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Calorimetric investigation of mixing enthalpy of liquid (Co + Cu + Zr) alloys at T = 1873 K

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ABSTRACT

The enthalpies of mixing of liquid (Co + Cu + Zr) alloys have been determined using the high-temperature isoperibolic calorimeter. The measurements have been performed along three sections (x_{Co}/x_{Cu} = 3/1, 1/1, 1/3) with x_{Zr} = 0 to 0.55 at T = 1873 K. Over the investigated composition range, the partial mixing enthalpies of zirconium are negative. The limiting partial enthalpies of mixing of undercooled liquid zirconium in liquid (Co + Cu) alloys are (−138 ± 18) kJ · mol^{-1} (the section x_{Co}/x_{Cu} = 3/1), (−155 ± 10) kJ · mol^{-1} (the section x_{Co}/x_{Cu} = 1/1), and (−130 ± 22) kJ · mol^{-1} (the section x_{Co}/x_{Cu} = 1/3). The integral mixing enthalpies are sign-changing. The isenthalpic curves have been plotted on the Gibbs triangle. The main features of the composition dependence of the integral mixing enthalpy of liquid ternary alloys are defined by the pair (Co + Zr) and (Cu + Zr) interactions.

1. Introduction

Recently, the (Co + Cu + Zr)-based alloys were recognized as a promising candidate for the creation of bulk metallic glass composites [1]. Such materials, which consist of a crystalline shape-memory phase and amorphous matrix, are expected to overcome the general brittleness of bulk metallic glasses [2]. The (Co + Cu + Zr) system is also of particular interest due to the occurrence of the liquid demixing of ternary alloys with low zirconium content [3]. This particular feature of the phase equilibria could allow the synthesizing of the crystalline/amorphous composite through liquid immiscibility. As a consequence, the information on the thermodynamic properties of liquid alloys is required for prediction of the glass-forming ranges as well as the accurate calculation of the phase diagram. To the best of our knowledge, no experimental data of such type are available in the literature for this system. Thus, the aim of this work is a calorimetric investigation of the mixing enthalpies of liquid (Co + Cu + Zr) alloys.

2. Literature review

In order to determine the mixing enthalpy function for liquid ternary alloys properly, it is important to have reliable data on the same functions for liquid binary alloys. Therefore, a short review of the calorimetric results for the binary systems is given in the present section.

As for the binary (Co + Cu) system, the direct calorimetric measurements were performed by Dokken and Elliott [4] at T = 1473 K, Nikolaenko and Turchanin [5] at T = 1823 K, and Iguchi *et al.* [6] at T = 1834 K. According to the experimental results of these works, the mixing enthalpies of liquid (Co + Cu) alloys show moderate positive values (figure 1). From their experimental data, all authors proposed the equations for the description of the composition dependence of the integral mixing enthalpy. The coefficients of the simple polynomials from [4–6] are given in table 1. The data presented in table 1 indicate the necessity of introducing at least three parameters for the proper description of the experimental data in the whole composition range.

Turchanin *et al.* [8] at T = 1873 K, Lück *et al.* [9] at T = 1873 K, and Esin *et al.* [10] at T = 1963 K measured the mixing enthalpies of liquid (Co + Zr) alloys using the direct calorimetric methods. The literature data [8–10] are combined in figure 2. The experimental results obtained by various authors are in good agreement. In general, the mixing enthalpies with substantial negative deviation from ideal mixing were established for the (Co + Zr) system. Turchanin *et al.* [8] and Esin *et al.* [10] applied simple polynomials to describe a $\alpha_{Zr}(x_{Zr})$-function. The coefficients of the equations according [8,10] are listed in table 2. In both cases, as many as four parameters were required to describe the composition dependence of the integral mixing enthalpy properly.

By calorimetry, numerous investigations on the mixing enthalpy of liquid alloys were carried out in the (Cu + Zr) system by Kleppa

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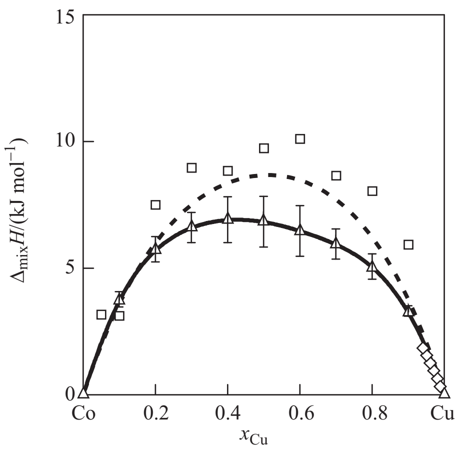

FIGURE 1. The integral mixing enthalpy $\Delta_{mix}H$ of liquid (Co + Cu) alloys. Experimental data points: ◇ [4] at T = 1473 K, –△– [5] at T = 1823 K, □ [6] at T = 1834 K. Line: --- calculation according [7]. The vertical bars show confidence intervals. The standard states are pure liquid metals.

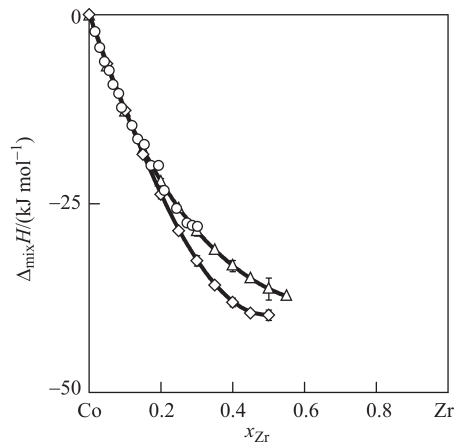

FIGURE 2. The integral mixing enthalpy of liquid (Co + Zr) alloys. Experimental data points: ○ [9] at T = 1873 K, –△– [8] at T = 1873 K, –◇– [10] at T = 1963 K. The vertical bars show confidence intervals. The standard states are pure liquid metals.

TABLE 2
Composition ranges in mole fractions of zirconium x_{Zr}, temperatures T of the experimental investigations of the mixing enthalpy $\Delta_{mix}H$ for the liquid (Co + Zr) alloys and coefficients of the simple polynomials q_n for the $\Delta_{mix}H$ function.

Reference	Investigated composition range, x_{Zr}	T/K	$\Delta H = x_{Zr}(1-x_{Zr})(q_0 + q_1x_{Zr} + q_2\,x_{Zr}^2 + \cdots + q_n\,x_{Zr}^n)$/(kJ · mol^{-1})			
			q_0	q_1	q_2	q_3
[8]	0–0.52	1873	−149.74	69.88	−37.83	−168.56
[10]	0–0.49	1963	−131.6	−95.27	18.89	121.4

and Watanabe [11] at T = 1373 K, Yamaguchi *et al.* [12] at T = 1443 K, Sommer and Choi [13] at T = 1473 K, Sudavtsova *et al.* [14] at T = 1480 K, Witusievicz *et al.* [15] at T = 1480 K, Turchanin *et al.* [16] at T = (1573 and 1873) K, Sidorov *et al.* [17] at T = 1973 K. The experimental results [11–17] are summarized in figure 3. All authors reported high negative values except for the less negative data of Sidorov [17]. The experimental results were represented by the simple polynomials using six parameters in [15], three parameters in [16], and five parameters in [17] (table 3).

The coefficients of the simple polynomial from [8,16] were taken to assess the binary interaction parameters for the (Cu + Zr) and (Co + Zr) systems, since the measurements of [8,16] were performed using the experimental procedure and experimental set-up adopted in the present work and at the corresponding temperature. For the (Co + Cu) system, the parameters were directly taken from [7], because this thermodynamic assessment allows to obtain a satisfactory fit to the thermochemical data [4–6] using only three interaction parameters (figure 1).

3. Experimental procedure

The partial mixing enthalpies of zirconium in liquid (Co + Cu + Zr) alloys were investigated using a high-temperature isoperibolic calorimeter designed and assembled in Laboratory of physicochemical properties of metallic liquid alloys (Donbass State Engineering Academy, Ukraine). The experimental set-up is described in details in [18]. Two thermopiles were used for the measurements. One with sixteen differential thermocouples was used for the integration of the heat flux between the bath of liquid metal and an isothermal enclosure of the calorimetric cell. The other consisting of three thermocouples measured the

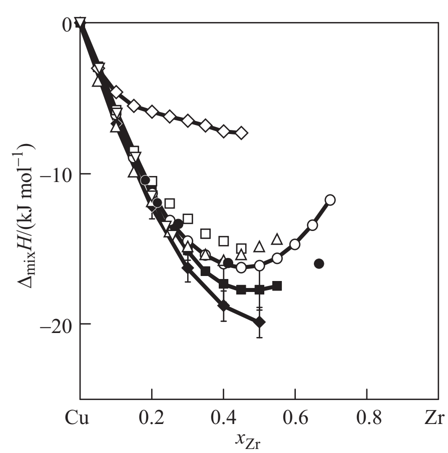

FIGURE 3. The integral mixing enthalpy of liquid (Cu + Zr) alloys. Experimental data points: △ [11] at T = 1373 K; ● [12] at T = 1443 K; □ [13] at T = 1473 K; ▽ [14] at T = 1480 K; –○– [15] at T = 1480 K; –◆– [16] at T = 1573 K; –■– [16] at T = 1873 K; –◇– [17] at T = 1973 K. The vertical bars show confidence intervals. The standard states: pure liquid metals.

TABLE 1
Composition ranges in mole fractions of cobalt x_{Co}, temperatures T of the experimental investigations of the mixing enthalpy $\Delta_{mix}H$ for the liquid (Co + Cu) alloys and the coefficients of simple polynomials q_n for the $\Delta_{mix}H$ function.

Reference	Investigated composition range, x_{Co}	T/K	$\Delta_{mix}H = x_{Co}\cdot(1-x_{Co})\cdot(q_0 + q_1\cdot x_{Co} + q_2\cdot x_{Co}^2 + \cdots + q_n\cdot x_{Co}^n)$/(kJ · mol^{-1})							
			q_0	q_1	q_2	q_3	q_4	q_5	q_6	q_7
[4]	0–0.06	1473	33.5	−10.5						
[5]	0–1	1823	44.3	−100.0	358.7	−1594.5	4980.3	−8223.0	6730.3	−2152.3
[6]	$0 < x_{Co} < 0.5$	1834	73.2	−138.1	138.1					
	$0.5 < x_{Co} < 1$		52.3	−54.4	54.4					