

# C-Cr-Fe-Mo (Carbon-Chromium-Iron-Molybdenum)

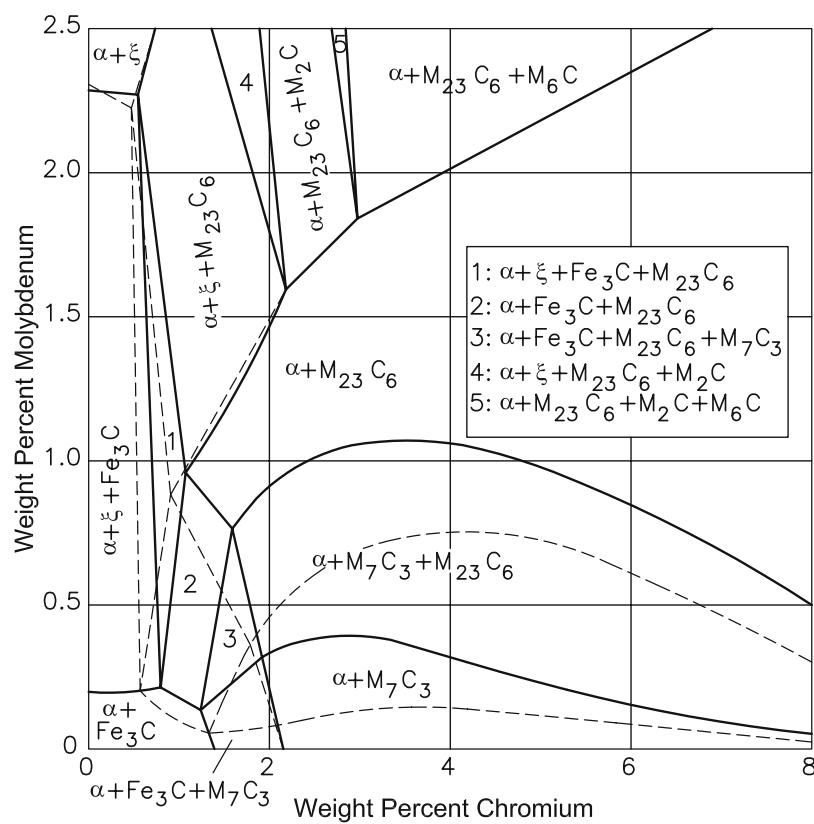
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Chromium-molybdenum steels are an important group of alloy steels for the development of high speed steels and die materials. The previous review of this quaternary system by [1996Rag] presented for Fe-rich alloys an isothermal section at 700 °C and 0.35 wt.% C from [1962Cad], two isothermal sections at 1050 °C and at 1 and 2 wt.% Mo respectively and a section at 850 °C and 2 wt.% Mo from [1967Bun], two isothermal sections at 1000 °C and at C activities of 0.410 and 0.177, respectively, and two computed isothermal sections from [1992Qiu] at 700 °C and at 0.12 and 1.5 wt.% C respectively. Recently, [2005Bra] used new experimental results in the optimization and recalculated the phase equilibria of this system, which gives better agreement with the experimental data than before.

## Binary Systems

The Cr-C system contains three carbides:  $\text{Cr}_{23}\text{C}_6$  ( $D8_4$ -type cubic),  $\text{Cr}_7\text{C}_3$  ( $D10_1$ -type orthorhombic), and  $\text{Cr}_3\text{C}_2$

( $D5_{10}$ -type orthorhombic). [2005Bra] used an improved estimate of the properties of the metastable carbide  $\text{CrC}$  ( $B1$ ,  $\text{NaCl}$ -type cubic) in their description of the Cr-C system. An experimental determination of the thermodynamic properties of  $\text{Cr}_3\text{C}_2$  and a reassessment of the Cr-C system was recently reported by [2004Ten]. The Fe-C phase diagram is in the form of a double diagram, corresponding to metastable equilibrium with cementite ( $\text{Fe}_3\text{C}$ ) ( $D0_{11}$ -type orthorhombic) or stable equilibrium with graphite (denoted gr). In the C-Mo system, the C-deficient monocarbide (denoted MoC) exists in three polymorphic forms:  $\gamma\text{MoC}$  ( $B_h$ , WC-type hexagonal),  $\eta\text{MoC}$  ( $B_i$ , AsTi-type hexagonal), and  $\delta\text{MoC}$  ( $B1$ ,  $\text{NaCl}$ -type cubic).  $\text{Mo}_2\text{C}$  has at least two forms:  $\varepsilon\text{Fe}_2\text{N}$ -type hexagonal and  $\text{PbO}_2$ -type orthorhombic. In the Fe-Cr phase diagram, a gamma loop restricts the face-centered cubic (fcc) phase  $\gamma$  to about 11 wt.% Cr. The body-centered cubic (bcc) solid solution  $\alpha$  is stable over a large region. The intermediate phase  $\sigma$  ( $D8_b$ -type tetragonal) forms congruently from  $\alpha$  at 820 °C and decomposes eutectoidally at 545 °C to Fe-rich and Cr-rich bcc phases. Cr and Mo form a continuous bcc solid solution



**Fig. 1** C-Cr-Fe-Mo computed isothermal section at 700 °C and 0.35 wt.% C [2005Bra]

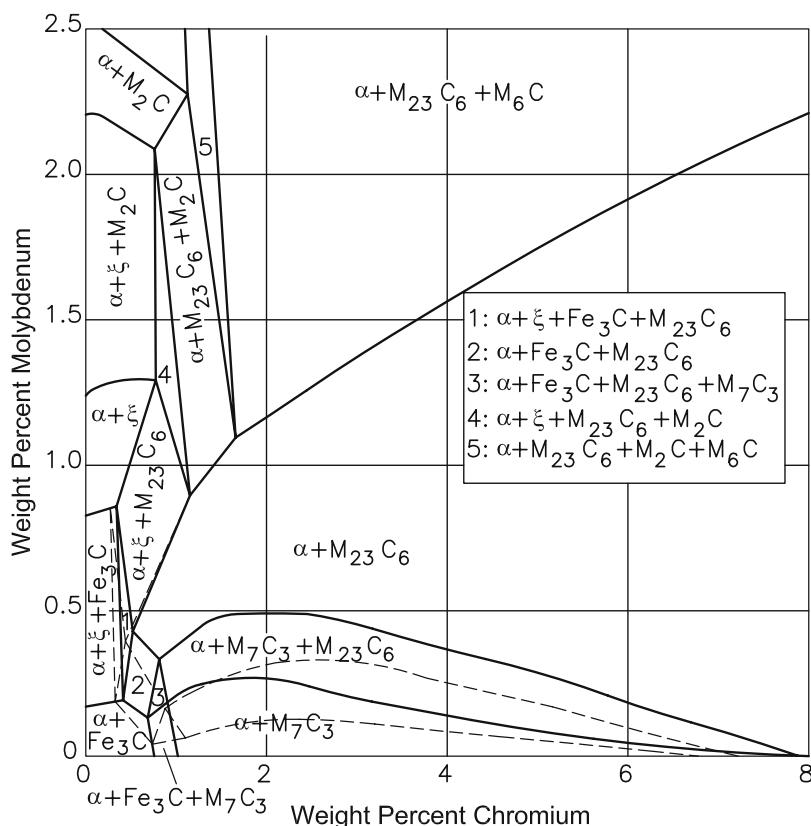


Fig. 2 C-Cr-Fe-Mo computed isothermal section at 700 °C and 0.12 wt.% C [2005Bra]

$\alpha$  at high temperatures. Below 880 °C, a miscibility gap is present. In the Fe-Mo system, the C14-type Laves phase Fe<sub>2</sub>Mo ( $\lambda$ ) forms at the stoichiometric composition. The R-phase (33.9–38.5 at.% Mo) is rhombohedral. Fe<sub>7</sub>Mo<sub>6</sub> ( $\mu$ ) is D<sub>85</sub>, Fe<sub>7</sub>W<sub>6</sub>-type rhombohedral and FeMo ( $\sigma$ ) is D<sub>85</sub>-type tetragonal.

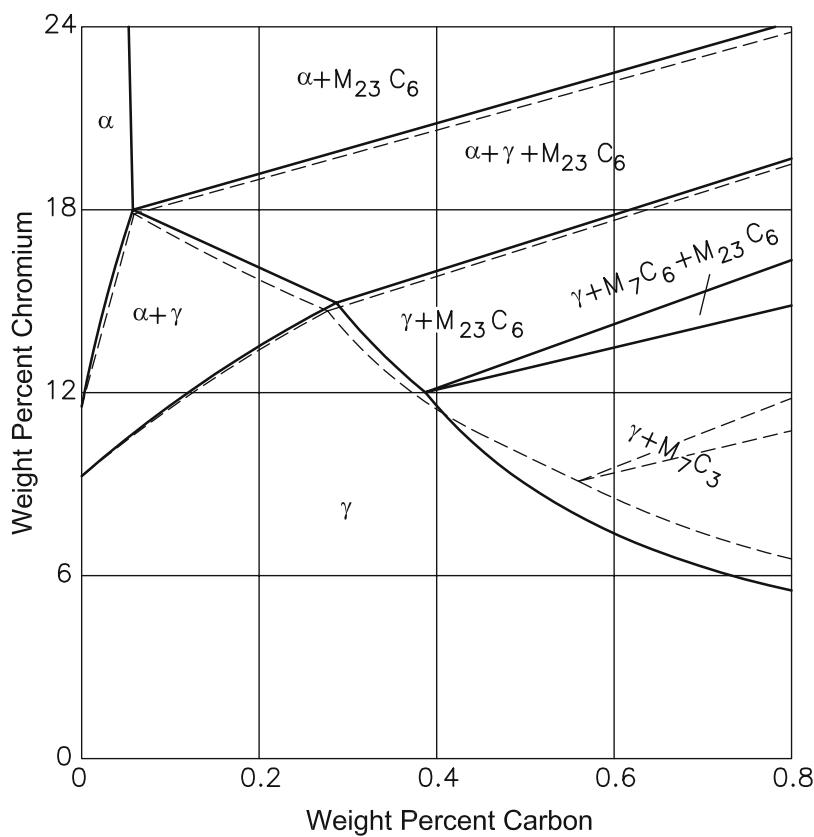
## Ternary Systems

The assessment of [1988Ray1] of the C-Cr-Fe system contains a liquidus projection and a number of isothermal sections between 1150 and 700 °C. There are no ternary phases in the system. The binary carbides dissolve appreciable amounts of the third component. The binary carbides with more than one metal are denoted by the usual notation M<sub>3</sub>C, M<sub>7</sub>C<sub>3</sub>, etc. In the C-Cr-Mo system, the Mo<sub>2</sub>C-derivative M<sub>2</sub>C dissolves ~ 50 wt.% Cr. The review of the C-Fe-Mo system by [1988Ray2] presented a liquidus projection and a number of isothermal sections between 1800 and 700 °C. The ternary compound M<sub>6</sub>C has the E9<sub>3</sub>, Fe<sub>3</sub>W<sub>3</sub>C-type cubic structure. Fe<sub>2</sub>MoC ( $\xi$ ) is orthorhombic. In the Cr-Fe-Mo system, an  $\alpha$ -Mn type cubic ternary phase exists at the composition ~ Cr<sub>12</sub>Fe<sub>36</sub>-Mo<sub>10</sub>.

## Quaternary Phase Equilibria

[2005Bra] began the quaternary evaluation with the computation of the phase equilibria, using the TCFE3 database [2002TCF], which incorporates the interaction parameters optimized by [1992Qiu] for this quaternary system. The aim was to bracket the composition of the model alloys required to provide critical information regarding the phase fraction and composition of the alloy carbides. Two model alloys, containing additional elements V and W, were designed and produced by induction melting. For general validation, [2005Bra] also investigated three commercial steels containing (in weight percent): 1.3–2.0 C, 3.7–4.8 Cr, 1.9–4.9 Mo, 3.0–4.9 V, 6.1–14.5 W, 7.8–11.1 Co, 0.6 Si, and 0.3 Mn. All specimens were annealed at 1150 °C for 500 h or at 1000 °C for 1000 h. The microstructures of the heat treated samples were examined by scanning electron microscopy. The composition of the coexisting phases was determined with wavelength-dispersive and energy-dispersive spectroscopy. The phase fractions were measured by quantitative image analysis. The experimental phase fractions and composition of the phases were listed and compared with the values computed using the TCFE3 database and the database developed by [2005Bra], after re-optimization of the parameters incorporating the new

## Section II: Phase Diagram Evaluations



**Fig. 3** C-Cr-Fe-Mo computed isothermal section at 1050 °C and 1.0 wt.% Mo [2005Bra]

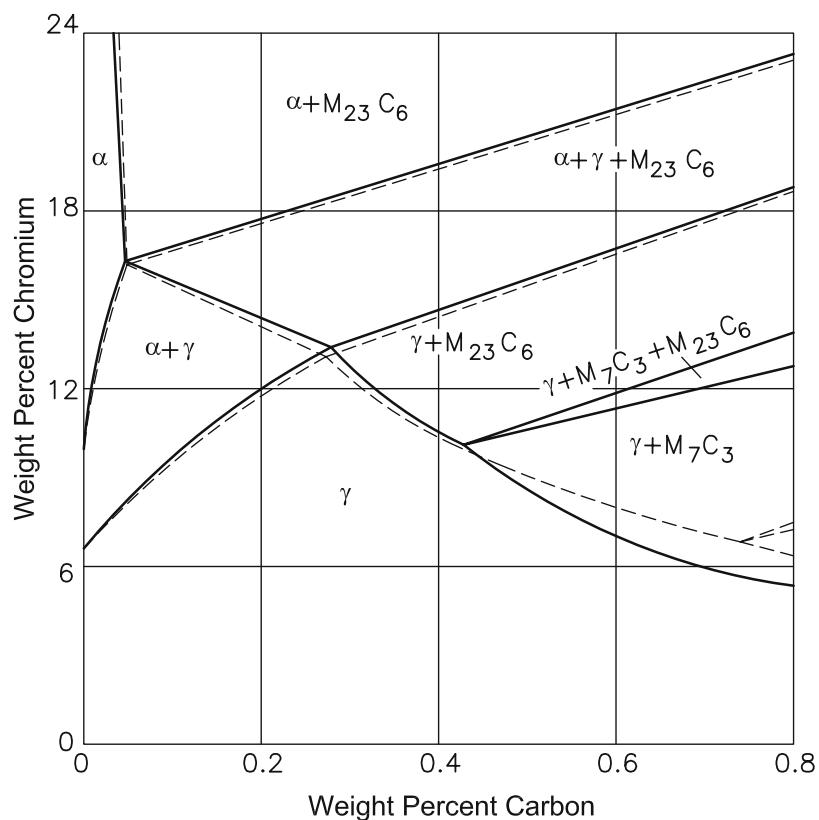
experimental results. The  ${}^0L_{Cr,Mo:C}$  interaction parameters for the MC and  $M_7C_3$  carbides were revised. The comparison shows that the calculations based on the TCFE3 database failed to predict the existence of the bcc phase at 1000 °C in a model alloy. Also, the TCFE3 base consistently overestimated the Cr contents in MC and  $M_7C_3$  and the Mo content in MC. The predictions of the improved parameters of [2005Bra] are more in line with the experimental findings.

Four isothermal sections for Fe-rich alloys of this quaternary system were recalculated by [2005Bra]. Figure 1 shows the section at 700 °C and 0.35 wt.% C. Figure 2 shows the section at 700 °C and 0.12 wt.% C. The computed sections of [1992Qiu] are also shown dotted for comparison. The labeled phase fields correspond to the phase boundaries computed by [2005Bra]. The comparison shows that, in the revised sections of [2005Bra], the  $(\alpha + M_7C_3)$  and  $(\alpha + M_7C_3 + M_{23}C_6)$  fields occupy a larger area. Figures 3 and 4 compare the sections of [2005Bra] and [1992Qiu] at 1050 °C and at 1 and 2 wt.% Mo, respectively. The  $\gamma$  corner in the

three-phase equilibrium of  $(\gamma + M_7C_3 + M_{23}C_6)$  is shifted to lower C contents in the revised description of [2005Bra].

## References

- 1962Cad:** J. Cadek, R. Freiwillig, and H.S. Hsien, Equilibrium Diagram of Fe-Cr-Mo-C Alloys Rich in Iron Containing 0.35 wt.% C at 700 °C, *Hutn. Listy.*, 1962, **17**(7), p 507-516, in Czech
- 1967Bun:** K. Bungardt, E. Kunze, and E. Horn, Effect of Various Alloying Elements on the Size of the  $\gamma$  Region in the System Fe-Cr-C. I. The System Fe-Cr-C-Mo, *Arch. Eisenhüttenwes.*, 1967, **38**(4), p 309-320, in German
- 1988Ray1:** G.V. Raynor and V.G. Rivlin, C-Cr-Fe, *Phase Equilibria in Iron Ternary Alloys*, Inst. Metals, London, 1988, p 143-156
- 1988Ray2:** G.V. Raynor and V.G. Rivlin, C-Fe-Mo, *Phase Equilibria in Iron Ternary Alloys*, Inst. Metals, London, 1988, p 177-191



**Fig. 4** C-Cr-Fe-Mo computed isothermal section at 1050 °C and 2.0 wt.% Mo [2005Bra]

**1992Qiu:** C. Qiu, An Analysis of the Cr-Fe-Mo-C System and Modification of Thermodynamic Parameters, *ISIJ Int.*, 1992, **32**(10), p 1117-1127

**1996Rag:** V. Raghavan, C-Cr-Fe-Mo (Carbon-Chromium-Iron-Molybdenum), *Phase Diagrams of Quaternary Iron Alloys*, Ind. Inst. Metals, Calcutta, 1996, p 120-134

**2002TCF:** TCFE3 Steels/Fe-Alloys Database, Thermo-Calc Software, Stockholm, Sweden, 2002

**2005Bra:** J. Bratberg, Investigation and Modification of Carbide Sub-Systems in the Multicomponent Fe-C-Co-Cr-Mo-Si-V-W System, *Z. Metallkd.*, 2005, **96**(4), p 335-344

**2004Ten:** L.D. Teng, X.G. Lu, R.E. Aune, and S. Seetharaman, Thermodynamic Investigations of  $Cr_3C_2$  and Reassessment of the Cr-C System, *Metall. Mater. Trans. A*, 2004, **35A**, p 3673-3680