Monatshefte für Chemie 111, 113—117 (1980)

Monatshefte für Chemie

The Ternary System Chromium—Manganese—Carbon

Julius C. Schuster and **Hans Nowotny***

Institute of Materials Science,
The University of Connecticut, Storrs, CT 06268, U.S.A.

(Received 31 May 1979. Accepted 22 June 1979)

The phase equilibria have been established for three isothermal sections by means of X-ray diffraction measurements.

(Keywords: Carbides; Chromium—Mn—*carbides; Manganese*—Cr—*carbides; Phase diagram*, Cr—Mn—C*)*

Der Dreistoff Chrom—Mangan—Kohlenstoff

Die Aufteilung der Phasenfelder wird für drei isotherme Schnitte auf Grund röntgenographischer Messungen erstellt.

Introduction

Despite the fact that there are no technical alloys within the chromium—manganese—carbon system, the exploration is of interest with respect to iron base superalloys. Newly developed aligned ferrous alloys[1] containing chromium and manganese clearly have shown the requirement for a more detailed study of the participating ternary combination Cr—Mn—C. The binary systems, chromium—manganese[2], chromium—carbon[3], and manganese—carbon[4], are rather well known from constitutional analysis with the exception of the liquidus lines in the Mn—C system around the high temperature ε-phase. The phase equilibria in general are more complex at the manganese rich region because of the allotropy of manganese and the large variety of manganese carbides. The mutual substitution of chromium and manganese in the $M_{23}C_6$ and M_7C_3 carbides (M for metal) has been mentioned in literature[5], however, only few data, e.g., lattice parameters, appear to be reported. Furthermore, there is some disagreement concerning the stability of the hexagonal Mn_7C_3 and its crystal structure, whether there is a Cr_7C_3 type present or just a related

0026-9247/80/0111/0113/$ 01.00

structure type occurring[6]. In a more recent study[7] no orthorhombic split was found for Mn_7C_3 and powder diagrams of Mn_7C_3 and Cr_7C_3 are virtually identical, ignoring the small difference in lattice parameters. It should be pointed out that because of coincidence of characteristic lines the decision on the basis of powder patterns only whether or not a lower symmetry occurs, is somewhat ambiguous.

Experimental

Powder mixtures of the components Cr 99.95%, Alpha Ventron Corp., Mn 99%, Alpha Ventron Corp., and C Graphite powder, 0.2% ash, Union Carbide Corp., have been arc melted in an inert atmosphere and the obtained buttons were annealed for 170 h at 1100 °C, 170 h at 1000 °C, and 340 h at 700 °C in evacuated quartz tubes. Results of the evaluated X-ray powder patterns are shown in Table 1. These findings together with literature data of the binary systems allow the establishment of isothermal sections which can be seen in Figs. 1*a*–1*c*. The ternary system is dominated by the formation of a complete series of solid solutions $(Cr,Mn)_7C_3$ obviously over the whole temperature range (up to at least 1150 °C) and by the formation of an analogous series $(Cr,Mn)_{23}C_6$

Table 1. *Phase analysis of chromium—manganese—carbon alloys*

Composition (at%)			annealing temperature (°C)		
Cr	Mn	C	700	1000	1100
24	72	4	α-Mn (8.93_5); σ^{a} 23/6 (10.61_9)	23/6; σ^{a}	23/6; σ^{a}
5	85	10	α-Mn (8.97_0) 23/6 (10.57_3)	α-Mn 23/6 (10.58_9)	5/2; 7/3 (13.90_9)^{b} (γ-Mn)
10	80	10	α-Mn (8.96_1) 23/6 (10.58_6)	23/6 (10.59_7) 7/3	σ^{a}; 7/3 (13.91_6)^{b} (γ-Mn)
15	75	10	α-Mn (8.96_0) 23/6 (10.59_6)	α-Mn (8.96_4) 23/6 (10.60_1)	σ^{a}; 7/3 (13.92_2)^{b} (γ-Mn)
20	70	10	α-Mn (8.95_6) 23/6 (10.60_9)	α-Mn; σ^{a} 23/6 (10.60_4)	σ^{a} 7/3 (13.92_2)^{b}
25	65	10	α-Mn (8.94_4) 23/6 (10.62_0)	α-Mn (8.93_1); σ^{a} 23/6 (10.60_0)	σ^{a} 7/3 (13.95_3)
45	45	10	σ 23/6 (10.61_9)	23/6	σ^{a}; 23/6
55	35	10	Cr s. s. 23/6 (10.62_5)	23/6	23/6
65	25	10	Cr s. s. 23/6 (10.63_0)	23/6	23/6

[a] Parameters of σ-phase, the same as in binary Cr—Mn system.

[b] *c*-parameter almost unchanged (4.53 Å).

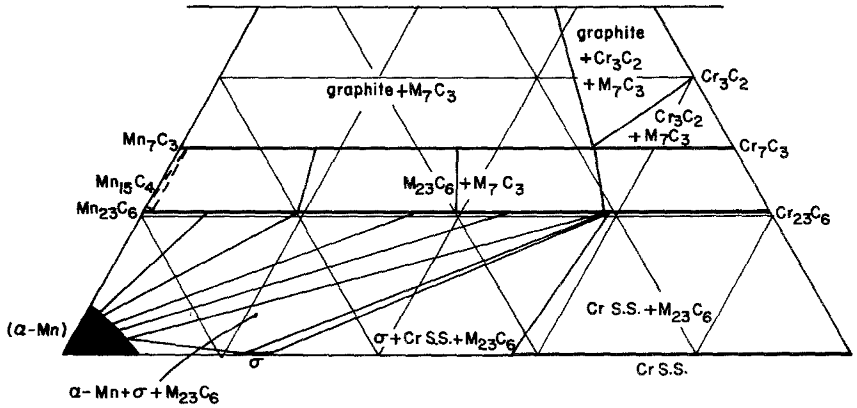

Fig. 1*a*. Isothermal section at 700 °C

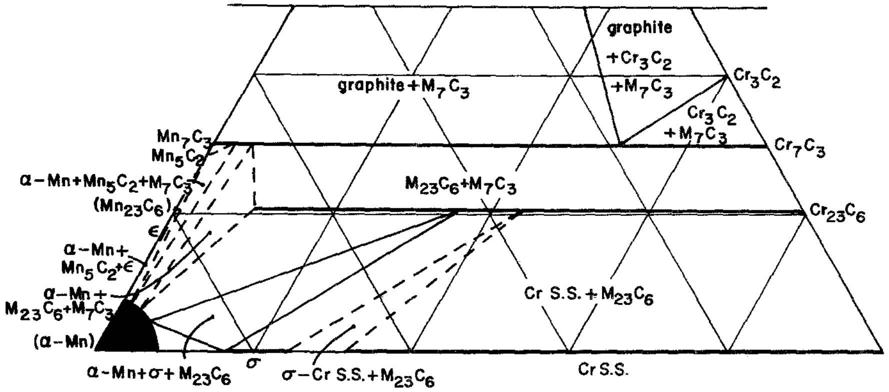

Fig. 1*b*. Isothermal section at 1 000 °C

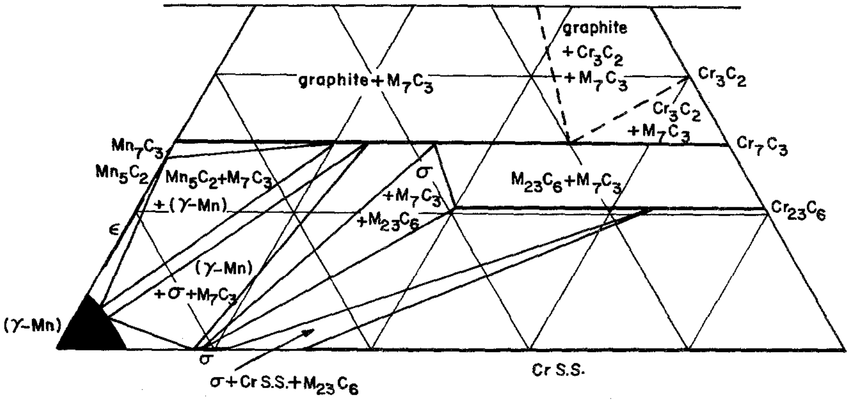

Fig. 1*c*. Isothermal section at 1 100 °C

up to approximately 1000 °C. It is of interest to notice that the carbon rich carbide Cr_3C_2 does not dissolve any manganese (carbide). Similarly the manganese carbides ε, $Mn_{15}C_4$ and Mn_5C_2 do not display any solubility for chromium (carbide). The σ-phase ($CrMn_3$) as most of the σ-phases does not show either a significant solubility for carbon, although the various forms of manganese dissolve a considerable amount of carbon.

Within the two-phase field $(Cr,Mn)_{23}C_6$ and $(Cr,Mn)_7C_3$ chromium and manganese distribute fairly equally in contrast to the equilibria between the metal solid solutions and the carbides. As is expected from the high stability of the chromium carbides the tie-lines correspond to a much higher amount of manganese in the metal phase rather than in the carbide. At the manganese rich side the α-modification stable below ca. 900 °C definitely shows up at 1000 °C (quench and anneal), that means the stability of the α-Mn solid solution increases with chromium and carbon. This behavior is consistent with the fact that the σ-phase does not dissolve any carbon and obviously narrows the homogenous region.

Results and Discussion

The α-Mn *Solid Solution*

Carbon increases the lattice parameter of α-Mn almost independent of temperature up to 8.97_2 Å[8] a value which is close to 8.970 Å for 10 at% C and 5 at% Cr. For such a composition α-Mn solid solutions coexist with $(Cr,Mn)_{23}C_6$. At the same amount of carbon, however, with increasing chromium the lattice parameter is found to be: $a = 8.944$ Å. As chromium alone surprisingly diminishes the α-Mn parameter[9], the interstitial effect by carbon at 700 °C is almost ($a = 8.93_5$ Å) and at 1000 °C fully compensated ($a = 8.93_1$ Å). This anomaly, shrinking by manganese/chromium substitution does not occur with the extended carbide solid solution, where larger lattice parameters are always found for the chromium rich side as expected from the atomic size of manganese and chromium respectively. At 1100 °C the findings at the binaries are already contradicting and because of the high reactivity of manganese with the surrounding material it could not be decided unambiguously which of the high temperature forms of manganese is present. At least one can exclude α-Mn at this temperature, while the γ-modification is most likely present.

Extended Carbide Solid Solutions

Lattice parameters of the continuous solid solutions $(Cr,Mn)_{23}C_6$ and $(Cr,Mn)_7C_3$ will be published elsewhere[1]; in Table 2 lattice parameters for the coexistent carbides are listed for alloys with 25 at% C. It should be mentioned that samples of composition 75 at% Mn and 25 at% C after anneal at 700 °C mainly consisted of $Mn_{15}C_4$ ($a = 7.491$; $c = 12.019$ Å in agreement with literature data[6,7]). It might well be that the $Mn_{15}C_4$ carbide decomposes at lower temperature.

At 1000 °C the $M_{23}C_6$ carbide starts to become unstable on the manganese rich side. At this temperature a small miscibility gap might already occur, which is taken into account in Fig. 1*b* although the lattice parameter of an alloy with 5 at% C and 10 at% C is 10.589 Å, very close to that for $Mn_{23}C_6$. No manganese/chromium substitution takes place in the ε-Mn carbide, while the manganese cementite Mn_3C reported to be stable around 1000 °C does not show up at all. Besides the narrow temperature region of existence, one can assume that chromium destabilizes furthermore, this carbide. On the other hand, Mn_5C_2 still appears to be stable at 1100 °C inasfar as a fairly large three phase field consisting of Mn_5C_2, M_7C_3 and very likely γ-Mn has been observed. A narrow three phase field ($Mn_5C_2 + \varepsilon + \gamma$—Mn s.s.) must be present, as indicated in Fig. 1*c*. The equilibrium: graphite + Cr_3C_2 + M_7C_3 does not change very much for the inspected temperatures, as can be seen from the lattice parameters of the M_7C_3 carbide. The approximate composition was found to be $Cr_{\sim 5.2}Mn_{\sim 1.8}C_3$, shifting to a somewhat higher Mn/Cr ratio for the higher temperature.

Table 2. *Lattice parameters of the coexistent* $M_{23}C_6$ *and* M_7C_3 *carbides*

Cr	Mn	C(at%)	$a\,(M_{23}C_6)$	a	$c\,(M_7C_3)$	anneal (°C)
18.75	56.25	25	10.59_0	13.90_5	4.52_8	700
			10.59_6	13.89_8	4.53_6	1000
37.5	37.5	25	10.61_0	13.95_5	4.53_2	700
			10.60_1	13.94_3	4.53_5	1000
56.25	18.75	25	10.61_8	13.98_0	4.53_3	700
			10.63_6	13.97_9	4.52_7	1000
75.0	—	25	10.65_4	14.01_8	4.53_4	700
			10.66_5	14.01_2	4.53_6	1000

References

[1] *F. D. Lemkey, J. C. Schuster, E. R. Thompson*, and *H. Nowotny*, to be published.

[2] See, Metals Hdb. **8**, 8th edition.

[3] *E. Rudy*, Compendium of Phase Diagram Data, Ohio: AFML Wright-Patterson AF. 1969.

[4] *R. Benz*, Met. Trans. **5**, 2217 (1974).

[5] *W. Schatt*, Intermetallische Phasen. Leipzig: VEB. 1977.

[6] *J.-P. Bouchaud, R. Fruchart*, C. R. Acad Sci., Paris, **259**, 160 (1964).

[7] *G. Papesch*, Thesis, University of Vienna, 1977.

[8] *K. Kuo, L. E. Persson*, J. Iron Steel Inst. **178**, 39 (1954).

[9] *W. B. Pearson*, Handbook of Lattice Spacings. London: Pergamon Press. 1958.