The Mn-Ni-Zr System (Manganese-Nickel-Zirconium)

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Introduction

The Mn-Ni-Zr system has been studied in only a few investigations. Most of these studies have been made along the Mn_2Zr-Ni_2Zr line to determine the compositional ranges of the two Laves phases, which are of potential use as hydrogen storage materials. Only one incomplete partial isothermal section at 900 °C has been established.

Binary Systems

The Mn-Ni binary system [1991 Nas] is shown in Fig. 1. The evaluated system is indicated to contain 13 phases: (αMn), (βMn), (γMn,Ni), (δMn), (ηMnNi), (η'MnNi), (η''MnNi), (εMn_2Ni), ψMn_3Ni, ($\zeta°MnNi_2$), ($\zeta'MnNi_2$), ($\gamma MnNi_3$), and L. All phases exhibit ranges of homogeneity except ψ, and the stoichiometry and composition range of the ψ phase are uncertain. The fcc (γMn,Ni) phase forms a complete series of solid solutions across the range from Mn to Ni. This (γMn,Ni) phase (1) transforms congruently at 911 °C to η, at 720 °C to ε, and at 710 ° to ζ; (2) undergoes eutectoidal decomposition to η' and $\zeta°$ at 655 °C, to ε and η' at 640 °C, and to (βMn) and ε at 615 °C; and (3) decomposes peritecticly to (δMn) and L at 1164 °C. The L phase has a melting minimum at 1020 °C near 38 at.% Ni. The η, η', ε, and $\zeta°$ phases all decompose eutectoidally at temperatures of 560 °C or above. The ψ, η'', ζ', and γ' phases all form peritectoidally at or below 520 °C. Neel transformations are observed in the ψ, η'', and ζ' phases, while Curie transformations are observed in the γ' and the Ni-rich (γMn,Ni) phases.

The Mn-Zr system of [Massalski 2] is shown in Fig. 2 and indicates the presence of a single intermediate phase Mn_2Zr (ζ), which is a Laves phase of the $MgZn_2$ type with a range of homogeneity. It melts congruently at 1340 °C. Two eutectic reactions, L $\rightleftharpoons$ (δMn) + ζ and L $\rightleftharpoons$ ζ + (βZr), occur at 1160 °C and 1095 °C, respectively. A eutectoid reaction (βZr) $\rightleftharpoons$ ζ + (αZr) occurs at 795 °C. At the Mn-rich end of the system, phase equilibria involving (δMn), (γMn), and (βMn) are not well established, but a peritectoid reaction, (βMn) + ζ $\rightleftharpoons$ (αMn), occurs near 730 °C and another, (γMn) + ζ $\rightleftharpoons$ (βMn), occurs near 1140 °C.

The Ni-Zr system [1991Nas] in Fig. 3 shows the presence of eight intermediate phases: Ni_5Zr, Ni_7Zr_2, Ni_3Zr, $Ni_{21}Zr_8$, $Ni_{10}Zr_7$, $Ni_{11}Zr_9$, NiZr, and $NiZr_2$, of which the Ni_7Zr_2, NiZr, and $NiZr_2$ phases melt congruently at 1440, 1260, and 1120 °C, respectively, whereas all the other phases form through peritectic or peritectoid reactions: L + Ni_7Zr_2 $\rightleftharpoons$ Ni_5Zr at 1300 °C, L + Ni_7Zr_2 $\rightleftharpoons$ $Ni_{21}Zr_8$ at 1180 °C, L + $Ni_{11}Zr_9$ $\rightleftharpoons$ $Ni_{10}Zr_7$ at 1160 °C, L + NiZr $\rightleftharpoons$ $Ni_{11}Zr_9$ at 1170 °C, and Ni_7Zr_2 + $Ni_{21}Zr_8$ $\rightleftharpoons$ Ni_3Zr at 920 °C. Two eutectoid reactions, $Ni_{11}Zr_9$ $\rightleftharpoons$ NiZr + $Ni_{10}Zr_7$ and (βZr) $\rightleftharpoons$ (αZr) + $NiZr_2$, occur at 978 and 843 °C, respectively.

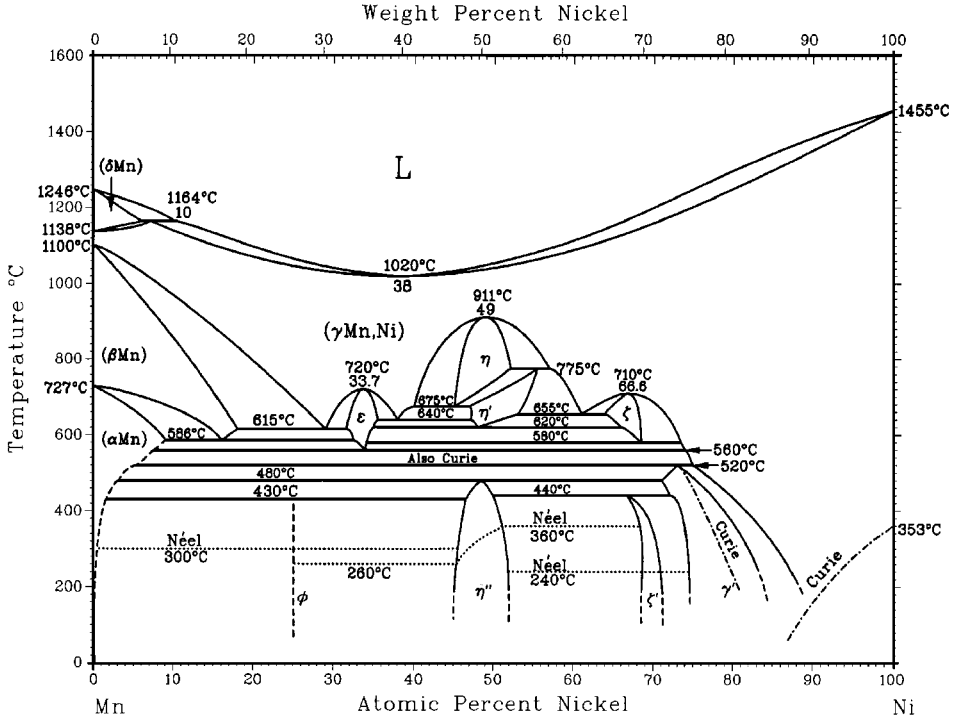

Fig. 1 The binary Mn-Ni diagram [1991Nas]

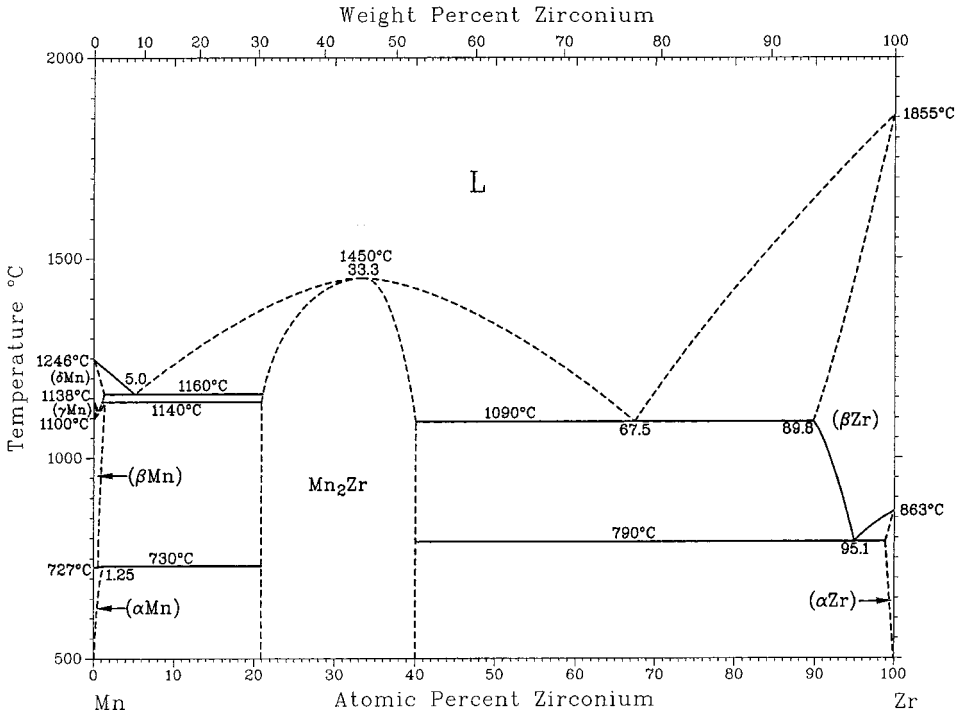

Fig. 2 The binary Mn-Zr diagram [Massalski2]

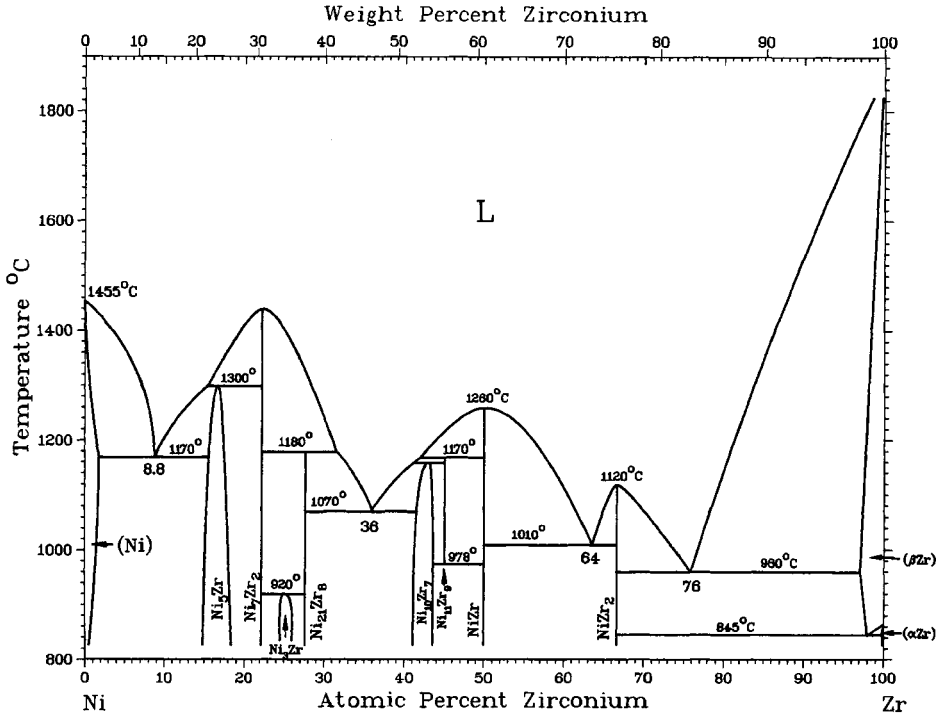

Fig. 3 The binary Ni-Zr diagram [1991Nas]

Binary and Ternary Phases

A total of 17 intermediate phases occur in the three binary systems. Limited information for the Mn-Ni-Zr ternary system is available but so far as is known only one ternary intermediate phase, a cubic Cu_2Mg type Laves phase, exists. All intermediate phases and their structure data are given in Table 1.

Ternary System

[1958Che] made a cursory study of $(Mn,Ni)_2Zr$ alloys around the MnNiZr composition. The alloys were melted in

Table 1 Phases in the binary Mn-Ni, Mn-Zr, and Ni-Zr and ternary Mn-Ni-Zr systems and their structure data

Phase designation	Composition	Pearson's symbol	Space group	Type	Lattice parameter, nm
γ	(Ni),(γ-Mn)	*c*F4	$Fm\bar{3}m$	Cu	…
α	(β-Zr),(δ-Mn)	*cI*2	$Im\bar{3}m$	W	…
ω	(α-Zr)	*hP*2	$P6_3/mmc$	Mg	…
α-Mn	(α-Mn)	*cI*58	$I\bar{4}3m$	α-Mn	…
β-Mn	(β-Mn)	*cP*20	$P4_132$	β-Mn	…
γ'	$MnNi_3$	*cP*4	$Pm\bar{3}m$	$AuCu_3$	a = 0.3598
ζ°	$MnNi_2$	…	…	…	…
ζ' ψ_2(l)	$MnNi_2$	…	…	…	…
η	MnNi	*cP*2	$Pm\bar{3}m$	CsCl	a = 0.29743
η' β_2(m)	MnNi	*tP*4	*P*4/*mmm*	AuCu	a = 0.37218
					c = 0.35295
$\eta''\beta_3$(l)	MnNi	…	…	…	…
ε	Mn_2Ni	…	…	…	…
ψ	Mn_3Ni	…	…	…	…
ζ	Mn_2Zr	*hP*12	$P6_3/mmc$	$MgZn_2$	a = 0.5036
					c = 0.3269
κ	Ni_5Zr	*cF*24	$F\bar{4}3m$	$AuBe_5$	a = 0.671
π	Ni_7Zr_2	*mC*36	*C*2/*m*	Ni_7Zr_2	a = 0.4698
					b = 0.8235
					c = 1.2193
					β = 95.83°
λ	Ni_3Zr	*hP*8	$P6_3/mmc$	Ni_3Sn	a = 0.5309
					c = 0.4303
θ	$Ni_{21}Zr_8$	*aP*29	*P*I	Hf_8Ni_{21}	a = 0.6472
					b = 0.8065
					c = 0.8588
					α = 75.19°
					β = 68.04°
					γ = 75.26°
μ	$Ni_{10}Zr_7$	*oC*68(a)	*Aba*2	$Ni_{10}Zr_7$	a = 0.9211
					b = 0.9156
					c = 1.2386
		*oP*68(b)	*Pbca*	$Ni_{10}Zr_7$	a = 1.2497
					b = 0.9210
					c = 0.9325
ν	$Ni_{11}Zr_9$	*tI*40	*I*4/*m*	$Pt_{11}Zr$	a = 0.990
					c = 0.662
ϕ	NiZr	*oC*8	*Cmcm*	CrB	a = 0.3268
					b = 0.9936
					c = 0.4101
ζ	$NiZr_2$	*tI*12	*I*4/*mcm*	Al_2Cu	a = 0.6483
					c = 0.5267
Γ	MnNiZr(c)	*cF*24	$Fd\bar{3}m$	Cu_2Mg	a = 0.707

(a) Zr poor
(b) Zr rich
(c) The phase is stable over a wide composition region

quartz crucibles in a graphite resistance furnace under argon atmosphere and the alloys were annealed at 400 °C for 10 days. The alloys showed the presence of a Cu_2Mg type cubic Laves phase near equiatomic MnNiZr composition with lattice parameter variation between 0.7017 and 0.7045 nm. Neither the alloy compositions nor the extent to which the cubic Laves phase extended were reported. The lattice parameter values given by [1950Che] agree reasonably well with those due to [1972Pet] given in Fig. 4 for compositions along the $(Mn_{1-x}Ni_x)_2Zr$ composition line.

High-purity (99.9+ mass%) Mn and Ni and iodide-process Zr were used by [1972Pet] to prepare arc-melted alloys along the Mn_2Zr-Ni_2Zr line. The alloys were annealed at 900 °C for 1000 h and phase analysis was done with optical microscopy and X-ray diffraction (XRD). A lattice parameter-composition plot was used to find the extent to which the Laves

phases extended along the AB_2 line. [1972 Pet] confirmed the presence of a cubic Laves phase in the Mn-Ni-Zr system. While a phase with Ni_2Zr stoichiometry is not an equilibrium phase in the binary Ni-Zr system [1984Suz, 1991Nas], the lattice parameter variation with Mn content in Fig. 4 shows that a cubic Laves phase extends from near the Ni_2Zr composition up to ~33 at.% Mn and an $MgZn_2$ type hexagonal Laves phase extends from ~40 to 100 at.% Mn.

[1984 Suz], in their study of hydrogen absorption in Mn-Ni-Zr alloys, prepared three ternary alloys $(Mn_{1-x}Ni_x)_2Zr$ with x = 0.2, 0.5, and 0.8 and a binary Ni_2Zr alloy. Arc-melted alloys, prepared with commercial grade Ni, 99.5 mass% pure Zr, and 99.95 mass% pure Mn, were heat treated (temperature and time not mentioned) and characterized by XRD. While their report shows no Ni_2Zr Laves phase, the $MgZn_2$ type laves phase was reported to extend up to x = 0.5. The alloy with x = 0.8 was reported to be two phase (the second phase was not identified). The hexagonal Laves phase boundary was suggested to be somewhere between x = 0.5 and 0.8. The reported lattice parameters for the hexagonal Laves phase are a = 0.5029 nm and c = 0.8238 nm for x = 0.2 and a = 0.5015 nm and c = 0.8216 nm for x = 0.5. Lattice parameters a = 0.5016 nm and c = 0.82138 nm for an alloy with x = 0.2 were measured using the neutron diffraction technique by [1993Aki] and are somewhat smaller than those reported by [1984Suz].

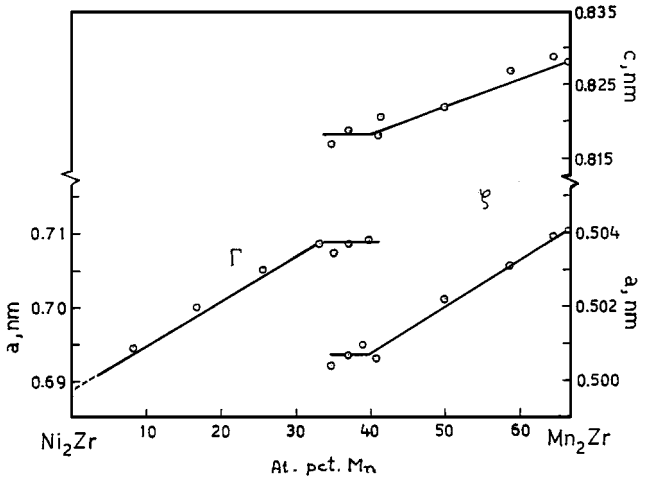

Fig. 4 The lattice parameters of $(Mn,Ni)_2Zr$ alloys [1972Pet]

[1984 Hou] made a more complete investigation of the Mn-Ni-Zr system. In this study, ZrO_2, MnO, and NiO, prepared by the coprecipitation process, were reduced by reacting with Ca-hydride at 900 to 1000°C to prepare the Mn-Ni-Zr alloy powders of different compositions. The alloy powders were annealed at 900 °C (annealing time not specified) and the phase analysis was done by XRD only. The Mn-Ni-Zr isothermal section of [1984Hou] at 900 °C is given in Fig. 5. The isothermal section shows the presence of a wide Cu_2Mg type cubic Laves phase (Γ) region, covering the MnNiZr composition, and the Γ phase is the only ternary intermediate phase so far found in the Mn-Ni-Zr system. The binary hexagonal Laves phase Mn_2Zr (ζ) was also found to extend reasonably far into the ternary system.

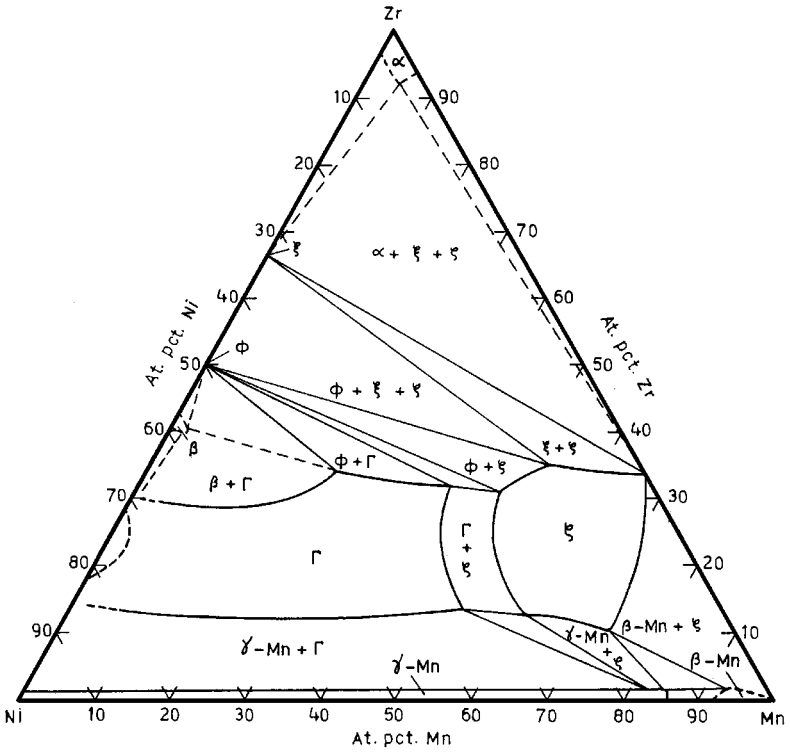

Fig. 5 900 °C isothermal section of Mn-Ni-Zr sytem [1984Hou]

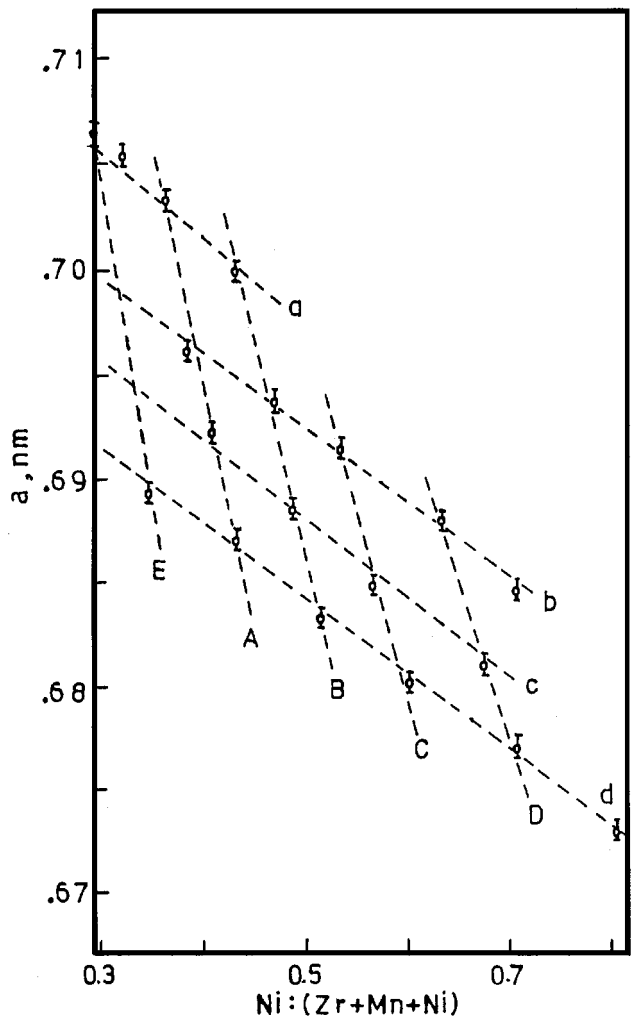

Fig. 6 The lattice parameters of Γ phase as a function of Ni: (Mn + Ni + Zr) ratio [1984Hou]. Atomic ratio Mn/Ni: $A = 1.0$, $B = 0.66$, $C = 0.43$, $D = 0.2$, and $E = 1.5$. Atomic ratio Zr/metal: $a = 0.3$, $b = 0.25$, $c = 0.2$, and $d = 0.15$

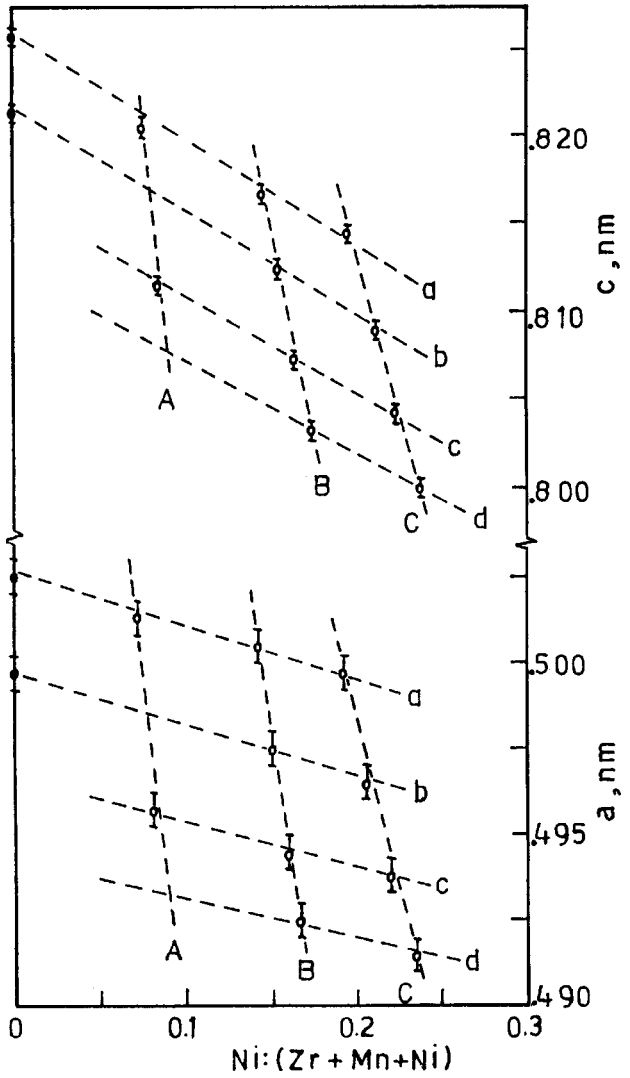

Fig. 7 Lattice parameter of ξ phase as a function of Ni/metal ratio [1984Hou]. Atomic ratio Mn/Ni: $A = 0.11$, $B = 0.25$, and $C = 0.37$. Atomic ratio Zr/metal: $a = 0.3$, $b = 0.25$, $c = 0.2$ and $d = 0.15$

Both Laves phases, Γ and ζ, show extensions toward lower Zr content.

[1984Hou] found the ζ phase to extend from ~34 at.% Zr to ~10 at.% Zr and from the Mn-Zr binary to ~21 at.% Ni, which is slightly smaller than that reported by [1972 Pet]. The ζ phase was found in equilibrium with the α, ξ, φ, βMn, γ, and Γ phases. [1984Hou] terminated the ζ/(ζ + βMn) phase boundary at 24 at.% Zr at the Mn-Zr binary limit. Since the composition range of the Mn_2Zr phase in the binary system is not known, the phase boundary between the ζ and ζ + βMn phase regions has been drawn with the assumption that the binary phase is stoichiometric.

In the ternary system, the Γ phase exists between ~12 and 34 at.% Zr in regions of lower Ni content and narrows to ~12 to ~29 at.% Zr for Ni contents above 50 at.%. This agrees with the observation of [1984Suz] that a $(Mn_{1-x}Ni_x)_2Zr$ alloy with $x = 0.8$ was two phase. The phase boundary of the Γ phase in regions of low Mn content were not determined nor were the phase equilibria involving the Γ phase and the binary phases of the Ni-Zr system. The available data show that the Γ phase extends down to ~5 at.% Mn from ~50 at.% Mn and also does not show the existence of the Ni_2Zr Laves phase.

The main point of controversy that remains to be resolved is whether the phase near a stoichiometric MnNiZr composition is a cubic Laves phase. On the basis of a low intensity diffraction line with $d = 0.2322$ nm, which could not be indexed on the basis of a cubic Laves phase but could be indexed on the basis of hexagonal Laves phase, [1984Suz] suggested that the MnNiZr alloy has a hexagonal $MgZn_2$ type structure. Since none of the other investigators give their XRD patterns through which they identified the cubic and the hexagonal Laves phases, it is not possible to resolve this controversy. Careful XRD study of the Γ and ζ phases and metallography of the two phase alloys containing Γ and ζ phases are required for proper identification of phases.

Lattice Parameter

The lattice parameters of the ζ phase along the 33.3 at.% Zr line by [1984Suz] and [1972Pet] are in reasonable agreement with each other. [1984 Hou] measured lattice parameters of the ζ and Γ phases over the entire composition region of their stabilities and these data are given in Fig. 6 and 7. The lattice parameters of both the phases were found to decrease with increase in Ni content and decrease in Zr content. The lattice parameters of the Γ phase determined by [1958Che]. [1972Pet], and [1984Hou] are in agreement with each other.

Hydrogen Absorption Characteristics of Mn-Ni-Zr Laves Phase

Some information regarding the hydrogen absorption characteristics of the $(Mn_{1-x}Ni_x)_2Zr$ Laves phase alloys are given by [1984Suz]. The XRD of hydrogen absorbed alloys was studied and dissociation pressures of alloys with varying hydrogen contents were measured. The results may be summarized as follows.

- Hydrogen saturation of an MnNiZr alloy shows the presence of two phases—a hydrogen-saturated hexagonal C14 Laves phase and a hydride with C15 type Cubic Laves phase structure. The lattice parameters and the cell volume per formula unit (V) for the MnNiZr, hydrogen-saturated MnNiZr, and the hydride phases were reported to be $a = 0.5015$ nm, $c = 0.8216$ nm, and $V = 0.04474$ $(nm)^3$; $a = 0.4987$ nm, $c = 0.8125$ nm, and $V = 0.04375$ $(nm)^3$; and $a = 0.7590$ nm, and $V = 0.5465$ $(nm)^3$, respectively.
- The dissociation pressure versus hydrogen concentration curves show the following.
- There is an increase in dissociation pressure of the Mn_2Zr phase with an increase in Ni content.
- A flat plateau region for Ni substituted Mn_2Zr phase, occurs in the dissociation pressure versus hydrogen concentration curve in the temperature range between 350 and 400 K.
- The estimated hydrogen saturation of the MnNiZr-H_2 system appears to be the same as that of the Mn_2Zr-H_2 system.
- The thermodynamic quantities ΔH, ΔS, and ΔG for the MnNiZr $-$ H_x for $0.8 \leq x \leq 2.2$ at 25 °C (298 K) were estimated and tabulated. The ΔG values for the MnNiZr-H_x alloys were found to change only very slightly with hydrogen concentration of the alloys. The ΔH, ΔS, and ΔG values for the MnNiZr-$H_{1.0}$ alloy are given as -30.2 kJ/mol·H_2, -89.7 J/deg mol·H_2, and -3.5 kJ/mol·H_2.

The ΔH and ΔG values for the Ni modified alloy are found to be smaller than the corresponding values for the $Mn_2ZrH_{1.0}$ alloy, which have been estimated to be -41.3 kJ/mol·H_2 and -13.0 kJ/mol·H_2, respectively.

Acknowledgments

The author thanks Dr. J Joubert, Centre National de la Recherche Scientifique, Laboratoire de Chimie Metallurgique et Sprectroscopie des Terres Rares (Cedex, France), for providing photocopies of the relevant part of the postdoctoral thesis by B. Houvert. Financial support for the evaluation of Co and Ni ternary systems was provided by the Department of Science and Technology, Government of India, New Delhi.

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*Indicates key paper.
#Indicates presence of a phase diagram.

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