Journal of Alloys and Compounds 742 (2018) 1058–1082

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

On the constitution and thermodynamic modelling of the system Zr-Ni-Sn

P. Sauerschnig [a, b, c], A. Grytsiv [a, b, c], J. Vrestal [d], V.V. Romaka [e], B. Smetana [f], G. Giester [g], E. Bauer [b, c], P. Rogl [a, b, *]

[a] Institute of Material Chemistry and Research, University of Vienna, Währingerstrasse 42, A-1090 Wien, Austria
[b] Christian Doppler Laboratory for Thermoelectricity, Wien, Austria
[c] Institute of Solid State Physics, TU-Wien, Wiedner Hauptstrasse, 8-10, A-1040 Wien, Austria
[d] Masaryk University, CEITEC, Kamenice 753/5, Brno, Czech Republic
[e] Department of Materials Science and Engineering, Lviv Polytechnic National University, 79013 Lviv, Ustiyanovycha Str. 5, Ukraine
[f] Faculty of Metallurgy and Materials Engineering, VŠB - Technical University of Ostrava, 17. Listopadu 15/2172, Poruba, Ostrava, Czech Republic
[g] Institute of Mineralogy and Crystallography, University of Vienna, Althanstrasse 14, A-1090 Wien, Austria

ARTICLE INFO

Article history:
Received 3 April 2017
Received in revised form
27 November 2017
Accepted 2 December 2017
Available online 6 December 2017

Keywords:
Zr-Ni-Sn
Isothermal section
Liquidus projection
Solidus projection
Scheil diagram
Thermodynamic modelling
Crystal structure
DFT calculations

ABSTRACT

In continuation of our optimization of {Ti,Zr}NiSn-based thermoelectrics, we herein determined the constitution of the system Zr-Ni-Sn (liquidus surface and isothermal section at 950 °C) employing X-ray powder diffraction (XPD) and electron probe micro analysis (EPMA) of about 80 ternary alloys in as cast and annealed state. The system is characterized by the existence of four ternary compounds labelled τ_1 to τ_4. At 950 °C no significant homogeneity regions are found for the compounds τ_1-ZrNiSn (Half-Heusler phase, MgAgAs-type), τ_2-$ZrNi_2Sn$ (Heusler phase, $MnCu_2Al$-type) and τ_4-Zr_6NiSn_2 (K_2UF_6-type, ordered Fe_2P-type), but τ_3-$Zr_{2+x}Ni_{2+y}Sn_{1-x-y}$ exhibits a significant solution range for $0.0 \le x \le 0.25$ and $0.0 \le y \le 0.06$. Extended solid solutions starting from binary phases at 950 °C have been evaluated for $Zr_5(Ni_x\square_ySn_{1-x-y})_4$ (filled Mn_5Si_3 - Ti_5Ga_4-type; $0 \le x \le 0.216$, $0.002 \le y \le 1$) and $Zr_{1-x}(Ni_{1-y}Sn_y)_{5+x}$ ($AuBe_5$-type) reaching a maximum solubility at $x = 0.022$, $y = 0.146$ (the symbol □ denotes a vacancy). From differential thermal analysis (DTA) measurements a complete liquidus surface has been elucidated revealing congruent melting for τ_1-ZrNiSn (at 1465 ± 10 °C) and τ_2-$ZrNi_2Sn$ at 1469 ± 10 °C, but incongruent melting for τ_3-Zr_2Ni_2Sn (pseudobinary peritectic formation: $\ell + Zr_5(Ni_x\square_ySn_{1-x-y})_4 \leftrightarrow \tau_3$ at 1406 ± 10 °C), and for τ_4-Zr_6NiSn_2 (ternary P-type reaction: $L + Zr_5(Ni_x\square_ySn_{1-x-y})_4 + (Zr) \leftrightarrow \tau_4$-$Zr_6NiSn_2$ at 1124 ± 8 °C). A Schultz-Scheil diagram for the solidification behavior was constructed for the entire diagram. X-ray single crystal data have defined precise atom site occupancies in τ_4-Zr_6NiSn_2 ($R_{F^2} = 0.0113$) as well as close to the end point of the solid solution $Zr_5Ni_{1-x}Sn_3$ (stuffed Mn_5Si_3-type; $x = 0.21$, $R_{F^2} = 0.0238$) and isostructural $Hf_5Ni_{1-x}Sn_3$ ($x = 0.26$, $R_{F^2} = 0.0242$). As thermodynamic data in the ternary system were only available in the literature for ZrNiSn, heat of formation data were supplied by our DFT calculations for $ZrNi_2Sn$, Zr_2Ni_2Sn and Zr_6NiSn_2 as well as for the solid solutions $Zr_5(Ni_x\square_ySn_{1-x-y})_4$ and $Zr_{1-x}(Ni_{1-y}Sn_y)_{5+x}$ for $y = 0$ and $x = 0.25$ or $y = 0.20$. For these cases DFT calculations also provide details on electronic properties and bonding. Thermodynamic CALPHAD calculation was performed with the Pandat software and resulted in reasonably good agreement for all the 29 invariant reaction isotherms involving the liquid.

1. Introduction

Quinary (i.e. quasi-ternary) solid solutions of the so-called "Half-Heusler" (HH) compounds TiNiSn, ZrNiSn and HfNiSn, known as n-type semiconductors since 1986 [1,2], have proven a remarkably high efficiency in thermoelectric conversion of (waste) heat into electricity: a dimensionless thermoelectric figure of merit $ZT = 1.5$ was reached at 700 K for the alloy $Ti_{0.5}Zr_{0.25}Hf_{0.25}NiSn_{0.998}Sb_{0.002}$ slightly doped with Sb [3]. In order to avoid the high-price element hafnium, recent thermoelectric research focused mainly on the optimization

* Corresponding author. Institute of Material Chemistry and Research, University of Vienna, Währingerstrasse 42, A-1090 Wien, Austria.
E-mail address: peter.franz.rogl@univie.ac.at (P. Rogl).

https://doi.org/10.1016/j.jallcom.2017.12.012
0925-8388/