



Enthalpies of formation of Nb–Ru and Nb–Ru–Al alloys

My.Y. Benarchid, N. David*, J.-M. Fiorani, M. Vilasi, T. Benlaharache

Laboratoire de Chimie du Solide Minéral, UMR 7555-CNRS, Université Henri Poincaré, 54506 Vandœuvre-Les-Nancy, France

ARTICLE INFO

Article history:

Received 22 July 2008

Received in revised form 6 October 2008

Accepted 14 October 2008

Available online 1 November 2008

Keywords:

Thermodynamics

Niobium alloys

Enthalpy of formation

High-temperature calorimetry

ABSTRACT

The enthalpies of formation of Nb–Ru alloys in the whole range of composition and of two compositions in the Nb–Ru–Al ternary system corresponding to Nb(Ru,Al)₂ and NbRu₂Al identified by Cerba et al. [P. Cerba, M. Vilasi, B. Malaman, J. Steinmetz, J. Alloys Compd. 201 (1993), 57–60], have been measured by high-temperature direct reaction synthesis calorimetry at 1775 K. For some binary alloys the experiment cannot provide results because the direct reaction synthesis is not completed contrarily to ternary alloys experiments. The results are compared with predicted *ab initio* data.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The phase diagram of the Nb–Ru system was first compiled by Massalski [2] based mainly on the studies of several authors [3–7], showing the existence of two solid solutions (Nb) and (Ru), and two intermediate phases NbRu and NbRu₃. The NbRu phase is a congruent compound which melts at 2215 K and exhibits a large homogeneity domain ranging from about 40 at.% Ru at 1423 K to 58 at.% Ru corresponding to the border of the invariant of the peritectoid reaction NbRu + (Ru) ↔ NbRu₃ (1813 K). The near-equiatomic compositions of Nb–Ru system has been reinvestigated by Fonda et al. [8]. They showed that NbRu compound exhibits two structural transitions as a function of the temperature: the first as a martensitic transformation at the temperature of about 1173 K from the β-cubic (CsCl-type) to the β'-tetragonal structure (AuCu-type). This high-temperature phase transition has been reported to be responsible of the shape memory phenomenon observed in the equiatomic NbRu compound. The second one occurs at the temperature 1023 K from the β'-tetragonal structure to the β''-orthorhombic or monoclinic allotropic form [9,10]. Recently, the experimental work of Zamoum [11] revealed the existence of a new phase NbRu₂ with peritectoid formation, while the NbRu₃ phase with cubic structure AuCu₃-type and the space group *Pm3m*, was not identified.

The phase diagram of the Nb–Ru–Al system was investigated by Cerba et al. [1] at 1373 K, indicating the existence of two aluminide

compounds: NbRu₂Al as Heusler phase alloy with cubic structure AlCu₂Mn-type and space group *Fm3m*. The second compound has a formula Nb₂(Ru_xAl_{1-x})₄ with 0.19 < x < 0.26. The structure of which determined by X-ray analysis is characterised by the hexagonal structure of the Laves phase MgZn₂-type (C14 phase) with the space group *P6₃/mmc* [1].

In the literature, none experimental studies are devoted to the thermodynamic data of Nb–Ru and Nb–Ru–Al alloys. Moreover, enthalpies of formation values calculated by means of *ab initio* method are available for binary alloys and for NbRu₂Al [12,13]. The aim of the present work is to measure the enthalpies of formation of primary binary solid solutions which exhibits a large solubility range, NbRu (B2 phase), NbRu₂ compound in the Nb–Ru system, and two compositions Nb_{0.33}Ru_{0.15}Al_{0.52} and Nb_{0.25}Ru_{0.50}Al_{0.25} in the Nb–Ru–Al system, by direct reaction synthesis calorimetry at high-temperature.

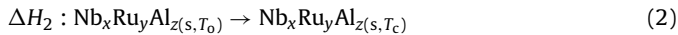
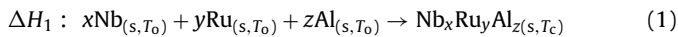
2. Experimental

The investigated starting samples were synthesised, inside a glove box under purified argon gas, from metals reagent grade as powder: Nb (Cerac; purity > 99.98%; Ø < 5 µm), Ru (Chempur; purity > 99.95%; Ø < 25 µm) and Al (Cerac; purity > 99.97%; Ø < 100 µm). Stoichiometric mixtures in the appropriate molar ratio were carefully homogenised in an agate mortar and compacted into 4 mm diameter pellets. The pellets were cut into pieces, weighted and placed alternatively with pure α-alumina in a special Ar-tight container in order to prevent any oxidation with air atmosphere. α-alumina is used for calibration because its enthalpy variation between room and experimental temperatures is well established

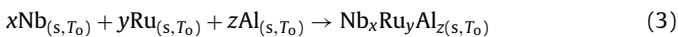
* Corresponding author. Tel.: +33 3 83 68 46 57; fax: +33 3 83 68 46 11.
E-mail address: nicolas.david@lcsm.uhp-nancy.fr (N. David).

by [14]. The container is transferred from the glove box to the top of the calorimeter (MultiHTC-96, SETARAM) for thermalisation at room temperature which is measured prior to each drop. At constant chosen temperature, the heat flow exchanged was measured by time integration of the instantaneous heat flow over the whole duration of the occurring phenomenon. After each set of drop measurements, the alloys resulting from the direct reaction inside the calorimeter were analysed by means of X-ray powder diffraction ($\lambda_{Cu} = 1.54056 \text{ \AA}$) and scanning electron microscopy with electron-probe microanalysis.

The drop measurements are performed from room temperature T_0 into the calorimeter maintained at appropriate temperature T_c (1775 K). The standard molar enthalpy of formation of the $Nb_xRu_yAl_z$ alloys at the reaction temperature T_c , is calculated from the enthalpy effects associated with the following reactions:

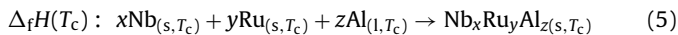
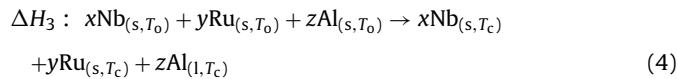


The reaction (2) represents the enthalpy increment between T_0 and T_c of the $Nb_xRu_yAl_z$ products of complete reaction (1), which have reached the room temperature equilibrium state. The difference between the two corresponding thermal effects gives the standard enthalpy of formation $\Delta_f H^{298.15K} = \Delta H_1 - \Delta H_2$:



The values of ΔH_1 and ΔH_2 are averages of nine individual sample drops with standard deviations σ_1 and σ_2 , respectively. The overall uncertainty in the measured standard enthalpy of formation is calculated from $\sigma = \sqrt{\sigma_1^2 + \sigma_2^2}$.

It is important to note that for the NbRu (B2) which is unstable at low temperature, we cannot measure ΔH_2 and consequently the standard enthalpy of formation can not be calculated. In this case, the high temperature enthalpy of formation is given from the contributions of the reactions (1) and (4):



The reaction (4) represents the enthalpy increment between T_0 and T_c of the pure elements Nb, Ru and Al, which is well established [15], including the melting of Al in Nb–Ru–Al compounds. The reaction (5) represents the enthalpy of formation of the $Nb_xRu_yAl_z$ compounds at the calorimeter temperature T_c , referred to solid Nb (bcc), solid Ru (hcp) and liquid Al at the reaction temperature (1775 K).

3. Results and discussion

In the present investigation, we have used stoichiometric starting compositions at 10, 20, 30, 40, 50, 66.5, 75 and 84 at.% Ru for the

Nb–Ru system and $Nb_{0.33}Ru_{0.15}Al_{0.52}$ and $Nb_{0.25}Ru_{0.50}Al_{0.25}$ for the Nb–Ru–Al system. The results obtained by XRD and SEM-EPMA on the final products after each set of measurements, indicate that the complete reactions inside the calorimeter are not achieved for all the products. Thus, we give below the results of the experiments corresponding only to the complete reactions. The experimental results obtained in the present investigation compared with the reported *ab initio* data [12–13] are given in Tables 1 and 2. From Table 2, we can observe that the uncertainty in standard enthalpy of formation $\Delta_f H_{Nb_xRu_yAl_z}^{298.15K}$ extends $\pm 3 \text{ kJ/mol}$ at. This is due probably to the working temperature used in our measurements, which is high and considered as an appropriate experimental temperature to reach the complete reaction inside the calorimeter especially for the Nb–Ru and Nb–Ru–Al refractory systems.

3.1. NbRu (B2)

The XRD analysis of NbRu sample at starting composition 40 at.% Ru indicates the formation of the NbRu cubic phase CsCl-type with the space group $Pm\bar{3}m$ (No. 221), $Z=1$, and the lattice parameter $a=3.184 \text{ \AA}$ [9]. The composition found by means of EPMA is 42.31 at.% Ru. The value of standard enthalpy of formation obtained is $-9.0 \pm 3.9 \text{ kJ/mol}$ at. In the case of equiatomic NbRu sample, the XRD analysis shows a single phase with the room temperature orthorhombic structure ($Z=12$, $a=7.387 \text{ \AA}$, $b=5.452 \text{ \AA}$, $c=8.774 \text{ \AA}$, $\alpha=90^\circ$, $\beta=90^\circ$, $\gamma=90^\circ$) [5]. This result is more consistent with the reported orthorhombic [9,16] for the NbRu compound at 50 at.% Ru than monoclinic structure [10] stabilised below 1023 K according to polymorphism of NbRu as function of the temperature. The composition of NbRu equiatomic compound measured by EPMA is about of 51.45 at.% Ru. This result confirms the work of Fonda et al. [8] who found the low-temperature β'' -NbRu in the near-equiatomic compositions of the Nb–Ru phase diagram. The high-temperature enthalpy of formation measured by direct reaction synthesis of this compound is found to be $-13.2 \pm 2.8 \text{ kJ/mol}$ at. This value is the magnitude than those obtained by *ab initio* calculations (-14.68 and -15.72 kJ/mol at.) [12].

3.2. Solid solution of Ru (A3)

The X-ray analysis of the (Ru) solid solution indicates the complete formation of the hexagonal structure similar to that of the Ru (Mg-type) with the space group $P6_3/mmc$ (No. 194), $Z=2$, and the lattice parameters $a=2.706 \text{ \AA}$, $b=2.706 \text{ \AA}$, $c=4.282 \text{ \AA}$, $\alpha=90^\circ$, $\beta=90^\circ$, $\gamma=120^\circ$ [17]. Indeed, the XRD peaks of the (Ru) solid solution synthesised inside the calorimeter are shifted towards lower 2θ values compared to the peaks of the pure Ru (hcp) due mainly to the incorporation of the Nb at 13.31 at.% in the Ru crystal lattice without modification in its symmetry. Both X-ray diffraction and SEM and EPMA analyses reveal the formation of a single phase of (Ru) solid solution at 86.69 at.% Ru. The obtained standard enthalpy of formation is of about $-7.9 \pm 4.0 \text{ kJ/mol}$ at.

Table 1
Measured heats of reaction (kJ/mol at.) in each set of drop measurements.

Phase	at.% Nb	at.% Ru	at.% Al	Strukturbericht designation	ΔH_1		ΔH_2		ΔH_3
					Average	σ_1	Average	σ_2	Average
NbRu	57.69	42.31	0.00	B2	35.9	2.8	44.9	2.7	42.1 ^a
NbRu	48.55	51.45	0.00	B2	28.7	2.8	–	–	41.9 ^a
(Ru)	13.31	86.69	0.00	A3	36.5	3.4	44.4	2.2	42.1 ^a
Nb(Ru,Al) ₂	34.99	16.03	48.98	C14	–7.5	3.4	51.6	3.1	48.1 ^b
NbRu ₂ Al	22.93	52.48	24.59	L2 ₁	–21.6	3.1	42.7	1.3	44.8 ^b

^a Increment of enthalpy of Nb and Ru between T_c (1775 K) and T_0 (25 °C) tabulated in [15].

^b Increment of enthalpy of Nb, Ru and Al between T_c (1775 K) and T_0 (25 °C) tabulated in [15], including the melting of Al.

Table 2Calculated enthalpies of formation (kJ/mol at.) of Nb–Ru and Nb–Ru–Al compounds compared with reported *ab initio* data.

Phase	at.% Nb	at.% Ru	at.% Al	Strukturbericht designation	$\Delta_f H^{298.15K}$		$\Delta_f H^{1775K}$		$\Delta_f H^{ab\ initio}$	Ref.
					Average	σ	Average	σ		
NbRu	57.69	42.31	0.00	B2	−9.0	3.9	−6.2	2.8	–	This work
NbRu	48.55	51.45	0.00	B2	–	–	−13.2	2.8	–	This work
	50.00	50.00	0.00						−14.68	[12]
	50.00	50.00	0.00						−15.72	[12]
(Ru)	13.31	86.69	0.00	A3	−7.9	4.0	−5.6	3.4	–	This work
Nb(Ru,Al) ₂	34.99	16.03	48.98	C14	−59.1	4.6	−55.6	3.4	–	This work
NbRu ₂ Al	22.93	52.48	24.59	L2 ₁	−64.3	3.4	−66.4	3.1	–	This work
	25.00	50.00	25.00						−62.25	[12]
	25.00	50.00	25.00						−63.96	[12]
	25.00	50.00	25.00						−63.00	[13]

3.3. Nb(Ru,Al)₂ (C14)

The XRD analysis of Nb(Ru,Al)₂ sample synthesised by direct reaction compared to the Powder Cell simulation for Nb₂RuAl₃ using the crystallographic data given in [1], shows the predominance of Nb(Ru,Al)₂ phase in the hexagonal form MgZn₂-type with the space group P6₃/mmc (No. 194), Z = 4, and the lattice parameters $a = 5.107 \text{ \AA}$, $b = 5.107 \text{ \AA}$, $c = 8.329 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$ [1]. The composition of the phase determined by EMPA was 34.99 at.% Nb, 16.03 at.% Ru and 48.98 at.% Al. Negligible quantity of Nb₂Al phase as impurity is also observed. This will not introduce a significant error in the reliability of the measured standard enthalpy of formation. The value of the standard enthalpy of formation measured for this composition is $-59.1 \pm 4.6 \text{ kJ/mol at.}$

3.4. NbRu₂Al (L2₁)

The XRD analysis shows that the NbRu₂Al sample synthesised at 1775 K is mostly constituted by the Heusler phase alloy NbRu₂Al in the cubic form AlCu₂Mn-type with the space group $Fm\bar{3}m$ (No. 225), Z = 4, and the lattice parameter $a = 6.135 \text{ \AA}$ [1]. The composition measured by EPMA is 22.93 at.% Nb, 52.48 at.% Ru and 24.59 at.% Al. Very small amount of the (Ru) solid solution phase is also detected. Thus, the measured heat effect by direct reaction is well due to the formation of the NbRu₂Al. The obtained standard enthalpy of formation ($-64.3 \pm 3.4 \text{ kJ/mol at.}$) is close to those calculated by *ab initio* method (-62.25 , -63.0 and $-63.96 \text{ kJ/mol at.}$) [12–13] regarding the composition and temperature of calculation differences.

Acknowledgements

The authors gratefully acknowledge the financial support of ANR through grant ANR-06-Blan-0181. Special thanks to the SCMEM of the Université Henri Poincaré which carried out the SEM and micro-probe analysis of the samples.

References

- [1] P. Cerba, M. Vilasi, B. Malaman, J. Steinmetz, J. Alloys Compd. 201 (1993) 57–60.
- [2] T.B. Massalski, in: T.B. Massalski (Ed.), Binary Alloy Phase Diagrams, Second edition, ASM International, Ohio, 1990.
- [3] A.E. Dwight, Trans. AIME 215 (1959) 283–286.
- [4] D. Bender, E. Bucher, J. Muller, Phys. Condens. Mater. 1 (1963) 225–231.
- [5] E. Raub, W. Fritzsche, Z. Metallkd. 54 (1963) 317–319.
- [6] G.F. Hurley, J.H. Brophy, J. Less-Common Met. 7 (1964) 267–277.
- [7] T. Tsukamoto, K. Koyama, A. Oota, S. Nogushi, Cryogenics 28 (1988) 580–584.
- [8] R.W. Fonda, H.N. Jones, R.A. Vandermeer, Scripta Mater. 39 (1998) 1031–1037.
- [9] B.H. Chen, H.F. Franzen, J. Less-Common Met. 153 (1989) L13–19.
- [10] V.F. Sears, Neutron News 3 (1992) 26–37.
- [11] F. Zamoum, Thesis, Univ. Henri Poincaré, Nancy, France, 2008.
- [12] G. Ghosh, G.B. Olson, Acta Mater. 55 (2007) 3281–3303.
- [13] R.E. Watson, M. Weinert, M. Alatalo, Phys. Rev. B 57 (1998) 12134–12139.
- [14] D.A. Ditmars, S. Ishihara, S.S. Chang, G. Bernstein, E.D. West, J. Res. N.B.S. 87 (1982) 159–163.
- [15] I. Barin, Thermochemical Data of Pure Substances, Third edition, VCH, Weinheim, Germany, 1995 (Part 1 and 2).
- [16] S.M. Shapiro, G. Xu, G. Gu, J. Gardner, R.W. Fonda, Phys. Rev. B 73 (2006), 214114/1–214114/6.
- [17] V.A. Finkel, M.I. Palatnik, G.P. Kovtun, Phys. Met. Metall. 32 (1971) 231.