Supplementary Material for Manuscript ID: CP-ART-06-2016-004542

The Ti-Mn system revisited: Experimental investigation and thermodynamic modelling

A.U. Khan[a,#] , P. Brož[b,c], M. Premović[b,♣] , J. Pavlů[c,b], J. Vřešťál[b,c], X. Yan[a,&] , D. Maccio[d], A. Saccone[d], G. Giester[e] and P. Rogl[a,f,♦]

Abstract:

As the Ti-Mn phase diagram is part of numerous ternary and higher order systems of technological importance, the present paper defines phase relations which have been experimentally established throughout this work from 800°C to the melting range based on Differential Thermal Analyses (DTA), X-ray powder diffraction, metallography and Electron Probe Micro Analysis (EPMA) techniques on ~50 alloys, which were prepared by arc melting or high frequency melting under high purity argon starting from freshly cleaned metal ingots. Novel compounds were identified and reaction isotherms were redefined accordingly. In the Ti-rich region a novel compound TiMn was detected, sandwiched between the known phases $TiMn_{1-x}$ (~45 at.% Mn) and $TiMn_{1+x}$ (~55 at.% Mn). In the Mn-rich region the hitherto unknown crystal structure of $TiMn_{\sim 3}$ was solved from X-ray single crystal diffraction data and found to be of a unique structure type $Ti_6(Ti_{1-x}Mn_x)_6Mn_{25}$ (x = 0.462; space group *Pbam* (#55); a = 0.79081(3) nm, b = 2.58557(9) nm, c = 0.47931(2) nm), which consists of two consecutive layers of the hexagonal $MgZn_2$-type Laves phase ($TiMn_2$) and a combined layer of alternate structure blocks of $MgZn_2$ type and Zr_4Al_3 type. Whereas TiMn can be considered as a line compound (solubility range <~1 at.%), the homogeneity regions of the Ti-Mn compounds are significant (determined by EPMA): $TiMn_{1-x}$ (44.0 to 46.6 at.% Mn), $TiMn_{1+x}$ (54.6 to 56.3 at.% Mn), $Ti_{1+x}Mn_{2-x}$ ($MgZn_2$-type, 59 to 69 at.% Mn at 1000°C: -0.08<x<0.23), $TiMn_{\sim 3}$ (unique type; 74 to 76.5 at.% Mn) and $TiMn_{\sim 4}$ (R-phase: $Ti_8(Ti_xMn_{1-x})_6Mn_{39}$, 80 to 84 at.% Ti). Supported by ab initio calculations of the ground state energy for the Laves phase, the new experimental results enabled a thermodynamic modelling of the entire Ti-Mn phase diagram providing a complete and novel set of thermodynamic data thus providing a sound basis for future thermodynamic predictions of higher order Ti-Mn-X-Y systems.

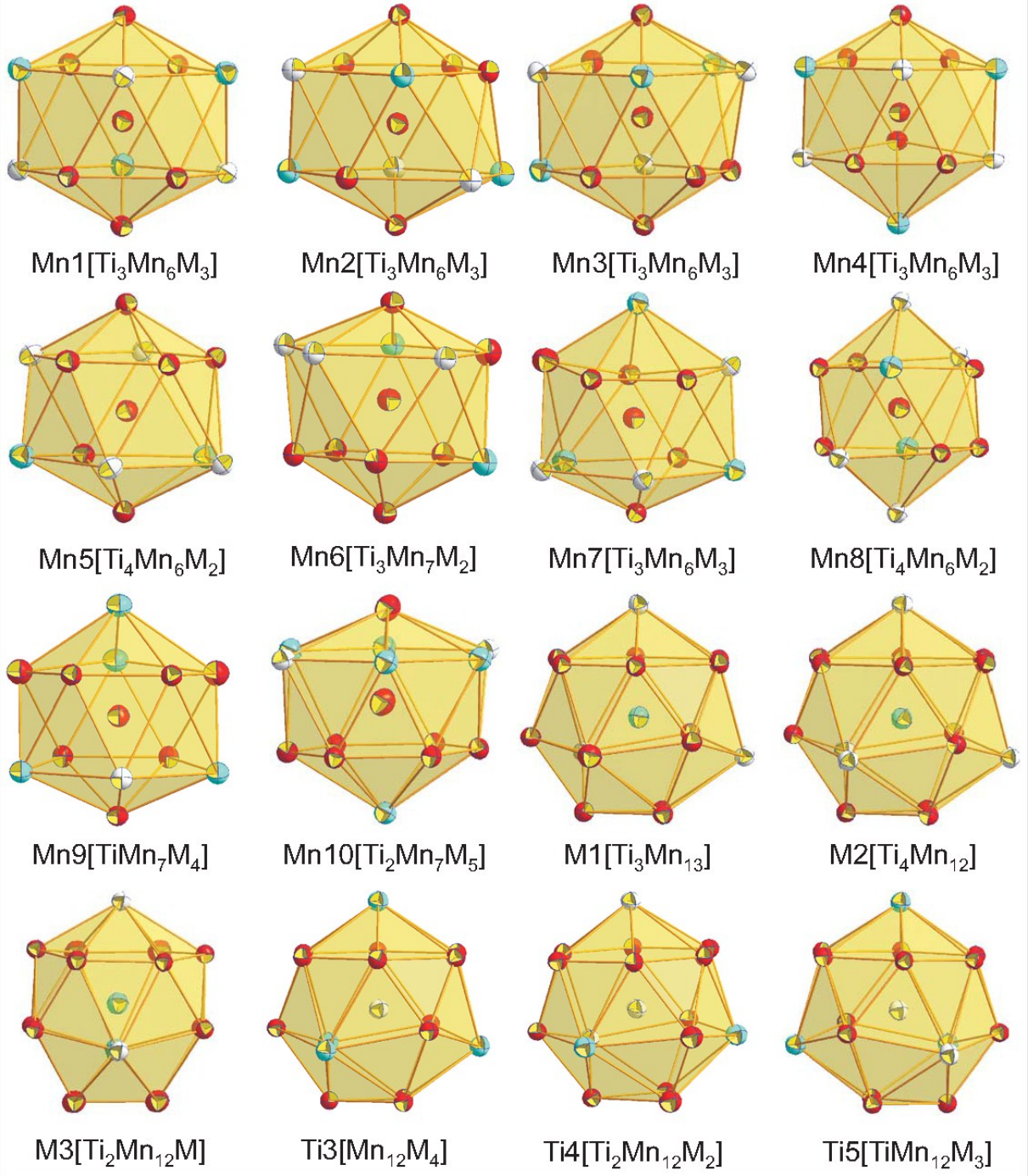

Figure I: Coordination polyhedra of $Ti_6(Ti_{1-x}Mn_x)_6Mn_{25}$, x = 0.462 ($TiMn_{\sim 3}$) with anisotropic displacement parameters from X-ray single crystal refinement. The coordinating atoms around each cental atom are given in brackets. For atom numbers see Table 3 of the corresponding paper.

Table I: Interatomic distances (nm) for $Ti_6(Ti_{1-x}Mn_x)_6Mn_{25}$, x = 0.462 ($TiMn_{\sim 3}$); standard deviation ≤0.0002. For atom numbers see the corresponding paper

Mn1-	2Mn2	0.2435		2Mn1	0.2823		1Mn10	0.2639
CN = 12	2Mn2	0.2442		2Mn2	0.2828		1Ti4	0.2729
	1Mn3	0.2465		1Mn4	0.2829		1M3	0.2734
	1Mn3	0.2470		1Mn9	0.2839		1M1	0.2807
	1M1	0.2788		2Mn7	0.2857		1Ti5	0.2817
	2M2	0.2817		2M1	0.2927		1Ti4	0.2829
	1Ti5	0.2818		1M2	0.2937	Mn7-	1Mn7	0.2354
	2Ti3	0.2822		1M2	0.2971	CN = 12	1Mn3	0.2368
Mn2-	1Mn2	0.2313	Ti4-	2Mn6	0.2729		1Mn5	0.2383
CN = 12	1Mn4	0.2361	CN = 16	2Mn7	0.2772		1Mn9	0.2392
	1Mn1	0.2435		2Mn5	0.2824		1Mn7	0.2440
	1Mn1	0.2442		2Mn6	0.2829		1Mn10	0.2659
	1Mn2	0.2480		2Mn8	0.2830		1Ti4	0.2772
	1Mn3	0.2511		2M3	0.2864		1M3	0.2811
	1M1	0.2798		1Ti5	0.2955		1M1	0.2852
	1M2	0.2811		1Ti4	0.3010		1Ti5	0.2854
	1Ti3	0.2816		1Mn10	0.3049		1Ti3	0.2857
	1M1	0.2825		1Mn10	0.3200		1M2	0.2871
	1Ti5	0.2827	Ti5-	1Mn3	0.2797	Mn8-	4Mn6	0.2429
	1Ti3	0.2828	CN = 16	2Mn5	0.2807	CN = 12	2Mn5	0.2438
Mn3-	2Mn7	0.2367		2Mn6	0.2817		2M3	0.2714
CN = 12	1Mn1	0.2465		1Mn1	0.2818		4Ti4	0.2830
	1Mn1	0.2470		2Mn4	0.2818	Mn9-	2Mn7	0.2392
	2Mn2	0.2511		2Mn2	0.2827	CN = 12	2Mn6	0.2447
	1M1	0.2788		2Mn7	0.2854		1Mn4	0.2451
	1Ti5	0.2797		1M1	0.2946		2Mn10	0.2682
	2M2	0.2810		2M2	0.2946		1M3	0.2697
	2Ti3	0.2813		1Ti4	0.2955		1M3	0.2734
M1-	1Mn10	0.2754	Mn4-	2Mn2	0.2361		1Ti3	0.2839
CN = 16	1Mn3	0.2788	CN = 12	1Mn5	0.2438		2M1	0.2854
	1Mn1	0.2788		1Mn9	0.2451	Mn10-	1Mn10	0.2330
	2Mn2	0.2798		2Mn6	0.2478	CN = 14	2Mn6	0.2639
	2Mn6	0.2807		2M1	0.2808		2Mn7	0.2659
	2Mn4	0.2808		2Ti5	0.2818		2Mn9	0.2682
	2Mn7	0.2852		1Ti3	0.2829		1M1	0.2754
	2Mn9	0.2854		1M2	0.2847		2M3	0.2949
	2Ti3	0.2927	Mn5-	2Mn7	0.2383		2M3	0.3008
	1Ti5	0.2946	CN = 12	1Mn8	0.2438		1Ti4	0.3049
M2-	1Mn5	0.2786		1Mn4	0.2438		1Ti4	0.3200
CN = 16	2Mn3	0.2810		2Mn6	0.2528	M3-	1M3	0.2664
	2Mn2	0.2812		1M3	0.2745	CN = 15	1Mn9	0.2697
	2Mn1	0.2817		1M2	0.2786		1Mn8	0.2714
	2Mn2	0.2825		2Ti5	0.2807		2Mn6	0.2734
	1Mn4	0.2847		2Ti4	0.2824		1Mn9	0.2734
	2Mn7	0.2871	Mn6-	1Mn6	0.2213		1Mn5	0.2745
	1Ti3	0.2937	CN = 12	1Mn8	0.2429		2Mn7	0.2811
	2Ti5	0.2946		1Mn9	0.2447		2Ti4	0.2864
	1Ti3	0.2971		1Mn4	0.2478		2Mn10	0.2949
Ti3-	2Mn3	0.2813		1Mn5	0.2528		2Mn10	0.3008
CN = 16	2Mn2	0.2816		1Mn6	0.2580			