The Co-Y (Cobalt-Yttrium) System

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Equilibrium Diagram

The assessed Y-Co phase diagram is presented in Fig. 1. The Corich portion (>55 at.% Co) is drawn mainly from data reported by [65Str] and includes some features from [71Bus1] and [74Kha]. The region 25 to 50 at.% Co is based on the results of [82Gro]. In addition, the melting points of Co and Y and the $\alpha \leftrightarrow \beta$ transformation temperature of Y were adjusted to bring them into agreement with the accepted values [83Nis] and [86Gsc], respectively. Invariant temperatures and compositions are listed in Table 1.

The Y-Co system has been studied by several research groups, with some inconsistency in their reported results. [65Pel] investigated the Y-Co system with thermal analysis, metallography, and X-ray methods. Their alloys were prepared from 99.9 wt.% pure Co and Y. Samples were arc melted under an inert gas atmosphere. [65Pel] reported nine intermetallic compounds—Y₃Co (peritectic at 885 ± 3 °C), Y₃Co₂ (peritectic at 735 ± 6 °C), YCo (peritectic at 803 ± 5 °C), Y₂Co₃ (peritectic at 855 ± 7 °C), YCo₂ (peritectic at 1155 ± 4 °C), YCo₃ (peritectic at 1325 ± 6 °C), "YCo₄" (congruently melting at 1500 ± 5 °C), YCo₅ (peritectic at 1420 ± 5 °C), and Y₂Co₁₇ (peritectic at 1365 ± 7 °C). In addition, they observed two eutectic reactions in this system—Y₃Co-Y₃Co₂ at 725 ± 2 °C and 37.5 at.% Co and (α Co)-Y₂Co₁₇ at 1340 ± 5 °C and 93.0 at.% Co. They found that the solid solubility of Y in (Co) does not exceed 0.14 at.% Y at room temperature.

[65Str] also investigated the Y-Co system by thermal analysis, Xray diffraction (XRD), and metallography. Their Co was of 99.5 wt.% or 99.99 wt.% purity, and their Y was of 99.9 wt.% purity. The metallographic and X-ray samples were prepared by comelting the two metals and casting them in a levitation furnace in argon atmosphere, with subsequent vacuum annealing when ap-

Table 1 Special Points of the Assessed Y-Co Phase Diagram

propriate. The thermal analysis was performed immediately after sample preparation by melting together the component metals directly in the recrystallized alumina crucible.

The phase diagram proposed by [65Str] differs rather significantly from that of [65Pel] between 50 and 90 at.% Co. [65Str] did not observe the peritectic phase YCo and the congruently melting phase "YCo₄," but rather the peritectic phase Y₂Co₇. They also found that the phase Y₂Co₁₇ was congruently melting rather than peritectic. They positively identified seven intermediate phases in this system—Y₃Co (peritectic at 880 °C), Y₂Co₃ (peritectic at 790 °C), YCo₂ (peritectic at 1150 °C), YCo₃ (peritectic at 1315 °C), Y₂Co₇ (peritectic at 1325 °C), YCo₅ (peritectic at 1352 °C), and Y₂Co₁₇ (congruently melting at 1362 °C)—and reported the possible existence of another phase, Y₃Co₂ (peritectic at 730 °C) near 40 at.% Co. In addition, [65Str] observed two eutectic reactions in this system, in substantial agreement with those reported by [65Pel].

[65Str] reported that in the as-cast condition an alloy of 88.6 at.% Co is single phase, whereas an alloy of stoichiometric composition Y_2Co_{17} (89.5 at.% Co) has an appreciable amount of eutectic between primary Y_2Co_{17} grains and an 88.0 at.% Co alloy shows Y_2Co_{17} surrounded by dark-etching YCo₅. This indicates that Y_2Co_{17} melts congruently at the approximate composition 88.6 at.% Co. [65Str] outlined a finite homogeneity range for Y_2Co_{17} at 1200 °C with limiting compositions of 88.0 and 89.5 at.% Co.

However, of the same alloys annealed at 800 °C, only the 88.0 at.% Co sample was single phase. In addition, they found that the alloys of 84.4 and 85.2 at.% Co are very nearly single-phase YCo_5 in the as-cast condition. This seems to indicate that the YCo_5 may be single phase between the above two concentrations in the as-cast condition and probably is a congruently melting phase.

Reaction		Composition of the respective phases, at.% Co		Temperature, °C	Reaction type	Reference
L⇔βY		0		1522	Melting	[86Gsc]
βY ↔ αY		0		1478	Allotropic	[86Gsc]
$L+(\alpha Y) \leftrightarrow Y_3Co$	~28.7	0	25.0	880	Peritectic	[65Str,71Bus1]
$L \leftrightarrow Y_3C_0 + Y_8C_{05}$	37.0	25.0	38.46	735 ± 2	Eutectic	[82Gro]
$L + YC_0 \leftrightarrow Y_8C_{05}$	~37.7	50.0	38.46	740 ± 2	Peritectic	[82Gro]
$YC_0 + Y_8C_0 \leftrightarrow Y_9C_0$	50.0	38.46	43.75	725 ± 5	Peritectoid	[82Gro]
$L+Y_2Co_3 \leftrightarrow YCo$	-43.0	60.0	50.0	802 ± 2	Peritectic	[65Pel.82Gro]
$L + YCo_2 \leftrightarrow Y_2Co_3$	-45.5	66.7	60.0	855 ± 7	Peritectic	[65Pel]
$L + YCo_3 \leftrightarrow YCo_2$	~59.0	75.0	66.7	1150	Peritectic	[65Str.71Bus1]
$L + Y_2 Co_7 \leftrightarrow Y Co_3$	~72.0	77.8	75.0	1315	Peritectic	[65Str]
$L + YCo_5 \leftrightarrow Y_2Co_7$	~73.0	83.3	77.8	1325	Peritectic	[65Str]
L + YCos		~85.0		~1350	Congruent	[74Kha]
$L \leftrightarrow Y_2 Co_{17} + Y Co_5$	-87.0		~85.5	-1330	Eutectic	[74Kha]
$L \leftrightarrow Y_2 Co_{17}$		88.6		1362	Congruent	[65Str]
$L \leftrightarrow (\alpha Co) + Y_2 Co_{17}$	93.0	~100	89.5	1340 ± 5	Eutectic	[65Pel]
L ↔ aCo		100		1495	Melting	[83Nis]

Section II: Phase Diagram Evaluations

The phase diagram of this system was reinvestigated by [71Bus1] with metallography, thermal analysis, and XRD techniques. The Co and Y used in preparing his samples were of 99.9 wt.% and 99.99 wt.% purity, and samples were prepared by arc melting. [71Bus1] observed seven intermetallic compounds in this system—Y₃Co (peritectic at 880 °C), "Y₄Co₃" (peritectic at 725 °C), YCo₂ (peritectic at 1150 °C), YCo₃ (peritectic at 1330 °C), Y₂Co₇

(peritectic at 1340 °C), YCo₅ (peritectic at 1350 °C), and Y_2Co_{17} (congruently melting at 1370 °C). His results are in fair agreement with those reported by [65Str], except for some minor differences in the melting temperatures in the Co-rich region.

[71Bus1] observed by metallography that in addition to that of Y_2Co_{17} , a homogeneity region also exists for YCo₅ at high



Phase	Composition, at.% Co	Pearson symbol	Space group	Struktur- bericht designation	Prototype
(αΥ)(a)	-0	hP2	P6_mmc	A3	Mg
(βΥ)(b)	~ 0	cľ2	Im3m	A2	Ŵ
¥ ₃ Co	25.0	<i>o</i> P 16	Pnma	$D0_{20}$	Al ₃ Ni
Y ₂ Co ₅	38.46	mP52	$P2_1/c$		
Y ₉ C0 ₇	43.75	(c)			,
YCo	50.0	•••			
Y ₂ Co ₃	60.0				Gd ₂ Co ₃
YCo ₂	66.7	cF24	Fd3m	C15	Cu ₂ Mg
YC03	75.0	hR12	R3m		Be ₃ Nb
		hP24	P6 ₃ /mmc	•••	CeNi ₃
Y ₂ Co ₇	77.8	hR18	R3m	•••	Gd ₂ Co ₇
YCos	83.3	hP6	P6/mmm	$D2_d$	CaCus
Y ₂ Co ₁₇	89.3	hP38	P6 ₃ /mmc		Th ₂ Ni ₁₇
		hR19	R3m	•••	Th ₂ Zn ₁₇
(αCo)(d)	~100	cF4	Fm3m	A1	Cu
Metastable phase					
Y ₃ Co ₂	40.0	oP20	Pnnm		
(a) Below 1478 °C. (b) From 1478 to 1522 °C. (c) Hexagonal. (d)	From 422 to 1495 *	C at 100 at.% Co.			

Table 2 Y-Co Crystal Structure Data

temperatures, with limiting compositions of 83.05 and 85.71 at.% Co; however in a sample of 82.6 at.% Co, an appreciable amount of Y_2Co_7 was present after quenching from 1200 and 1300 °C. [69Sch] also reported a small homogeneity range for YCo₅, with limiting compositions of 82.6 and 85.71 at.% Co. [73Bus] showed that YCo₅ is unstable below about 725 °C. [71Bus1] asserted that there are two phases—not identified—with compositions close to the "Y₄Co₃" phase. One of these was identified later by [76Mor] as a monoclinic compound, Y₈Co₅, and the other was identified by [75Mor] as orthorhombic Y₃Co₂ and was assumed to be a low-temperature phase. However, [82Gro] showed that Y₃Co₂ is a metastable phase in as-cast alloy.

[74Kha] prepared Y-Co alloys from Co and Y metal of 99.9 wt.% purity. The alloys were melted in a medium-frequency oven under purified argon atmosphere and cast in copper mold. He reported a Co-rich (≥ 60 at.% Co) region that differed significantly from those proposed by [65Str] and [71Bus1], [74Kha] observed the peritectic phase "Y₅Co₁₉" (1300 °C), which decomposed eutectoidally to Y₂Co₇ and YCo₅ at elevated temperature (~1200 °C). YCo₅ was reported as a congruently melting rather than as peritectically melting. It decomposed eutectoidally to Y₂Co₁₇ and Y₂Co₇ phases at about 975 °C. [74Kha] also reported that YCo₅ and Y₂Co₁₇ possess finite homogeneity ranges at high temperatures, but did not report the congruent temperatures and compositions for YCo₅ and the Y₂Co₁₇. However, by scaling of his phase diagram, these are about 1350 °C at 85 at.% Co and 1360 °C at 89.3 at.% Co, respectively.

[74Kha] observed two eutectic reactions in the Co-rich portion of the Co-Y system, but did not propose values for the eutectic temperatures and eutectic compositions. Scaling of his phase diagram indicates the values for eutectic temperatures and compositions of YCo₅-Y₂Co₁₇ and Y₂Co₁₇-(α Co) to be about 1330 °C at 87.5 at.% Co and 1335 °C at 92.5 at.% Co, respectively. The values for the eutectic temperature and composition of the Y_2Co_{17} -(α Co) reaction are in reasonable agreement with the values reported by [65Str] (1320 °C at ~92 at.% Co) and [65Pel] (1340 °C at 93 at.% Co).

[85Sub] determined the thermodynamic functions of formation for Y-Co alloys by emf measurements, and the " Y_5Co_{19} " phase was not observed.

The Y-Co phase diagram in the region 25 to 50 at.% Co was restudied carefully by [82Gro]. They showed clearly that the stable phase diagram in this range includes four phases-Y₃Co (25 at.% Co, peritectic at 885 °C), Y₈Co₅ (38.46 at.% Co, peritectic at 740 ± 2 °C), Y₉Co₇ (43.75 at.% Co, peritectoid at 725 ± 5 °C), and YCo (50 at.% Co, peritectic at 802 ± 2 °C). Y₉Co₇, which forms by a peritectoid reaction at 725 °C, formerly was thought to be "Y4Co3". Y3Co2 is a metastable phase that was found only in ascast alloys. However, [83Yvo] studied a minute single crystal of irregular shape isolated from an arc-melted and annealed sample of nominal composition Y₉Co₇ by X-ray diffraction analysis. They proposed that the sample is Y_4Co_3 rather than Y_9Co_7 . [85Sub] reported that YCo was not observed from their emf measurements. They believed that Y-Co alloys with minor differences in impurity content might differ with respect to the presence or absence of one or another phase.

Metastable Phases

[82Gro] reported the metastable phase Y_3Co_2 as occurring only in as-cast alloys. [75Mor] presented data for the crystal structure of Y_3Co_2 and concluded that it is a low-temperature phase. These conflicting reports have not been resolved.

Section II: Phase Diagram Evaluations

Table 3 Y-Co Lattice Parameter Data

	Composition,	Lattice parameters, nm				
Phase	at.% Co	a b		с	Comment	Reference
αΥ	0	0.36482	•••	0.57318	At 25 °C	[86Gsc]
βΥ	0	0.407		• •••		[86Gsc]
Y ₃ Co	25.0	0.7026	0.9454	0.629		[71Bus1]
Y ₈ Co ₅	38.46	0.7058	0.7286	2.4227	$\beta = 102.11^{\circ}(a)$	[76Mor]
Y ₄ Co ₁	42.90	1.1521		0.4042	6	[83Yvo]
Y ₀ C ₀₇	43.75	1.1529		1.2123		[82Gro]
Y ₂ Co ₃	60.0	0.7996			Cubic(c)	[65Pel]
YCo	66.7	0.7217			(d)	[61Dwi.65Pel]
-		0.7215			(e)	[72Bur]
		0.7216			ຕິ	[60Bea.60Wer.65Str]
YCo1	75.0	0.5020		2.440	As cast	[65Smi]
,		0.51033		2.4371	(g)	[66Vuc]
		0.5005		2.427	(8/	[71Bus1]
		0.5015		1.628	(h)	[65Ost.65Str]
Y ₂ Co ₇	77.8	0.5002		3.615	< <i>y</i>	[71Bus1]
2)		0.4998		3.618	(i)	[67Ost]
YCoc	83.3	0.4935		0.3964	U /	[68Vel]
5		0.4995		0.3994		[65Pel]
		0.4931		0.3980	(k)	[65Str]
		0.4956		0.3969	(m)	[61Dwi]
		0.4928		0.3992	()	[59Wer]
Y ₂ Co ₁₇	89.5	0.8355		0.8128	As cast	[73Kha]
2 1)		0.8341		0.8125	At 1000 °C	[66Bus]
		0.8355		1.2192	Below 1100 °C	[73Kha]
		0.8344		1.2190	(n)	[66Bus]
		0.8331		1.2186	(D)	[65Ost.65Str]
αCo	100	0.35446	•••			[83Nis]
Metastable phase						
Y ₃ Co ₂	40.0	1.2248	0.9389	0.3975		[75Mor]

Note: Sample previously heat treated at: (a) 700 °C for 48 h. (b) 550 °C for five weeks. (c) 700 °C for 75 h. (d) 700 °C. (e) 800 °C for 24 h. (f) 690 °C. (g) 1000 °C for 48 h. (h) 960 °C for 224 h. (j) 900 °C for 400 h. (k) 960 °C. (m) 900 °C. (n) 1000 °C for 15 days. (p) 800 °C for 200 h.

Crystal Structures and Lattice Parameters

Y has two allotropic forms, and it transforms from cph to bcc at 1478 °C on heating [86Gsc]. Co also has two allotropic modifications. α Co is stable from 422 to 1495 °C (melting point) and has a fcc structure [83Nis]. Crystal structure and lattice parameter data for the stable and metastable intermediate phases in the Y-Co system are listed in Tables 2 and 3, respectively.

Thermodynamics

[85Sub] determined the Gibbs energies, enthalpies, and entropies of phase formation of nine Y-Co intermetallic compounds by emf measurements over the temperature range 850 to 1200 K. They assumed that the solid solubility of Y in (Co) in negligible and that there is no appreciable range of homogeneity in any of these intermetallic compounds at the temperature of measurement. On this basis, the pure solid phases can be chosen as standard states, with invariant activities in the alloys. Therefore, the experimentally measured emf data yield standard Gibbs energies of phase formation as follows:

 $\Delta_{\rm f} G^0 ({\rm Y}_2 {\rm Co}_{17}) = -144.39 - (4.05 \times 10^{-3}) T \, \rm kJ/mol$

Table 4Thermodynamic Functions for the Formation ofY-Co Alloys: Gibbs Energies of Formation at 973 K andMean Values for Enthalpies and Entropies of Formation inthe Range 850 to 1200 K

Phase	$-\Delta_f G^0$ (973 K), kJ/mol of atoms	$-\Delta_t H^0$ (850 to 1200 K), kJ/mol of atoms	$-\Delta_f S^0$ (850 to 1200 K), J/K·mol of atoms
Y ₂ Co ₁₇	. 7.81 ± 0.10	7.60 ± 0.80	-0.21 ± 0.73
YCo5	12.08 ± 0.11	12.20 ± 0.87	0.15 ± 0.80
Y ₂ Co ₇	. 15.93 ± 0.12	17.25 ± 0.96	1.35 ± 0.87
YC01	. 17.81 ± 0.13	19.35 ± 1.05	1.57 ± 0.94
YC02	20.41 ± 0.14	22.76 ± 1.33	2.38 ± 1.25
Y ₂ Co ₃	20.72 ± 0.16	27.06 ± 1.90	6.49 ± 1.81
Y ₉ C07	19.00 ± 0.18	26.02 ± 3.07	7.16 ± 3.11
Y ₈ Co	18.63 ± 0.23	21.83 ± 4.07	3.25 ± 4.21
Y ₃ Co	16.51 ± 0.36	15.80 ± 4.98	-0.72 ± 5.27
From [85S	ub].		

 $\Delta_{\rm f} G^0 ({\rm YCo}_5) = -73.18 + (0.72 \times 10^{-3}) \, T \, \rm kJ/mol$

 $\Delta_{\rm f} G^0 ({\rm Y}_2 {\rm Co}_7) = -155.23 + (12.15 \times 10^{-3}) T \, \rm kJ/mol$

 $\Delta_{\rm f} G^0 ({\rm YCo}_3) = -77.38 + (6.27 \times 10^{-3}) T \, \rm kJ/mol$

 Table 5
 Magnetic Properties of Intermetallic Compounds of Y and Co

Phase	Composition, at.% Co	Magnetic moment, µB	Curie temperature, K, <i>T</i> C	Comment	Reference
Y ₃ Co	25.0	-0	<2		[71Giv]
Y ₄ Co ₃	42.90	0.11	13		[68Ber]
Y ₀ C0 ₇	43.75	0.85	•••	(a)	[82Sar]
YCo ₂	66.7	0.23	296		[64Wal]
-		~0	<2	•	[66Lem]
YCo3	75.0	1.4	301	(b)	[66Lem,69Kre]
		1.6	402	(c)	[66Lem]
		•••	310		[71Bus2]
Y ₂ Co ₇	77.8	7.4	639		[66Lem]
		•••	545		[71Bus2]
YCo ₅	83.3	7.7	975		[60Nas]
-		6.8	977		[66Lem]
		7.5			[68Vel]
		7.5	977		[69Kre]
		•••	955	•••	[71Bus2]
Y ₂ Co ₁₇	89.5	27.8	1167		[66Lem]
		27.37	1110	•••	[66Str]

(a) Superconducting transition T = 2.15 K [84Ora]; superconductivity at 2.8 K [82Sar]. (b) Sample previously annealed at 1000 °C. (c) Sample previously quenched from 1000 °C.

 $\Delta_{\rm f} G^0 ({\rm YCo}_2) = -68.27 + (7.17 \times 10^{-3}) T \, {\rm kJ/mol}$

 $\Delta_{\rm f} G^0({\rm Y}_2{\rm Co}_3) = -135.28 + (32.45 \times 10^{-3}) T \, {\rm kJ/mol}$

 $\Delta_{\rm f} G^0 ({\rm Y}_{\rm 9} {\rm Co}_7) = -416.23 + (114.58 \times 10^{-3}) T \, {\rm kJ/mol}$

 $\Delta_{\rm f} G^0({\rm Y}_8{\rm Co}_5) = -283.72 + (42.29 \times 10^{-3}) T \, {\rm kJ/mol}$

 $\Delta_{\rm f} G^0$ (Y₃Co) = -63.20 - (2.89 × 10⁻³) T kJ/mol

where mol is a mole of the formula unit, and T is in K. The reported data for the thermodynamic functions of formation for Y-Co intermediate phases are given in Table 4.

[83Nie] computed the theoretical enthalpies of Y-Co phase formation on the basis of Miedema's theory. Their calculated values for YCo₅, YCo₃, YCo₂, YCo, and Y₃Co are -18.0, -26.0, -31.0,-31.0, and -16.0 kJ/mol of atoms, respectively. The Miedema predictions and the experimental enthalpies of formation for some Y-Co phases (Table 4) are in fair agreement. [89Sid] determined and computed the enthalpy of formation for YCo₃ by calorimetry and based on Miedema's theory, respectively. Their experimental and theoretical enthalpies of formation for YCo₃ are 20 ± 3 and 18 kJ/mol of atoms, respectively.

Magnetism

The data of magnetic properties such as saturation moment (at 0 K or 4.2 K), expressed in Bohr magnetron/formula unit and Curie temperature, $T_{\rm C}$, given in K for intermetallic compounds of Y with Co, are listed in Table 5.

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