

C-Cr-Fe-V (Carbon-Chromium-Iron-Vanadium)

V. Raghavan

Chromium-vanadium steels are an important group of alloy steels for creep-resistant applications and wear/abrasion resistant materials. The relative stability of Cr- and V-carbides and the solubilities of Cr in V-rich carbides and V in Cr-rich carbides are important data needed to understand the microstructural evolution in commercial alloys. The previous review of this system by [1996Rag] included partial liquidus projections at 5, 9, and 15 wt.% Cr. Four computed isothermal sections for Fe-rich alloys at 0.3 wt.% C and at 1150, 1000, 850, and 700 °C, respectively and one section at 0.2 wt.% C and 700 °C were presented from [1992Lee2]. The review also included one experimental isothermal section at 1050 °C and 1 wt.% V, and two sections at 1100 °C and at 5 and 12 wt.% Cr, respectively. Recently, [2004Bra] used new experimental results in the optimization and recalculated the phase equilibria of this system, which gives better agreement with the experimental data than the results of [1992Lee2].

Binary Systems

The Cr-C system depicts three carbides: Cr_{23}C_6 ($D8_4$ -type cubic), Cr_7C_3 ($D10_1$ -type orthorhombic) and Cr_3C_2 ($D5_{10}$ -type orthorhombic). [2004Bra] used an improved estimate of the properties of the metastable carbide CrC ($B1$, NaCl-type cubic) in their description of the Cr-C system. An experimental determination of the thermodynamic properties of Cr_3C_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 (Fe_3C) ($D0_{11}$ -type orthorhombic) or stable equilibrium with graphite (denoted gr). Both [1992Lee2] and [2004Bra] used the thermodynamic description of [1985Gus] for the Fe-C system. The V-C system [Massalski2] depicts two carbides VC and V_2C , both with a homogeneity range on the C-deficient side. Several ordered forms are present in the low-temperature region of these carbides. Also, a third carbide of fixed composition is shown with stoichiometry near V_3C_2 (denoted as V_4C_{3-x} by [Massalaksi2]). [1991Hua1] modeled the composition variation of VC and V_2C and treated V_3C_2 as stoichiometric. This model was mainly adopted by [2004Bra]. In the Fe-Cr phase diagram, a gamma loop restricts the face-centered cubic (fcc) phase γ to about 11 wt.% Cr. The body-centered cubic (bcc) continuous solid solution α is stable over a large region. The intermediate phase σ ($D8_b$ -type tetragonal) forms from α at 820 °C around the mid-composition and decomposes eutectoidally at 545 °C to Fe-rich and Cr-rich bcc phases. The thermodynamic description of the Fe-Cr system by [1987And] was

adopted by both [1992Lee2] and [2004Bra]. A γ loop and an intermediate phase σ ($D8_b$ -type tetragonal) with a significant range of homogeneity are the characteristic features of the Fe-V system. The thermodynamic description of [1991Hua2] of the Fe-V system was used by [2004Bra] in their quaternary assessment. A continuous bcc solid solution exists in the Cr-V system. [2004Bra] used the thermodynamic description of [1992Lee3] for the Cr-V system.

Ternary Systems

The C-Cr-Fe description of [1992Lee1] was revised by [2004Bra] to fit their modified description of the properties of CrC. The C-Cr-V system was reassessed by [2004Bra], using the experimental data from a source different from that used by [1992Lee2]. For the Cr-Fe-V system, [2004Bra] adopted the description of [1992Lee2].

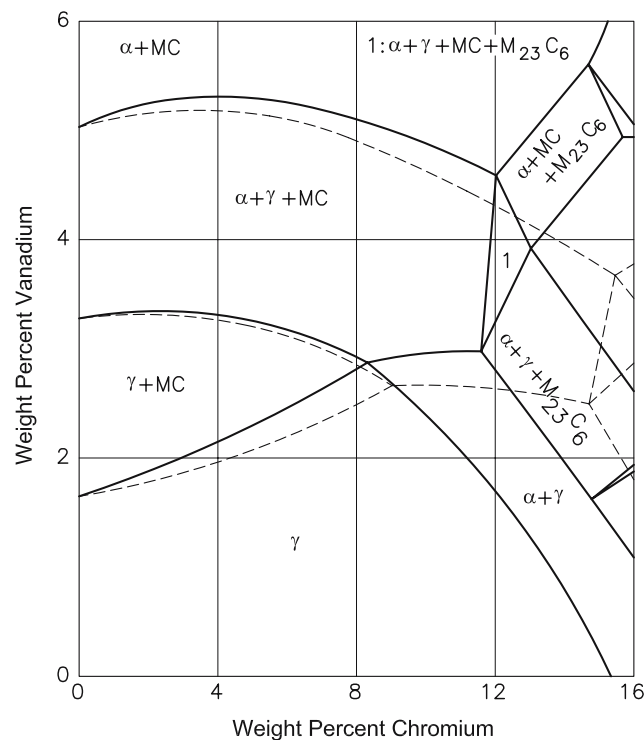


Fig. 1 C-Cr-Fe-V computed isothermal section at 1150 °C and 0.3 wt.% C [2004Bra]

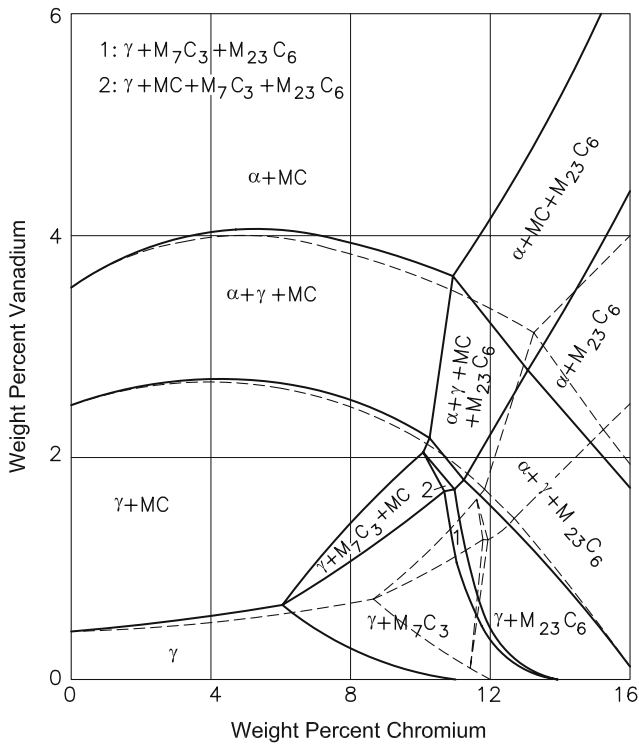


Fig. 2 C-Cr-Fe-V computed isothermal section at 1000 °C and 0.3 wt.% C [2004Bra]

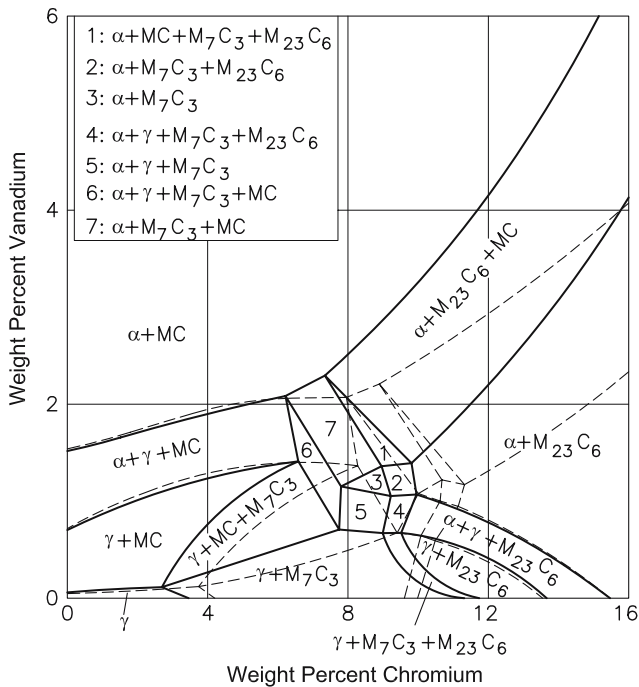


Fig. 3 C-Cr-Fe-V computed isothermal section at 850 °C and 0.3 wt.% C [2004Bra]

For the C-Fe-V system, [1992Lee2] used their own assessment, whereas [2004Bra] modified the description of [1991Hua2].

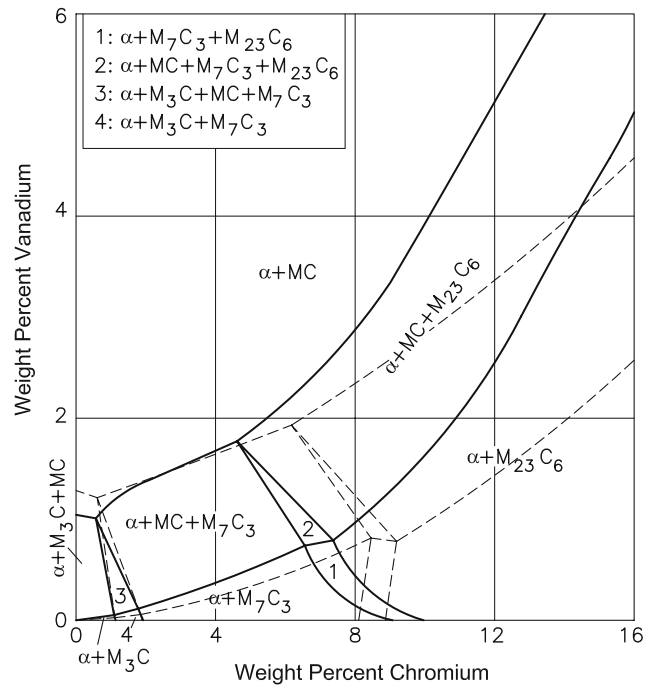


Fig. 4 C-Cr-Fe-V computed isothermal section at 700 °C and 0.3 wt.% C [2004Bra]

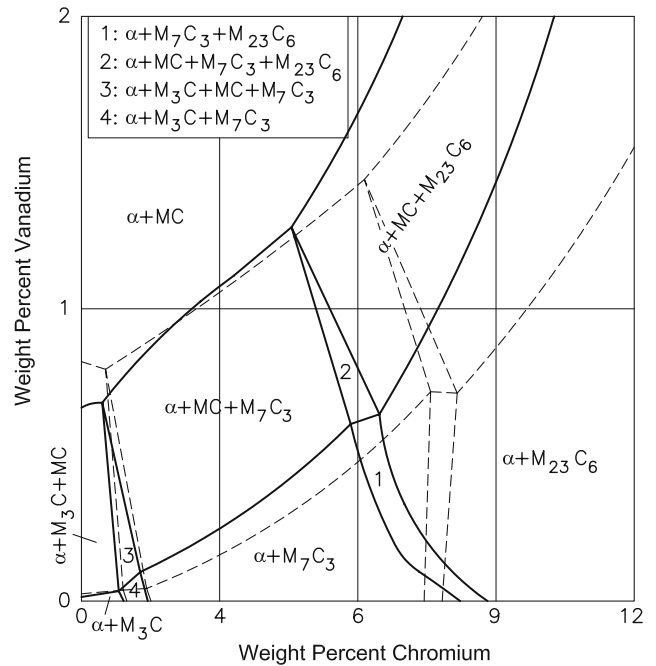


Fig. 5 C-Cr-Fe-V computed isothermal section at 700 °C and 0.2 wt.% C [2004Bra]

Quaternary Phase Equilibria

[2004Bra] began their quaternary evaluation with the computation of the phase equilibria using the earlier

Section II: Phase Diagram Evaluations

assessment of [1992Lee2], so that they could bracket the composition of the model alloys required to provide critical information regarding the phase fraction and composition of Cr-V carbides. Starting with 99.9995% C, 99.99% Cr, 99.98% Fe, 99.95% Mo and 99.7% V, [2004Bra] induction-melted two C-Cr-Fe-V alloys and one C-Cr-Fe-Mo-V alloy. To simulate the compositions of commercial alloys, they also prepared three more alloys which contained additionally Mn and Si. The alloys were annealed at 1150 °C for 500 h or at 1000 °C for 1000 h and quenched in water. The microstructures were studied by scanning electron microscopy. The composition of the coexisting phases was determined by wavelength-dispersive and energy-dispersive spectroscopy. The phase fractions were measured by quantitative image analysis. [2004Bra] listed the experimental results, the computed results from the model of [1992Lee2] and their own computed results for all the six alloys investigated and for the two heat treatments at 1150 and 1000 °C, respectively. A comparison of the results shows that the description of [1992Lee2] failed to predict the existence of M_7C_3 [$M = (Cr, Fe, Mo, V)$] at 1150 °C in two commercial alloys and the bcc phase at 1000 °C in a model alloy. Also, the description of [1992Lee2] overestimated the Cr content and underestimated the V content of MC and M_7C_3 in most alloys. In Mo-containing alloys, the model of [1992Lee2] overestimates the Mo content of the MC carbide. The improved model of [2004Bra] is more in line with the experimental findings. The ternary carbide M_6C does not appear at the low level of Mo in these alloys, which contained a maximum of 2.6 wt.% Mo.

[2004Bra] used their optimized interaction parameters to compute a number of isothermal sections of this quaternary system. Figures 1-4 show four computed isothermal

sections at 0.3 wt.% C and at 1150, 1000, 850 and 700 °C, respectively. Figure 5 shows the computed section at 0.2 wt.% C and 700 °C. For comparison, the phase boundaries computed by [1992Lee2] are shown dotted in the above figures. The labeled phase fields correspond to the phase boundaries computed by [2004Bra].

References

- 1985Gus:** P. Gustafson, A Thermodynamic Evaluation of the C-Fe System, *Scand. J. Metall.*, 1985, **14**(5), p 259-267
- 1987And:** J.O. Andersson and B. Sundman, Thermodynamic Properties of the Cr-Fe System, *CALPHAD*, 1987, **11**, p 83-92
- 1991Hua1:** W. Huang, An Assessment of the V-C System, *Z. Metallkd.*, 1991, **82**(2), p 174-181
- 1991Hua2:** W. Huang, A Thermodynamic Evaluation of the Fe-V-C System, *Z. Metallkd.*, 1991, **82**(5), p 391-401
- 1992Lee1:** B.J. Lee, On the Stability of Chromium Carbides, *CALPHAD*, 1992, **16**(2), p 121-149
- 1992Lee2:** B.J. Lee and D.N. Lee, A Thermodynamic Evaluation of the Fe-Cr-V-C System, *J. Phase Equilib.*, 1992, **13**(4), p 349-364
- 1992Lee3:** B.J. Lee, A Thermodynamic Evaluation of the Fe-Cr-V System, *Z. Metallkd.*, 1992, **83**(5), p 292-299
- 1996Rag:** V. Raghavan, C-Cr-Fe-V (Carbon-Chromium-Iron-Vanadium), *Phase Diagrams of Quaternary Iron Alloys*, Ind. Inst. Metals, Calcutta, 1996, p 193-207
- 2004Bra:** J. Bratberg and K. Frisk, An Experimental and Theoretical Analysis of the Phase Equilibria in the Fe-Cr-V-C System, *Metall. Mater. Trans. A*, 2004, **35A**, p 3649-3663
- 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