Experimental Investigations of the Fe-Mn-Ti System in the Concentration Range of up to 30 at.% Ti

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Abstract The ternary Fe-Mn-Ti system was investigated in the compositional range of up to 30 at.% Ti for temperatures ranging from 1000 °C to the melting temperature. Based on the metallographic investigation of as-cast alloys a partial liquidus projection was constructed, revealing large primary solidifying regions for the phases A1, A2, A12, A13, C14 and Mn₄Ti. Isothermal heat treatments at 1000 and 1200 °C revealed wide homogeneity ranges for the Mn-based phases A12 and A13 at Ti contents between 5 and 20 at.% and up to 65 at.% of Fe, indicating an electron-mediated stabilization of both phases for the simultaneous solution of Fe and Ti.

Keywords experimental phase equilibria · Fe-Mn-Ti · isothermal section · liquidus surface · ternary system

1 Introduction

The constitution of phase diagrams and the thermodynamic modelling of Fe-Mn-based systems is playing a remarkable role for several research groups over the last three

decades.^[1–5] This high importance is due to the variety of possible application fields ranging from precipitation- or transformation strengthened alloys and steels,^[6–8] to Fe-based shape memory alloys (SMAs).^[9–12] Especially for the SMAs based on the Al-Fe-Mn-Ni system, Ti additions were found to improve several technologically relevant properties and effects like the quenching sensitivity^[13] and the initiation of abnormal grain growth.^[14] To fully understand these phenomena, as well as to further enhance the properties of Fe-based SMAs, reliable constitutional phase-equilibria data of the corresponding multi-component systems is crucial. Therefore, the following work will provide important information for the further development of alloys based on the Fe-Mn-Ti system.

2 Experimental Procedure

The ternary alloys were prepared by arc melting of mixtures of high purity metal pieces (Fe: 99.99%, Mn: 99.95%, Ti: 99.995%). In the following, these alloys will be denoted by an adopted numbering, whereby the numbering of the as-cast alloys, the alloys which were heat treated at 1000 and 1200 °C start at #1, #21 and #41, respectively. The pure metal mixtures were arc melted on a water-cooled copper mold in an arc-melting furnace (Edmund Buehler GmbH, Germany) under an inert Ar atmosphere at a pressure of 800 mbar. To achieve sufficient homogeneity, the alloys were turned over and re-melted at least three times. For the heat treatments, the samples were sealed in fused silica ampoules under controlled Ar pressures between 200 and 300 mbar, depending on the subsequent heat-treatment temperature. The heat treatments were performed in a temperature calibrated (± 3 K) tube furnace (Linn Elektro Therm GmbH, Germany).

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The chemical composition of each phase and the overall composition of the alloys were determined using electron-probe microanalysis with wavelength-dispersive x-ray spectroscopy (EPMA/WDS). The chemical compositions of the individual phases were measured locally, whereas the overall chemical compositions were obtained from averaged EPMA line scans over 1 mm with a step size of 1 μm . The measurements were performed using a JSM-8900 RL (JEOL, Japan) microprobe at 20 kV accelerating voltage.

The spatial distribution of the individual phases in the different as-cast, as well as heat treated samples was obtained from micrographs in the scanning electron microscope (SEM) JSM-7800 F (JEOL, Japan). The micrographs were investigated using backscattered electron (BSE) and secondary electron (SE) contrasts¹. In order to correlate the SEM contrast with the local chemical compositions measured with EPMA, energy-dispersive x-ray spectroscopy (EDS) point measurements were performed on the respective grains using an EDAX/EDS system. Moreover, to relate information regarding the crystallography of the different phases in each alloy with the measured chemical compositions, electron backscatter diffraction (EBSD) was performed with an EDAX/EBSD system.

3 Phase Equilibria in the Fe-Mn-Ti System

3.1 Literature Review

There are only few works available considering the constitution of the ternary Fe-Mn-Ti phase diagram which are focused mainly on limited compositional regions.^[15–19]

The liquidus surface was investigated by Murakami et al.^[16] for Ti contents above 15 at.% by means of thermal analysis, showing reactions involving the phases A2, B2, MnTi and C14. For a detailed view, the crystal structures of the relevant phases are shown in Table 1. The liquidus surface of the Fe-Mn-Ti system was also investigated by Ivanchenko et al.^[18] with special emphasis on the isoplethal section at 33 at.% Ti by using differential thermal analysis (DTA). They reveal a complete miscibility of the C14 phase along the whole isoplethal section and the

formation of a lense-shaped two-phase region (Liquid + C14). The comparison of the experimentally determined melting temperatures of Murakami et al.^[16] and Ivanchenko et al.^[18] showed, that especially for the Fe-rich side of the C14-Laves phase, the melting temperatures were considerably higher in the work of Murakami et al.,^[16] which also contradicts the melting temperature of the C14 phase presented in the binary assessment of the Fe-Ti-system.^[20] Moreover, Ivanchenko et al.^[18] investigated the variation of the melting temperature of the C14 phase for a constant Fe content of 14 at.%, between 33 and 45 at.% Ti, showing a reduction of both, the liquidus and the solidus, temperatures with increasing Ti content.

Considering the solid-state phase equilibria in the Fe-Mn-Ti system, the isothermal section at 1000 °C was investigated in almost the whole compositional range by different authors.^[15,17,19] Murakami and Enjō^[15] performed x-ray diffraction (XRD) experiments on heat-treated and quenched samples with Ti contents higher than 15 at.%, showing the already mentioned complete miscibility of the C14 phase between its two binary end-members. Furthermore, a solubility of approximately 30 at.% Mn in the B2-TiFe phase was revealed by these investigations, which is in agreement with the work of Dew-Hughes and Kaufman,^[19] in which EPMA analyses were performed on heat-treated samples in the vicinity of the B2 phase. In the course of these investigations the three-phase triangle A2 + B2 + C14 was determined, indicating the extension of the solubility range of the C14 phase at 14 at.% Fe towards higher Ti contents. The Ti-poor part of the phase diagram was partially investigated by Panigrahy and Gupta^[17] using XRD, focusing mainly on the solubility ranges of the Mn-rich phases A13, A12 and Mn₄Ti. It was shown that all of these phases exhibit a large solubility for Fe (between 35 and 50 at.%) at almost constant molar fractions of Ti. Moreover, it was indicated that the solubility range of the A2 phase seems to extend from the binary Fe-Ti system up to 50 at.% Mn. In addition, two alloys with the chemical compositions 70Fe-28Mn-2Ti and 78Fe-20Mn-2Ti (numbers indicating wt.%) were heat treated at 800 °C by Chang and Morris^[6] in order to investigate the precipitation behaviour of homogenized A1 alloys. It was shown that for both alloys equilibria between A1 and C14 were established after the heat treatment for 480 h at 800 °C.

More information about the phase diagram constitution, thermodynamic and materials properties, together with possible applications of the Fe-Mn-Ti system can be found in the MSIT evaluation report initiated by Günther Effenberg.^[22]

Since the constitutional data in the Ti-poor region of the Fe-Mn-Ti system is scarce and a fundamental knowledge of the phase stabilities in this particular compositional

¹ It appears that the BSE intensity of, in particular, the A1 phase is smaller than that of the A12 and A13 phases, in contrast to what is expected from pure atomic-number (*Z*) contrast. In fact, the atomic numbers of Ti, Mn and Fe, but also the phase compositions are quite similar and, hence, *Z* contrast is expected to be not very pronounced. It appears that other effects contributing to BSE contrast like channeling were significant and lead to the partially counterintuitive BSE contrast between the phases. In any case, phase identification by local EDS and EBSD analysis was clear.

Table 1 Stable solid phases in the Ti-poor part of the Fe-Mn-Ti system relevant for the present work

Phase	Alternative notation in unary or binary systems	Prototype structure	Pearson symbol	Space group
A2	α -Fe, δ -Mn	W	<i>cI2</i>	<i>Im $\bar{3}m$</i>
A1	γ -Fe, γ -Mn	Cu	<i>cF4</i>	<i>Fm $\bar{3}m$</i>
A12		α -Mn	<i>cI58</i>	<i>I $\bar{4}3m$</i>
A13		β -Mn	<i>cP20</i>	<i>P 4₁32</i>
B2		CsCl	<i>cP2</i>	<i>Pm $\bar{3}m$</i>
C14	TiFe ₂	MgZn ₂	<i>hP12</i>	<i>P 6₃/mmc</i>
MnTi (ρ)		Zr ₂₁ Re ₂₅	<i>hR92</i>	<i>R $\bar{3}c$</i>
Mn ₄ Ti		Mo _{0.38} Cr _{0.16} Co _{0.46}	<i>hR53</i>	<i>R $\bar{3}$</i>
Mn ₃ Ti		Mn ₃ Ti	<i>oP74</i>	<i>Pbam</i>

The references for the different phases can be found in Ref. [21]

region is necessary for further development of Ti-containing Fe-based SMAs, additional experimental investigations are necessary.

The constructed phase diagrams of the present work are based on the assessed binary systems Fe-Mn,^[23] Fe-Ti^[20] and Mn-Ti.^[21] The phase diagrams of the binary systems by Huang^[23] and Kumar et al.^[20] were already chosen in the course of an ongoing development of a five-component (Al-Fe-Mn-Ni-Ti) thermodynamic database using the Cal-PhaD (Calculation of Phase Diagrams) approach. Therefore, they were accepted by the authors of the present work. Especially the most recent experimental investigations of Khan et al.^[21] were of high importance for the construction of reliable phase diagrams, since they investigated also the Mn₃Ti and Mn₄Ti phases, indicating that these phases exhibit a certain homogeneity range in the binary subsystem, rather than being line compounds, as described in earlier works.^[24]

3.2 Liquidus Projection

For the construction of a partial liquidus projection up to 30 at.% Ti, metallographic investigations of twelve as-cast alloys were performed. Based on the as-cast microstructures, the primary solidifying phases and the phases, which solidify in the last step of the solidification process were determined, and thus the liquidus surface and the course of the corresponding monovariant curves were estimated. A summary of the investigated alloys together with the formed phases and their chemical composition is given in Table 2.

In the first set of alloys (#1, #2 and #3), A1 is the primary solidifying phase, as it can be seen in Fig. 1. Upon further cooling A13 was found to solidify in alloy #1, with increasing iron content alloy #2 formed a mixture of A13 and A12, whereas in alloy #3 A12 has been formed as the interdendritic phase. This phase change indicates the

presence of an invariant reaction in the vicinity of the solidification path of these alloys. A comparable evolution of the as-cast microstructures can be seen in the alloys #4–#7, which all exhibit primary solidifying C14, as shown in Fig. 1 exemplarily for the alloys #4, #5 and #6. For these alloys, the increasing Fe content leads to a change of the phase stability of Mn₄Ti in #4, over Mn₄Ti + A12 in #5, to A12 in #6 and #7, respectively. The character of the reaction of the last solidifying microstructural components seems to be peritectic. Consequently, an invariant peritectic reaction (Liquid + C14 + A12 $\rightleftharpoons$ Mn₄Ti) is most likely present close to the composition of alloy #5.

The microstructures of the as-cast alloys #8–#12 showed the occurrence of four different primary solidifying phases, see Fig. 1. In alloy #8, the primary phase is Mn₄Ti with A2 as the last solidifying component. For alloy #9, a single phased sample consisting of A13 has formed upon solidification. Alloy #10 revealed a primary solidified A12 phase, whereas A13 was formed peritectically from the last portions of liquid during solidification, which agrees with the microstructure formed in alloy #9. The alloys #11 and #12 show both primary the A2 phase together with an eutectic microstructure (A2 + C14) in the interdendritic space.

Taking into account the observed microstructures of as-cast alloys, as well as the invariant reactions and the liquidus temperatures of the surrounding binary systems, and the experimentally determined liquidus temperatures of the C14-Laves phase by Ivanchenko et al.,^[18] a tentative partial liquidus projection for Ti contents below 30 at.% was constructed and is illustrated in Fig. 2 together with interpolated² isothermal lines ranging from 1250 to 1500 °C. The experimentally determined melting temperatures of Murakami et al.^[16] were not taken into account in the construction of the liquidus surface, since they contradict the melting temperatures of the assessed binary

² From the binaries into the ternary.

Table 2 Results of the metallographic investigation of as-cast alloys in the Fe-Mn-Ti system in the compositional range of up to 30 at.% Ti together with the overall chemical compositions and the composition of the interdendritic microstructural components measured with EPMA

Alloy	Alloy composition (EPMA), at. %			Primary solidified phases	Interdendritic phases	Chemical composition (EPMA), at. %		
	Fe	Mn	Ti			Fe	Mn	Ti
#1	40.4	58.1	1.5	A1	A13	37.9	60.2	1.9
#2	42.8	53.7	3.5	A1	A13 + A12	41.7	53.9	4.3
#3	52.1	46.0	1.9	A1	A12	44.1	47.6	8.3
#4	9.6	68.7	21.7	C14	Mn ₄ Ti	8.8	74.5	16.7
#5	22.4	53.3	24.3	C14	Mn ₄ Ti + A12	23.8	56.2	20.0
#6	33.8	44.0	22.2	C14	A12	31.5	53.0	15.5
#7	54.2	23.4	22.4	C14	A12	55.3	31.5	13.2
#8	8.4	77.2	14.4	Mn ₄ Ti	A2	6.4	90.8	2.8
#9	26.3	66.7	7.0	A13	...	...	...	...
#10	32.5	54.6	12.9	A12	A13	31.6	57.3	11.1
#11	70.5	21.3	8.2	A2	A2 + C14	64.7	18.3	17.0
#12	79.8	4.5	15.7	A2	A2 + C14	78.5	4.4	17.1

systems,^[20,21] as well as the liquidus temperatures of the C14-Laves phase determined by Ivanchenko et al.^[18] and were, therefore, not regarded as reliable data.

3.3 Isothermal Section at 1000 °C

Since, only limited experimental information regarding the isothermal section at 1000 °C is available in the compositional range of up to 30 at.% Ti,^[17] fourteen alloys were heat treated at 1000 °C for 168 h, subsequently quenched in ice water and metallographically investigated to construct the corresponding partial isothermal section in the Fe-Mn-Ti system. A detailed summary of the established phase equilibria including the experimentally determined average chemical composition of the alloys, as well as the chemical compositions of the corresponding phases is given in Table 3.

For the A13 phase, two tie-lines could be determined showing either an equilibrium with A1 in alloy #21, see Fig. 3, or A12 in alloy #22. Based on these two alloys the maximum solubility for Fe in the A13 phase was assessed to be 37 at.% for a Ti content of 2.5 at.%.

Considering the Ti-poor side of the homogeneity range of the A12 phase, the alloys #23, #24 and #25 formed equilibria with the A1 phase with increasing Fe and Ti contents. Exemplarily the microstructure of alloy #23 is shown in Fig. 3. From the direction of the tie-lines of the alloys #21, #22 and #23 it is inferred, that in the vicinity of these alloy compositions a tie-triangle (A1 + A12 + A13) has to be present.

The maximum solubility of Fe in the A12 phase at 1000 °C was determined based on the three-phase equilibria (A1 + A12 + C14) formed in alloy #26, see Fig. 3,

which is 63.8 at.% Fe. For the Ti-rich side of A12, the alloys #27, #28 and #29 formed two-phase equilibria with the C14 phase, exemplarily illustrated for alloy #28 in Fig. 3. For these alloys, the maximum solubility of Ti in the A12 phase was measured for alloy #27 as 17.0 at.%, which is comparable to the maximum solubility of Ti in the ternary extension of the A12 phase at 1000 °C in the Cr-Mn-Ti system.^[25]

Along the Mn-rich side, the alloys #30 and #31 show two-phase microstructures involving Mn₄Ti, C14 and A12, exemplarily illustrated for the A12 + Mn₄Ti microstructure of alloy #31 in Fig. 3. These alloys reveal a certain solubility of Fe at Ti contents between 15.5 and 18.7 at.% in Mn₄Ti. The maximum solubility of Fe in Mn₄Ti could not be determined directly, but needs to be smaller than 22 at.%, due to the presence of the A12 + C14 two phase microstructure in alloy #27.

In the Fe-rich corner, the alloys #32 and #33 show the presence of two different types of two-phase fields involving the C14 phase. In alloy #32, C14 was found to be in equilibrium with A2, shown in Fig. 3, whereas in alloy #33 a two-phase microstructure A1 + C14 was formed. This finding is in agreement with the tie-triangle determined in alloy #26. Consequently, in the compositional range between the alloys #32 and #33 the tie-triangle between the phases A1, A2 and C14 has to be present. Furthermore, the occurrence of the two-phase microstructure A1 + C14, found in alloy #33, contradicts the large solubility range of the A2 phase at the given temperature indicated by Panigrahy and Gupta.^[17]

The partial isothermal section at 1000 °C for Ti contents up to 30 at.% derived from the experimentally determined phase equilibria of the present work is illustrated in Fig. 4,

Fig. 1 SEM/BSE micrographs contrast of several cross-sectional polished as-cast alloys (#1–#12, see Table 2). The labels indicate the present phases (Table 1). The inset at alloy #2 indicates an EBSD phase-map of an enlarged area showing the presence of the

A12 + A13 phase mixture as the interdendritic phases. The black features in the microstructures resemble cracks and pores induced during the solidification and the subsequent mechanical treatment of the alloys

Fig. 2 Constructed tentative partial liquidus projection of the Fe-Mn-Ti system for Ti contents up to 30 at.%, together with isothermal lines, interpolated based on the binary systems, ranging from 1250 to 1500 °C. The dashed lines indicate expected monovariant curves which could not be determined experimentally. The experimental datapoints of the alloys #1–#12 show the overall chemical

compositions of the alloys (triangles), the eutectic compositions (circles) and the chemical compositions of the microstructural components formed in the interdendritic space (crosses). The arrows indicate the course of the monovariant lines on the liquidus surface pointing to lower temperatures

Table 3 EPMA measurement results of the individual phases, as well as the averaged alloy compositions of the samples heat treated at 1000 °C for 168 h

Alloy	Alloy composition (EPMA), at. %			Phase	Phase composition (EPMA), at. %		
	Fe	Mn	Ti		Fe	Mn	Ti
#21	40.0	58.6	1.4	A1	41.4	57.9	0.7
				A13	36.7	61.1	2.2
#22	35.5	60.5	4.0	A12	35.7	58.9	5.4
				A13	34.3	63.3	2.4
#23	43.4	52.6	4.0	A1	45.7	53.3	1.0
				A12	41.7	52.2	6.1
#24	54.0	44.6	1.4	A1	54.3	44.6	1.1
				A12	49.3	43.6	7.1
#25	65.4	28.5	6.1	A1	68.3	29.4	2.3
				A12	62.3	27.7	10.0
#26	67.3	23.7	9.0	A1	71.5	25.9	2.7
				A12	63.8	24.8	11.4
				C14	60.1	14.9	25.0
#27	24.6	52.1	23.3	A12	22.7	60.3	17.0
				C14	26.6	44.5	28.9
#28	33.6	42.4	24.0	A12	31.3	53.0	15.7
				C14	35.8	36.3	27.9
#29	53.7	22.6	23.7	A12	54.5	33.1	12.4
				C14	53.8	19.5	26.7
#30	9.4	64.7	25.9	C14	10.1	61.2	28.7
				Mn ₄ Ti	8.9	72.4	18.7
#31	8.1	76.6	15.3	A12	7.7	79.6	12.7
				Mn ₄ Ti	8.3	76.2	15.5
#32	78.4	4.1	17.5	A2	89.9	4.6	5.5
				C14	67.4	3.6	29.0
#33	72.5	17.8	9.7	A1	77.3	20.2	2.5
				C14	63.0	13.0	24.0
#34	34.4	52.8	12.8	A12	34.4	52.8	12.8

the dashed lines indicate the assessed homogeneity ranges and tie-triangles which could not be determined experimentally.

3.4 Isothermal Section at 1200 °C

In order to investigate the phase equilibria at elevated temperatures, eight alloys were heat treated at 1200 °C for 72 h, subsequently quenched in ice water and afterwards metallographically examined. A summary of the experimentally determined phase equilibria, together with the averaged chemical compositions of the alloys, as well as the compositions of the corresponding phases is given in Table 4.

The main feature of the isothermal section at 1000 °C, namely the large homogeneity range for A12 phase, was also found to be present at 1200 °C. The alloys #41 and #42 formed two-phase A12 + C14 microstructures, as shown in Fig. 5, indicating a slightly increased maximum

solubility of Ti up to 18.1 at.% in the A12 phase. A comparable increase of the maximum solubility was found for Fe in the A12 phase in alloy #43. In this alloy, a two-phase A12 + A2 microstructure was formed (Fig. 5) revealing a solubility for Fe of at least 64.9 at.%. The maximum solubility, however, should be slightly higher and is limited by a tie-triangle involving the C14 phase.

For the A13 phase, two-phase equilibria involving the phase A1 were found in the alloys #44 and #45, see Fig. 5. Moreover, alloy #46 exhibits a two-phase A12 + A13 microstructure, which is illustrated in Fig. 5. Considering that both, the A12 and the A13 phases are not stable at 1200 °C in the adjacent binary systems, a strong stabilizing effect of Fe in combination with Ti was observed for these phases. For A12 this can be explained taking into account its structural similarity with the χ -type Frank-Kasper phase.^[26] For this phase, the d-electron concentration is one of the limiting factors for possible homogeneity ranges, which have found to be ranging from 4.7 in Mn-Ti to 5.3 in

Fig. 3 SEM/BSE micrographs contrast of several cross-sectional polished alloys after heat treatment at 1000 °C for 168 h and subsequent ice-water quenching (#21–#34, see Table 3). The labels

indicate the present phases (Table 1). The black features in the microstructures resemble cracks and pores induced during the solidification and the subsequent mechanical treatment of the alloys

Fig. 4 Constructed partial isothermal section at 1000 °C of the Fe-Mn-Ti system for Ti contents up to 30 at.% together with the tie-lines and tie-triangle determined in the present work. The triangles and the crosses mark the corresponding chemical compositions of the phases

and the overall chemical compositions of the alloys, respectively. The dashed lines indicate the assessed homogeneity ranges and tie-triangles which could not be determined experimentally

Mn-Fe.^[27] At the maximum solubilities of Ti, 18.1 at.% in alloy #43, and Fe, 64.9 at.% in alloy #46, the d-electron concentrations were calculated as 4.8 and 5.2, respectively, which falls within the limits of the two surrounding binary systems. Even though, the d-electron concentration is comparable with the binaries, the homogeneity range is significantly expanded, due to the combined effect of Ti, which tends to reduce the number of d-electrons, and Fe, which increases the number of d-electrons in the A12 phase. A comparable electron concentration mediated stabilization also applies for the A13 phase, as described by Bardos et al.^[28]

The Mn-rich alloy #47 exhibits a two-phase $\text{Mn}_4\text{Ti} + \text{C14}$ microstructure, see Fig. 5, which indicates a comparable solubility range of the Mn_4Ti phase compared to 1000 °C. Additionally, a remarkable ternary extension of the A2 phase field, compared to the isothermal section at 1000 °C was detected in alloy #48. The corresponding two-phase $\text{C14} + \text{A2}$ microstructure is illustrated in Fig. 5. From the experimentally determined phase equilibria, a partial isothermal section at 1200 °C was constructed and is shown in Fig. 6(a). The enlarged region in Fig. 6(b) shows the phase equilibria, which were assessed based on the observations made for the alloys #43 and #48.

Table 4 EPMA measurement results of the individual phases, as well as the averaged alloy compositions of the samples heat treated at 1200 °C for 72 h

Alloy	Alloy composition (EPMA), at. %			Phase	Phase composition (EPMA), at. %		
	Fe	Mn	Ti		Fe	Mn	Ti
#41	37.3	39.0	23.7	A12	35.9	46.0	18.1
				C14	38.9	33.2	27.9
#42	41.4	37.0	21.6	A12	40.8	43.5	15.7
				C14	42.3	30.3	27.4
#43	68.2	21.6	10.2	A1	71.1	21.7	7.2
				A12	64.9	21.6	13.5
#44	43.6	52.2	4.1	A1	45.3	52.2	2.4
				A13	42.1	52.3	5.6
#45	41.9	53.9	4.2	A1	44.0	53.8	2.2
				A13	40.9	53.9	5.2
#46	38.3	49.0	12.7	A13	38.3	50.5	11.2
				A12	38.2	48.1	13.7
#47	10.0	65.9	24.2	Mn ₄ Ti	9.3	70.8	19.9
				C14	10.2	63.4	26.4
#48	66.0	16.7	17.3	A2(a)	72.3	20.1	7.6
				C14	59.6	13.0	27.4

(a) The phase which was stable at the heat-treatment temperature prior to the quenching

A more detailed view into the microstructures of the alloys #43 and #48 indicate the presence of possible phase transitions taking place upon cooling from the heat-treatment temperature of 1200 °C.

In alloy #43, at the grain boundaries of A2 and at phase boundaries between A2 and A12, A2 starts to transform into the A1 phase, which indicates a decreasing solubility for Mn of the A2 phase at lower temperatures and thus, a change of the position of the two-phase field in the vicinity of the chemical composition of the former A2 phase (from A2 + A12 to A1 + A12). In alloy #48, the A2 phase was found to be decomposed upon quenching, supporting the already mentioned decreasing solubility for Mn in the A2 phase with decreasing temperatures. This is in agreement with the experimental investigations at 1000 °C, showing the presence of an A1 + C14 two-phase field at the chemical composition of the former A2 phase. Microstructural observations of the former A2 areas, showing a fine mixture of the phases A1 and C14, indicate the eutectoid character of the decomposition reaction. As a direct consequence of the decreasing solubility of the A2 phase with decreasing temperature, the eutectoidly decomposed microstructure in alloy #48 and formation of the A1 phase in A2-phase areas in alloy #43, a transition type of reaction ($A12 + A2 \rightleftharpoons C14 + A1$) was assumed at temperatures close to 1200 °C. As a consequence of this reaction, the former three-phase triangles A1 + A2 + A12 and A2 + A12 + C14 will be transformed into A1 + A12 + C14 and A1 + A2 + C14 upon cooling, which agrees with the experimental findings of the present work

at 1000 °C, where the three-phase triangle A1 + A12 + C14 was experimentally determined.

Taking into account the experimental findings at 1000 and 1200 °C a sequence of partial isothermal sections near the phase boundaries of A1, A2, A12 and C14 at temperatures close to 1200 °C can be constructed, as shown in Fig. 7.

4 Summary

In the present work, comprehensive experimental investigations in the Ti-poor side of the Fe-Mn-Ti system at temperatures above 1000 °C were performed based on as-cast, as well as heat-treated alloys. The main outcome of the present investigations can be summarized as follows:

1. A partial tentative liquidus projection was constructed based on metallographically examined as-cast alloys in the compositional range up to 30 at.% Ti. Consequently, together with literature data, experimental information regarding the liquidus surface in the whole compositional region of the ternary system is now available and a complete liquidus projection can be constructed.
2. Experimental investigations at 1000 °C, covering almost all two-phase areas in the corresponding compositional range, remarkably enhance the knowledge of the constitution of the Fe-Mn-Ti phase diagram. Moreover, a tie-triangle A1 + A12 + C14 was experimentally determined.

Fig. 5 SEM/BSE micrographs contrast of several cross-sectional polished alloys after heat treatment at 1200 °C for 72 h and subsequent ice-water quenching (#41–#48, see Table 4). The labels indicate the present phases (Table 1). The asterisk symbol (*) indicates the stable phase prior to the quenching induced eutectoid decomposition. The colored micrograph of alloy #43 shows an enlarged EBSD-phase map of the microstructure near the former

phase boundary of the phases A2 and A12, where the A1 phase has formed during quenching. The red colored frame shows an enlarged EBSD-phase map of the marked microstructural components for alloy #48. The black features in the microstructures resemble cracks and pores induced during the solidification and the subsequent mechanical treatment of the alloys

Fig. 6 Constructed partial isothermal section at 1200 °C of the Fe-Mn-Ti system for Ti concentrations up to 30 at.% together with the tie-lines determined in the present work. The triangles and the crosses mark the corresponding chemical compositions of the phases and the

overall chemical compositions of the alloys, respectively. The dashed lines indicate expected homogeneity ranges and tie-triangles which could not be determined experimentally. The marked section (b) shows an enlarged part of the partial isothermal section

Fig. 7 Sequence of partial isothermal sections close to 1200 °C with $T_2 > T_1 > 0$ K showing the transition reaction ($A12 + A2 \rightleftharpoons C14 + A1$) and the formed phase equilibria as a function of temperature

3. The phases A12 and A13 revealed both a very high stability at elevated temperatures inside the ternary system, since both phases at 1200 °C, as well as in the liquidus projection, possess no connection to the surrounding binaries. This feature of the phase diagram indicates the combined stabilizing effect of Fe and Ti.

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References

1. A. Forsberg and J. Ågren, Thermodynamic Evaluation of the Fe-Mn-Si System and the Gamma/Epsilon Martensitic Transformation, *J. Phase Equilib.*, 1993, **14**, p 354–363
2. B.J. Lee, A Thermodynamic Evaluation of the Cr-Mn and Fe-Cr-Mn Systems, *Metall. Trans. A*, 1993, **24**, p 1919–1933
3. A.V. Khvan and B. Hallstedt, Thermodynamic Description of the Fe-Mn-Nb-C System, *Calphad*, 2012, **39**, p 62–69
4. S. Liu, B. Hallstedt, D. Music, and Y. Du, Ab Initio Calculations and Thermodynamic Modeling for the Fe-Mn-Nb System, *Calphad*, 2012, **38**, p 43–58
5. A. Walnsch, M.J. Kriegel, O. Fabrichnaya, and A. Leineweber, Thermodynamic Assessment and Experimental Investigation of the Systems Al-Fe-Mn and Al-Fe-Mn-Ni, *Calphad*, 2019, **66**, p 101621
6. K.M. Chang and J.W. Morris, Precipitation-Strengthened Austenitic Fe-Mn-Ti Alloys, *Metall. Trans. A*, 1979, **10**, p 1377–1387
7. C. Scott, B. Remy, J.-L. Collet, A. Cael, C. Bao, F. Danoix, B. Malard, and C. Curfs, Precipitation Strengthening in High Manganese Austenitic TWIP Steels, *Int. J. Mater. Res.*, 2011, **102**, p 538–549
8. K. Oikawa, K. Ishida, and T. Nishizawa, Effect of Titanium Addition on the Formation and Distribution of MnS Inclusions in Steel During Solidification, *ISIJ Int.*, 1997, **37**, p 332–338
9. K. Ando, T. Omori, I. Ohnuma, R. Kainuma, and K. Ishida, Ferromagnetic to Weak-Magnetic Transition Accompanied by BCC to FCC Transformation in Fe-Mn-Al Alloy, *Appl. Phys. Lett.*, 2009, **95**, p 212504
10. T. Omori, K. Ando, M. Okano, X. Xu, Y. Tanaka, I. Ohnuma, R. Kainuma et al., Superelastic Effect in Polycrystalline Ferrous Alloys, *Science*, 2011, **333**, p 68–71
11. T. Omori, M. Nagasako, M. Okano, K. Endo, and R. Kainuma, Microstructure and Martensitic Transformation in the Fe-Mn-Al-Ni Shape Memory Alloy with B2-type Coherent Fine Particles, *Appl. Phys. Lett.*, 2012, **101**, p 231907
12. M. Vollmer, M.J. Kriegel, A. Walnsch, V. Klemm, A. Leineweber, and T. Niendorf, On the Microstructural and Functional Stability of Fe-Mn-Al-Ni at Ambient and Elevated Temperatures, *Scr. Mater.*, 2019, **162**, p 442–446
13. M. Vollmer, P. Krooß, I. Karaman, and T. Niendorf, On the Effect of Titanium on Quenching Sensitivity and Pseudoelastic Response in Fe-Mn-Al-Ni-Base Shape Memory Alloy, *Scr. Mater.*, 2017, **126**, p 20–23
14. M. Vollmer, T. Arold, M.J. Kriegel, V. Klemm, S. Degener, J. Freudenberger, and T. Niendorf, Promoting Abnormal Grain Growth in Fe-Based Shape Memory Alloys Through Compositional Adjustments, *Nat. Commun.*, 2019, **10**, p 2337
15. Y. Murakami and T. Enjyo, Investigation of the Ti-Rich Ti-Fe-Mn Alloy System (3rd Report). On the Solid Equilibrium Relation in Ti-Fe-Mn System, *Nippon Kinzoku Gakkaishi*, 1958, **22**, p 328–332
16. Y. Murakami, Y. Yukawa, and T. Enjyo, Investigation of the Ti-rich Ti-Fe-Mn Alloy System (2nd Report). On the Liquidus Surface of the Ti-Fe-Mn System, *Nippon Kinzoku Gakkaishi*, 1958, **22**, p 265–269
17. P.C. Panigrahy and K.P. Gupta, Some Observations on Alpha-Mn, Beta-Mn and R Phases in the Mn-Ti-Fe and Mn-Ti-Co Systems, *Trans. Metall. Soc. AIME*, 1969, **245**, p 1533–1536
18. V. Ivanchenko, V. Dekhtyarenko, T. Kosorukova, and T. Pryadko, Phase Equilibria in the TiMn2-TiFe2 Polythermal Section, *Chem. Met. Alloys*, 2008, **1**, p 137–139
19. D. Dew-Hughes and L. Kaufman, Ternary Phase Diagrams of the Manganese-Titanium-Iron and the Aluminum-Titanium-Iron Systems: A Comparison of Computer Calculations with Experiment, *Calphad*, 1979, **3**, p 175–203
20. K.C.H. Kumar, P. Wollants, and L. Delaey, Thermodynamic Reassessment and Calculations of Fe-Ti Phase Diagram, *Calphad*, 1994, **18**, p 223–234
21. A.U. Khan, P. Brož, M. Premović, J. Pavlů, J. Vřešťál, X. Yan, D. Maccio, A. Saccone, G. Giester, and P. Rogl, The Ti-Mn System Revisited: Experimental Investigation and Thermodynamic Modelling, *Phys. Chem. Chem. Phys.*, 2016, **18**, p 23326–23339

22. V. Ivanchenko and T. Pryadko, Iron–Manganese–Titanium, *Numerical Data and Functional Relationships in Science and Technology: New Series*, G. Effenberg, H. Landolt, R. Börnstein, and W. Martienssen, Ed., Springer, Berlin, 2008, p 359–373
23. W. Huang, An Assessment of the Fe-Mn System, *Calphad*, 1989, **13**, p 243–252
24. I. Ansara, A.T. Dinsdale, M.H. Rand, COST507 Thermochemical Database for Light Metal Alloys, vol. 2, European Commission, EUR 18499EN, Luxembourg (1998), p 241–244.
25. Y. Le Chen, C.H. Li, K. Wang, H.Q. Dong, X.G. Lu, and W.Z. Ding, Thermodynamic Modeling of Ti-Cr-Mn Ternary System, *Calphad*, 2009, **33**, p 658–663
26. A.J. Bradley and J. Thewlis, The Crystal Structure of α -Manganese, *Proc. R. Soc. A*, 1927, **115**, p 456–471
27. J.-M. Joubert and M. Phejar, Crystal Chemistry and Calphad Modelling of the χ Phase, *Prog. Mater. Sci.*, 2009, **54**, p 945–980
28. D.I. Bardos, R.K. Malik, F.X. Spiegel, and P.A. Beck, Beta-Manganese Phases in Ternary Systems of Transition Elements with Silicon, Germanium or Tin, *Trans. Metall. Soc. AIME*, 1966, **236**, p 40–48

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