



**HAL**  
open science

# THERMODYNAMICS OF STABLE AND METASTABLE PHASES IN THE Ni-Zr AND THE Co-Zr SYSTEM AND THEIR APPLICATION TO AMORPHOUS PHASE FORMATION

F. Gärtner, R. Bormann

► **To cite this version:**

F. Gärtner, R. Bormann. THERMODYNAMICS OF STABLE AND METASTABLE PHASES IN THE Ni-Zr AND THE Co-Zr SYSTEM AND THEIR APPLICATION TO AMORPHOUS PHASE FORMATION. *Journal de Physique Colloques*, 1990, 51 (C4), pp.C4-95-C4-99. <10.1051/jphyscol:1990411>. <jpa-00230771>

**HAL Id: jpa-00230771**

**<https://hal.science/jpa-00230771v1>**

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

**THERMODYNAMICS OF STABLE AND METASTABLE PHASES IN THE Ni-Zr AND THE Co-Zr SYSTEM AND THEIR APPLICATION TO AMORPHOUS PHASE FORMATION**

F. GÄRTNER and R. BORMANN\*

*Institut für Metallphysik, Universität Göttingen and SFB 126  
Göttingen/Clausthal, D-3400 Göttingen, F.R.G.*

*\*Institut für Werkstofforschung, GKSS-Forschungszentrum Geesthacht  
GmbH, D-2054 Geesthacht, F.R.G.*

Abstract - The thermodynamic functions of the phases in the Ni-Zr and the Co-Zr system are calculated from the experimental data by applying the CALPHAD method. In the case of the undercooled liquid its excess specific heat is taken into account resulting of a pronounced stabilization of the liquid state at lower temperatures. Below  $T_g$  the amorphous phase is considered which exhibits a free energy comparable to the one of the intermetallic compounds. From the calculated free energy functions the concentration ranges of amorphous phase formation can be determined and compared to the experiments. Results obtained by mechanical alloying and ion-mixing of the components will be discussed with respect to the assumption of a metastable equilibrium between the phases involved, whereas  $T_O$  lines of the terminal solid solutions are used for the interpretation of amorphous phase formation by melt-spinning.

1 - INTRODUCTION

Due to their metastable state amorphous alloys can be prepared by an interdiffusion of crystalline phases as first being demonstrated by Schwarz and Johnson /1/. For the quantitative description of the occurring phase reactions and phase transformations the thermodynamic and kinetic properties of the involved phase must be taken into account. In particular, this requires the determination of the Gibbs free energies of the stable and metastable phases of the investigated system which can be done most favorably by the CALPHAD method /2/. The advantage of the method is based on the utilization of the specific thermodynamic data of the system with regard to the calculation of the thermodynamic functions. In this paper we report on the results of the Ni-Zr and Co-Zr system, which will be discussed with respect to the concentration ranges of amorphous phases by several preparation techniques such as interdiffusion, mechanical alloying and ion mixing of the components as well as quenching of the melt.

2 - ANALYTICAL DESCRIPTION OF THE THERMODYNAMIC FUNCTIONS

For the calculations a slightly modified least-square-fitting program developed by Lukas et al. /3/ was used. In principle, the free energy  $G^\Phi$  of a binary solution phase in dependence of the temperature  $T$  and the mole fractions  $x_A$  and  $x_B$  of A and B atoms can be described as

$$G^\Phi = x_A G_A^\Phi + x_B G_B^\Phi + \Delta G^{\text{ex}} - T S^{\text{mix}}$$

where  $G_A^\Phi$  and  $G_B^\Phi$  represent the phase stability values of the pure components.  $S^{\text{mix}}$  is the ideal entropy of mixing and  $\Delta G^{\text{ex}}$  is the excess free energy of mixing, which is expressed in our calculation by

$$\begin{aligned} \Delta G^{\text{ex}} = & A_1 x_A x_B + A_2 x_A x_B (x_A - x_B) + A_3 x_A x_B (x_A - x_B)^2 \\ & - T [B_1 x_A x_B + B_2 x_A x_B (x_A - x_B) + B_3 x_A x_B (x_A - x_B)^2] \\ & - 1/T [C_1 x_A x_B + C_2 x_A x_B (x_A - x_B) + C_3 x_A x_B (x_A - x_B)^2] \end{aligned}$$

The first line is related to the enthalpy of mixing taking into account deviations from the parabolic concentration dependence. The second line describes a non-ideal behavior of the entropy of mixing. The contribution of an excess specific heat to the free energy given in the third line is only considered in the case of the undercooled liquid /2/. The  $1/T$  dependence of the free energy corresponds to an  $1/T^2$  dependence of the specific heat. This representation was chosen with respect to the hole model describing the influence of defects in the short-range order of liquid alloys on the specific heat with rising temperature. In most systems suitable for amorphous phase formation the excess specific heat causes a pronounced temperature dependence of the enthalpy and the entropy of mixing stabilizing the undercooled liquid with respect to the crystalline phases at lower temperatures. In addition, the entropy of the undercooled liquid at the glass transition temperature  $T_g$  becomes comparable to the entropy of the stable crystalline phases, demonstrating the pronounced short-range order in the undercooled liquid close to  $T_g$  /2/. At  $T_g$  its specific heat decreases to a value comparable of the crystalline phases. In our calculation the glass transition is formally treated as a second order phase transformation and neglects the difference between the specific heat of the amorphous and the crystalline phases.

The free energy of stoichiometric compounds  $G^\Phi$  is composed of the phase stability values and a temperature independent enthalpy  $H^\Phi$  and entropy  $S^\Phi$  of formation

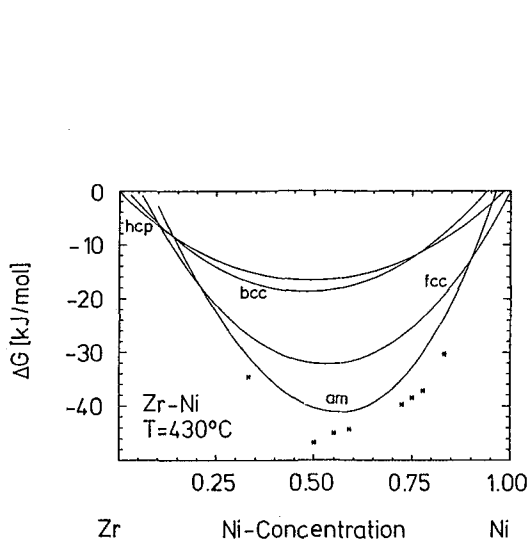
$$G^\Phi = x_A G_A^\Phi + x_B G_B^\Phi + H^\Phi - T S^\Phi$$

The coefficients  $A_i$ ,  $B_i$  and  $C_i$  ( $i=1-3$ ) as well as  $H^\Phi$  and  $S^\Phi$  of each phase are calculated from the thermodynamic data of the system. The required input data consist in the case of the Ni-Zr and Co-Zr system of the 2-phase and 3-phase equilibria as well as of the heats of formation of the intermetallic compounds. The thermodynamic characterization of the amorphous phase is based on crystallization enthalpies into the equilibrium phases and on the heats of formation. Details of the calculation and the derived coefficients will be published in a separate paper.

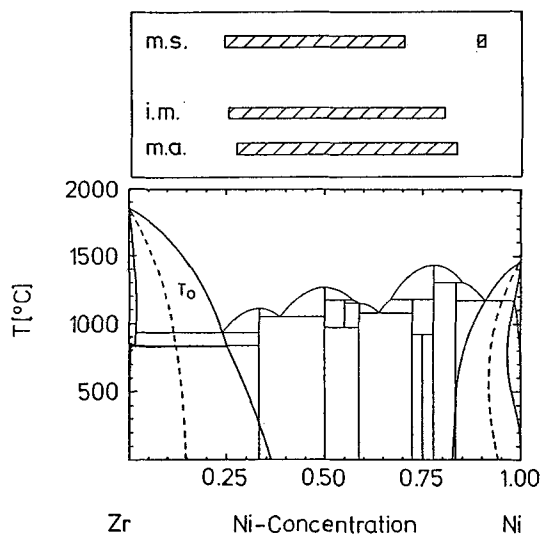
### 3 - RESULTS IN THE NI-ZR SYSTEM

With the used input data a self consistent description of the thermodynamics in the Ni-Zr system could be obtained. In Fig. 1 the free energies of the stable and the metastable phases are represented at a temperature of 430°C (being close to the glass transition temperature for equiatomic compositions). It demonstrates the relatively high stability of the intermetallic compounds as well as of the amorphous phase. The small differences between the free energies of the glassy and the equilibrium states result in similar chemical driving forces for the nucleation of the respective phases. However, it is reasonable for most cases to assume a much lower interface energy for the amorphous phase with respect to the intermetallic compounds /4/. This would favor the formation of an amorphous phase during nucleation. In addition, a growth selection of the different phases can further stabilize the amorphous phase as described by Gösele and Tu /5/ for example.

If the amorphous phase is formed by an interdiffusion process of the crystalline components the interfaces are considered to be close to a metastable equilibrium, where the chemical potentials of each component on both sides of the interface are equal. Under this assumption the concentration range of amorphous phase formation can be anticipated from the free energy curves by applying the common-tangent rule. The results for different temperatures can be summarized in a metastable phase diagram (Fig. 2), exhibiting the enhanced solid solutions and the homogeneity range of the amorphous phase. The later extends for temperatures close to  $T_g$  from 32 to 83 at.% Ni.



**Fig. 1:** Diagram of the free energies vs. concentration for the Zr-Ni system. \*represent the free energy of the intermetallic line compounds. The free energy of h.c.p. Zr and f.c.c. Ni are chosen as reference states.



**Fig. 2:** The calculated equilibrium (thin lines) and metastable (bold lines) phase diagram of the Ni-Zr system. In addition, the calculated  $T_0$  lines for the b.c.c. and h.c.p. Zr-rich and the f.c.c. Ni-rich alloys are shown. The hatched concentration ranges indicate the compositions of amorphous phase formation by melt-spinning (m.s.)/8/, ion-beam mixing (i.m.)/6/ and mechanical alloying (m.a.)/7/ of the elemental components.

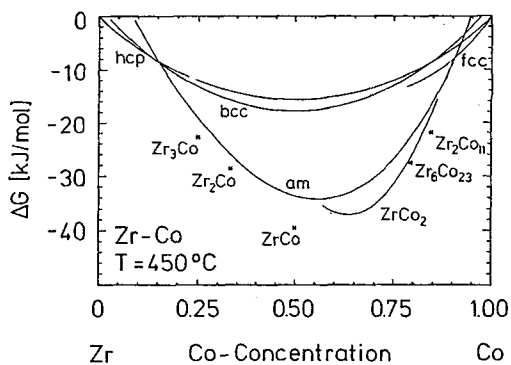
Amorphous phases prepared by a melt-quench process are unlikely to achieve an equilibrium with respect to other phases formed during the quench. This results from the difficulty of long-range diffusion usually required in order to equal the chemical potentials in the involved phases. However, polymorphous transformations might occur, in particular by forming the terminal solid solutions. The concentration ranges favorable for such reactions can also be derived from the free energy curves and are limited by the so-called  $T_0$ -values given by the intersection of the free energy curves of the undercooled liquid and the terminal solid solution. For compositions between the  $T_0$ -values no thermodynamic driving force exists for a polymorphous transformation of the undercooled liquid into a terminal solid solution. The corresponding  $T_0$  lines for the b.c.c. and h.c.p. Zr-rich and the f.c.c. Ni-rich alloys are also given in Fig. 2. For temperatures close to  $T_0$  the composition range of the amorphous phase is limited by the  $T_0$ -values between 14 and 93<sup>g</sup> at.% Ni.

The comparison with the results obtained by different preparation processes such as ion-mixing (at  $T = 300^\circ\text{C}$ ) /6/ and mechanical alloying /7/ demonstrates (Fig. 2), that the ranges of amorphous phase formation can be described under the assumption of a metastable equilibrium between the amorphous and solid solution phases, if a reaction temperature of about  $300\text{--}350^\circ\text{C}$  is presupposed. On the other hand the composition for which metallic glasses are obtained by melt spinning /8/ are in good agreement with the regions predicted by the calculated  $T_0$  lines. However, for concentrations of about 80 at.% Ni the nucleation of the intermetallic compounds can not be avoided for the used quenching rates of about  $10^6$  K/sec.

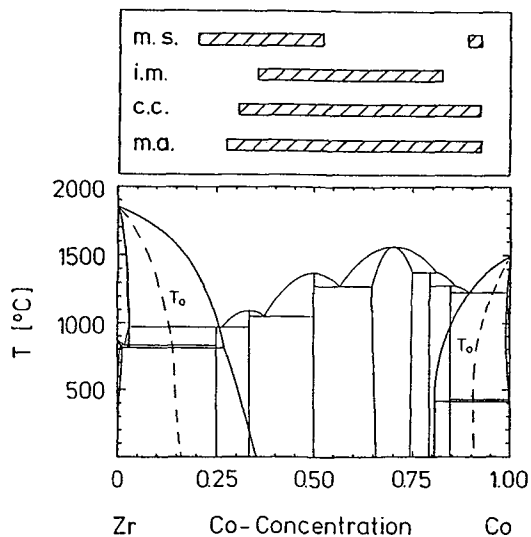
## 4 - RESULTS IN THE CO-ZR SYSTEM

In addition to the Ni-Zr system the thermodynamic functions of the Co-Zr system could be determined from the experimental data self-consistently. Fig. 3 represents the calculated free energies at a temperature of 450°C. Because of its extended homogeneity range the  $\text{Co}_2\text{Zr}$  phase is treated as a solid solution, whereas the remaining intermetallic alloys are described as line compounds. Like Ni-Zr, the Co-Zr system is distinguished by a relatively high stability of the equilibrium phases as well as of the amorphous alloy. Fig. 4 exhibits the metastable phase diagram and the corresponding  $T_0$  lines. The assumption of a metastable equilibrium between the amorphous phase and the terminal solid solutions predicts a composition range of amorphous formation between 31 and 81 at.% Co in good agreement with the results obtained by ion mixing at higher temperatures /6/. For alloys prepared by mechanical alloying /7/ and by co-condensation /9/ of the components the assumption of a metastable equilibrium seems only applicable for Zr-rich alloys. The deviations on the Co-rich side are yet not understood and will be further investigated.

The  $T_0$  lines limit the amorphization range at 15 and 91 at.% Co if a polymorphous transformation into the terminal solid solutions are taken into account. Like in the Ni-Zr system this concentration range agrees well with the results obtained by a melt-spinning process /8/. However, the precipitation of Zr-poor intermetallic compounds can not be suppressed completely for the used quenching rates, similar as in other Zr-based transition metal systems.



**Fig. 3:** Diagram of the free energies vs. concentration for the Co-Zr system. \*represent the free energy of the intermetallic line compounds. The free energy of the f.c.c. Co and h.c.p. Zr are chosen as reference states.



**Fig. 4:** The calculated equilibrium (thin lines) and metastable (bold lines) phase diagram of the Co-Zr system. The  $T_0$  lines are calculated for the f.c.c. and h.c.p. Co as well as for the b.c.c. and the h.c.p. Zr-rich alloys. The hatched concentration ranges indicate the compositions of amorphous phase formation by melt spinning (m.s.)/8/, ion mixing (i.m.) /6/, co-condensation (c.c.)/9/, and mechanical alloying (m.a.)/7/ of the components.

## 5 - CONCLUSIONS

The thermodynamics of the Ni-Zr and the Co-Zr system can be calculated by the CALPHAD method from the experimental data reported in the literature. Both systems exhibit a high stability of the amorphous phase and the intermetallic compounds. This originates from the strong attractive interactions of the components and the pronounced short-range order in the amorphous phase which develops during the undercooling of the melt. The higher stability of the amorphous phase with respect to the terminal solid solutions favors the formation of an amorphous phase during the interdiffusion reaction of the pure components. Under the assumption of a metastable equilibrium the concentration ranges of amorphous phase formation obtained by ion mixing (at higher temperatures) and by mechanical alloying of Ni and Zr can be described. However, this result which also holds for the Nb-Al system /10/ can not be generalized, as experiments in the Nb-Ni /4/ and the Zr-Co system demonstrate. The concentration ranges of amorphous phases prepared by a melt-spinning process extend up to the  $T_0$  lines supporting the assumption that a polymorphous phase transformation into the terminal solutions limits formation range of metallic glasses attainable by conventional quench techniques.

## REFERENCES

- /1/ R.B. Schwarz and W.L. Johnson, Phys. Rev. Lett. 51 (1983), 4/5
- /2/ R. Bormann, F. Gärtner and K. Zöltzer, J. Less - Comm. Met. 145 (1988), 283
- /3/ H.L. Lukas, E.T. Henig and B. Zimmermann, CALPHAD 1 (1977), 225
- /4/ R. Bormann and R. Busch, Proc. DGM Conference on New Materials by Mechanical Alloying Techniques, eds. E. Arzt and L. Schultz, DGM Informationsgesellschaft 1989, p. 73
- /5/ U. Gösele and K.N. Tu, J. Appl. Phys. 53 (1982), 3252
- /6/ J. Boettiger, K. Dyrbye and R. Paulsen, in: Nuclear Physics Application on Materials Science, eds. E. Recknagel and J.C. Soares, Kluwer Academic Publ., London 1988, p. 209
- /7/ J. Eckert and L. Schultz, J. Less-Comm. Met. 145 (1988), 283
- /8/ Z. Altounian, Tu Guo-hua and J.O. Strom-Olsen, J. Appl. Phys. 54 (1983), 3111  
Z. Altounian, R.J. Shank and J.O. Strom-Olsen, J. Appl. Phys. 58 (1985), 1192  
Z. Altounian, E. Batalla and J.O. Strom-Olsen, J. Appl. Phys. 59 (1986), 2364
- /9/ A. Regenbrecht, PhD thesis, Göttingen 1988
- /10/ E. Hellstern, L. Schultz, R. Bormann and D. Lee, Appl. Phys. Lett. 53 (1988), 1399