

The Co-Cr-W (Cobalt-Chromium-Tungsten) System

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Introduction

The Co-Cr-W system has been investigated to establish an isothermal section, and a study of aging characteristics of Co-rich alloys has been made. The existence of a ternary R phase has been reported in the Co-Cr-W system.

Binary Systems

The Co-Cr phase diagram [1978All, Massalski2] (Fig. 1) shows a simple eutectic system with a eutectic reaction $L \leftrightarrow \alpha + \beta_2$ occurring at 1395 °C. The α and β_2 phases are the terminal solid solutions of Cr in face-centered cubic (fcc) α Co and Co in (Cr), respectively. In the wide β_2 phase field $\beta_2 \leftrightarrow \sigma$ congruent transformation occurs at 1280 °C. A eutectoid reaction $\beta_2 \leftrightarrow \alpha + \sigma$ occurs at ~1260 °C. A peritectoid reaction $\alpha + \sigma \leftrightarrow \epsilon$, where ϵ is the hexagonal close-packed (hcp) terminal solid solution of Cr in ϵ Co, occurs at 967 °C. In the wide ϵ -phase field, the existence of three intermediate phases, Co_3Cr , Co_2Cr , and Co_3Cr_2 , has been suggested by [1961Gri] to form through congruent transformations at 620, 640, and 625 °C, respectively. This lower-temperature Co-rich region is highly questionable because

of sluggish kinetics, and the diagram of [Massalski2] indicates the uncertainty.

The Co-W system [Massalski2] (Fig. 2) shows the presence of two intermediate phases, Co_7W_6 (μ) and Co_3W (κ). The μ phase forms through a peritectic reaction $L + (\text{W}) \leftrightarrow \mu$ at 1689 °C, and the κ phase forms through a peritectoid reaction, $\alpha + \mu \leftrightarrow \kappa$ at 1093 °C. A eutectic reaction, $L \leftrightarrow \alpha + \mu$, occurs at 1471 °C. The α phase melts congruently at 1505 °C and ~10 at.% W. The Cr-W system [Massalski2] (Fig. 3) is an isomorphous system. A wide miscibility gap exists in the bcc β phase below the critical point at 1677 °C, and gives the W-rich β_1 and Cr-rich β_2 phases.

Binary and Ternary Phases

In the three binary systems Co-Cr, Co-W, and Cr-W, three intermediate phases exist (or six if the three phases reported by [1961Gri] are included). A ternary intermediate phase, R, has been reported in the Co-Cr-W system at an approximate stoichiometry of $\text{Co}_{23}\text{Cr}_{15}\text{W}_{15}$. The structure data for the binary and ternary phases are given in Table 1.

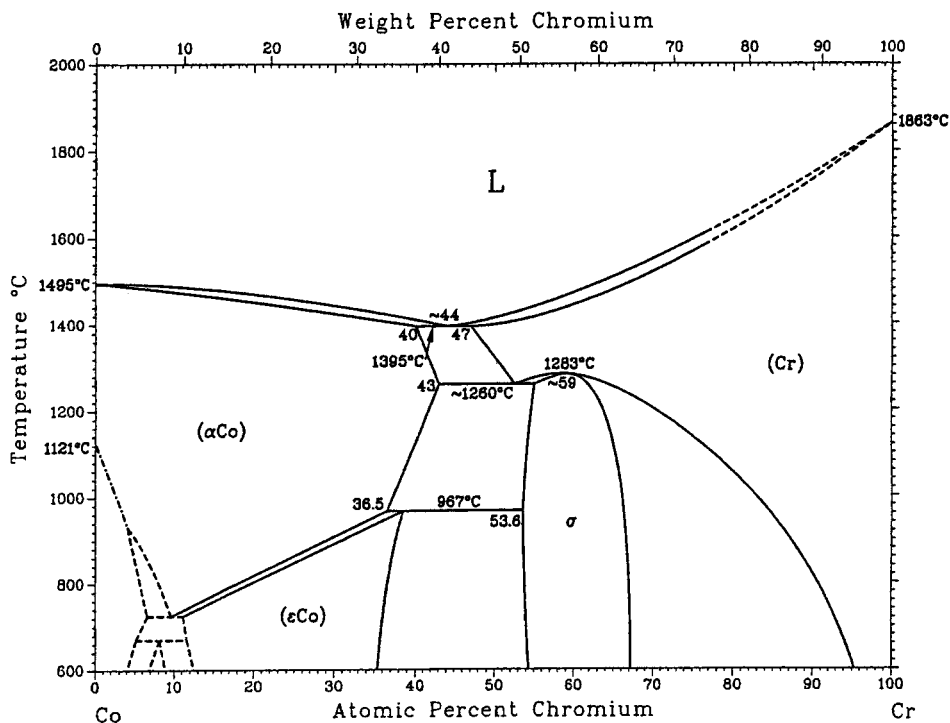


Fig. 1 Co-Cr binary phase diagram [Massalski2]

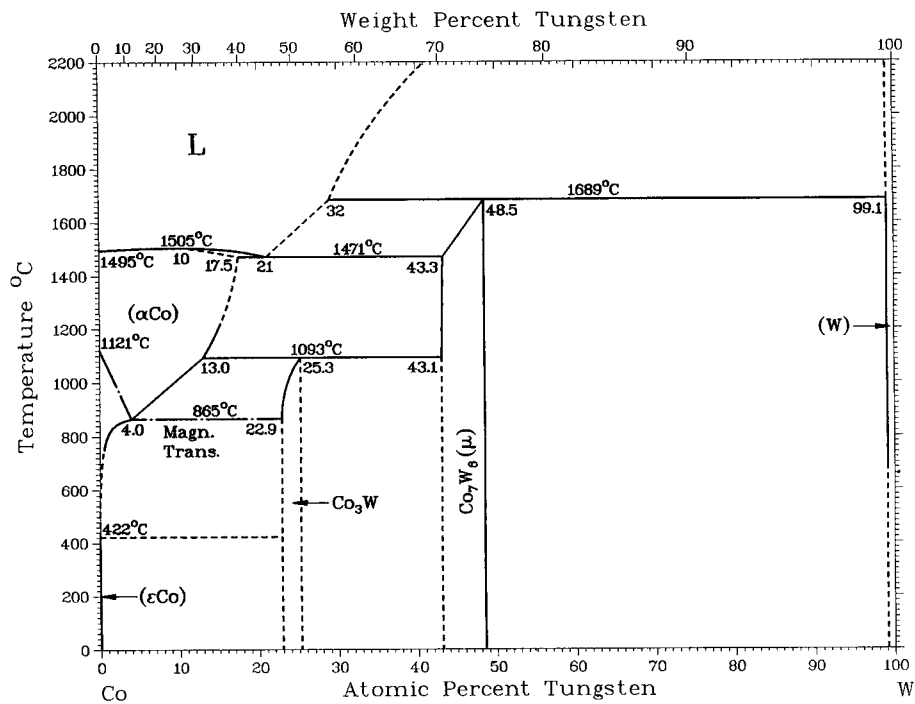


Fig. 2 Co-W binary phase diagram [Massalski2]

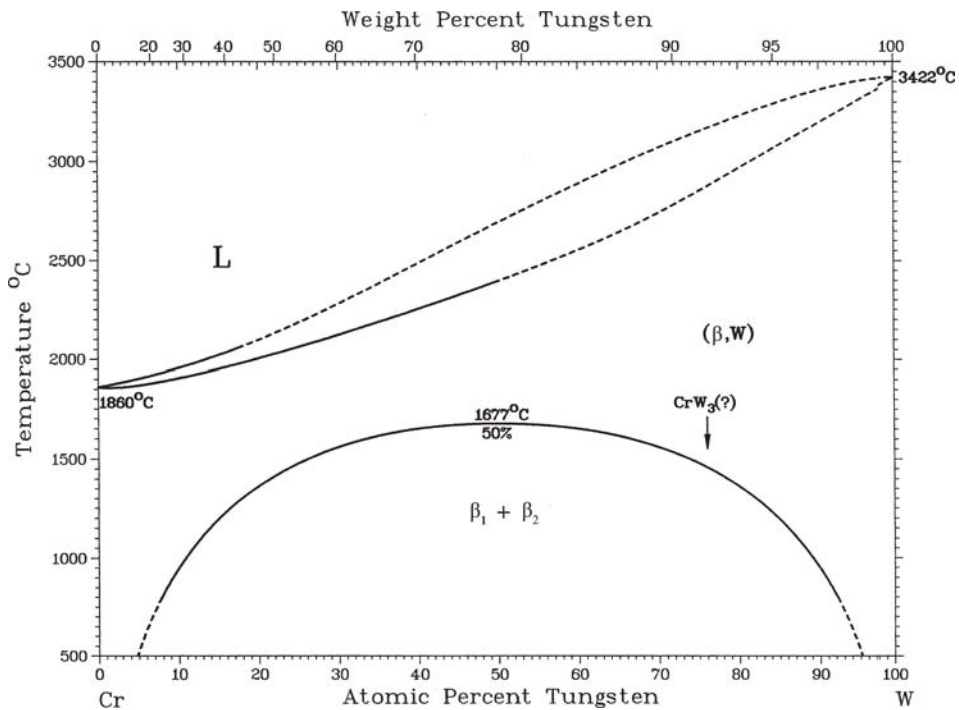


Fig. 3 Cr-W binary phase diagram [Massalski2]

Ternary Systems

The Co-Cr-W system was investigated by [1965Dra] to establish a part of the fcc α phase boundary and to study the aging characteristics of some Co-Cr-W alloys. Alloys in the composition region up to 25 wt.% Cr and 35 wt.% W were

prepared by arc melting pure component elements (99.9 mass% Co, 99.35 mass% Cr, and 99.8 mass% W). The melting atmosphere was not mentioned. The alloys were sealed in quartz capsules, annealed at 1200 °C for 1000 h, and lastly water-quenched. For the study of aging characteristics, the solution treated (at 1200 °C) and quenched

Section II: Phase Diagram Evaluations

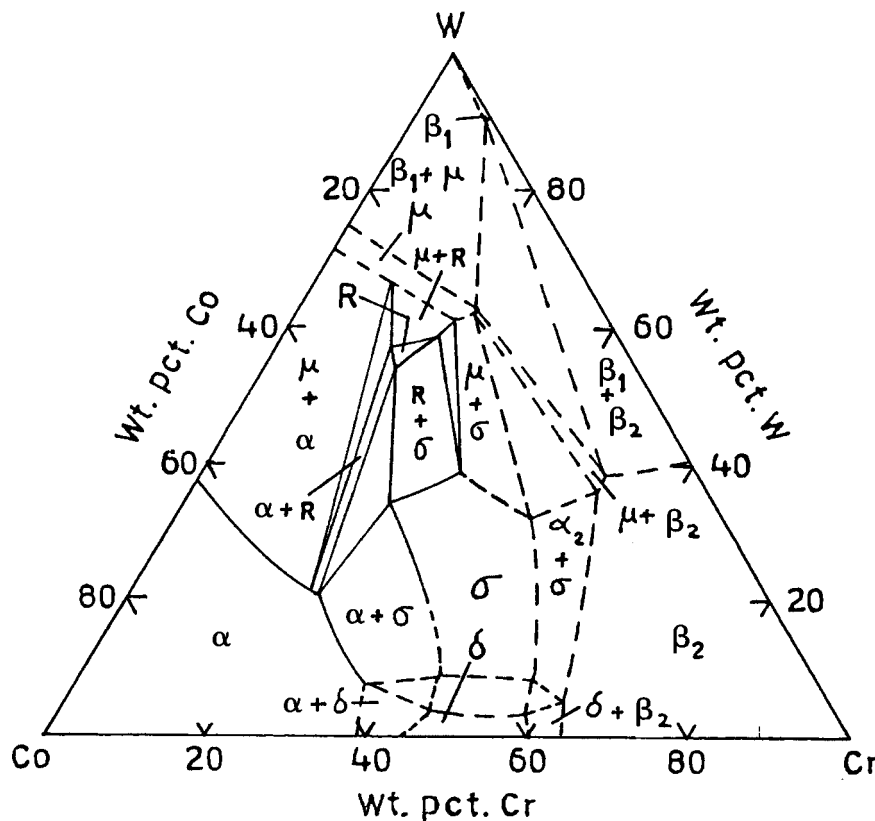


Fig. 4 An isothermal section of the Co-Cr-W system at 1350 °C

Table 1 Binary and ternary phases of the Co-Cr-W system

Phase designation	Composition	Pearson symbol	Space group	Type	Lattice parameter, nm		
					a	b	c
β	(W, Cr)	<i>cI2</i>	$Im\bar{3}m$	W
β_1	(W,Co), (W,Cr)	<i>cI2</i>	$Im\bar{3}m$	W
β_2	(Cr,Co), (Cr,W)	<i>cI2</i>	$Im\bar{3}m$	W
α	α Co	<i>cF4</i>	$Fm\bar{3}m$	Cu
ϵ	ϵ Co	<i>hP2</i>	$P6_3/mmc$	Mg
σ	Co_7Cr_8	<i>tP30</i>	$P4_2/mnm$	σ (Cr,Fe)	0.8758	...	0.4536
μ	Co_7W_6	<i>hR13</i>	$R\bar{3}m$	Fe_7W_6	0.4761	...	2.572(a)
κ	Co_3W	<i>hP8</i>	$P6_3/mmc$	Ni_3Sn	0.5130	...	0.4128
R	$Co_{23}Cr_{15}W_{15}$	<i>hR53</i>	$R\bar{3}$	R(Co,Cr,Mo)	1.08819	...	1.92536(a)(b)
π	Co_3Cr	<i>hP8</i>	$P6_3/mmc$	Ni_3Sn	0.5028	...	0.4034
γ	Co_2Cr
ρ	Co_3Cr_2

(a) Lattice parameter for hexagonal cell. (b) Lattice parameter for $Co_{29.9}Cr_{16.3}W_{53.8}$ R phase [1972Bar]

alloys were aged at 600, 700, 800, and 1000 °C for 2 to 250 h. Alloy characterization was done using optical microscopy, x-ray diffraction (XRD), hardness measurement, and transmission electron microscopy.

Metallography of alloys annealed at 1200 °C for 1000 h was used to determine the solubility limit of the α phase at 1200 °C; this is shown in Fig. 5 which is later discussed in more detail. The second and third phases present in the high Cr and high W in all the alloys were not identified.

The aging of alloys at different temperatures showed an

increase in hardness with an increase in Cr and W content of the alloys. The maximum hardness was obtained for all alloys at 800 °C. Most of the alloys showed the presence of both fcc α and hcp ϵ phases, and the precipitated phase was usually Co_3W . The highest Cr and W content alloy, however, showed the presence of a new phase. Electron probe microanalysis (EPMA) and XRD of this phase showed it to be of Co_4Cr_3W stoichiometry with a tetragonal structure having lattice parameters $a = 0.655$ nm and $c = 0.471$ nm. A detailed investigation of aging was carried out with one

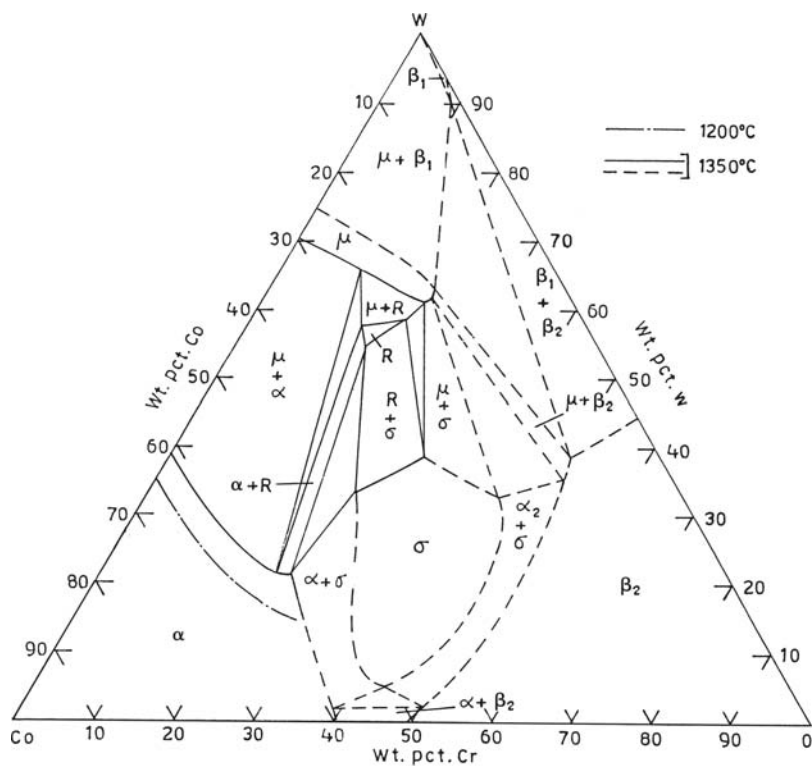


Fig. 5 Proposed modification of the isothermal section of the Co-Cr-W system at 1350 °C

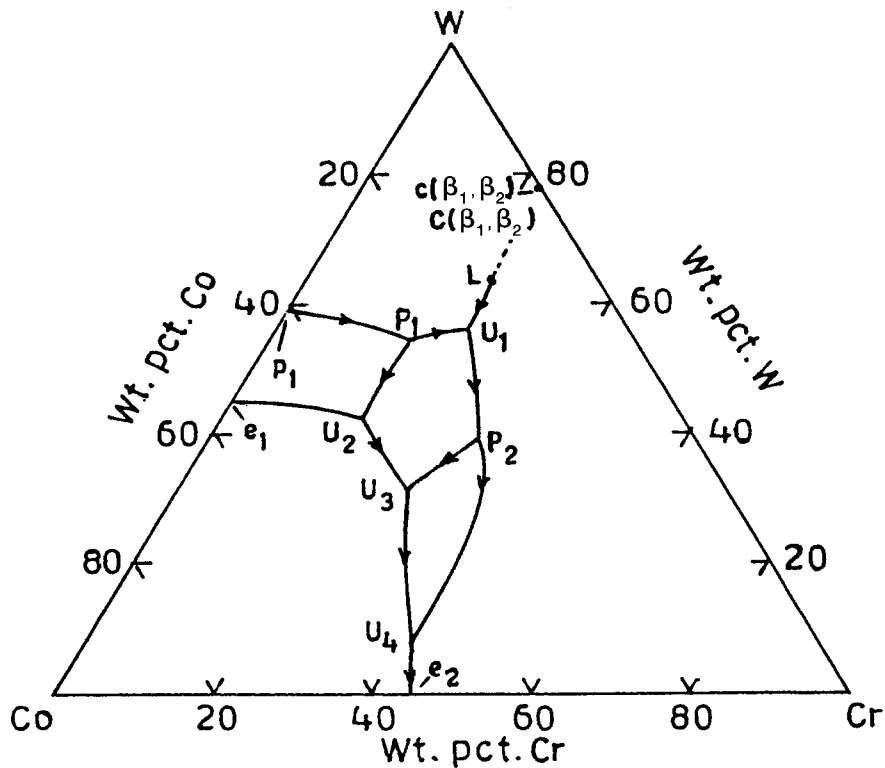


Fig. 6 A proposed liquidus projection (schematic) for the Co-Cr-W system

alloy containing 15 wt.% Cr and 15 wt.% W. The solution-treated alloy (1200 °C, 2 h) was aged at 600, 700, 800, and 1000 °C for 2 to 100 h. Maximum hardness was achieved at

800 °C in 100 h. At 800 °C, the alloy consisted of both an fcc α phase as well as hcp ϵ phase with Co_3W -precipitated phases. The hardness increase of the alloy is due to the

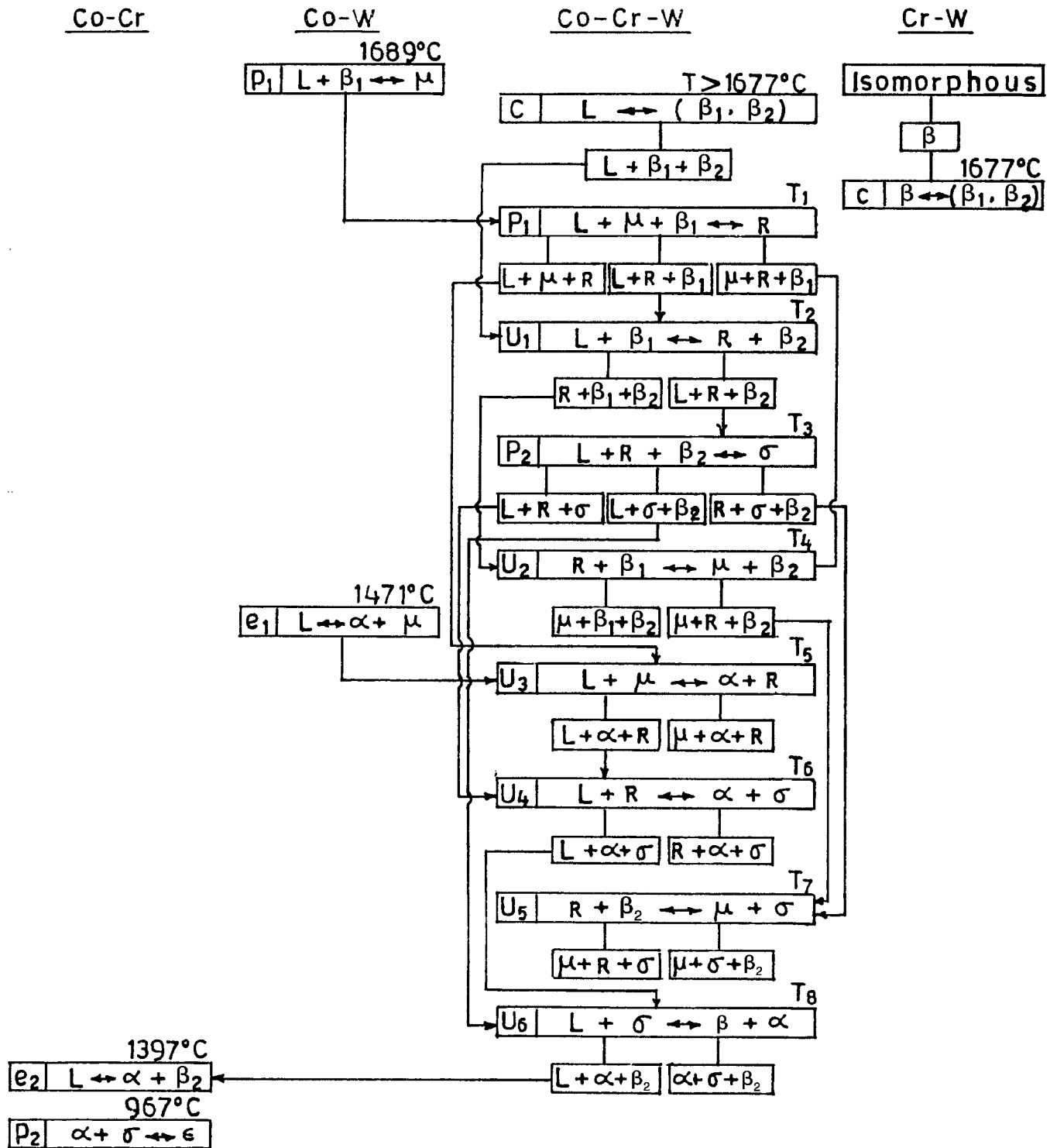


Fig. 7 Reaction scheme for the Co-Cr-W system

precipitated Co_3W phase. Transmission electron microscopy of the alloy aged at 700 °C for 100 h showed the precipitation of the Co_3W phase only in the hcp ϵ phase. Electron diffraction patterns indicated an epitaxial relationship between the ϵ and Co_3W phases: $[10\bar{1}2]_\epsilon \parallel [10\bar{1}1]_\kappa$, and $[12\bar{1}0]_\epsilon \parallel [12\bar{1}02]_\kappa$. The coherence relationship between the ϵ and κ phase is simple; the c parameters of the two

phases are approximately equal, and the a parameters are in the ratio 1:2, respectively.

[1972Bar] studied the Co-Cr-W system in somewhat more detail. High-purity elements (with 0.001 mass% impurities) were arc-melted under a Zr-gettered argon atmosphere. The alloys, which were placed on alumina boats, were annealed at 1350 ± 10 °C in a flowing Zr-gettered

argon atmosphere for 44 h (annealing for up to 210 h did not produce any significant changes in the microstructure of alloys). The annealed alloys were characterized with optical microscopy, microhardness measurement, XRD of powdered alloys as well as of residues left after electrolytic dissolution of some alloy samples, and EPMA. An isothermal section was constructed on the basis of analyses of the alloys and is given in Fig. 4, which used the available binary data available at the time of investigation.

The isothermal section at 1350 °C (Fig. 4) was established [1972Bar] with data from the investigated alloys containing up to 34 wt.% Cr and 65 wt.% W. The presence of an R-phase region was detected around the alloy composition 27.7 wt.% Co, 16.4 wt.% Cr, and 55.9 wt.% W, and the R phase was found to be in equilibrium with the μ , σ , and α phases. The μ phase extends from the Co-W binary up to 21 wt.% Cr. For the higher Cr and higher W regions the expected phase equilibria, on the basis of the binary data available at that time, is shown in Fig. 4. The Co-Cr diagram [Hansen] shows the presence of a δ phase at temperatures above 1300 °C, and a σ phase at temperatures below 1300 °C. On that basis, the probable phase equilibria involving the δ phase is given in Fig. 4. The accepted binary diagram of the Co-Cr system described earlier does not have a δ phase. The σ phase in the Co-Cr system forms from the bcc β_2 phase through a congruent transformation at 1283 °C. The σ phase of the Co-Cr-W system is thus an extension of the binary σ phase that is stabilized to higher temperatures when W is added to Co-Cr alloys. The 1350 °C isothermal section given in Fig. 4 has to be modified, and the expected phase equilibria in Co-Cr-W system is given in Fig. 5.

[1972Bar] used a few alloys close to the α phase boundary with a Cr content of ~22 to 25 wt.% and a W content of ~20 wt.% to see whether the R phase is stable at other temperatures and how the α phase boundary changes with temperature. The volume fractions of the minor phases in some of the alloys close to the α phase boundary of the composition mentioned above were measured after long annealing at 1350 °C (215 h) and then at 1380 °C (150 h). At 1380 °C, there was a considerable decrease in the volume fraction of the minor phases, indicating that the α phase region expands with the increase in temperature. This trend is in agreement with the α phase boundary locations given in Fig. 5 at 1200 and 1350 °C. The three-phase region $\alpha + \sigma + R$ of an alloy at 1350 °C was also found to change to $\alpha + R$ region at 1380 °C, indicating a shift of the phase regions toward higher Cr contents. The same alloys annealed at 1200 °C for 1000 min and at 800 °C for 72 h also indicated the R phase to be stable at these temperatures without any change in the amount of the phase. An alloy with 23.2 wt.% Cr and 23.6 wt.% W at 1350 °C was found to have three phases of $\alpha + R + \sigma$. This alloy, on annealing at 1400 °C for 35 h and quenching in water, showed primary α and R phases and a small amount of liquid phase. The liquid phase on quenching gave a very fine eutectic structure. The phases of this eutectic structure could not be identified, but EPMA gave an average composition of the eu-

tectic region in the $\alpha + \sigma$ region. [1972Bar] suggested that the eutectic structure results from a U-type reaction, $R + L \leftrightarrow \alpha + \sigma$, occurring close to 1400 °C. These results thus suggest the R phase is stable over a wide temperature range and forms through a reaction involving the liquid phase.

The isothermal section based on the data of [1972Bar] (Fig. 5) and the observed change of phase in a few alloys with increases in temperature [1972Bar] can be used to show the possible reactions that may take place involving the liquid phase and to show how the proposed phase equilibria for the high-Cr and high-W side of the Co-Cr-W system develops. For this purpose, we have to make a few assumptions:

- The R phase forms through a reaction involving the liquid phase.
- The σ phase also forms through a reaction involving the liquid phase.
- A critical reaction, $L \leftrightarrow (\beta_1, \beta_2)$ should occur in the ternary; that is, the critical point $c(\beta_1, \beta_2)$ of the Cr-W binary system should rise with the addition of Co to a ternary critical point $C(\beta_1, \beta_2)$, and at this critical point β_1 and β_2 merge to come into equilibrium with liquid L.

A schematic liquidus projection for the Co-Cr-W system, based on these assumptions, is given in Fig. 6, and the corresponding reaction scheme is given in Fig. 7. P_1 and P_2 are the two ternary peritectic-type reactions through which the R and σ phases are proposed to form, respectively. The liquid composition finally terminates at the eutectic point e_2 of the Co-Cr binary.

The reaction scheme of Fig. 7 not only shows the reactions involving the liquid phase but it also shows the reactions involving solid phases that lead to the formation of the $\mu + \beta_1 + \beta_2$, $\mu + \sigma + \beta_2$, and $\mu + R + \sigma$ three phase equilibrium regions through the reactions U_2 and U_5 . All of the phase regions observed experimentally and those proposed by [1972Bar] can be accounted for completely on the basis of the reaction scheme of Fig. 7. Experimental investigation of the Co-Cr-W system should be carried out to verify the assumptions made and the liquidus projection and reaction scheme proposed.

References

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Indicates presence of phase diagram.

Co-Cr-W 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 1996. Dr. Gupta is the Alloy Phase Diagram Co-Category Program Editor for ternary nickel alloys.