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THE IRON-RICH CORNER OF THE TERNARY SYSTEM Fe-Mo-C

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SUMMARY

The iron-rich corner of the ternary system Fe-Mo-C was investigated by X-ray and metallographic methods, by microprobe and DTA. An isothermal section at 1000°C and the liquidus surface were constructed from the results. The existence of a small field of primary crystallization of the ξ-phase ($Fe_{11}Mo_6C_5$) was established. Furthermore, it could be shown that at 1000°C Mo_2C is in equilibrium with α-Fe and not with γ-Fe as reported previously.

INTRODUCTION

Although the constitution of the ternary system iron molybdenum-carbon seemed to be well established (refs. 1-9), some disagreement remained about the existence (refs. 1,6,10,11) or nonexistence (refs. 12,13) of ξ-"Fe_2MoC" at 700°C. Whereas the crystal structures of η-Fe_3Mo_3C (cubic, Fd3m, a = 1.114 nm, $E9_3$-type, Fe_3W_3C-type structure (ref. 14)) and τ-$Fe_{21}Mo_2C_6$ (cubic, Fm3m, a = 1.056 nm, $D8_4$-type, $Cr_{23}C_6$-type structure (ref. 14)) were known, the crystal structure of ξ-"Fe_2MoC" could only be determined after Wayne and Nowotny succeeded in obtaining a single crystal from the melt (ref. 15). The correct composition for the ξ-phase was found to be $Fe_{11}Mo_6C_5$ (monoclinic, C2/m, a = 1.0865 nm, b = 0.7671 nm, c = 0.6559 nm, β = 120.13° (ref. 16)). This indicated that contrary to the accepted melting surface for the system Fe-Mo-C (refs. 1,7,9) a field of primary crystallization must exist for the ξ-phase. Additionally, during attempts to determine the solubility of iron in Mo_2C at 1000°C the coexistence of α-Fe (and not γ-Fe) with Mo_2C was observed at this temperature (ref. 17), which is at variance with the established isothermal section (refs. 4,5,7). Thus it was decided to reexamine this part of the ternary system.

EXPERIMENTAL METHODS

Fourteen ternary samples with molybdenum contents of up to 40 at% and carbon contents of up to 20 at% were prepared from powder mixtures (Mo: Metallwerk Plansee, Reutte, Austria; Fe: Fluka, Buchs, Switzerland; C: reactor grade graphite); they were cold pressed and arc melted under pure argon. The ingots were annealed in vaccum ($p \leq 5 \times 10^{-4}$ Pa) at 1200°C (50 h), 1000°C (50 h), and

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800°C (600 h). All samples were investigated by X-ray (Guinier powder method), metallography (SEM), microprobe, and differential thermal analyses (DTA). The DTA-measurements were performed on a DTA 404S/3 (Netzsch, Selb, F.R.G.) using samples annealed at 1000°C with a mass of 200-300 mg in alumina crucibles; a heating rate of 5 K min^{-1} was selected.

RESULTS AND DISCUSSION

Using the reactions and their temperatures reported by Jellinghaus (ref. 1) as well as the binary boundary systems from Massalski's handbook (ref. 18) as starting points, it was possible to develop a hypothetical reaction sequence capable to explain all DTA-signals above 1000°C. Isothermal sections were constructed at the temperatures of the different four-phase equilibria, and comparing expected and observed DTA-peaks led to an unambiguous assignment of each reaction to the corresponding temperature as well as to accurate equilibrium compositions of the liquid phase. The resulting liquidus surface in the iron-rich corner of the ternary Fe-Mo-C system is shown in Fig. 1. In agreement with

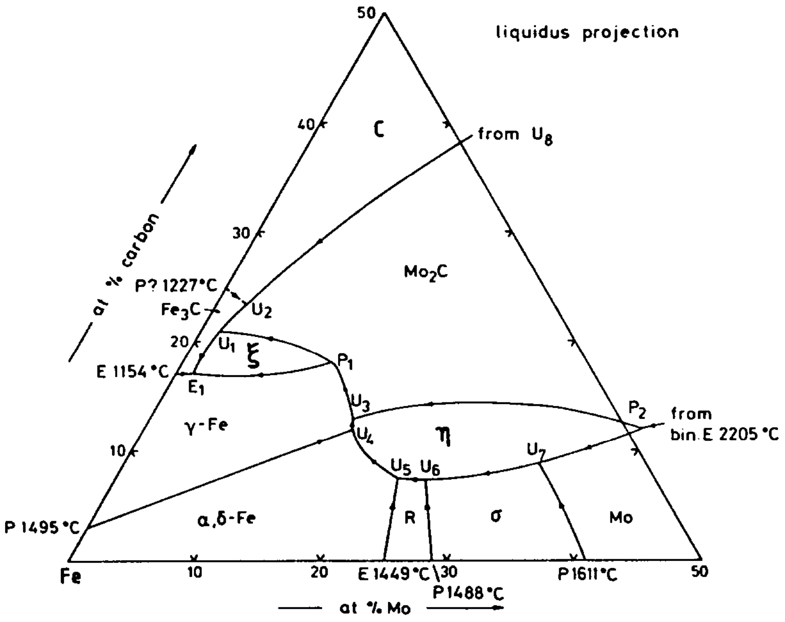

Fig. 1. Liquidus surface of the iron-rich part of the ternary Fe-Mo-C system with fields of primary crystallization. E,P = binary eutectic or peritectic, resp.; E_1..., U_1...,P_1...= ternary four-phase equilibria of class I, class II, and class III, resp. ξ = $Fe_{11}Mo_6C_5$; η = Fe_3Mo_3C; R and σ are binary Fe-Mo phases.

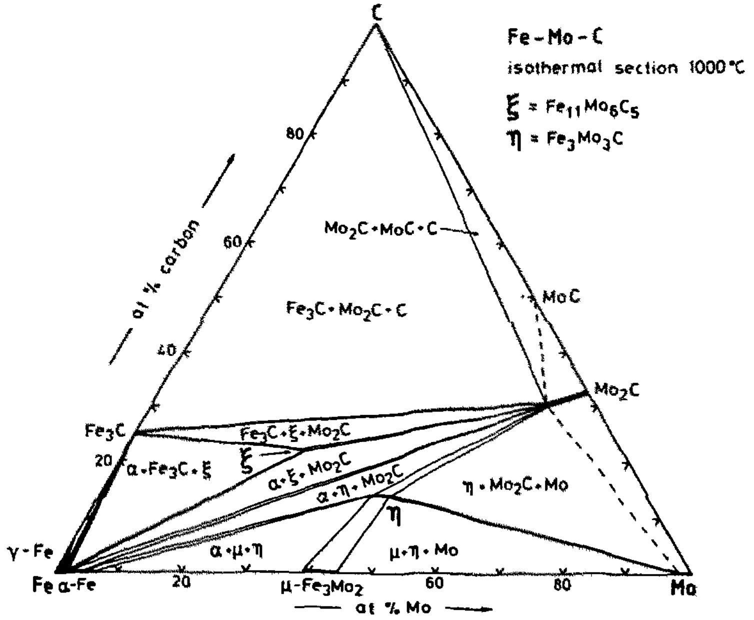

Fig. 2. Isothermal section of the ternary system Fe-Mo-C at 1000°C. For nomenclature see caption of Fig. 1; μ is a binary Fe-Mo phase.

the results of Wayne and Nowotny (ref. 15) a field of primary crystallization does exist for the ξ-phase which forms in a class III four-phase equilibrium at 1202°C from (liq.+γ-Fe+Mo_2C). This field of primary crystallization is rather small which explains the difficulty in obtaining single phase samples (ref. 17).

In alloys ($x_C \leq 0.2$; $x_{Mo} \leq 0.4$) quenched from 1000°C the following three-phase fields were observed by X-ray analysis: (α-Fe+Fe_3C+ξ), (α-Fe+ξ+Mo_2C), (α-Fe+η+Mo_2C), and (α-Fe+μ+η) where μ is a binary Fe-Mo phase. The corresponding isothermal section is shown in Fig. 2. As can be seen, at 1000°C Mo_2C coexists with α-Fe, but not with γ-Fe as reported by Nishizawa (ref. 4) and Uhrenius and Harvig (ref. 5). However, it has to be mentioned, that these authors identified the coexisting phases by metallographic etching rather than by X-ray diffraction. All other observations in the present study at 1000°C confirm the established isothermal section (ref. 7) including the fact that cementite Fe_3C has to be regarded a stable phase in the ternary Fe-Mo-C system at this temperature.

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