 with the experimental data in the literature [13,16,17]. The calculated values are in reasonable agreement with the reported values.

Since no information about the heat capacity of UNi_2 and UNi_5 is available in the literature, the heat capacities were roughly estimated from the harmonic–vibrational and dilatational contributions. Fig. 7 reveals the temperature dependence of the heat capacities of UNi_2 and UNi_5 with temperature. Owing to the dilatational term, the heat capacity of UNi_5 shows larger temperature dependence than that of UNi_2. The empirical equations for the temperature dependence of heat capacity are given as follows:

$$C_p(\mathrm{J\,mol^{-1}\,K^{-1}}) = 74.8 + 1.03 \times 10^{-2}T - 2.21 \times 10^5/T^2 \text{ for } UNi_2$$

$$C_p(\mathrm{J\,mol^{-1}\,K^{-1}}) = 149 + 1.88 \times 10^{-2}T - 7.69 \times 10^5/T^2 \text{ for } UNi_5 .$$

4. Conclusions

The structures and lattice parameters of UFe_2, UNi_5,,UNi_2, UPd_3, URh_3 and URu_3 were examined by X-ray diffraction method. Thermal expansion coefficients for UNi_5, UNi_2, UPd_3, URh_3 and URu_3 were evaluated from high-temperature X-ray diffraction data. The longitudinal and shear sound velocities of the intermetallic compounds obtained by ultrasonic pulse echo method enabled us to estimate the elastic properties. Though the intermetallic compounds were found to have higher bulk moduli than pure uranium, no marked deviations from the rule of mixture were observed for their modulus–composition curves. The values of microhardness of these intermetallic compounds were much higher than pure uranium, except for UFe_2.

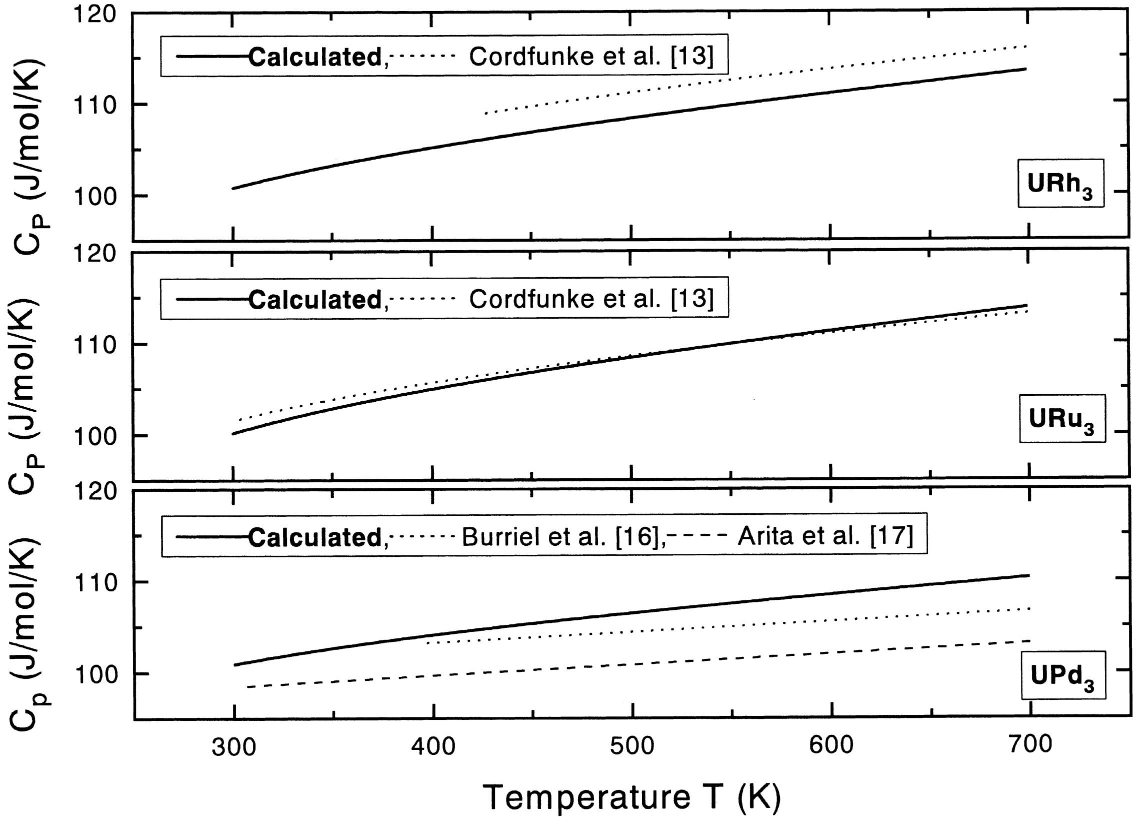

Fig. 6. Temperature dependence of heat capacities C_p of URh_3, URu_3, and UPd_3.

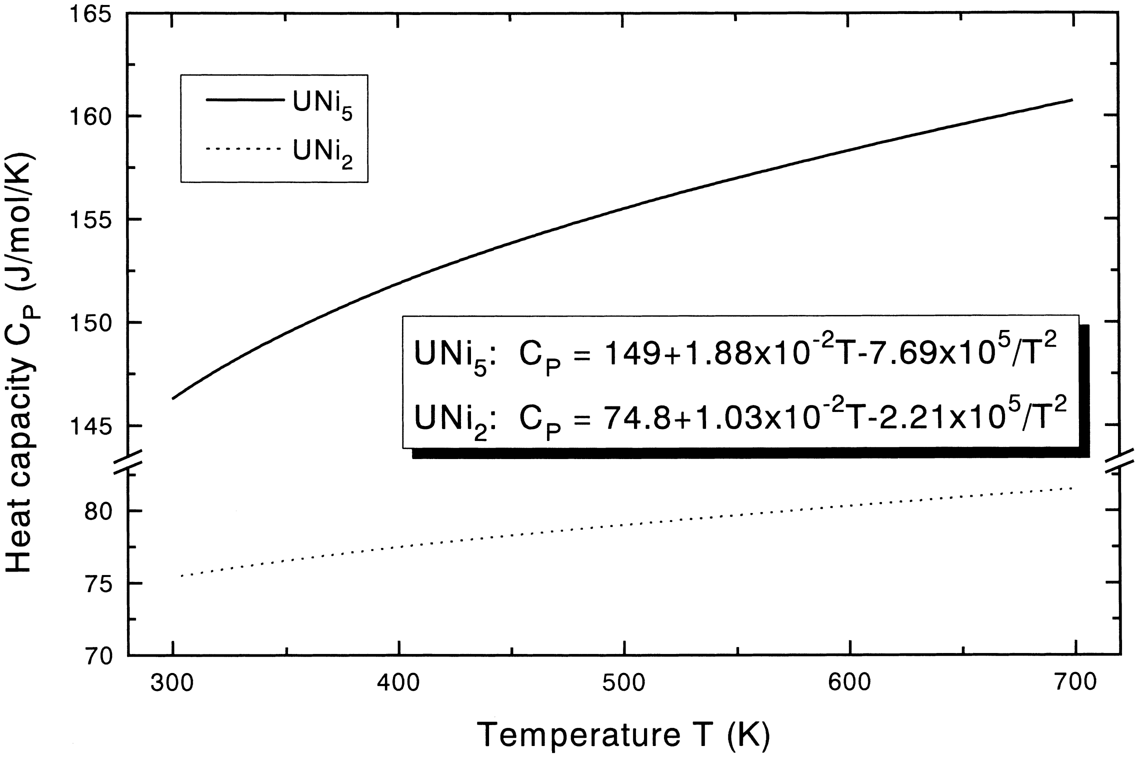

Fig. 7. Temperature dependence of heat capacities C_p of UNi_2 and UNi_5.

The physico–chemical properties of the uranium intermetallic compounds such as Debye temperature and heat capacity were estimated from the sound velocities and thermal expansion data. The correlations between the physico–chemical properties were able to be expressed by the existing physical laws. As for the relationships analyzed (Figs. 1 and 2 and Fig. 5), the characteristics of the metallic bonding in the uranium intermetallic compounds does not markedly differ from that of pure metals. However, a matter to be clarified yet is the case of UFe_2 whose properties were slightly different from those observed for the other intermetallics.

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