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Enthalpy of formation of intermetallic phases from Al–Zr system determined by calorimetric solution method

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Abstract

Intermetallic phases represent a group of materials of unique properties. Many of those materials have found practical application, whereas others are still intensively examined. There are ten stable intermetallic phases in Al–Zr system, among which few are prospective materials to work at elevated temperature, nuclear reactors, etc. On top of that, researches are focused on obtaining amorphous phases, nanoparticles and zirconium-based pressure pipes covered with aluminum. As a result, better understanding of thermal effects accompanying those compounds formation becomes crucial. In this paper, solution calorimetry method was used for determination of formation enthalpy $\Delta_f H$ of intermetallic phases from Al–Zr system at room temperature (298 K). Experiments were conducted using test station built by author. Material used as bath was aluminum. Additionally, alloys preparation methodology was described and presented. Calorimetric measurements were taken on phases: Al_3Zr, Al_2Zr, Al_3Zr_2, $AlZr$, Al_2Zr_3, $AlZr_2$ and $AlZr_3$. Heat of dissolution of zirconium in aluminum bath at temperature 1073 K was determined experimentally and was equal to -244.5 ± 5.4 kJ mol^{-1}. Obtained results of enthalpy of formation were summarized and compared with the literature data.

Keywords Calorimetry · Al–Zr system · Intermetallics · Enthalpy of formation

Introduction

Modern material engineering keeps searching for materials being able to work in various conditions; therefore, a lot of attention is put for intermetallic phases. Those phases characterize with ordered structure and often stoichiometric composition. As a result, properties are substantially different from alloys in which they appear. They are described as indirect materials among ceramics and alloys, mostly due to brittleness at room temperature and high melting point, resistance to oxidation and corrosion, elevated temperature strength and relatively low density. Particularly, interesting intermetallic phases from practical point of view are those containing aluminum and transition metals (Ni, Ti, Zr, Hf, V, Nb, Ta) [1, 2]. Some of them have found practical application long time ago, e.g., NiAl

for coating materials or Ni_3Al for high-temperature structural materials [3–5]. Others, like aluminum–zirconium intermetallics, may be potentially applied in thermal nuclear reactors [6, 7], also extensive work on the Al–Zr-based amorphous and nanocrystalline alloys has been reported [8–10]. Phase Al_3Zr is desirable candidate for high-temperature structural applications [1, 2].

Al–Zr system shown in Fig. 1 is one of the most complicated of all the transition metal aluminide binary phase diagrams [11]. According to the evaluation of Murray et al., there are ten stable intermetallic phases: Al_3Zr, Al_2Zr, Al_3Zr_2, $AlZr$, Al_4Zr_5, Al_3Zr_4, Al_2Zr_3, Al_3Zr_5, $AlZr_2$ and $AlZr_3$; all of which experimentally are found to have extremely narrow concentration ranges [12]. Two of them Al_4Zr_5 and Al_3Zr_5 are high-temperature phases. Available in the literature crystallographic data of Al–Zr intermetallics are listed in Table 1 [13].

This paper is focused on thermodynamic data, specifically on thermal effects accompanying formation of intermetallic phases from Al–Zr system. The literature data present minor results obtained from experiments, whereas major of them originate from computational methods. In

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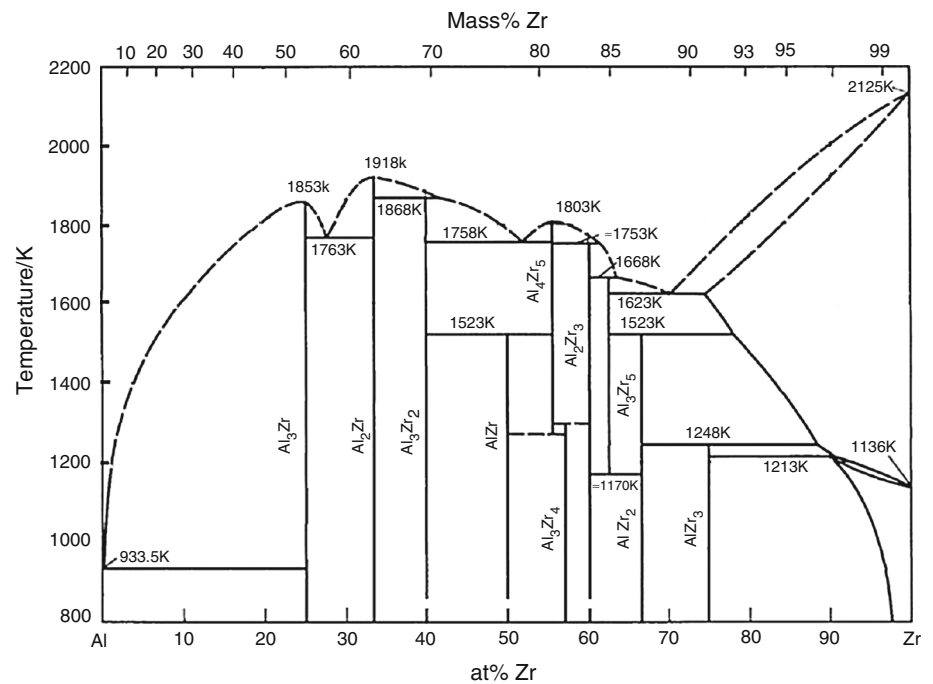**Fig. 1** Al–Zr phase diagram with marked intermetallic phases

Table 1 Crystallographic data of Al–Zr intermetallics [13]

Phase	Pearson symbol	Strukturbericht designation	Space group (#)	Prototype
Al_3Zr	$tI16$	$D0_{23}$	$I4/mmm$ (139)	Al_3Zr
Al_2Zr	$hP12$	$C14$	$P6_3/mmc$ (194)	$MgZn_2$
Al_3Zr_2	$oF40$	–	$Fdd2$ (43)	Al_3Zr_2
$AlZr$	$oC8$	B_f	$Cmcm$ (63)	CrB
Al_4Zr_5	$hP18$	–	$P6_3/mcm$ (193)	Ga_4Ti_5
Al_3Zr_4	$hP7$	–	$P6$ (174)	Al_3Zr_4
Al_2Zr_3	$tP20$	–	$P4_2/mnm$ (136)	Al_2Zr_3
Al_3Zr_5	$tI32$	$D8_m$	$I4/mcm$ (140)	Si_3W_5
$AlZr_2$	$hP6$	$B8_2$	P63/mmc (194)	Ni_2In
$AlZr_3$	$cP4$	$L1_2$	$Pm3\,m$ (221)	$AuCu_3$

this work, high-temperature calorimetric solution method for determination of formation enthalpy $\Delta_f H$ of intermetallic phases from Al–Zr system at room temperature (298 K) is proposed. Calorimetric measurement allows for determination of molar enthalpy of formation that is one of the most important thermodynamic data used in computing and phase diagrams optimization. Formation enthalpy is determined using high-temperature solution calorimeter with indirect method. For binary alloys AB, value of enthalpy of formation results from the difference between heat effects accompanying dissolution of A, B components and AB alloy separately in metallic bath. It is worth to mention that the alloy obtained before the calorimetric experiment and its components are dissolved in the same type of solvent. In presented research, aluminum bath is used, and additionally preparation of intermetallic phases from Al–Zr system as well as results analysis is described.

High-temperature phases Al_4Zr_5 and Al_3Zr_5 are not part of this research.

Phases preparation and analysis

Preparation of alloys with precisely defined stoichiometry from pure components requires application of proper melting method. One of the most commonly used is melting in electric-arc furnace. Disadvantage of this method is poor stirring, inhomogeneous structure and composition of alloy resulting from high-temperature gradient [14]. Therefore, in this work, levitation melting was selected as method of alloying. It allows for obtaining homogeneous casts without segregation effects thanks to fast crystallization. Additional advantage is also high purity of alloys resulting from no contact with crucible material

which could contaminate sample [15]. Levitation furnace uses inductive heating effect which bases on heat generation during eddy current flow, induced from electromagnetic induction phenomenon in elements magnetically coupled. For the phenomenon of levitation, it is necessary to create gradient and the value of magnetic component of the field to compensate the mass of metal and to keep it in the stable position by magnetic forces. In order to form the field of particular geometry, appropriately shaped coil is required. It is usually made from copper tube and is intensively water cooled. The coil is powered by high-frequency generator, with an output of at least few kilowatts. Then, in the central part of the coil the field is weakest, and the metal is pushed to this zone occupying more or less stable position [14–17].

For obtaining intermetallic phases from Al–Zr system, metals of high purity were used: aluminum 99.999% and zirconium 99.99%. Based on stoichiometry of phases, eight analytical samples in particular mass ratio were prepared. They were melted in induction levitation furnace, which diagram is presented in Fig. 2. Furnace is equipped with high-frequency generator GIS-10 (10 kW in 415 kHz). It allows for metal casting of approximately 2 cm^3 volume.

All casts were performed in protective atmosphere of argon (N6.0). Within seconds, metals were melted during which, intensive stirring and overheating was occurring. Short time of melting using levitation method allowed for minimizing of oxidizing risk of alloys. After reducing power of generator, melted metal felled on water-cooled cooper mold, shaped in inverted cone and immediately solidified with the same shape. Mass decrement of alloy after casting compared to metallic charge was negligible.

Due to overcooling, amorphous structure in alloys occurred. Tendency to the formation of amorphous phases during overcooling on the example of $AlZr_3$ was presented by Ma [8]. Samples were submitted to long-lasting annealing at elevated temperature. Casts were cut with electro-erosion saw in half and vacuum-sealed in quartz capsules. They were placed on ceramic pad in order to separate samples from quartz wall. Conoidal shape of samples reduced also contact with pad. Alloys were heated in resistance furnace at temperature 1123 K for 672 h (28 days). Cooling was performed together with furnace.

Subsequently, phase composition was verified using X-ray phase analysis, performed on X-ray diffractometer PW 1710 (Philips). Filtered radiation of CoKα was used for measurement. Analysis results are presented in Table 2. In
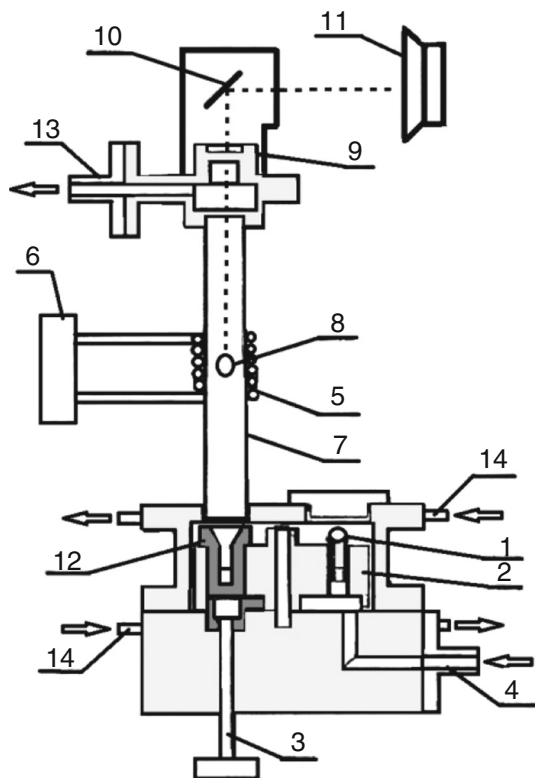

Fig. 2 Diagram of the laboratory levitation melting apparatus: 1—metal sample, 2—turning table, 3—manipulating rod, 4—gas inlet, 5—coil, 6—generator of high-frequency current, 7—quartz tube, 8—metal droplet, 9—looking window, 10—mirror, 11—pyrometer, 12—copper mold, 13—gas outlet, 14—water heating

Table 2 Phase analysis results

No.	Sample	Phase composition (XRD)
1	Al_3Zr	0.15% Al_3Zr_5
		99.42% Al_3Zr
		0.27% $AlZr$
		0.17% Al
2	Al_2Zr	97.83% Al_2Zr
		1.82% Al
		0.35% $AlZr$
3	Al_3Zr_2	98.22% Al_3Zr_2
		1.78% Al_3Zr_5
4	$AlZr$	92.72% $AlZr$
		1.71% Al_3Zr_2
		2.30% Al_3Zr_4
		3.17% Al_3Zr_5
5	Al_3Zr_4	50.24% Al_3Zr_5
		49.76% Al_3Zr_4
6	Al_2Zr_3	96.3% Al_2Zr_3
		3.67% Al
		0.30% Al_3Zr_4
7	$AlZr_2$	95.20% $AlZr_2$
		4.80% Al
8	$AlZr_3$	95.80% $AlZr_3$
		4.20% Al

majority of samples, apart from identified phases from Al–Zr system, presence of aluminum was revealed. It was taken into consideration while computing accompanying enthalpy of formation measurements. Also presence of other phases than investigated is stated. Its quantity is negligible in case of samples: Al_3Zr, Al_2Zr and Al_2Zr_3; only in case of samples marked as AlZr and Al_3Zr_4, content of expected phase is below 95%. Sample AlZr was used in calorimetric measurements; on contrary, sample Al_3Zr_4 was rejected due to significant presence of high-temperature phase Al_3Zr_5. X-ray pattern of sample AlZr is presented in Fig. 3, and that of sample Al_3Zr_4 is shown in Fig. 4. In parallel, metallographic specimen was prepared, which was analyzed on scanning electron microscope PHILIPS XL30 integrated with energy-dispersive X-ray spectrometer LINK ISIS (EDS). Figures 5 and 6 present images of heated alloys obtained in the light of backward scattered electrons (BSE) and results of chemical composition analysis obtained using EDS analysis. In case of AlZr sample are visible clear precipitations in form of dendrites (Fig. 5). Dark places visible on microstructure of Al_3Zr_4 sample are pores created during fast solidification of sample (Fig. 6).

Calorimetric measurements

Measurements of enthalpy of formation Δ_fH at temperature 298 K of intermetallic phases from Al–Zr system were taken on test station equipped with high-temperature solution calorimeter (Fig. 7). It consists of calorimeter, vacuum pump set, bottle with argon of spectral purity (N6.0), module for signal recording and computer. The calorimeter is a pipe furnace containing calorimetric block that is locked in casing shaped as barrel. It is connected with locks used for entering of samples, set of valves ensuring protective atmosphere during measurements, thermoelements and also temperature controllers. Detailed description of the calorimeter as well as problems related to calibration of the device can be found in other papers of the author [18, 19]. In this work, only most important element that is calorimetric block will be discussed. It consists of elements presented in Fig. 8.

Alundum crucible (1 in Fig. 8) has internal diameter around 35 mm and can contain aluminum bath of 50 g mass. Mass of examined samples represents minimal part of the bath. Small change in degree of fulfillment of crucible during experiment is crucial in calorimetric experiment. Directly under crucible bottom is presented thermopile (2 in Fig. 8) consisting of around seventy thermocouples type S (PtRh10-Pt), connected in series. Thermopile is used for measuring thermal effect

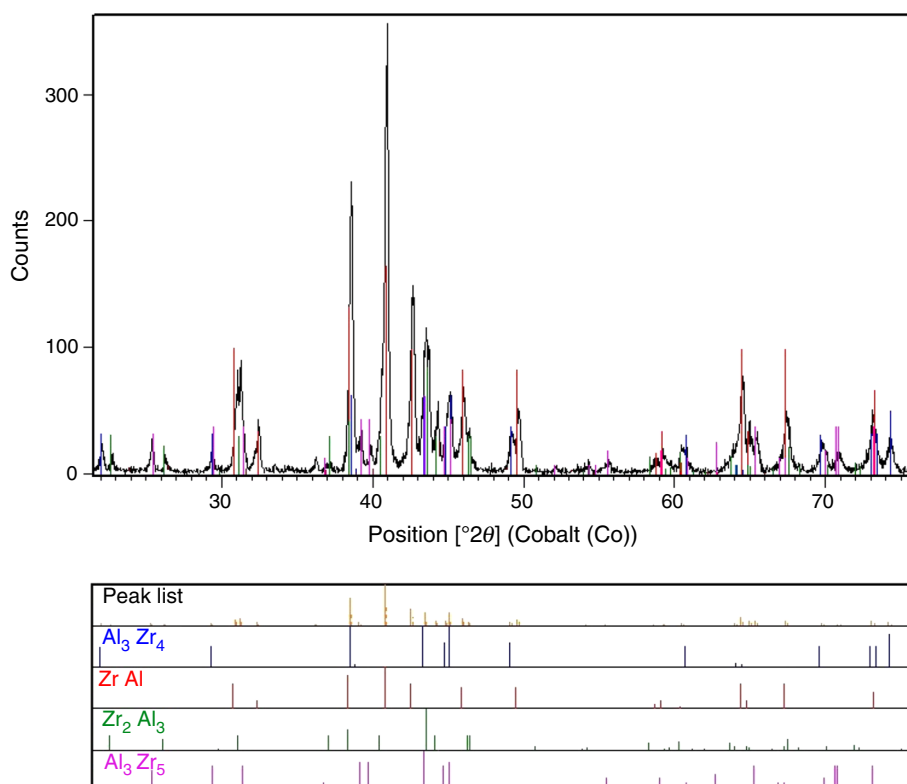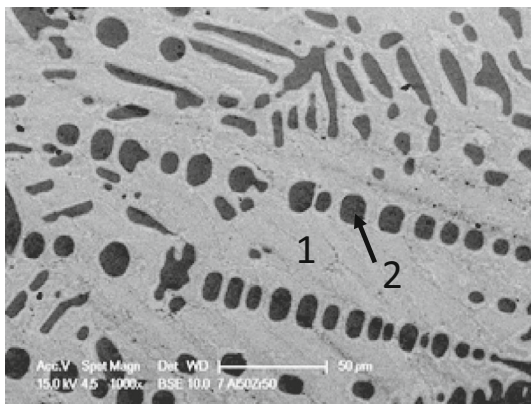**Fig. 3** X-ray pattern of AlZr sample after annealing at temperature 1123 K for 672 h
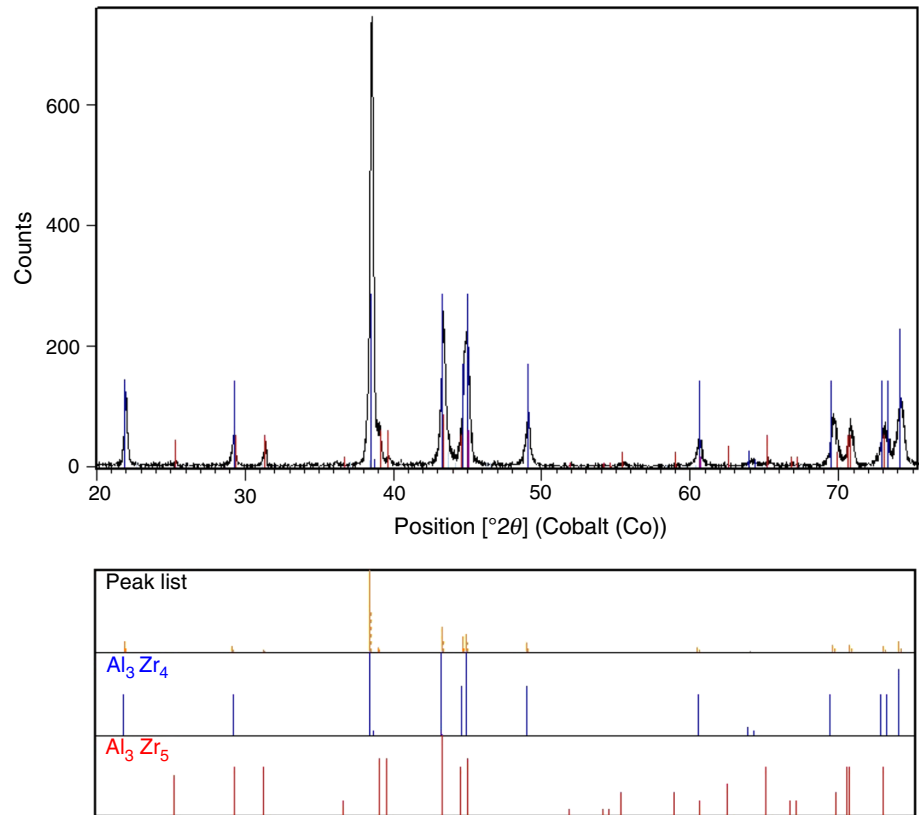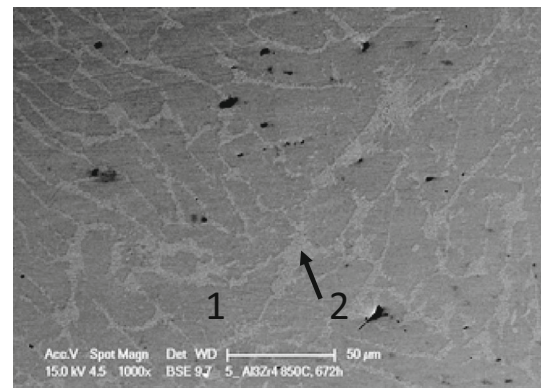
Fig. 4 X-ray pattern of Al₃Zr₄ sample after annealing at temperature 1123 K for 672 h

Chemical composition (EDS)

	Mass%		At%	
	Al	Zr	Al	Zr
1	21.33	78.67	47.83	52.17
2	28.01	71.99	56.82	43.18

Fig. 5 BSE image of AlZr sample after annealing at temperature 1123 K for 672 h with results of the EDS analysis

Chemical composition (EDS)

	Mass%		At%	
	Al	Zr	Al	Zr
1	16.88	83.12	40.71	59.29
2	15.29	84.71	37.90	62.10

Fig. 6 BSE image of Al₃Zr₄ sample after annealing at temperature 1123 K for 672 h with results of the EDS analysis

accompanying dropping the sample into the bath. Alundum stirrer (3 in Fig. 8) is used for obtaining homogeneous composition of bath bulk and increasing measurement accuracy. The sample is dropped into the bath by the tube

(4 in Fig. 8). Temperature of calorimetric block is measured with thermocouple type N (NiCrSi–NiSi) (5 in Fig. 8). Main body of calorimetric block (6 in Fig. 8) is made of heat-resisting steel. It is placed in heat-resisting
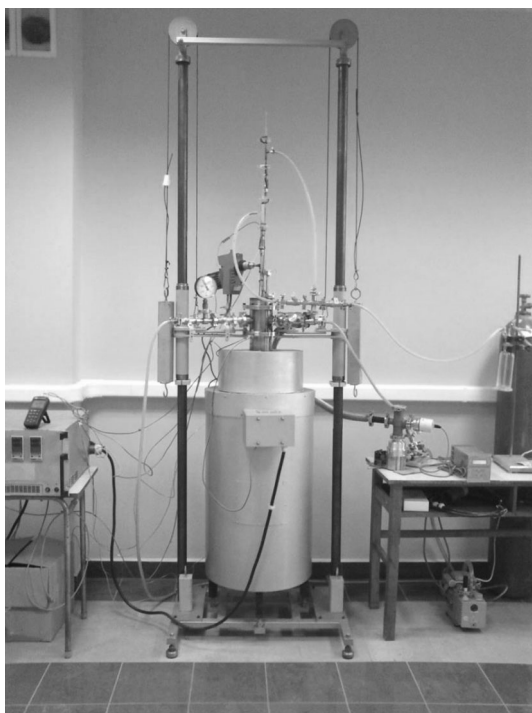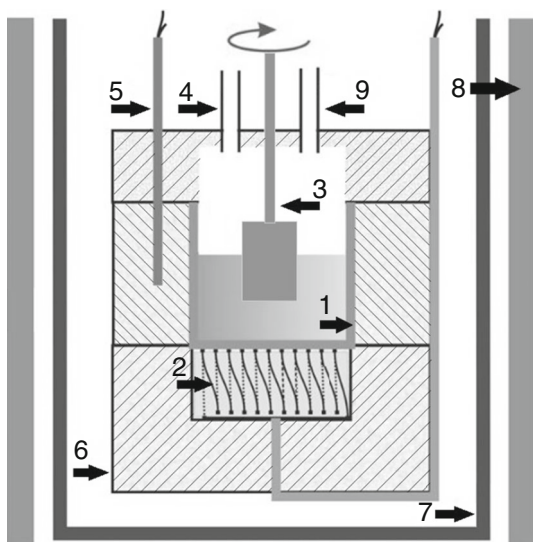
Fig. 8 Calorimetric block scheme: 1—alundum crucible, 2—thermopile, 3—alundum stirrer, 4—sample inlet, 5—thermocouple, 6—block housing, 7—block container, 8—furnace, 9—sample inlet from intermediate container

steel container (7 in Fig. 8), which is located inside calorimeter furnace (8 in Fig. 8) and is characterized by significant thermal inertia.

Measurement principle

Measurement principle of thermal effects in solution method relies on the change in the temperature of a bath, into which sample is dropped. Base temperature (temperature of calorimetric block between single measurements) in one series of measurement remains stable. Determination of formation enthalpy with use of high-temperature solution calorimeter bases on comparison of heat effects accompanying dissolving of alloys and its components in metallic bath. For binary alloys, it can be presented as:

$$\Delta_f H = x_A \Delta H_A^{\text{ef.}} + x_B \Delta H_B^{\text{ef.}} - \Delta H_{A_{x_A} B_{x_B}}^{\text{ef.}} \tag{1}$$

where $\Delta_f H$—formation enthalpy of the alloy; x_A, x_B—concentrations (mole fractions) of the alloy components; $\Delta H_A^{\text{ef.}}$, $\Delta H_B^{\text{ef.}}$, $\Delta H_{A_{x_A} B_{x_B}}^{\text{ef.}}$—heat effects accompanying dissolution of the components and the alloy in the bath.

It is worth mentioning that thermal effect consists of: heating, melting and solving of the sample in the bath. Enthalpy of formation is determined for temperature, from which sample is dropped into the bath.

Experimental

In order to prepare samples for calorimetric measurements, it was necessary to cut it using electro-erosion saw so that it could fit dosing pipe of internal diameter approx. 4 mm. Preparation of the experiment started with placing of aluminum roll (of 99.99% purity) in the crucible, closing of the device and triple gas pumping out from the interior of calorimeter with use of turbomolecular pump; alternately, argon was introduced. All experiments were conducted in argon atmosphere. In parallel, temperature of aluminum bath was raised up to 1073 K. Device was left for 24 h in order to obtain equilibrium state that is being identified as stabilized baseline observed on computer monitor. Next, stirrer was installed, and device was ready for experiment. During the first measurements of the series, the device was calibrated by dissolving aluminum samples; in this manner, amount of energy per conventional unit was determined [18]. After calibration, experimental samples were dropped into aluminum bath from room temperature (298 K). Heat effect was registered by computer, and special software allowed to determine value of enthalpy accompanying dissolving samples in bath as well as enthalpy of formation of alloys.

Table 3 Formation enthalpy $\Delta_f H$ (at temperature 298 K) of intermetallic phases from Al–Zr system determined with solution calorimetric method

No.	Formation enthalpy $\Delta_f H$ (298 K)/kJ mol^{-1}						
	Al$_3$Zr	Al$_2$Zr	Al$_3$Zr$_2$	AlZr	Al$_2$Zr$_3$	AlZr$_2$	AlZr$_3$
1	− 49.9	− 57.8	− 60.5	− 69.1	− 51.6	− 50.7	− 45.9
2	− 51.2	− 57.2	− 60.9	− 76.5	− 44.7	− 57.5	− 45.3
3	− 51.7	− 52.2	− 63.4	− 70.9	− 52.9	− 59.2	− 41.5
4	− 52.6	− 55.6	− 57.4	− 67.1	− 48.4	− 58.7	− 45.2
5	− 50.8	− 58.3	− 58.4	− 67.5	− 49.8	− 55.3	− 40.1
6	− 53.2	− 56.8	− 57.1	− 76.9	− 46.4	− 55.4	− 43.7
Average	− 51.6 ± 1.2	− 56.3 ± 2.2	− 59.6 ± 2.4	− 71.3 ± 4.4	− 49.0 ± 3.1	− 56.1 ± 3.1	− 43.6 ± 2.3

Results

Table 3 presents results of formation enthalpy $\Delta_f H$ of intermetallic phases from Al–Zr system determined with solution calorimetric method. Partial dissolving heat of zirconium in liquid aluminum at temperature 1073 K (Table 4) was evaluated in own measurements, that is critical for formation enthalpy of intermetallic phases from Al–Zr system determination. The heat effect accompanying dissolving of the second compound (aluminum) was considered when series of calibration were performed. Calculations were corrected also taking into account the presence of Al in samples, which was stated based on phase analysis.

Enthalpy of formation is one of the most important thermodynamic data used for computing and optimization of phase diagrams. Among various methods of determining this value, the calorimetric measurement is one of the most precise ones. Due to the difficulty of measuring the formation enthalpy of alloys, many thermodynamic data available in the literature are based only on computational methods.

In Table 5, results obtained in this work are compared with the literature data, among which experimental data are presented [12, 20–22] as well as results obtained with computational methods, mostly from CALPHAD

procedure (CALculations of PHAse Diagrams) [23, 24] and Miedema's Model [25]. Kematick and Franzen [20] combined several measurements to obtain enthalpies of formation of compounds Al$_3$Zr$_5$, Al$_2$Zr$_3$, Al$_4$Zr$_5$, AlZr, Al$_3$Zr$_2$, Al$_2$Zr and Al$_3$Zr. They measured the equilibrium vapor pressure of Al by the Knudsen-effusion technique. The enthalpies of formation of the compounds were evaluated by means of the second- and third-law methods. Kematick and Franzen results were adjusted by Murray et al. [12] since they did not take into account the difference between the free energies of the liquid and solid phases of pure Al above its melting point. Murray also estimated the associated error to be ± 4 kJ mol^{-1}. Meschel and Kleppa [21] measured standard enthalpies of Al$_2$Zr and Al$_3$Zr by direct synthesis calorimetry at 1473 K. Klein et al. [22] determined standard enthalpy of formation for the AlZr$_2$ phase also from calorimetric measurements. There are no experimental data for phase Al$_3$Zr$_4$ that is particularly interesting, considering difficulty in obtaining it, that is presented in this work.

Results of formation enthalpy $\Delta_f H$ of intermetallic phases from Al–Zr system, presented in this paper, show good compatibility with experimental data available in the literature. Only in case of phase AlZr, distinct difference is visible. It can be a result of a presence of small quantity of other phases like Al$_3$Zr$_2$, Al$_3$Zr$_4$ and Al$_3$Zr$_5$, which was stated during X-ray analysis (Fig. 3). The best compatibility with computational method is recognized with work of Wang et al. [24]. Differences occur in case of phases AlZr$_3$ and AlZr$_2$, still it is worth to emphasize that results of formation enthalpy from this paper represent experimental data shown for the first time.

Table 4 Partial dissolving heat $\Delta \overline{H}_{Zr}^0$ accompanying zirconium dissolution in liquid aluminum at temperature 1073 K

No.	$\Delta \overline{H}_{Zr}^0$/kJ mol^{-1}
1	− 239.9
2	− 246.1
3	− 247.0
4	− 241.6
5	− 253.3
6	− 239.1
Average	− 244.5 ± 5.4

Table 5 Enthalpy of formation of stable Al–Zr intermetallics phases

Ref.	Enthalpy of formation $\Delta_f H$/kJ mol^{-1}										
	$AlZr_3$	$AlZr_2$	Al_3Zr_5	Al_2Zr_3	Al_3Zr_4	Al_4Zr_5	$AlZr$	Al_3Zr_2	Al_2Zr	Al_3Zr	
This work	− 43.6 ± 2.3	− 56.1 ± 3.1	–	− 49.0 ± 3.1	–	–	− 71.3 ± 4.4	− 59.6 ± 2.4	− 56.3 ± 2.2	− 51.6 ± 1.2	E
[20]	–	–	− 39 ± 4	− 41 ± 4	–	− 44 ± 4	− 45 ± 4	− 47 ± 4	− 46 ± 4	− 41 ± 4	E
[12]	–	–	− 48 ± 4	− 49 ± 4	–	− 52 ± 4	− 53 ± 4	− 55 ± 4	− 54 ± 4	− 49 ± 4	E
[21]	–	–	–	–	–	–	–	–	− 52.1 ± 1.6	− 48.4 ± 1.3	E
[22]	–	–	–	–	–	–	–	–	− 51.3 ± 4.3	–	E
[13]	− 31.1	− 36.8	− 37.6	− 39.3	− 47.6	− 42.0	− 46.2	− 51.6	− 53.3	− 49.1	C
[23]	− 27.0	− 33.4	− 36.2	− 38.4	–	− 41.0	− 44.5	− 46.9	− 45.8	− 40.5	C
[24]	− 36.2	− 48.4	− 51.5	− 55.2	− 58.5	− 55.4	− 65.0	− 56.6	− 52.6	− 48.5	C
[25]	− 50	− 65	− 72	− 75	–	− 83	− 80	− 72	− 57	–	C

E experiment, *C* computation

Conclusions

1. For the preparation of eight intermetallic phases stable at room temperature from Al–Zr system, melting in levitation furnace was used. Phase analysis XRD indicated that only in case of alloy denoted as Al_3Zr_4 it was impossible to obtain sufficient intermetallic phase; therefore, it was not taken into consideration in calorimetric measurements.

2. High-temperature solution calorimeter was used in order to determine formation enthalpy $\Delta_f H$ of intermetallic phases from Al–Zr system at room temperature (298 K). Partial dissolving heat of zirconium in aluminum at temperature 1073 K which is crucial value in described experiment was evaluated as -244.5 ± 5.4 kJ mol^{-1}.

3. The value of formation enthalpy $\Delta_f H$ of intermetallic phases from the Al–Zr system at 298 K was determined: Al_3Zr (-51.6 ± 1.2 kJ mol^{-1}), Al_2Zr (-56.3 ± 2.2 kJ mol^{-1}), Al_3Zr_2 (-59.6 ± 2.4 kJ mol^{-1}), $AlZr$ (-71.3 ± 4.4 kJ mol^{-1}), Al_2Zr_3 (-49.0 ± 3.1 kJ mol^{-1}), $AlZr_2$ (-56.1 ± 3.1 kJ mol^{-1}) and $AlZr_3$ (-43.6 ± 2.3 kJ mol^{-1}).

4. Obtained results were compared with data available in the literature. For the first time, experimental value of enthalpy of formation for phases $AlZr_3$ and $AlZr_2$ was presented.

5. Presented calorimeter, thanks to applied preheating intermediate container, can be used in the future for determination of formation enthalpy of high-temperature phases from Al–Zr system that is: Al_4Zr_5 and Al_3Zr_5.

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