Manganese – Titanium – Zirconium

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Introduction

The Mn-Ti-Zr system is of high importance for a number of practical applications. Firstly, Zr and Mn are often used as alloying elements in the titanium industries. Secondly, alloys of this system are considered to be promising candidates for reversible hydrogen storage [1978Oes, 2000Bob] as well as for hydrogen storage tanks in proton exchange membrane fuel cell technology [2004Tai]. Thirdly, promising candidate solders may emerge from that system. Eutectics reactions with relatively low melting temperatures in the Mn-Ti and Ti-Zr systems plus a minimum in the fusibility diagram of the Ti-Zr system have draw the attention to this ternary system in developing new solders. Possible applications are reaction brazing of Ti-based alloys and, especially, titanium aluminide based materials [2004Kho]. The knowledge of the constitution of the Mn-Ti-Zr system therefore is important for developing new advanced materials. Nevertheless, the information on the equilibrium phases in this system is restricted to a few publications only.
[1980Jac, 1987Bla] showed the formation of continuous solid solutions between isostructural $TiMn_2$ and $ZrMn_2$ compounds and [2006Iva1, 2006Iva2] studied the phase equilibria in composition range Ti-$TiMn_2$-$ZrMn_2$-Zr. The same authors constructed experimentally the solidus surface in the Ti rich part of the system, projections of solidus and liquidus surfaces as well as some polythermal sections [2006Iva1, 2006Iva2]. A section with metastable phases formed in as cast brazing alloys was presented by [2004Kho]. The hydrogen sorption and desorption properties of $(Ti_{1-x}Zr_x)Mn_{2-y}$ base materials have been studied by [1978Oes, 1980Jac, 2000Bob, 2004Tai]. The investigations of phase relations, structures and thermodynamics of the Mn-Ti-Zr alloys are summarized in Table 1.

Binary Systems

The Ti-Zr binary systems is accepted as published by [Mas2] as well as the Mn-Ti binary system, Fig. 1. An amendment has been applied to the temperature of the peritectic formation of βTiMn which was definied to be 1225°C by [2004Iva] in comparison with value ~1200°C presented by [Mas2]. The Mn-Zr system is accepted from [1999Sch] where the homogenity region of $ZrMn_2$ is determined more accurately then in [Mas2]. The temperature of the eutectic reaction $L \rightleftharpoons \beta(Zr)+ZrMn_2$ however has been corrected to 1125 ± 7°C, Fig. 2. This is 35°C higher then presented by [1999Sch] and results from the experiments on the binary and ternary alloys performed by the author of the present evaluation. The liquidus temperature at 50 at.% Mn - 50 at.% Zr was measured as 1420°C. In the light of the results of [1999Sch, 2006Iva2] the present evaluation does not assume that an MnZr intermetallic compound exist.

Solid Phases

The known solid phases are listed in Table 2 with continious solid solutions being formed between $TiMn_2$ and $MnZr_2$ intermetallic compounds. In the Ti-Zr binary system the (αZr) and (αTi) form a continuous solid solution (α) which can dissolve a limited amount of Mn (1-2 at.%). The (βZr) and (βTi) also form a series of continious solid solutions (β) dissolving Mn from 10 at.% at the Zr reach side to 30 at.% at Ti rich part. In the ternary system the βTiMn phase dissolves up to 5 at.% Zr. The βTiMn phase in binary alloys was detected in as cast conditions only after dead melting during 30 min in the solid-liquid state at a temperature of 1190°C, which is a little higher than the eutectic temperature (1175°C) but lower than the temperature of the peritectic reaction (1225°C) [2004Iva]. The same situation with the βTiMn phase formation was detected in the ternary alloys study [2006Iva2]. A phase isotypic with φHfRe had also been found in the system Mn-Ti at approximately 50.15 at.% Mn (αTiMn) [1962Wat]. In analogy with the cell reported for φHfRe , the αTiMn phase has also been tentatively indexed with a tetragonal cell with a = 819 pm and c = 1281 pm. As it was later shown by [1986Cen], it can be indexed with a new $Zr_{21}Re_{25}$ type rhombohedral

structure containing 1200 pm-thick infinite $MgZn_2$ (Laves)-type columns. [1986Cen] expected that the still unknown structure of βTiMn, which appears at an intermediate composition between $Ti_{21}Mn_{25}$ and $TiMn_2$, also contains Friauf polyhedra [1986Cen]. The new intermetallic phase is described here as metastable in accordance with [1999Sch], although it may in fact be part of the equilibrium diagram. The tentatively assigned stoichiometry is $Zr_{21}Mn_{25}$ [1999Sch], by analogy with a similar phase in the Mn-Ti system [1986Cen].

Quasibinary Systems

According to the study of [2006Iva2] there must be two quasibinary sections in the Mn-Ti-Zr system. One of them, $TiMn_2$-$ZrMn_2$, is characterized by continuous solid solutions between these Laves phases with the maximum of melting point at 2 at.% Ti. The phase diagram of this quasibinary system is presented in Fig. 3. The second one may be presented by the temperature-composition section oriented along the tie-line connecting the β solid solution with the $(Zr,Ti)Mn_2$ solid solution. The end points of this section are for $(Zr,Ti)Mn_2$: the point "max" at 1470°C in Fig. 6 and for the β phase: the minimum point at 1040°C on β the solidus line in Fig. 5.

Invariant Equilibria

The data on invariant ternary reactions are tabulated according to [2006Iva2] in Table 3.

Liquidus, Solidus and Solvus Surfaces

The solidus surface in the Ti corner of the phase diagram was constructed by [2006Iva1] based on DTA measurements. Due to the absence of ternary phases, this part of the solidus surface should be smooth and may be described by a power function as:
$T_S = 1670 - 29.053\ x_{Mn} + 0.4246\ x_{Mn}^2 - 5.692\ x_{Zr} + 0.0566\ x_{Zr}^2 + 0.6478\ x_{Zr}\ x_{Mn} - 0.0307\ x_{Zr}^2\ x_{Mn} - 0.0065\ x_{Zr} x_{Mn}^2$. The calculated isothermal lines at temperatures of 1175-1540°C are presented in Fig. 4. The solidus surface and liquidus surface projections of the partial Ti-TMn_2-$ZrMn_2$-Zr system are presented in Fig. 5 and Fig. 6, respectively, according to [2006Iva2].

Temperature – Composition Sections

Two vertical sections along the $Ti_{48}Mn_{52}$-$Zr_{50}Mn_{50}$ and $Ti_{61}Mn_{39}$-$Zr_{67.5}Mn_{32.5}$ lines reflect the smooth transition from the quasibinary $TiMn_2$-$ZrMn_2$ section with maximum on the fusibility diagram to the binary Ti-Zr system with minimum on the solidus and liquidus curves. They are shown in Fig. 7 and Fig. 8. As it was noted by [2004Iva], cooling with the rate of 0.7 $K \cdot s^{-1}$ did not lead to the βTiMn phase formation on eutectic crystallization in the binary system and this situation is retained in ternary alloys. The phase composition realised in as cast alloys cooled with the rate above 0.1 $K \cdot s^{-1}$ is presented in Fig. 9 in accordance with [2004Kho], where phase equilibria involving the βTiMn intermetallic compound are missing.

Notes on Materials Properties and Applications

The experimental investigations of materials properties are summarised in Table 4. Microhardness of the $(Zr_xTi_{1-x})Mn_2$ solid solutions lineary varies from 5817 MPa for $TiMn_2$ to 7750 MPa for $ZrMn_2$ [1987Bla]. Butt brased joints in γTiAl (47XD) were made by the vacuum brazing method, using adhesive active filler metals of the Mn-Ti-Zr system. Short-time strength of the butt brazed joints is on the level of ~690 MPa at 20°C and ~310 MPa at 700°C [2004Kho]. The maximum absorption capacity N_H of the $(Zr_xTi_{1-x})Mn_2$ system steeply increased from $N_H = 0.3$ H atoms $(f.u.)^{-1}$ for $x = 0$ to $N_H = 3.65$ H atoms $(f.u.)^{-1}$ for $x = 0.4$; it stays practically constant at approximately 4 H atoms $(f.u.)^{-1}$ for $0.6 < x < 1$ [1978Oes, 1980Jac]. The sorption-desorption characteristics are strongly dependent on the Mn content in the intermetallic compound [2000Bob, 2004Tai].

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Table 1: Investigations of the Mn-Ti-Zr Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1978Oes]	X-ray diffraction, Sieverts method	room temperature, $Zr_xTi_{1-x}Mn_2$, x = 0; 0.2; 0.4; 0.6; 0.8; 1.0, *C*14 Laves phase
[1980Jac]	X-ray diffraction, hydrogen absorption capacity	room temperature, $Zr_xTi_{1-x}Mn_2$, x = 0; 0.2; 0.4; 0.6; 0.8; 1.0, *C*14 Laves phase
[1987Bla]	X-ray diffraction, microhardness	annealed at 800 to 1500°C for 24 h, quenched at rate 100°C·h^{-1}, $Zr_{1-x}Ti_xMn_2$, x = 0; 0.2; 0.4; 0.6; 0.8; 1.0, hexagonal $MgZn_2$
[2000Bob]	X-ray diffraction, electron microprobe analysis	annealed at 800°C for 7 days, $Zr_{0.05}Ti_{0.95}Mn_{2-x}$ x = –0.05; 0; 0.05; 0.15; 0.35, C-14 Laves phase
[2004Kho]	X-ray diffraction, DTA investigation, light optical microscopy, electron microprobe analysis, mechanical properties	annealed at 1250°C, quenched at rate >0.1°C·s^{-1}, metastable polythermal section of $Ti_{60}Mn_{40}$ - $Zr_{67.5}Mn_{32.5}$
[2004Tai]	X-ray diffraction, induction coupled plasma spectroscopy, entropy and enthalpy of hydrogen desorption	annealed at 960°C for 6 h, room temperature, $Zr_xTi_{1-x}Mn_2$, x = 0; 0.1; 0.2; 0.3; 0.4, *C*14 Laves phase
[2006Iva1]	Optical light microscopy, DTA investigation	as cast and annealed 900°C for 35 h, Ti-(Ti-25 at.%Mn)-(Ti-20 at.% Zr-10 at.% Mn), (βTi), β+(Zr,Ti)Mn_2
[2006Iva2]	X-ray diffraction, DTA investigation, light optical microscopy, electron microprobe analysis	annealed at 950°C for 1 week, water quenching. Ti-$TiMn_2$-$ZrMn_2$-Zr β(Zr,Ti), (Zr,Ti)Mn_2, βTiMn

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(δMn) 1246 - 1138	*cI*2 $Im\bar{3}m$ W	a = 308.0	pure Mn [Mas2]
(γMn) 1138 - 1100	*cF*4 $Fm\bar{3}m$ Cu	a = 386.0	pure Mn [Mas2]
(βMn) 1100 - 727	*cP*20 $P4_132$ βMn	a = 631.52	pure Mn [Mas2]
(αMn) < 727	*cI*58 $I\bar{4}3m$ αMn	a = 891.26	pure Mn at 25°C [Mas2]
β, $\beta Zr_{1-x-y}\beta Ti_yMn_x$	*cI*2 $Im\bar{3}m$ W	 a = 337.7 a = 343.7 a = 349.7	$0 < x < 0.3$, $0 < y < 1$, x = 0, y = 0.3 x = 0, y = 0.5, x = 0, y = 0.7 [1981Mur1]
(βZr) 1855 - 863		a = 360.90	pure Zr, [Mas2]
(βTi) 1670 - 882		a = 330.65	pure Ti, [Mas2]
α, (αZr,αTi)	*hP*2 $P6_3/mmc$ Mg	a = 295.1 to 323.2 c = 468.4 to 515.0	0-100 at.% Zr, at 25°C [1981Mur1]
(αZr) < 863		a = 323.16 c = 514.75	pure Zr at 25°C, [Mas2]
(αTi) < 882		a = 295.06 c = 468.35 a = 295.11 c = 468.43	pure Zr, [Mas2] 0-0.4 at.% Mn [P]
βTiMn < 1200	-	-	52 at.% Mn [1962Wat] 48-52 at.% Mn, [2004Iva]
αTiMn < 950	*t**58	a = 819 c = 1281	at 50.15 at.% Mn [Mas2] [1962Wat]
$TiMn_3$ < 1250	*o*** $P2_12_12_1$	a = 481.2 c = 789.5	75.5 at.% Mn, at 1000°C [1981Mur2]
$TiMn_4$ 1230 - 930	*hR*159 $R\bar{3}m$ $Co_5Cr_2Mo_3$	a = 1100.03 c = 1944.6	[1961Wat] [VC2] Temperature interval from [1962Wat]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
$(Zr_xTi_{1-x})Mn_{2\pm y}$	*hP*12 $P6_3/mmc$ $MgZn_2$	a = 482.1 to 504.1 c = 791.4 to 824.9 a = 483.3 + 38.6 x – 19 x^2 ± 0.2 c = 792.3 ± 63.3 x – 31.2 x^2 ± 0.4	$0 < x < 1$, $y = 0$, [1987Bla] $0 < x < 1$, $y = 0$, [2006Iva2]
$ZrMn_2$ < 1450		a = 505.2 to 498.5 c = 831.5 to 819.0 a = 504.5 c = 828.0 a = 498.0 c = 817.6	60-72 at.% Mn, at 1510°C, [1976Sve], 64.3 at.% Mn, (βZr) - saturated, 77.3 at.% Mn, (βMn) - saturated, [1999Sch]
$TiMn_2$ < 1325		a = 485.7 to 481.8 c = 801.7 to 87.9	64-70 at.% Mn, at 1310°C [1976Sve]
$Zr_{21}Mn_{25}$ metastable	*hR*276 $R\bar{3}c$ $Zr_{21}Re_{25}$	-	[1997Kod] 54.4 at.% Mn [1999Sch]

Table 3: Invariant Equilibria

Reaction	T (°C)	Type	Phase	Composition (at.%)		
				Mn	Ti	Zr
l ⇌ (Zr,Ti)Mn_2	1470	max	l	~ 67	~ 2	~ 31
			(Ti,Zr)Mn_2	~ 67	~ 2	~ 31
l + βTiMn ⇌ β + (Zr,Ti)Mn_2	1090	U	l	~ 22	~ 51	~ 27
			βTiMn	~ 50	~ 45	~ 5
			β	~ 27	~ 69	~ 4
			(Ti,Zr)Mn_2	~ 57	~ 23	~ 20
l ⇌ β + (Zr,Ti)Mn_2	1040	e (min)	l	~ 21	~ 47	~ 32
			β	~ 15	~ 54	~ 31
			(Ti,Zr)Mn_2	~ 57	~ 8	~ 35

Table 4: Investigation of the Mn-Ti-Zr Materials Properties

Reference	Method/Experimental Technique	Type of Property
[1978Oes]	Sieverts method	Desorption isotherms of hydrogen
[1987Bla]	Vickers microhardness measurement	Microhardness under a load of 100 g
[2000Bob]	Sieverts method	Hydrogen sorption capacity
[2002Mit]	Sieverts method	Hydrogen sorption capacity
[2004Tai]	A gas reaction controller	Sorption-desorption isotherms

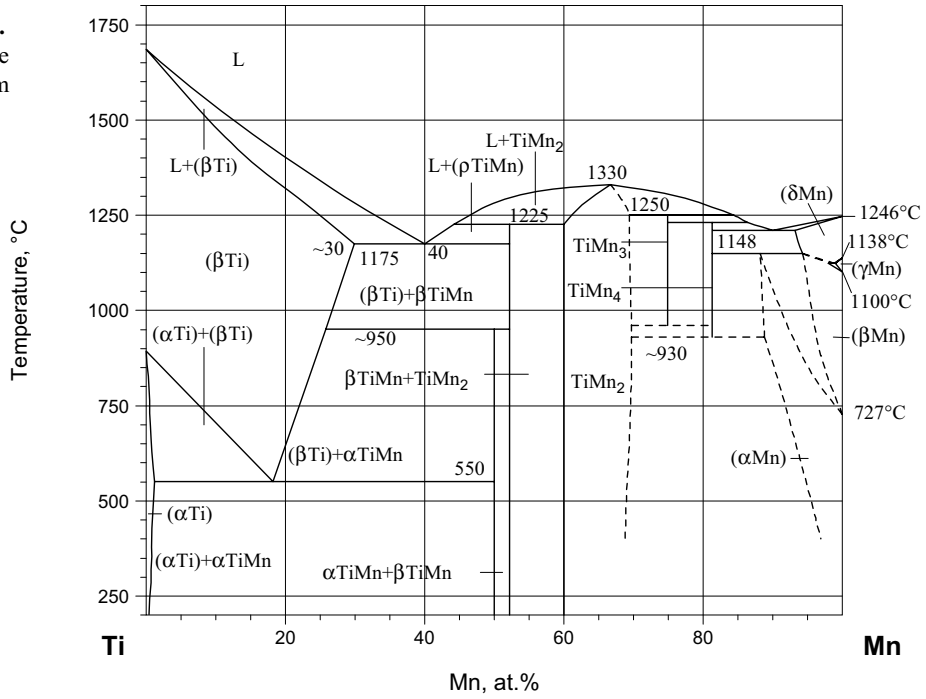

Fig. 1: Mn-Ti-Zr. Phase diagram of the Mn-Ti binary system

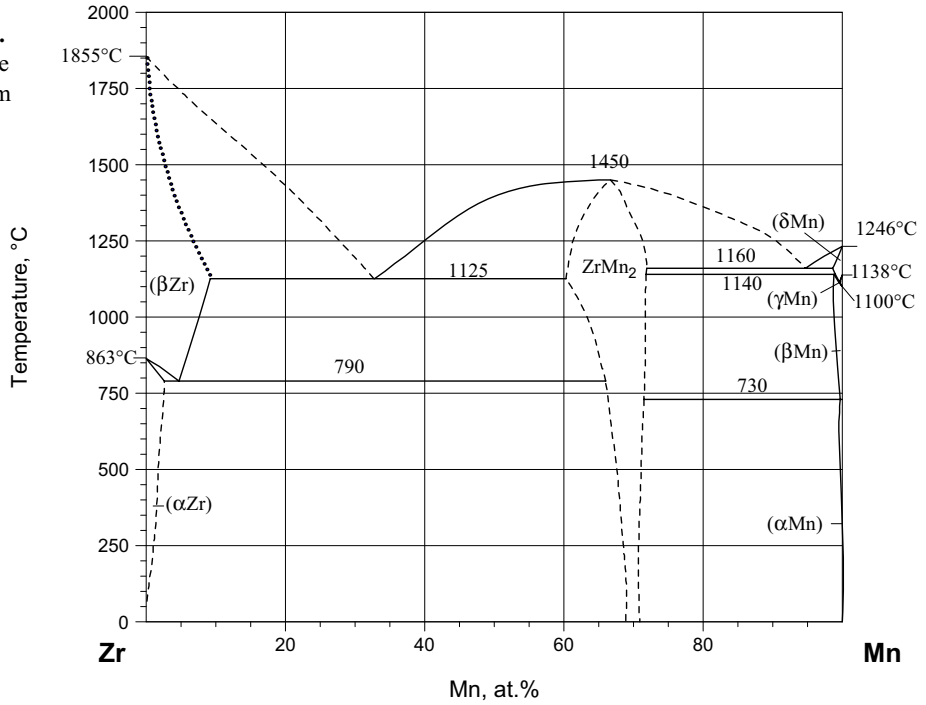

Fig. 2: Mn-Ti-Zr. Phase diagram of the Mn-Zr binary system

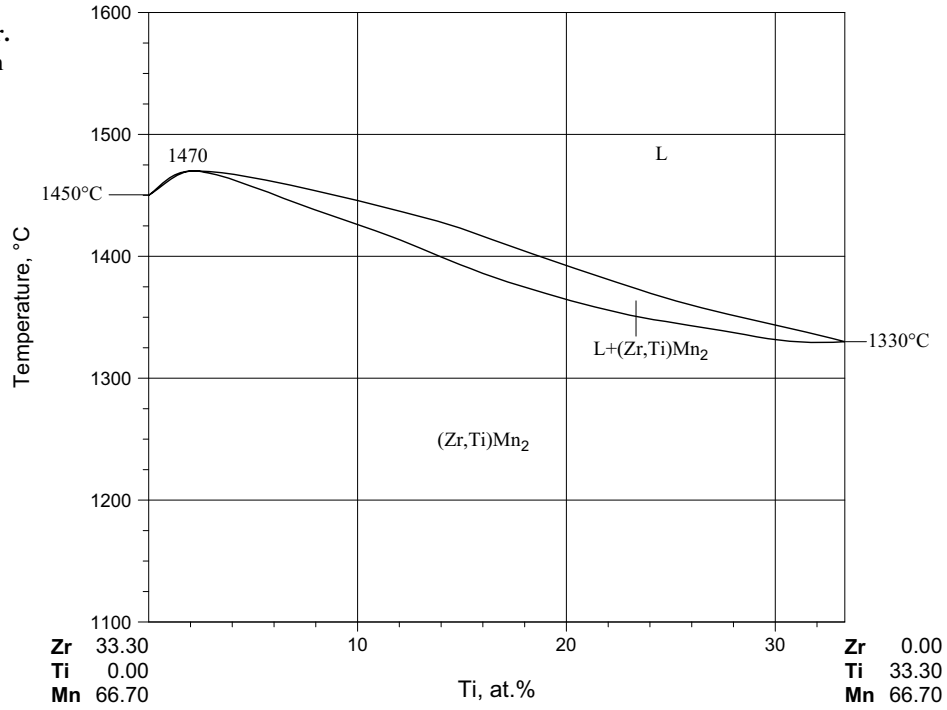

Fig. 3: Mn-Ti-Zr. Quasibinary section Zr33.3Mn66.7 - Ti33.3Mn66.7

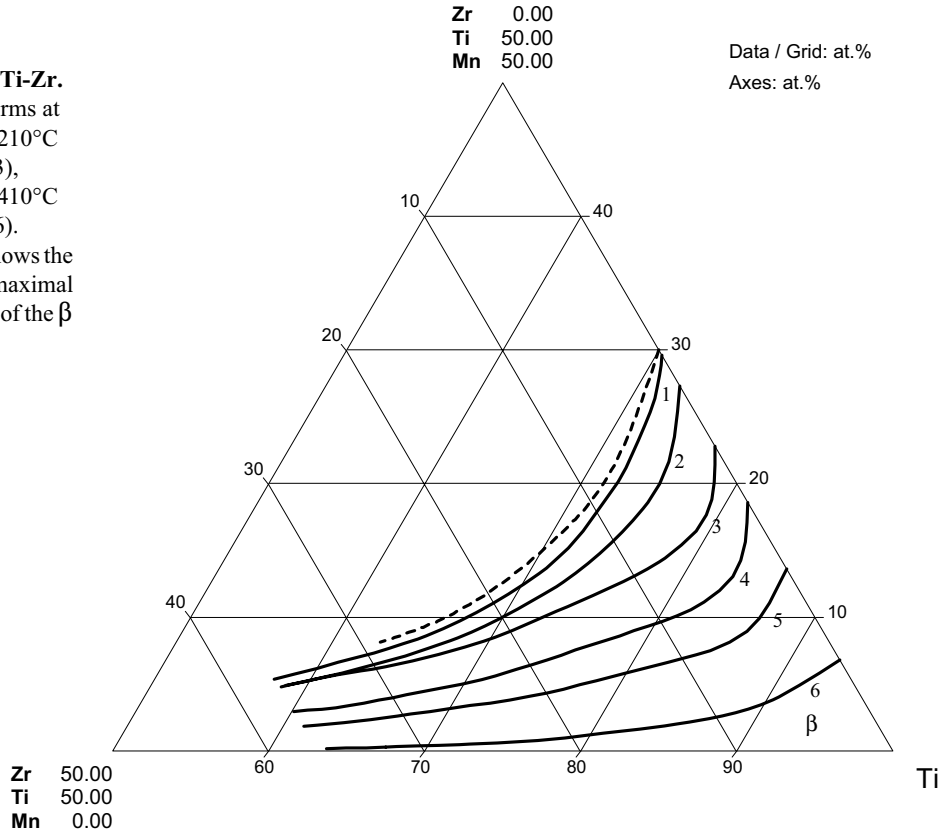

Fig. 4: Mn-Ti-Zr. Solidus isotherms at 1180°C (1), 1210°C (2), 1280°C (3), 1340°C (4), 1410°C (5), 1540°C (6). Dashed line shows the projection of maximal solubility line of the β solid solution

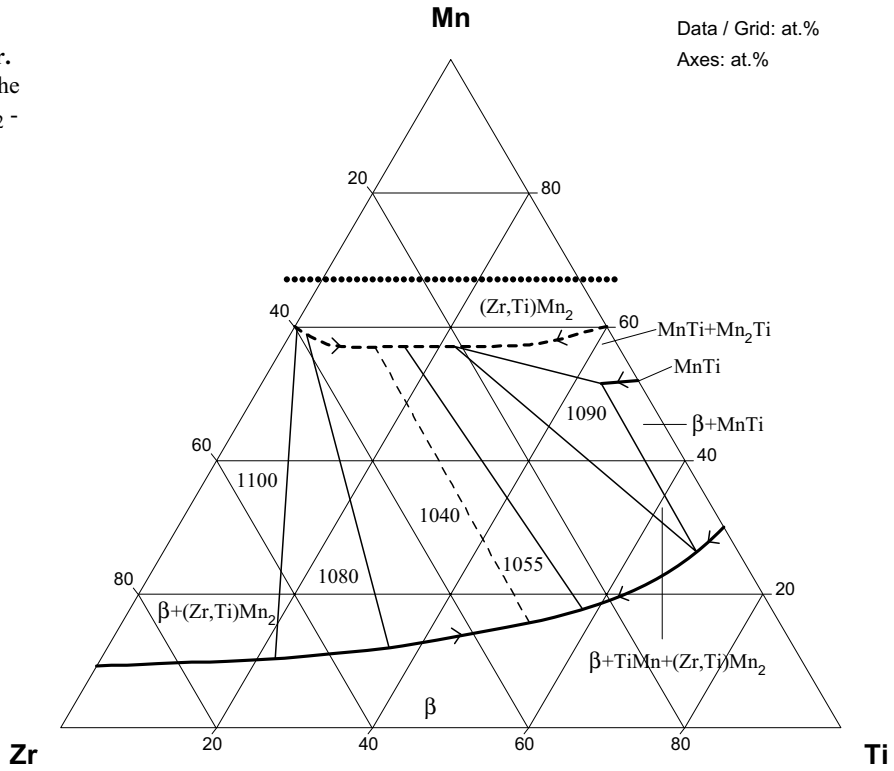

Fig. 5: Mn-Ti-Zr. Solidus surface of the Ti - $TiMn_2$ - $ZrMn_2$ - Zr partial system

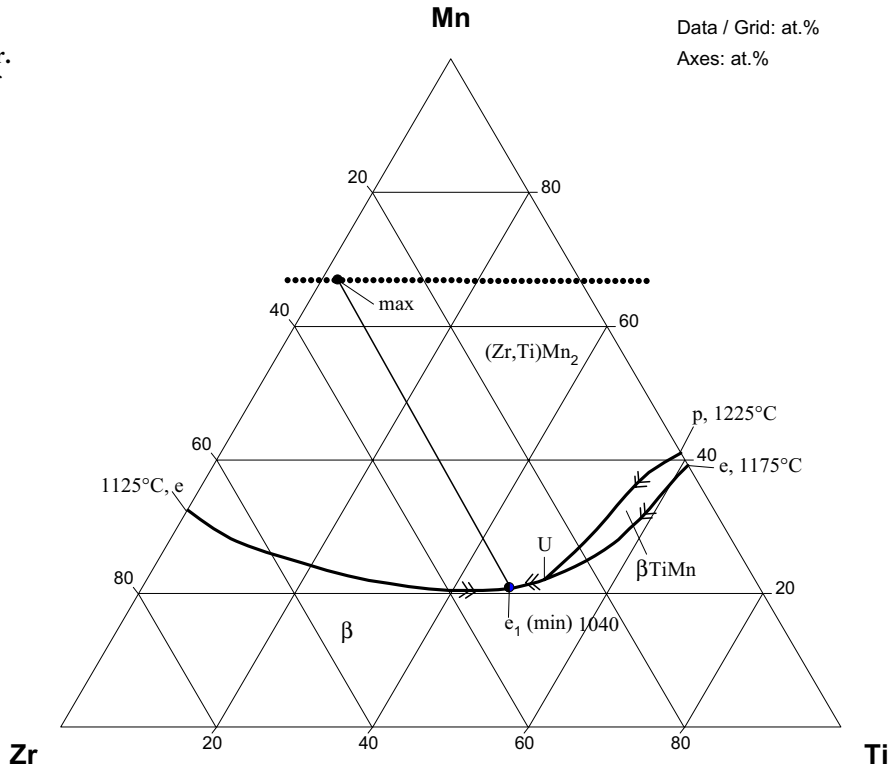

Fig. 6: Mn-Ti-Zr. Liquidus surface of the Ti - $TiMn_2$ - $ZrMn_2$ - Zr partial system

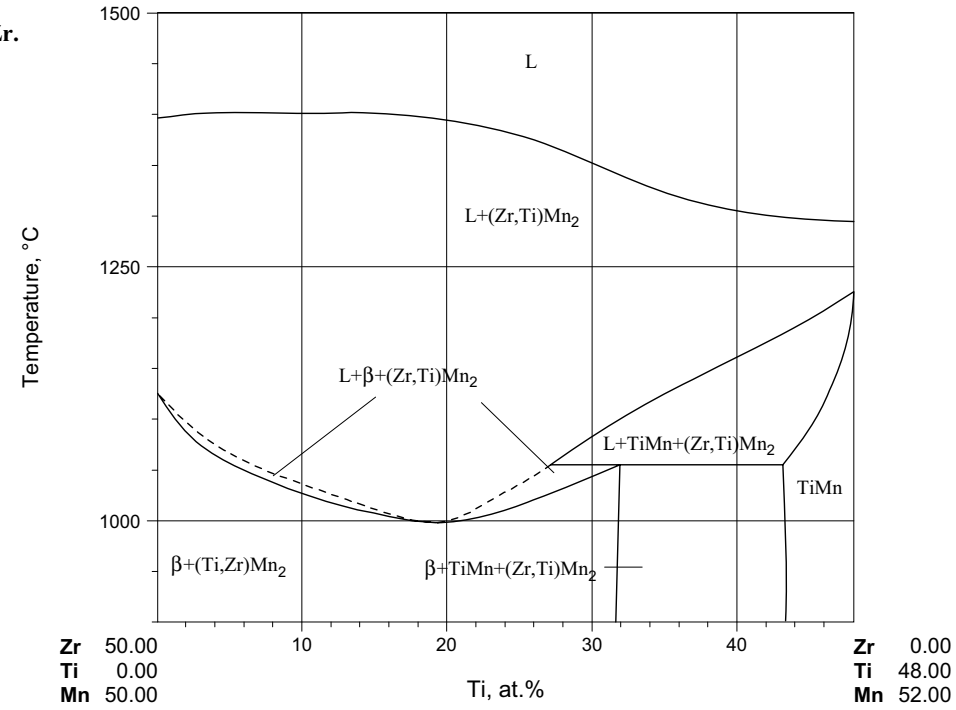

Fig. 7: Mn-Ti-Zr. Vertical section Zr50Mn50 -Ti48Mn52

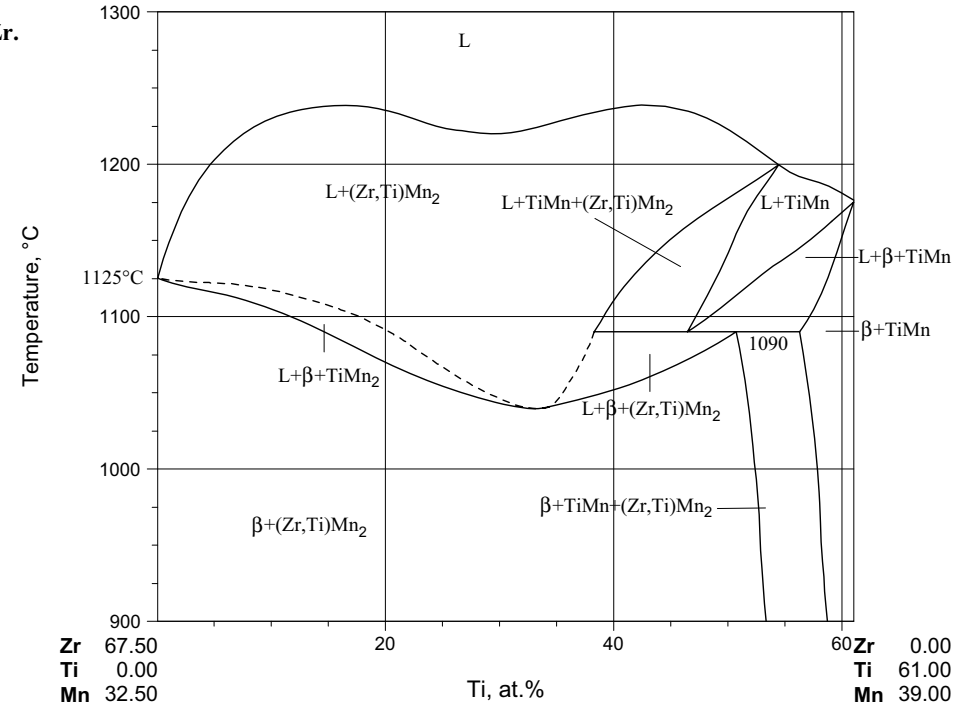

Fig. 8: Mn-Ti-Zr. Vertical section Zr67.5Mn32.5 - Ti61Mn39

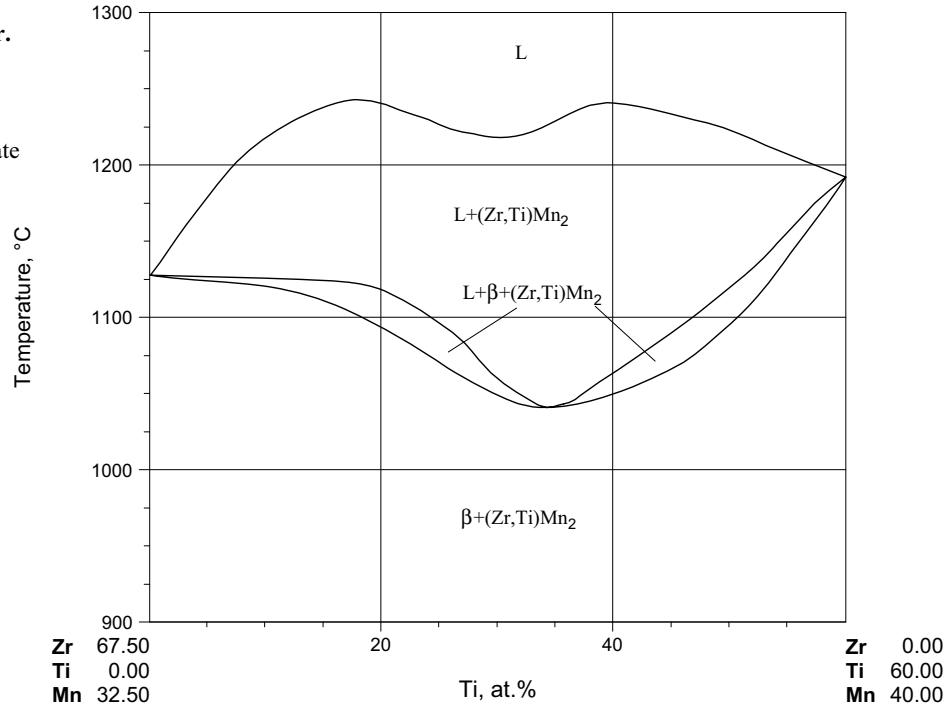

Fig. 9: Mn-Ti-Zr. Metastable Zr67.5Mn32.5 - Ti60Mn40 section under the cooling rate above 0.1 $K \cdot s^{-1}$