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Enthalpies of formation of Mo–Ru and Mo–Ru–Si compounds determined by high-temperature direct reaction synthesis calorimetry

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

Institut Jean Lamour, UMR 7198, CNRS, Université Henri Poincaré Nancy 1, 54506 Vandœuvre-Lès-Nancy, France

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ABSTRACT

The enthalpies of formation of (Ru) hcp solid solution and Mo_5Ru_3 (σ phase) in the Mo–Ru system and ternary extension in the Mo–Ru–Si system at $Mo_{56}Ru_{37}Si_7$ composition, have been determined by high-temperature direct reaction synthesis calorimetry at 1760 K. The following values are reported: $\Delta_f H^{1760\,\mathrm{K}}(\mathrm{Ru}) = -10.6 \pm 0.5$ kJ/mol at.%; $\Delta_f H^{1760\,\mathrm{K}}(\mathrm{Mo_5Ru_3}) = -7.4 \pm 0.4$ kJ/mol at.%; $\Delta_f H^{1760\,\mathrm{K}}(\mathrm{Mo_{56}Ru_{37}Si_7}) = -13.1 \pm 3.3$ kJ/mol at.%. The results are compared with the previous values derived from e.m.f. measurements. They are also compared with the predicted values obtained by Calphad, by *ab initio* method combined to Calphad modelling, and derived from a thermodynamic database named "TM16.TDB".

1. Introduction

The binary phase diagram of the Mo–Ru system was compiled by Massalski [2] based on the studies carried out by Anderson and Hume-Rothery [3] and by Kleykamp [4], indicating the existence of two solid solutions (Mo) and (Ru), and a high-temperature Mo_5Ru_3 intermediate compound (σ phase). The solubility of Ru in (Mo) bcc solid solution and Mo in (Ru) hcp solid solution was known to exhibit a large domain at very high-temperature [2]. In fact, at the eutectic reaction L ↔ (Mo) + (Ru) (2228 K), the maximum of this solubility reaches up to 32.4 at.% Ru and 51.5 at.% Mo, respectively. When the temperature decreases a significant decrease of the solubility of Ru in (Mo) was observed compared to that of Mo in (Ru). At 1416 K, solubilities were measured to be around 10 at.% Ru in (Mo) and 40 at.% Mo in (Ru). σ Phase, first discovered by Raub [5], is formed by a peritectoid reaction (Mo) + (Ru) ↔ Mo_5Ru_3 at the temperature of 2188 K and exhibited a narrow homogeneity domain ranging from about 36.7–39.4 at.% Ru [3,4]. Kleykamp showed by dilatometry analysis that the σ phase is decomposed by a eutectoid reaction to (Mo) and (Ru) solid solutions at 1416 K [4]. Recently, Gürler has reinvestigated the system Mo–Ru in the temperature range of 873–1473 K using ultra rapidly solidified samples [6]. He confirmed the existence of Mo_5Ru_3 at 1473 K and the absence of intermediate phase below 1388 K, which is consistent with the decomposition temperature reported by Kleykamp [4]. He indicated also by SEM analyses the narrow composition range of σ phase (38.2–39.3 at.% Ru). Recently, Oh et al. have assessed the Mo–Ru binary system using the Calphad method [7].

The crystallographic study of Mo_5Ru_3, carried out by Raub, Gürler and Rasmussen and Lundtoft, showed a tetragonal structure of FeCr-type with the space group $P4_2/mnm$ [5,6,8].

Even though enthalpies of formation of hcp Mo–Ru alloys at 1200 K are reported in the literature, they were derived from the electromotive forces (e.m.f.) data using solid galvanic cell [9,10]. Consequently, there is no experimental enthalpy of formation data by direct determination. However, these data have been calculated by Calphad [11], by *ab initio* method combined to Calphad modelling [12–14] and also derived from TM16.TDB [1] (Table 1). Kissavos et al. [12] and Shin et al. [13] noticed that the enthalpies of formation of hcp Mo–Ru compounds calculated only by *ab initio* method using lattice stabilities between Mo hcp and Mo bcc, which is of about 42 or 48 kJ/mol, are in disagreement with enthalpies of formation measured by Kleykamp [9,10]. In order to reproduce Kleykamp data, they suggested using instead of *ab initio* lattice stabilities those derived from the SGTE database for pure elements (11.55 kJ/mol) [15]. To clear up ambiguity we propose in our work to measure directly the enthalpy of formation data of binary Mo–Ru alloys by high-temperature synthesis calorimetry.

The isothermal section of the Mo–Ru–Si system at 1673 K, given in Fig. 1, was investigated by Littner et al. [16]. They observed that σ phase exhibits an extension in the ternary system. Contrary to binary Mo–Ru system, there is no experimental thermodynamic data for Mo–Ru–Si system.

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* Corresponding author. Tel.: +33 3 83 68 46 57; fax: +33 3 83 68 46 50.
E-mail address: nicolas.david@lcsm.uhp-nancy.fr (N. David).

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Table 1
Measured heat of reaction (kJ/mol at.%) in each set of drop measurements and calculated enthalpies of formation (kJ/mol at.%) of Mo–Ru and Mo–Ru–Si alloys compared with reported e.m.f. data and predicted data by Calphad, *ab initio* method combined to Calphad modelling, and from TM16.TDB database (referred to Mo bcc, Ru hcp and Si liquid).

Phase	Mo (at.%)	Ru (at.%)	Si (at.%)	Strukturbericht designation	ΔH_1		ΔH_2[a]	$\Delta H^{1760\,\mathrm{K}}_{\mathrm{formation}}$		$\Delta H^{\mathrm{calculated}}_{\mathrm{formation}}$	Ref.
					Average	σ	Average	Average	σ		
(Ru)	22.85	77.15	0.00	A3	31.4	0.5	42.0[a]	−10.6	0.5	–	This work
	25.00	75.00	0.00					–		−9.7	[9,10]
	20.00	80.00	0.00					–		−10.7	[9,10]
	25.00	75.00	0.00					–		−7.1	[12]
	25.00	75.00	0.00					–		−6.9	[13]
	25.00	75.00	0.00					–		−8.3	[13]
	25.00	75.00	0.00					–		−2.8	[1]
$Mo_{62.5}Ru_{37.5}$	61.72	38.28	0.00	$D8_b$	34.8	0.4	42.2[a]	−7.4	0.4	–	This work
	62.50	37.50	0.00					–		1.8	[14]
	62.50	37.50	0.00					–		4.4	[11]
$Mo_{56}Ru_{37}Si_7$	55.57	37.16	7.27	$D8_b$	32.1	3.3	45.2[b]	−13.1	3.3	–	This work

[a] Increment of enthalpy of Mo and Ru between T_c (1760 K) and T_o (298.15 K), tabulated in refs. [17,18].

[b] Increment of enthalpy of Mo, Ru and Si between T_c (1760 K) and T_o (298.15 K). tabulated in refs. [17,18], including the melting of Si.

In this paper, we report the first experimental measurements by direct reaction synthesis calorimetry at high-temperature of the formation enthalpies of primary (Ru) hcp solid solution and Mo_5Ru_3 (σ phase) in the Mo–Ru system, and ternary extension in the Mo–Ru–Si system for the $Mo_{56}Ru_{37}Si_7$ composition.

2. Experimental

The starting materials are the metals reagent grade as powder: Mo (Aldrich; purity > 99.9%; 1 μm < Ø < 2 μm), Ru (Chempur; purity > 99.95%; Ø < 25 μm) and Si (Alfa Aesar; purity > 99.9985%; Ø < 20 μm). The Stoichiometric mixtures, in the appropriate molar ratio, were carefully homogenised, inside a glove box under purified argon gas, in an agate mortar and compacted into 6 mm diameter pellets. The pellets were cut into pieces and transferred from the glove box to the calorimeter using a special Ar-tight container in order to prevent any oxidation with air atmosphere. MHTC-96 SETARAM calorimeter was used for the enthalpies of formation measurements. The starting samples were placed alternatively in the container with reference α-alumina used for calibration. The enthalpy variations of α-alumina between room and experimental temperatures are well established by Sabbah et al. [17]. The container is placed on the top of the calorimeter for thermalisation at room temperature, which is measured prior to each drop. Several scans of argon and primary vacuums were done at room temperature before heating and drops. 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. All calorimetric measurements were carried out with argon atmosphere scanning. After each set of drop measurements, the alloys resulting from the direct reaction inside the calorimeter were analysed by X-ray powder diffraction (Philips X'pert Pro; $\lambda_{Cu} = 1.54056$ Å) and scanning electron microscopy with electron-probe microanalysis (CAMECA SX-100).

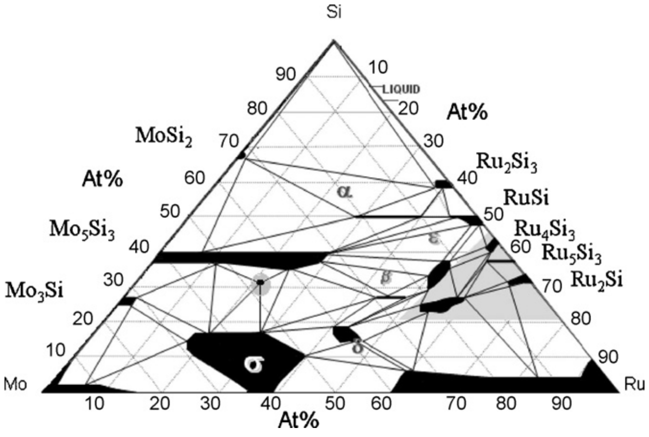

Fig. 1. Isothermal section at 1673 K of the Mo–Ru–Si phase diagram [16].

The drop measurements are performed from room temperature T_o into the calorimeter maintained at appropriate temperature T_c (1760 K). As the Mo_5Ru_3 (σ phase) is unstable at low temperature, we cannot measure the enthalpy increment between T_o and T_c of the $Mo_xRu_ySi_z$ products of complete reaction (1). Consequently, the standard enthalpy of formation cannot be obtained. In this work, we calculate the molar high-temperature enthalpy of formation of the $Mo_xRu_ySi_z$ alloys at the reaction temperature T_c from the enthalpy effects associated with the following reactions:

$$\Delta H_1 : \; x\mathrm{Mo}_{(s,T_o)} + y\mathrm{Ru}_{(s,T_o)} + z\mathrm{Si}_{(s,T_o)} \rightarrow \mathrm{Mo}_x\mathrm{Ru}_y\mathrm{Si}_{z(s,T_c)} \qquad (1)$$

H_1 can be decomposed into two contributions:

$$\Delta H_2 : \; x\mathrm{Mo}_{(s,T_o)} + y\mathrm{Ru}_{(s,T_o)} + z\mathrm{Si}_{(s,T_o)} \rightarrow x\mathrm{Mo}_{(s,T_c)} + y\mathrm{Ru}_{(s,T_c)} + z\mathrm{Si}_{(l,T_c)} \qquad (2)$$

$$\Delta_f H(T_c) = \Delta H_1 - \Delta H_2 : \; x\mathrm{Mo}_{(s,T_c)} + y\mathrm{Ru}_{(s,T_c)} + z\mathrm{Si}_{(l,T_c)} \rightarrow \mathrm{Mo}_x\mathrm{Ru}_y\mathrm{Si}_{z(s,T_c)} \qquad (3)$$

The reaction (2) represents the enthalpy increment between T_o and T_c of the pure elements Mo, Ru and Si established in refs. [17,18], including the melting of Si in Mo–Ru–Si compounds. The reaction (3) represents the enthalpy of formation of the $Mo_xRu_ySi_z$ compounds refereed to solid Mo bcc, solid Ru hcp and liquid Si at the reaction calorimeter temperature ($T_c = 1760$ K). The values of ΔH_1 are averages of nine individual sample drops with standard deviations σ.

3. Results and discussion

The experimental results obtained in the present investigation compared with the earlier values derived from e.m.f. measurements data [9,10] and that calculated by Calphad [11] and by *ab initio* method combined with Calphad modelling [12–14] and from TM16.TDB database [1], are given in Table 1 and plotted in Fig. 2.

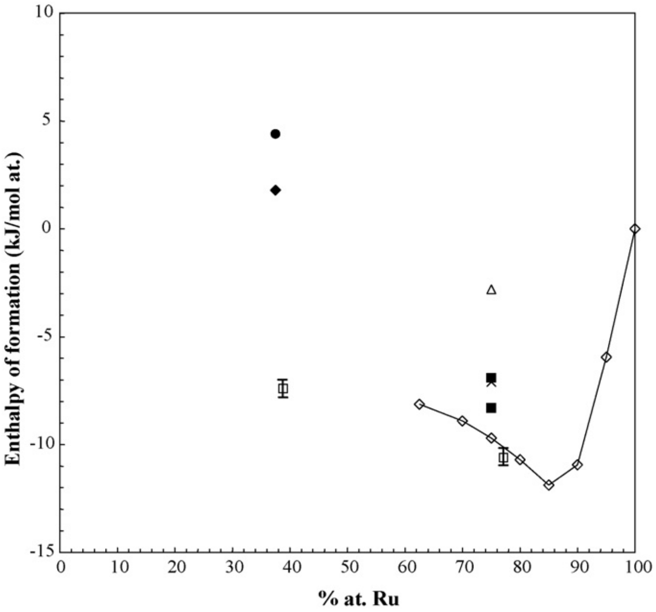

Fig. 2. Enthalpies of formation of Mo–Ru alloys *vs* x_{Ru} referred to Mo bcc and Ru hcp; (□) present work, (◇) Kleykamp [9,10], (●) Calphad [11], (×) *ab initio* combined to Calphad modelling [12], (■) *ab initio* combined to Calphad modelling [13], (◆) *ab initio* combined to Calphad modelling [14], and () TM16.TDB [1].

3.1. Solid solution of Ru (A3)

The sample XRD analysis, indicates the complete formation of the hexagonal structure comparable to that of (Ru) hcp with the space group $P6_3/mmc$ (no. 194), $Z=2$, and the lattice parameter $a=2.7059$ Å, $c=4.2815$ Å [19]. The XRD peaks of the synthesised (Ru) solid solution are shifted towards lower Bragg angles compared with the pure Ru, which agrees well with the results of Kleykamp [4] and Gürler [6]. The composition of (Ru) solid solution synthesised inside the calorimeter measured by EPMA is 77.15 at.% Ru. The enthalpy of formation at 1760 K of the (Ru) solid solution is -10.6 ± 0.5 kJ/mol at.%. As the difference between the enthalpy of formation data at 1200 K and 1760 K is fairly not very significant, we can conclude that our value measured by high-temperature direct reaction calorimetry is in very good agreement with those derived by Kleykamp [9,10] from the experimental e.m.f. data at 1200 K using Gibbs–Duhem integration and Gibbs–Helmholtz derivation: -9.7 and -10.7 kJ/mol at.% for 75 and 80 at.% Ru, respectively. Our value is the magnitude compared to those calculated using *ab initio* method combined to Calphad modelling at the stoichiometric composition 75 at.% Ru (-7.1 kJ/mol at.% [12], -6.9 kJ/mol at.% [13] and -8.3 kJ/mol at.% [13]). While, the derived one from TM16.TDB database (-2.8 kJ/mol at.%) reported by Aldinger et al. [1], is less exothermic than that measured in the present work.

3.2. Mo_5Ru_3 ($D8_b$)

The XRD analysis of Mo_5Ru_3 sample, shows the formation mainly of σ phase in tetragonal structure of FeCr-type with the space group $P4_2/mnm$ (no. 136), $Z=30$, and the lattice parameter $a=9.5652$ Å, $c=4.9362$ Å reported by Rasmussen et al. [8]. The composition of σ phase measured by EPMA is 38.28 at.% Ru. Small quantities of (Mo) and (Ru) solid solutions are detected, which correspond to compositions found by EPMA of 16.28 at.% Ru in (Mo) and 44.14 at.% Mo in (Ru), respectively. They are very close to the limit of the invariant reaction of the eutectoid decomposition $Mo_5Ru_3 \leftrightarrow (Mo)+(Ru)$ occurring at the temperature of 1416 K, previously reported by Kleykamp [4]. Therefore, the enthalpy of formation measured by direct reaction calorimetry is well associated to the complete formation of the σ phase at high-temperature (1760 K) taking into consideration that during cooling to room temperature after the set of drop measurements, this phase decomposes moderately to the (Mo) and (Ru) solid solutions. The obtained enthalpy of formation of Mo_5Ru_3 compound at 1760 K (-7.4 ± 0.4 kJ/mol at.%) is a little bit exothermic contrarily to that of the line compound at the composition of 37.5 at.% Ru, calculated at 0 K (1.8 kJ/mol at.%) using *ab initio* calculations considering SGTE value (11.55 kJ/mol) for Mo hcp lattice stability [14] and to that at 298.15 K determined by Calphad modelling (4.4 kJ/mol at.%) [11].

3.3. $Mo_{56}Ru_{37}Si_7$ ($D8_b$)

The measured composition using EPMA, is 55.57 at.% Mo, 37.16 at.% Ru and 7.27 at.% Si. The XRD pattern of the sample synthesised by direct reaction confirms the formation of single σ phase in the tetragonal structure of FeCr-type with the space group $P4_2/mnm$ similar to Mo_5Ru_3 compound [8]. Furthermore, the peaks of the $Mo_{56}Ru_{37}Si_7$ occur at higher 2θ values compared to that of Mo_5Ru_3, indicating that the lattice parameters of ternary σ phase were smaller than those for binary σ phase. That can be supported by the structural study of Mo_5Ru_3 by ref. [5] and of $Mo_{60}Ru_{30}Si_{10}$ by ref. [16], respectively. The measured enthalpy of formation at 1760 K is -13.1 ± 3.3 kJ/mol at.%, which seems to indicate an increasing of the stability of binary Mo_5Ru_3 with silicon addition.

4. Conclusion

In this work, experimental enthalpy of formation measurements by direct reaction high-temperature calorimetry of (Ru) hcp solid solution and binary and ternary σ phases, are presented. The enthalpy of formation of (Ru) solid solution is very close to that derived from previous electromotive forces data [9,10], which confirm them. First time values of enthalpy of formation of binary and σ ternary phases, are measured. The binary σ phase shows a significant discrepancy with predicted data by Calphad and by *ab initio* method combined to Calphad modelling [11,14]. The silicon addition in σ phase seems to stabilise it at low temperature in the ternary system.

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