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The Co-Mn-V (Cobalt-Manganese-Vanadium) System

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Introduction

The Co-Mn-V system was studied with a view to establish the σ phase field in the ternary diagram. Only one isothermal section was established and is reported here.

Binary Systems

The Co-Mn system [Massalski2] (Fig. 1) shows a peritectic reaction L + (δMn) ↔ (βMn) at 1185 °C and a eutectic reaction L ↔ γ + (βMn) at 1161 °C, where γ is the terminal solid solution of face-centered-cubic (fcc) γCo. The (γMn) phase forms through a peritectoid reaction (δMn) + (βMn) ↔ (γMn) at ~1154 °C. A wide (βMn) phase field exists from Mn to the middle of the phase diagram. At ≤727 °C, the βMn → αMn transformation occurs at the Mn end of the Co-Mn diagram. One intermediate phase CoMn forms through a peritectoid reaction (βMn) + γ ↔ CoMn at ~545 °C. At the Co end of the Co-Mn system, a γ → ε phase transformation occurs at ≤422 °C, where ε is the close-packed-hexagonal (cph) terminal solid solution of εCo.

The Co-V system [Massalski2] (Fig. 2) has three intermediate phases, Co_3V, CoV (σ), and CoV_3. The σ phase forms through a peritectic reaction L + α ↔ σ at 1422 °C. A eutectic reaction L ↔ γ + σ occurs at 1248 °C. The α and γ are the terminal solid solutions of body-centered-cubic (bcc) V and fcc γ Co, respectively. The γ phase transforms congruently at 1070 °C at the Co_3V stoichiometry to $AuCu_3$ type ordered γ′ phase.

The Co_3V phase undergoes a further phase change at temperatures a few degrees below 1070 °C to the hexagonal γ_1' phase. On the V-rich side of the system. CoV_3 forms through a peritectoid reaction (αV) + σ ↔ CoV_3 at 1025 °C. At the high Co end of the diagram, reactions are less certain because of the sluggish nature of the (εCo) ↔ (γCo) transition. Even in pure Co, the transition is confused because of extensive faulting of the close-packed layers. The presence of a peritectoid reaction at ~860 °C has been suggested [1979Aok], but the work of both Miodownik [1982Mio] and Inden [1981Ind1, 1981Ind2, 1982Ind] indicates that this temperature is the point at which the ferromagnetic-to-paramagnetic transition, (γ_fCo) ↔ (γ_pCo), in the Co-rich solid solution shifts from a second-order transition above this temperature to a first-order transition below this temperature. Such behavior has been reported for several binary systems of Co with transition metals (e.g., Co-Cr, Co-Mn, Co-V [Massalski2]). The α → ε transformation, where ε is the terminal solid solution to cph εCo has not been well established. The CoV_3 phase forms through a peritectoid reaction α + σ ↔ CoV_3 at 1025 °C. The σ phase is reported to undergo a phase change at ~550 °C.

The Mn-V system [Massalski2] (Fig. 3) shows at high temperatures a complete solid solubility of bcc V and bcc

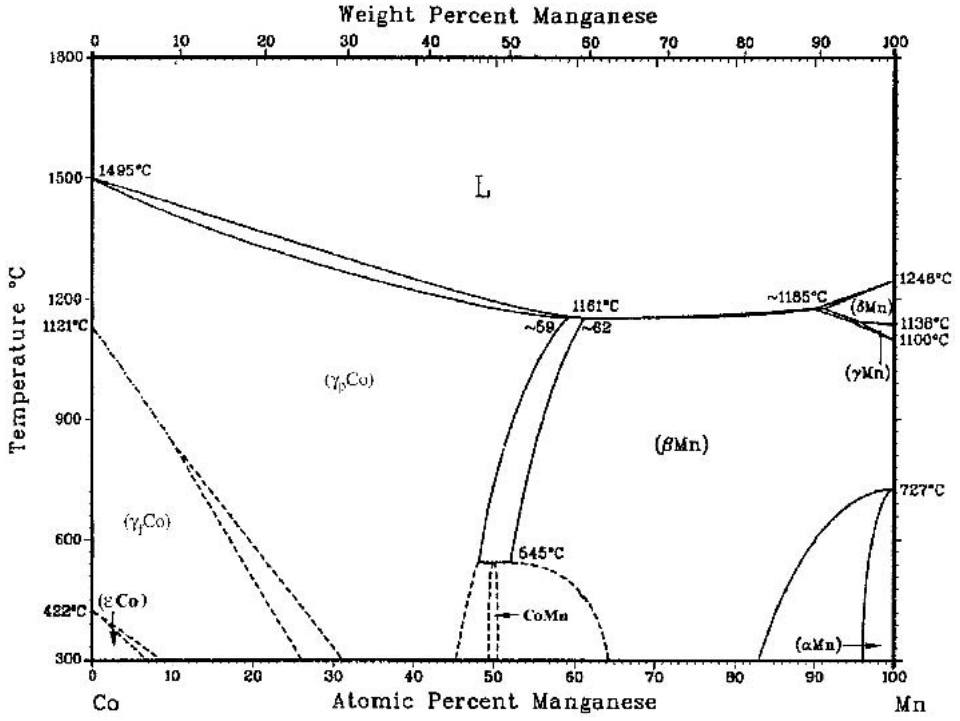

Fig. 1 Co-Mn binary phase diagram

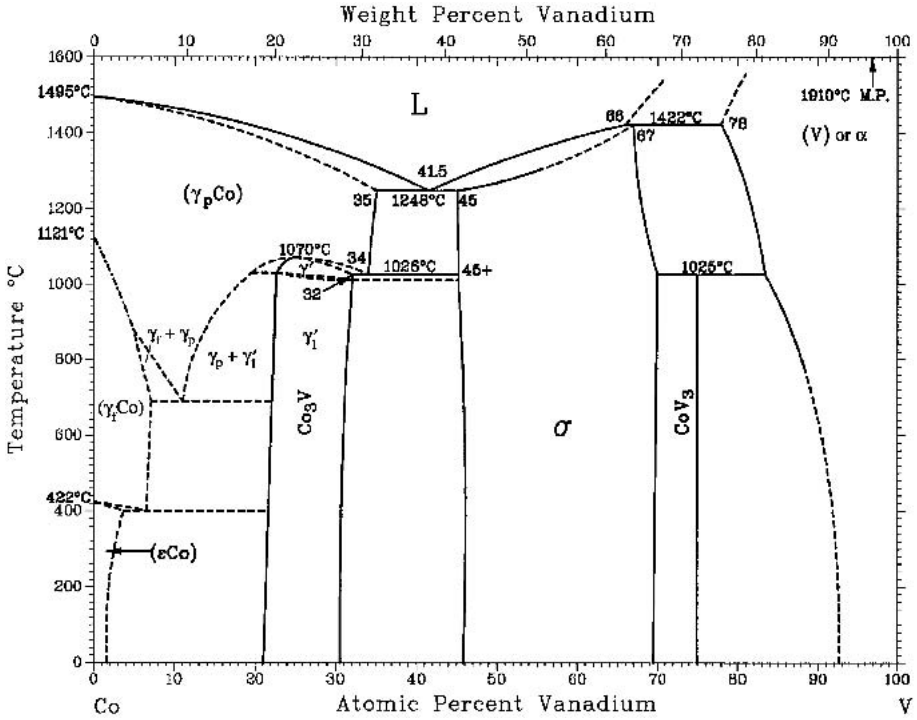

Fig. 2 Co-V binary phase diagram

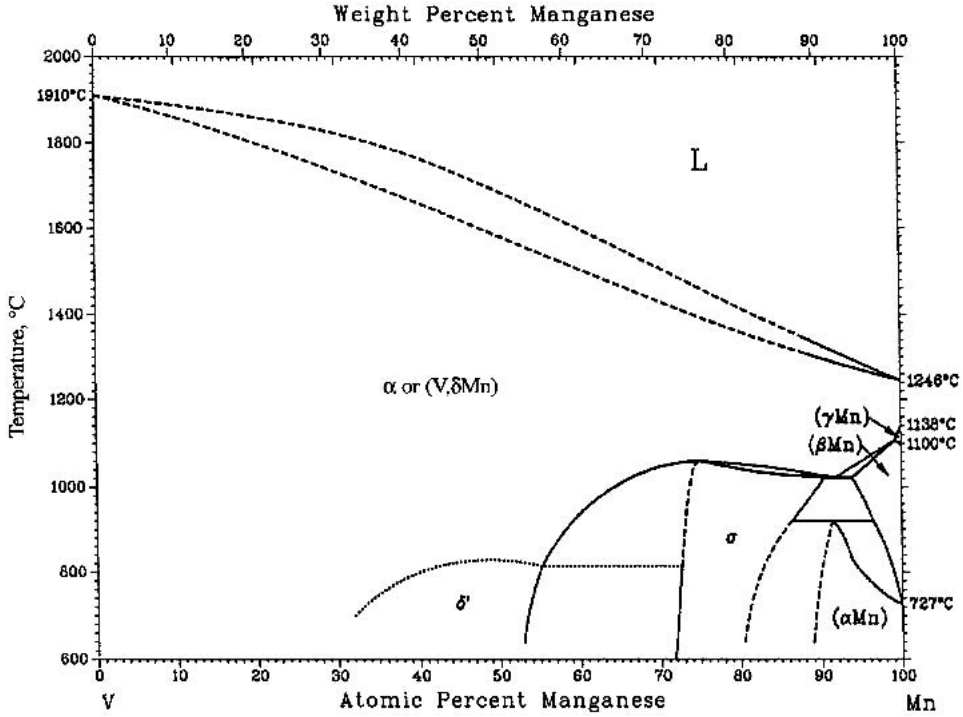

Fig. 3 Mn-V binary phase diagram

δMn in each other, and a simple isomorphous system has been suggested to exist at higher temperatures. The bcc solid-solution α phase undergoes a congruent transformation to σ phase at ~25 at.% V and ~1050 °C. At the Mn end, a peritectoid reaction, α + (γMn) ↔ (βMn), occurs at ~1108 °C, and a eutectoid reaction, α ↔ (βMn) + σ, occurs at ~1020 °C. The (αMn) phase forms through a peritectoid reaction, σ + (βMn) ↔ (αMn), at ~920 °C. The α solid

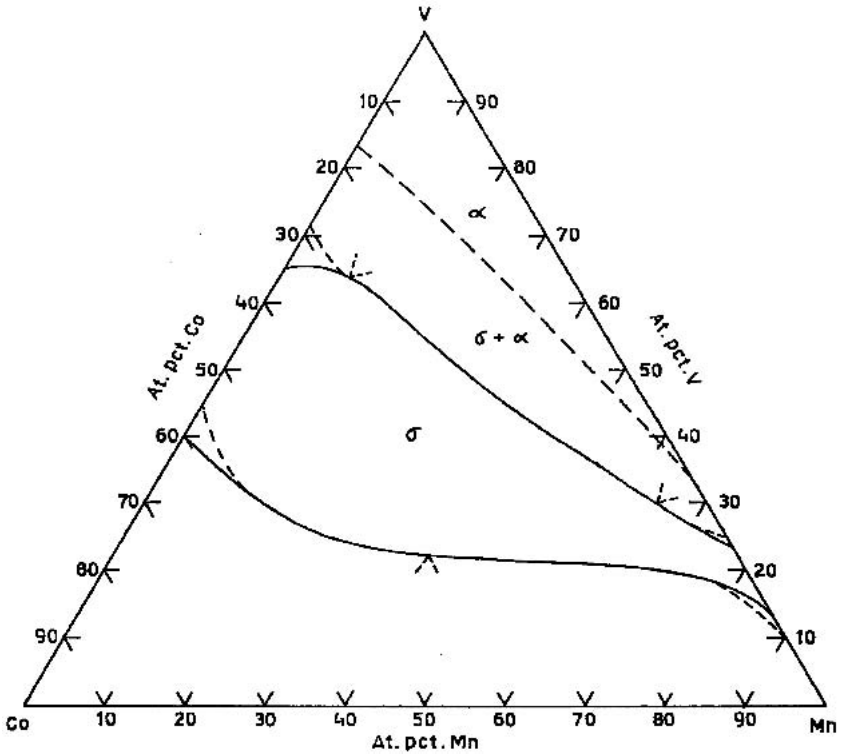

Fig. 4 A partial isothermal section of Co-Mn-V system at 1000°C [1957Dar]. The probable phase boundaries of the σ phase close to the Co-V and Mn-V binaries and the probable phase boundary of the bcc α phase are shown by dashed lines.

Table 1 Binary phases in the Co-Mn, Co-V, and Mn-V systems

Phase designation	Composition	Pearson's symbol	Space group	Type	Lattice parameter, nm	
					a	*c*
γ	(γCo), (γMn)	*cF*4	$Fm\bar{3}m$	Cu	…	…
α	(δMn,V), (δMn)	*cI*2	$Im\bar{3}m$	W	…	…
βMn	(βMn)	*cP*20	$P4_132$	βMn	…	…
αMn	(αMn)	*cI*58	$I\bar{4}3m$	αMn	…	…
ε	(εCo)	*hP*2	$P6_3/mmc$	Mg	…	…
ϕ	CoMn	…	…	(a)	…	…
γ′	Co_3V(h)	*cP*4	$Pm\bar{3}m$	$AuCu_3$	…	…
γ_1'	Co_3V(1)	*hP*24	$P6_3/mmc$	Al_3Pu	0.5032	1.227
σ	CoV(h)	*tP*30	$P4_2/mnm$	σ(CrFe)	0.8843	0.4586
	Mn_4V	…	…	…	0.8918	0.4613
δ′	MnV	*cP*2	$Pm\bar{3}m$	CsCl	…	…

(a) Reported to be σ type

solution phase changes to a δ′ form near ~800 °C at compositions in the range 30-55 at.% after very long annealing [1962Wat, 1963Dar]. The δ′ form is a CsCl-type ordering of the bcc structure analogous to the ordering in β-brass.

Binary and Ternary Phases

At least six intermediate phases form in the three binary systems, Co-Mn, Co-V, and Mn-V. No ternary phase has been reported to form in the Co-Mn-V system. The binary phases and their structure data are given in Table 1.

Ternary System

[1957Dar] studied the boundaries of the σ phase in various V-containing ternary systems, and the Co-Mn-V system was one of them. To prepare the alloys, electrolytic grade Co and Mn and V chips containing ~0.25% impurity

were vacuum induction melted in recrystallized alumina crucibles. The alloys were annealed in sealed, fused silica capsules at 1000 °C for long periods. X-ray diffraction (XRD) and optical microscopic studies of annealed alloys were made for phase identification and phase boundary determination. Only the σ phase boundaries were determined. A partial isothermal section of the Co-Mn-V system at 1000 °C is given in Fig. 4.

This 1000 °C isothermal section of the Co-Mn-V system shows Darby's boundaries [1963Dar] for the σ phase by solid lines. These lines extend continuously across the system from the Co-V binary boundary of the ternary system to the Mn-V binary boundary. The dashed line extrapolations of the Darby boundaries are included to indicate binary intercepts that are more compatible with currently accepted binary phase diagrams. The second phases in the two-phase regions on either side of the σ phase were not identified. However, on the basis of the changes in appearance in the microstructures of the second phase along the σ phase boundaries, the presence of three three-phase equilibria has been suggested: two along the high V boundary and one along the low V boundary of the σ phase. These are indicated in Fig. 4 by short dashed lines that converge at the suggested loci for the corners of the three-phase equilibria. The dashed line across the system in the V-rich region indicates a reasonable estimate of the boundary of the α phase if the formation of CoV_3 did not occur. However, 1000 °C is lower than the 1025 °C indicated as the formation temperature of CoV_3 in the binary phase diagram (Fig. 2), and the existence of a stable CoV_3 phase would be compatible with the existence of a three-phase region on the Co-V side of the diagram with the involvement of CoV_3, α, and σ. The existence of a second three-phase region in the V-rich region between the σ and α phases seems dubious, since there is no evidence for the existence of a ternary compound in the Co-Mn-V system. In comparison, the existence of a three-phase region involving the σ phase on the V-poor side seems quite probable because of the phase separation between (γCo) and (βMn) in the Co-Mn binary system at 1000 °C.

[1959Stu] made an attempt to describe the σ phase on the basis of a sphere-packing model. For this purpose, he measured lattice parameters of various binary and ternary σ phase alloys. For the $Co_{37.2}Mn_{19.9}V_{42.9}$ σ phase alloy, Stüwe reported the lattice parameter to be $a = 0.8901$ nm and $c = 0.4599$ nm.

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