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The Co-Cr-Nb (Cobalt-Chromium-Niobium) System

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Introduction

Very little work has been done in the Co-Cr-Nb system. Only a part of the face-centered cubic (fcc) (αCo) solid solution phase boundary has been established at high temperature and a study of mechanical properties after aging of low Cr and low Nb containing alloys have been reported.

Binary Systems

There exist two reviewed phase diagrams for the Co-Cr system, one by [1990Gup] (based on the experimental data of [1978All] and [1961Gri]) (Fig. 1) and the other by [Massalski2] (based on the experimental data of [1978All] and thermodynamic calculations by several investigators) (Fig. 2), which are more or less the same at temperatures higher than 900 °C but show differences at lower temperatures. The Co-Cr system is a single eutectic system with a eutectic reaction L ↔ (αCo) + (Cr) at 1397 °C [1990Gup] or 1395 °C [Massalski2]. The σ phase forms from the (Cr) solid solution through a congruent transformation at 1283 °C. The (Cr) solid solution further undergoes a eutectoid transformation (Cr) ↔ (αCo) + σ at 1266 °C (Fig. 1) or ~1260 °C Fig. 2. A peritectoid reaction (αCo) + σ ↔ (ϵCo) occurs at 967 °C. Thermodynamic calculations suggest a transformation involving the (αCo) and (ϵCo) ferromagnetic and paramagnetic states (Fig. 2). In the wide (ϵCo) phase region, [1961Gri] suggested the existence of three intermediate phases. Co_3Cr, Co_2Cr, and Co_3Cr_2 with congruent transformation temperatures of ~620, ~640, and ~625 °C, respectively (Fig. 1). [1969Sin] confirmed the existence of the Co_3Cr phase.

The Co-Nb system [Massalski2] (Fig. 3) shows three intermediate phases, Co_3Nb, Co_2Nb, and Co_6Nb_7 (μ), of which the Co_2Nb and μ phases melt congruently at 1480 and 1402 °C, respectively. The Co_3Nb phase forms through a peritectic reaction L + Co_2Nb ↔ Co_3Nb at 1247 °C. Three eutectic reactions L ↔ (αCo) + Co_3Nb, L ↔ Co_2Nb + μ, and L ↔ μ + (Cr) occur at 1237, 1278, and 1374 °C, respectively.

The Cr-Nb system (Fig. 4) [Massalski 2] has one intermediate phase, Cr_2Nb, with two polymorphic forms. The Cr_2Nb (H) phase melts congruently at 1770 °C, and the Cr_2Nb (L) phase exists down to room temperature. The transition temperature for the Cr_2Nb phase varies from ~1585 °C at the higher Cr content side to ~1625 °C at the higher Nb content side. The existence of the Cr_2Nb(H) phase was reported by [1961Pan1] and [1961Pan2]. [1961Pan2] in their study of the Cr-Nb-Ni system observed for the Cr_2Nb-$NbNi_3$ pseudobinary that the Cr_2Nb(H) phase gets stabilized at lower temperatures with the addition of Ni, the Cr_2Nb (L) phase is rather restricted, and a two-phase region, Cr_2Nb (L) + Cr_2Nb(H), exists between the two phases from the Cr_2Nb end of the pseudobinary. This led the authors to suggest that the Cr_2Nb (H) and Cr_2Nb (L) phases are two district phases, and that the so-called polymorphic transformation line of the Cr_2Nb phase is possibly a very narrow two-phase region between the Cr_2Nb(H) and Cr_2Nb (L) phases. The probable phase equilibria involving the Cr_2Nb phases is given schematically as an insert in Fig. 4, which shows a probable peritectoid reaction Cr_2Nb (H) + (Nb) ↔ Cr_2Nb (L) at 1625 °C and a eutectoid decomposition of the Cr_2Nb (H) phase, Cr_2Nb (H) ↔ (Cr) + Cr_2Nb (L) at ~1585 °C. Two eutectic reactions, L ↔ Cr_2Nb (H) + (Cr) and L ↔ Cr_2Nb (H) + (Nb) occur at 1620 and 1650 °C, respectively.

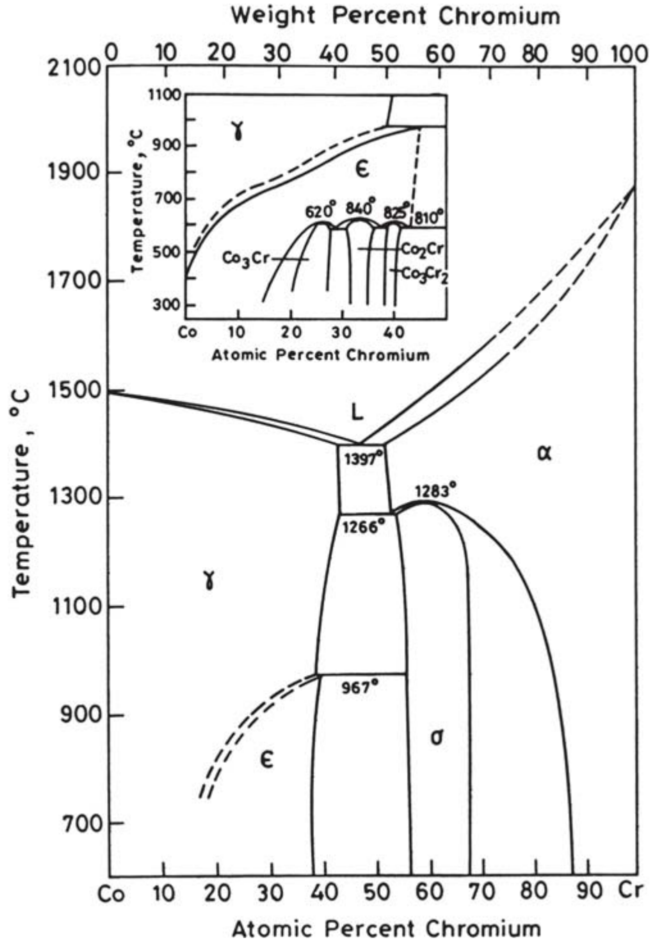

Fig. 1 The Co-Cr binary system [1990Gup, 1978All]. Insert shows the low-temperature transformations in the cph (ϵCo) phase [1961Gri].

Binary and Ternary Phases

In the three binary systems, there are nine intermediate phases. In the ternary system, the existence of a $MgZn_2$-type

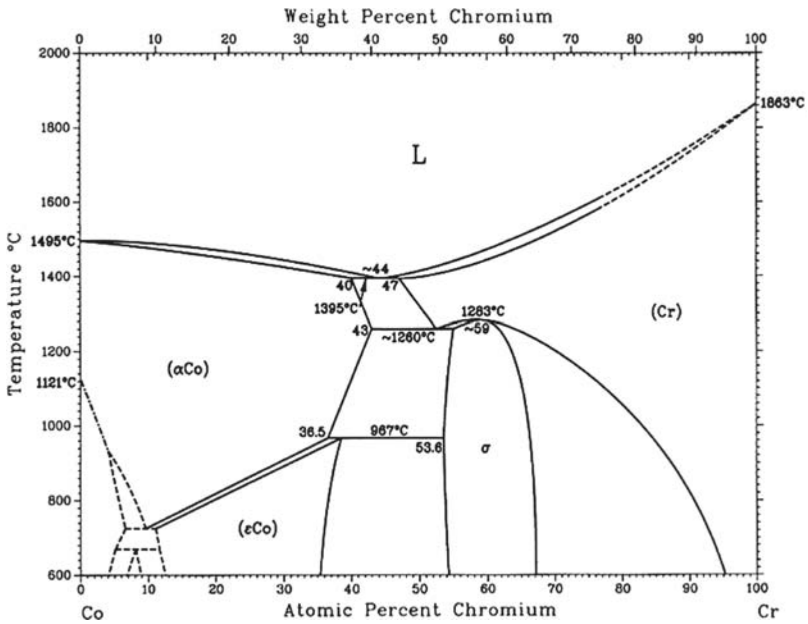

Fig. 2 The Co-Cr binary system [Massalski2]

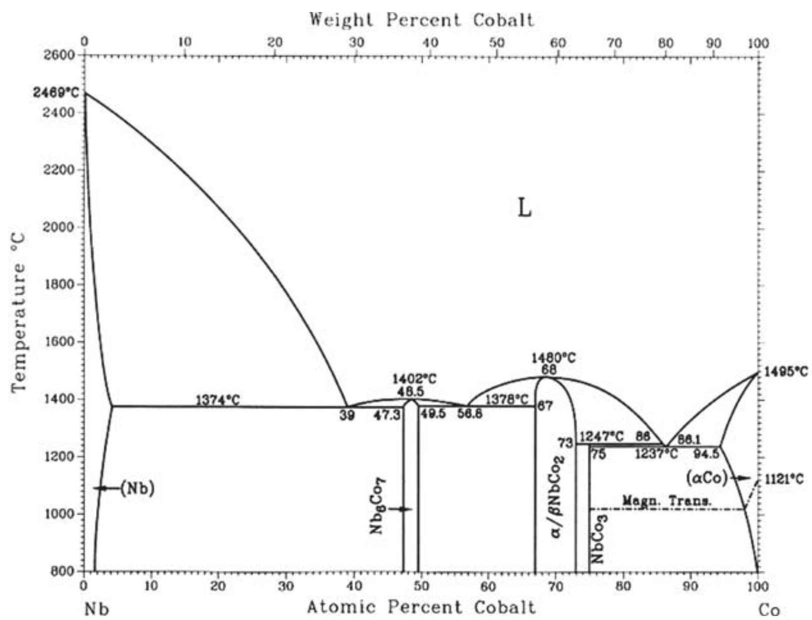

Fig. 3 The Co-Nb binary system [Massalski2]

phase at equiatomic composition has been reported, but it may not be a true ternary intermediate phase because the $NbCr_2$ (H) phase is a $MgZn_2$-type phase and the ternary phase is possibly an extension of the binary phase into the ternary. The structure data of the binary phases are given in Table 1.

Ternary System

[1962Pie] studied the aging characteristics and mechanical properties of Co alloys containing Cr, Nb, and Ni as alloying elements. Only one ternary Co alloy containing 6.5 wt.% Nb and 20.27 wt. % Cr (4.07 at. % Nb and 22.9 at.% Cr, respectively) was studied in this investigation. The alloys were induction-melted under vacuum using 99.6 mass% pure Co containing 0.37% Ni, 99.5 mass% Cr containing 0.2 mass% Fe, and 99.7 mass% Nb. Hot-swaged alloy specimens were first solution-treated in evacuated silica capsules at 1150 °C, next were water-quenched and then were aged at 850 °C for up to 1000 h, and were finally examined microscopically by x-ray diffraction (XRD) and by mechanical property studies. A precipitated phase was

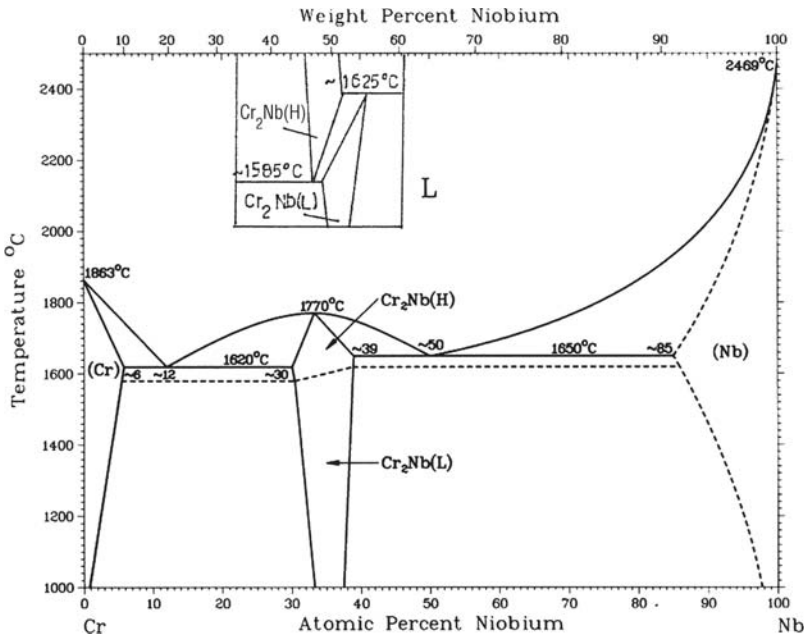

Fig. 4 The Cr-Nb binary system [Massalski2]. The insert shows the probable phase equilibria at the Cr_2Nb phase [1961Pan2].

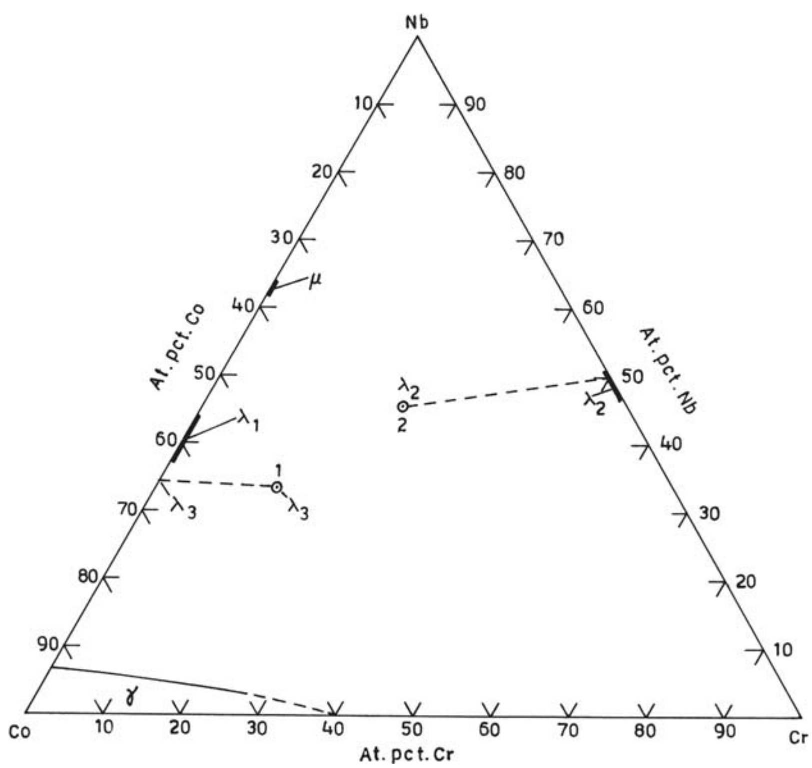

Fig. 5 A partial isothermal section of the Co-Cr-Nb system at 1200 °C. The approximate composition of the $MgNi_2$-type Laves phase (point 1) precipitates in a Co-Cr-Nb alloy at 850 °C [1962Pie], and the compositions of the $MgZn_2$-type Laves phase (point 2) reported by [1965Gan] are also shown.

extracted from the aged specimens for chemical analysis and phase identification by XRD.

The hardness of the alloys increased on aging at 850 °C and reached a maximum hardness after 100 h. Precipitate particles extracted from the aged specimen were found to contain 44.9 wt.% Co, 13.7 wt.% Cr, and 29.5 wt.% Nb (the total comes out to be only 88.1 wt.%) or approximately about 56 at.% Co, 20 at.% Cr, and 24 at.% Nb. Analysis of

Table 1 Structure data of binary phases in the Co-Cr-Nb system

Phase designation	Composition	Pearson symbol	Space group	Type	Lattice parameters, nm	
					a	*c*
α	(Cr)	*cI*2	$Im\bar{3}m$	W	…	…
	(αCo)	*cF*4	$Fm\bar{3}m$	Cu	…	…
ϵ	(ϵCo)	*hP*2	$P6_3/mmc$	Mg	…	…
Nb	(Nb)	*cI*2	$Im\bar{3}m$	*W*	…	…
σ	Co_7Cr_8	tP_3O	$P4_2/mnm$	σ (Cr, Fe)	0.8758	0.4536
ρ	Co_3Cr	*hP*8	$P6_3/mmc$	Ni_3Sn	0.5028	0.4034
ν	Co_2Cr	…	…	…	…	…
ζ	Co_3Cr_2	…	…	…	…	…
λ_2	$Cr_2Nb(H)$	*hP*12	$P6_3/mmc$	$MgZn_2$	0.493	0.807
λ_1	$Cr_2Nb(L)$	*cF*24	$Fd\bar{3}m$	Cu_2Mg	0.6987	…
λ_3	Co_3Nb	*hP*24	$P6_3mmc$	$MgNi_2$	0.67407	1.5425
λ_1	Co_2Nb	*cF*24	$Fd\bar{3}m$	Cu_2Mg	0.6758	…
μ	Co_6Nb_7	*hR*13	$R\bar{3}m$	Fe_7W_6	0.4893	2.664(a)

(a) Lattice parameter is for hexagonal cell with 39 atoms/cell.

the XRD pattern of the extracted precipitate particles showed them to be isostructural with the $MgNi_2$-type Laves phase with lattice parameter $a = 0.475$ nm and $c = 1.556$ nm. The Co-Nb system has an $MgNi_2$-type phase (Co_3Nb), and the above result shows that the Co_3Nb phase extends into the ternary at least up to ~14 wt.% Cr or ~20 at.% Cr.

In search of $MgZn_2$-type Laves phases in ternary alloys of Co and Ni containing V, Cr, Nb, Ta, or W, [1965Gan] studied the Co-Cr-Nb system. No experimental details regarding, for example, the purity of the component elements, the method of alloy melting, or the heat treatment temperature are given. The presence of an $MgZn_2$-type Laves phase at a Co-to-Cr-to-Nb atomic ratio of 1:1:1 (i.e., 28.9 wt.% Co, 23.5 wt.% Cr, and 45.6 wt.% Nb) was reported. Because an $MgZn_2$-type Laves phase exists at high temperatures in the Cr-Nb system (Cr_2Nb(H) phase), the Laves phase reported by [1965Gan] is possibly due to an extension of the high-temperature Cr_2Nb phase into the ternary system. The lattice parameter of the ternary $MgZn_2$ phase [1965Gan] is reported to be $a = 0.4849$ nm and $c = 0.7907$ nm, which are slightly smaller than those of the Cr_2Nb (H) phase (Table 1). Because in the Cr-Nb-Ni system [1990Gup] the Cr_2Nb (H) phase is stabilized by the addition of Ni, a similar effect may also be possible by addition of Co. It will be interesting to investigate the Co_2Nb-Cr_2Nb isopleth to see to which lower temperature the $MgZn_2$ phase persists.

[1965 Dra] also studied the aging behavior of Co-Cr-X alloys, in which X = Mo, Nb, Ta, or W, in the composition region of up to 25 wt.% Cr and 25 wt.% Nb. The alloys were arc-melted using 99.9 mass% Co, 99.35 mass% Cr, and 99.6 mass% Nb, homogenized in sealed silica capsules at 1200 °C for 1000 h, and water-quenched. After the solution treatment of a portion of the alloys at 1200 °C for 2 h, they were aged for 2 to 100 h at different temperatures between 1000 and 600 °C. Precipitated phases were extracted from the aged specimens for phase identification. Metallography, XRD, hardness measurement, transmission election microscopy (TEM), and electron diffraction were used for phase analysis and for study aging the behavior of the alloys.

The 1200 °C annealed alloys were used to establish the fcc (αCo) phase boundary (Fig. 5). The detailed phase analysis of all the alloys is not given by [1965Dra] to distinguish which phases are in equilibrium with the (αCo) phase at 1200 °C. The only information available from the reported data is that at 1200 °C the $MgNi_2$-type Laves phase exists in the investigated multiphase alloys. X-ray analysis of the alloys showed that the matrix phase contained both fcc (αCo) and hexagonal close-packed (hcp) (ϵCo) phases, with the latter phase formed during cooling of the fcc (αCo) phase.

Hardness of the aged alloys was found to increase with an increase in Cr and Nb content for all aging temperatures. This increase in hardness has been attributed to increased volume of precipitated phase with increase in alloying element content. A more detailed investigation was carried out with an alloy containing 5 wt.% Cr and 5 wt.% Nb aged at 600 °C. At this temperature maximum hardness was produced in this alloy. TEM and electron diffraction, studies of this alloy indicated superstructure formation in the fcc (αCo) matrix with the particles lying on the (111) plane of the (αCo) phase and additional diffraction spots were observed for the hcp (ϵCo) phase. The additional diffraction spots were identified as due to a hexagonal $MgZn_2$-type Laves phase. If the identification of the $MgZn_2$ phase is correct, it may mean that the $MgZn_2$ type Laves phase observed by [1965Gan] is stable down to at least 600 °C. As indicated earlier the Co_2Nb-Cr_2Nb isopleth should be investigated to throw more light on the stability of Laves phases in the Co-Cr-Nb system.

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# Indicates presence of phase diagram.

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