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The Co-Cr-Mo (Cobalt-Chromium-Molybdenum) System

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Introduction

The Co-Cr-Mo system was studied mostly by a group of investigators interested in the crystal chemistry of phases with complex crystal structures related to the σ phase. Two isothermal sections were established and are reported here.

Binary Systems

Two reviews [1990Gup, 1978All] (Fig. 1a) and [Massalski2] (Fig. 1b) of the binary Co-Cr phase equilibria have been published. The resultant phase diagrams are in close accord except in the high Co region at low temperatures. Points of agreement and disagreement between the two reviews are summarized in the binary Co-Cr portion of the article on "The Co-Cr-Ta System" on pages 93-97 of this issue. Since the interest in the present article is concerned with phase equilibria in the Co-Cr-Mo system at temperatures of the order of 1200-1300 °C, there are no relevant or significant differences between the two reviews at the temperatures of interest.

The Co-Mo system [Massalski2] (Fig. 2) has four intermediate phases Co_9Mo_2, Co_3Mo, $Co_7Mo_6(\mu)$, and σ. The σ and μ phases form through peritectic reactions $L + \alpha \leftrightarrow \sigma$ at 1620 °C and $L + \sigma \leftrightarrow \mu$ at ~1510 °C, respectively, where α is the body-centered-cubic (bcc) terminal solid solution of (Mo). A eutectic reaction $L \leftrightarrow \mu + \gamma$ occurs at 1355 °C. Three peritectoid reactions $\mu + \gamma \leftrightarrow Co_9Mo_2$, $Co_9Mo_2 + \mu \leftrightarrow Co_3Mo$, and possibly $\gamma + Co_3Mo \leftrightarrow \varepsilon$, occur at 1200, 1025, and ~700 °C, respectively. The Co_9Mo_2 and σ phases undergo eutectoid decomposition, $Co_9Mo_2 \leftrightarrow \gamma + Co_3Mo$ at 1018 °C and $\sigma \leftrightarrow \alpha + \mu$ at ~1000 °C.

The Cr-Mo system [1987Ven] (Fig. 3) is an isomorphous system with a minimum of 1820 °C at 12.5 at.% Cr. The bcc α solid solution of (Mo,Cr) has a miscibility gap below ~800 °C.

Binary and Ternary Phases

Eight intermediate phases have been reported to form in the Co-Cr, Co-Mo, and Cr-Mo binary systems. One ternary intermediate phase forms in the Co-Cr-Mo system. The phases and their structure data are given in Table 1.

Ternary System

The Co-Cr-Mo system was first studied by [1951Rid] at 1200 °C in the composition region up to ~65 mass% Cr and ~65 mass% Mo. The alloys were induction melted under a (He + 8% H_2) gas mixture in zirconia or alumina crucibles using elemental purities of 98.8 mass% Co, 99.27 mass% Cr, and 99.99 mass% Mo. The alloys that could be forged were annealed at 1200 °C for 90-120 h, and the others were annealed at the same temperature for 150 h. Metallography and x-ray diffraction (XRD) methods were used for identification as well as for the delineation of phase boundaries.

The 1200 °C isothermal section of the Co-Cr-Mo system is shown in Fig. 4. The isothermal section shows extensions of the σ phase from the Co-Cr binary and the μ phase from the Co-Mo binary, to ~30 mass% Mo and to ~10 mass% Cr, respectively, as narrow phase regions trending toward each other, roughly along a line of ~41 mass% Co. Between the two extended phase regions of the σ and μ phases, a ternary intermediate phase R was found to exist in the composition ranges of ~39-44 mass% Co and ~38-43 mass% Mo, respectively. The face-centered-cubic (fcc) γ-phase boundary was determined and shows a maximum solubility of Mo ~21 mass%. The bcc α-phase boundary was not determined.

Since it was known at the time of investigation of the 1200 °C isothermal section that a σ phase exists in the Co-Mo system above 1250 °C, an isothermal section at 1300 °C was established by [1955Dar] (Fig. 5) with a view to find whether the σ phase of the Co-Cr system extends toward the σ phase existing in the Co-Mo system. In this investigation, the alloys were mostly melted by vacuum induction, and high Mo alloys were arc melted and annealed for 72-240 h. Metallography and XRD were used for phase identification as well as phase boundary determination. The isothermal section of Fig. 5 shows a wide σ phase region extending from the Co-Cr to the Co-Mo binary. Near the Co-Mo binary, the σ phase boundary could not be determined accurately because of the segregation of phases in the alloys. The μ phase region was also not determined well; the approximate location of the μ phase boundary is given in Fig. 5 on the basis of the amount of μ phase found in several two-phase alloys. Between the σ and μ phase regions, [1955Dar] reported the presence of a new intermediate phase D, the XRD pattern of which showed some similarities with that of the R phase found at 1200 °C.

The differences in the XRD patterns of the R and D phases were rather small. While the major diffraction lines in the XRD patterns of the R and D phases were the same, a few weak and very weak diffraction lines in the two XRD patterns did not match. In order to check whether the R and D phases were two different phases, [1958Dar] used an alloy with 43 mass% Co, 16 mass% Cr, and 41 mass% Mo, which lies in the R phase region at 1200 °C and in the D phase region at 1300 °C, reannealed them at 1200 and 1300 °C and XRD patterns were taken. Both of the XRD patterns were found to be the same, indicating that the D phase is the same as the R phase.

[1959Stu] made an attempt to describe the σ-phase on

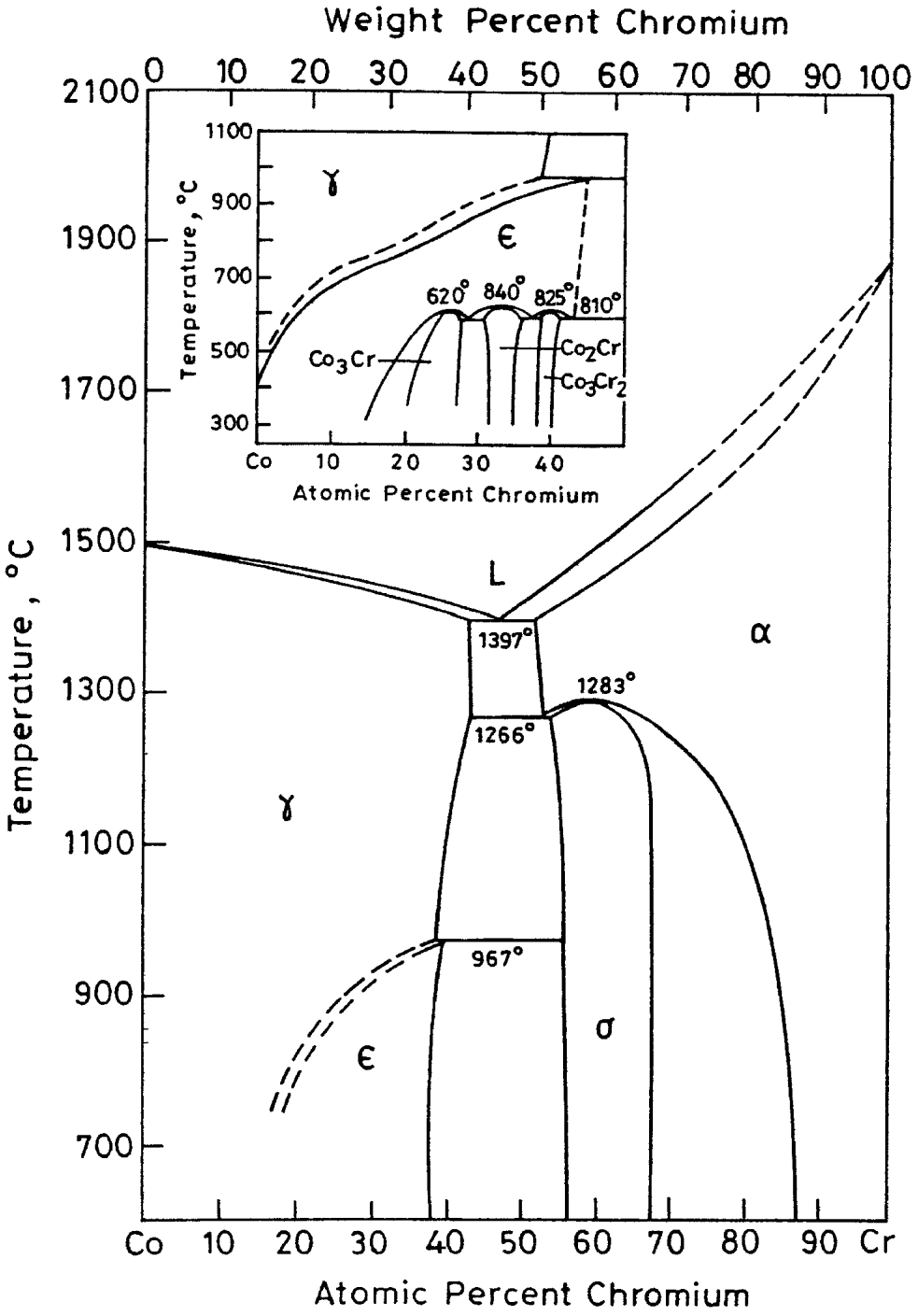

Fig. 1(a) Co-Cr binary phase diagram [1978All, 1990Gup]

the basis of a sphere-packing model. For this purpose, he measured the lattice parameters of various σ-phase alloys. For the Co-Cr-Mo system, he used a σ-phase alloy of composition $Co_{47.5}Cr_{31}Mo_{21.5}$, and the lattice parameter for this alloy was reported to be $a = 0.8916$ nm and $c = 0.4627$ nm.

[1965Dra] studied the aging characteristics of Co containing up to 25 mass% Cr and 25 mass% Mo. The alloys were arc melted from pure metals (Co 99.9 mass%, Cr 99.35 mass%, and Mo 99.9 mass%), annealed at 1200 °C for 1000 h in sealed quartz capsules, and water quenched. Aging of the alloys was done at 600, 700, 800, and 1000 °C for 250-2 h depending on the temperature. The hardness of the alloys increased with an increase in Cr and Mo content

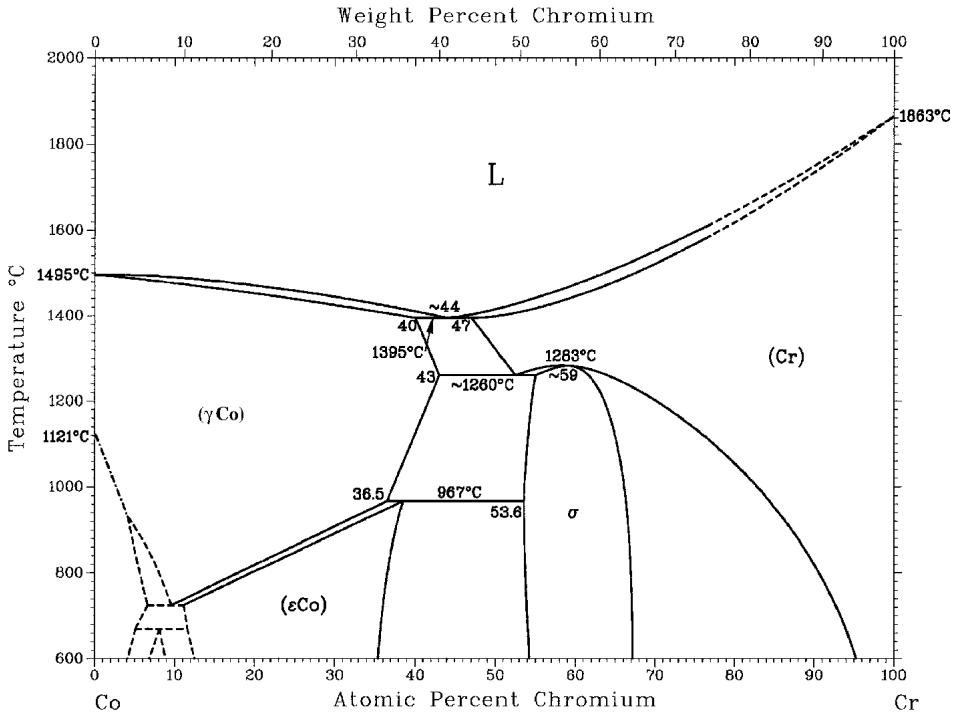

Fig. 1(b) Co-Cr binary phase diagram [Massalski2]

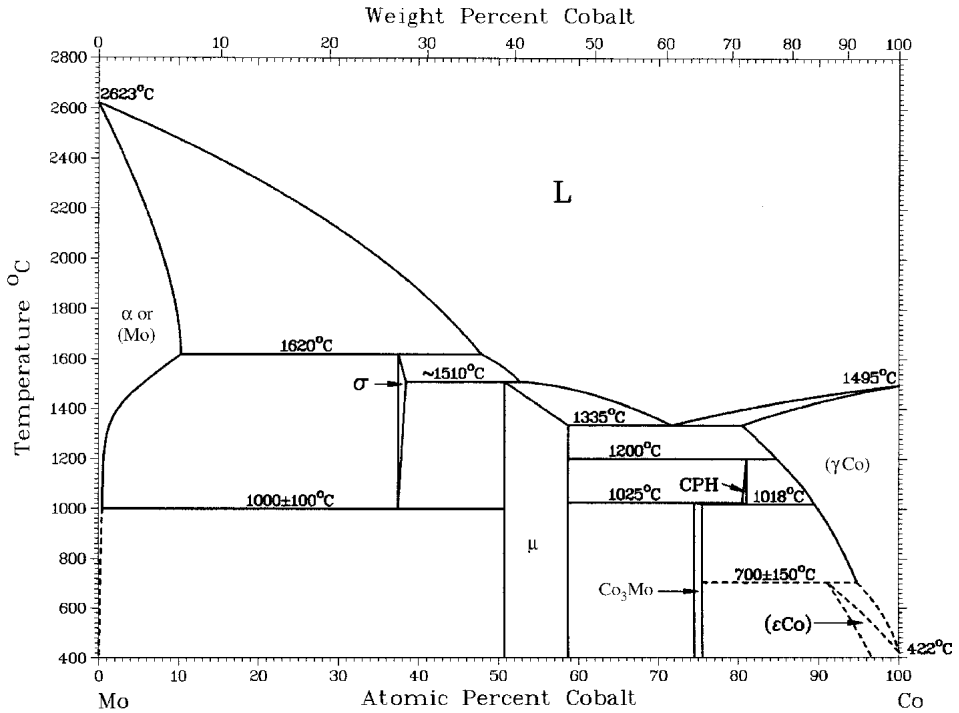

Fig. 2 Co-Mo binary phase diagram [Massalski2]

due to an increase in the volume of the precipitated phase. A more detailed study was made with an alloy containing 67 mass% Co, 18 mass% Cr, and 15 mass% Mo.

Maximum hardness was produced in this alloy after aging for 100 h at 800 °C. The precipitated phase is the R phase in close-packed-hexagonal (cph) (εCo) matrix. At

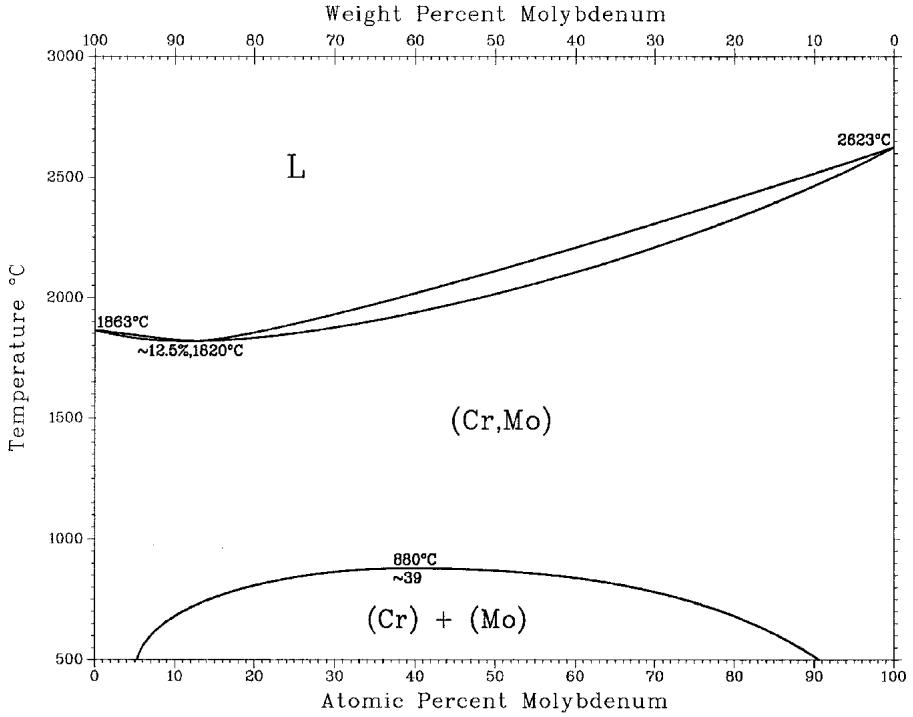

Fig. 3 Cr-Mo binary phase diagram [1987Ven]

Table 1 Binary and ternary phases of the Co-Cr-Mo system and their structure data

Phase designation	Composition	Pearson's symbol	Space group	Type	Lattice parameters, nm	
					a	*c*
α	(Cr), (Mo), (Cr,Mo)	*cI*2	$Im\bar{3}m$	W	…	…
γ	(γCo)	*cF*4	$Fm\bar{3}m$	Cu	…	…
ε	(εCo)	*hP*2	$P6_3/mmc$	Mg	…	…
σ	Cr_8Co_7	*tP*30	$P4_2/mnm$	σ(Fe,Cr)	0.8758	0.4536
	Co_9Mo_{15}				0.92287	0.48269
Co_3Cr	Co_3Cr	*hP*8	$P6_3/mmc$	Ni_3Sn	0.5028	0.4034
Co_2Cr	Co_2Cr	…	…	…	…	…
Co_3Cr_2	Co_3Cr_2	…	…	…	…	…
π	Co_9Mo_2	*h*	…	…	…	…
κ	Co_3Mo	*hP*8	$P6_3/mcm$	Ni_3Sn	0.51245	0.41125
μ	Co_7Mo_6	*hR*13	$R\bar{3}m$	Fe_7W_6	0.4762	2.5015(a)
R	$Co_{49}Cr_{21}Mo_{30}$	*hR*53	$R\bar{3}$	R(Co,Cr,Mo)	1.0903	1.9342(a)

(a) Lattice parameters for hexagonal cell

1000 °C, the matrix was found to be fcc (γCo). Thermal analysis showed the transition temperature to be ~900 °C.

The phase diagrams of Fig. 4 and 5 agree with the binary phase diagram information at the time of investigations made between 1955 and 1958. More recent data on Co-Cr and Co-Mo systems (Fig. 1 and 2), however, indicate that the phase boundary compositions of the σ, γ, and α phases are quite different from the earlier known data and that the σ phase is stable only below 1283 °C in the Co-Cr system and above 1000 ± 100 °C in the Co-Mo system. Thus, the phase boundaries shown in Fig. 4 and 5 need modification. Since the σ phase is not stable above 1283 °C in the Co-Cr system, at 1300 °C, the σ phase should have a three-phase equilibrium with α and γ phases at 1300 °C in the region of the Co-Cr binary. The probable 1300 °C isothermal section is given in Fig. 6. This suggested modification should be experimentally established. At 1200 °C, the σ phase region in the Co-Cr system is much wider. Also the σ phase is to be expected to extend toward the σ phase region of the Co-Mo system. At present, no other data are available for the Co-Cr-Mo system, and simple phase boundary adjustments may not be proper for the 1200 °C isothermal section.

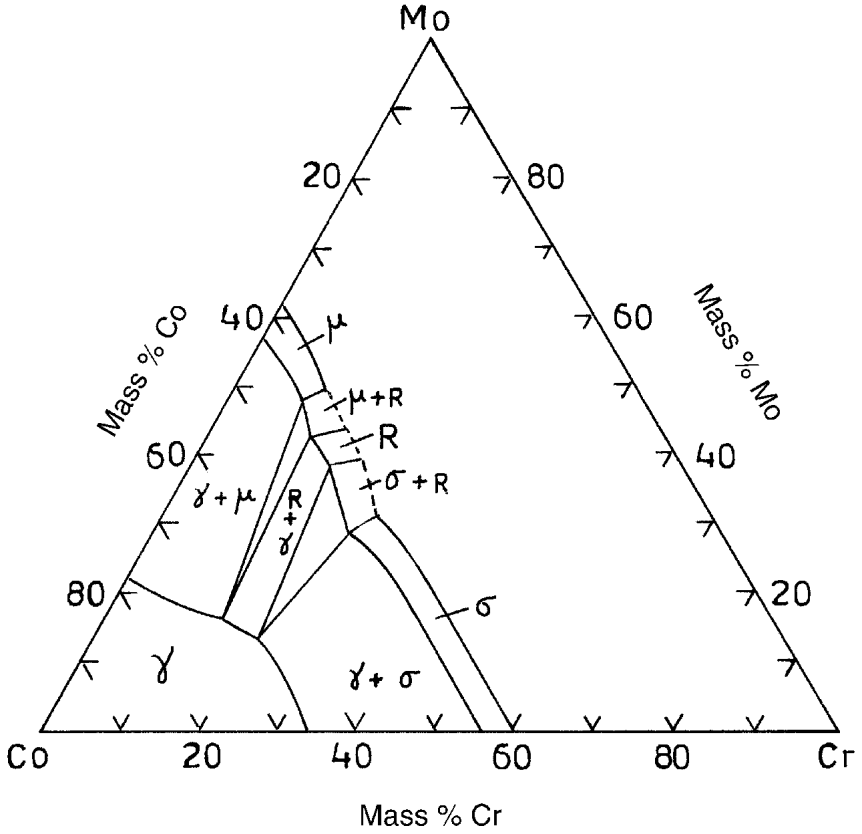

Fig. 4 A partial isothermal section of Co-Cr-Mo system at 1200 °C [1951Rid]

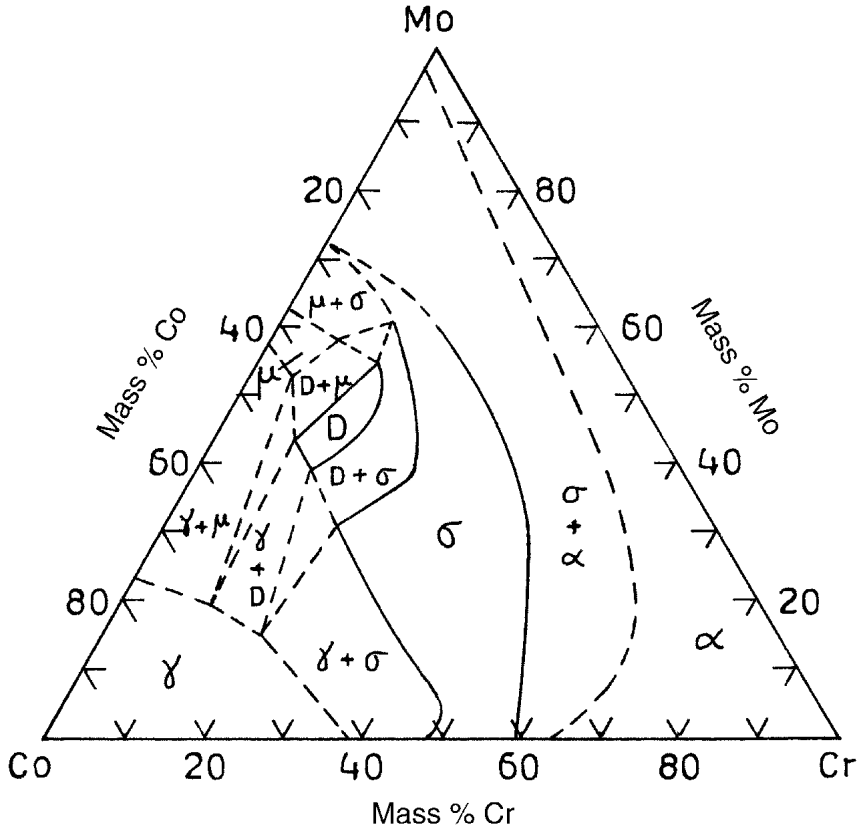

Fig. 5 An isothermal section of Co-Cr-Mo system at 1300 °C [1955Dar]

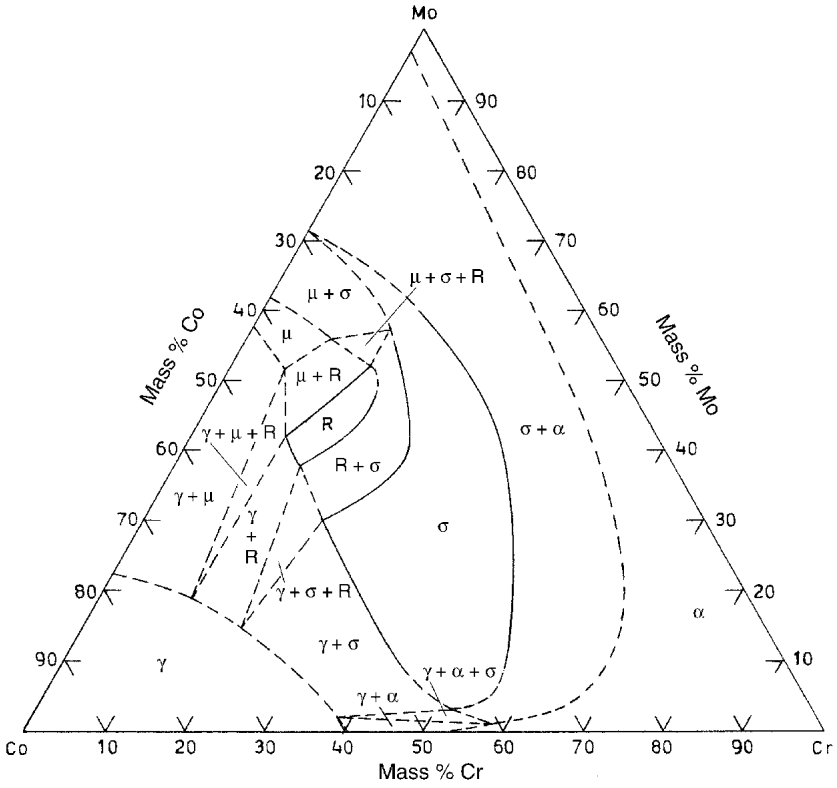

Fig. 6 A probable 1300 °C isothermal section of Co-Cr-Mo system

The 1200 °C isothermal section on the high Cr and high Mo sides of the Co-Cr-Mo system should be reinvestigated using arc-melted alloys and longer annealing times to achieve proper phase equilibrium.

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# Indicates presence of phase diagram.

Co-Cr-Mo evaluation contributed by **K.P. Gupta,** The Indian Institute of Metals, Metal House, Plot 13/4, Block AQ, Sector V, Calcutta, India. Literature searched through 1993. Dr. Gupta is the Alloy Phase Diagram Co-Category Program Editor for ternary nickel alloys.