

The Co-Ge-Mo (Cobalt-Germanium-Molybdenum) System

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Introduction

Only very limited information is available on the Co-rich side of the (Co,Ge)₂ Mo composition region of the Co-Ge-Mo system and is reported here.

Binary Systems

The Co-Ge system [Massalski2] (Fig. 1) shows the presence of six intermediate phases: Co₃Ge, Co₅Ge₂, Co₅Ge₃, CoGe, Co₅Ge₇, and CoGe₂, of which the Co₅Ge₃ phase exists in two polymorphic forms, the high-temperature βCo₅Ge₃ and the low-temperature (*T* < 382 °C) αCo₅Ge₃ phases. The βCo₅Ge₃ phase melts congruently at 1210 °C. Alloying Co with Ge stabilizes the hexagonal close packed (hcp) (εCo) phase to quite high temperatures. The (εCo), CoGe, and CoGe₂ phases form through peritectic reactions: L + (αCo) ↔ (εCo), L + βCo₅Ge₃ ↔ CoGe, and L + CoGe ↔ CoGe₂ at 1123, 985, and 832 °C, respectively. The Co₃Ge, Co₅Ge₂, and Co₅Ge₇ phases form through peritectoid reactions: (εCo) + βCo₅Ge₃ ↔ Co₃Ge at ~770 °C; (εCo) + βCo₅Ge₃ ↔ Co₅Ge₂ at 636 °C; and CoGe + CoGe₂ ↔ Co₅Ge₇ at 806 °C. The Co₃Ge and Co₅Ge₂ phases exist only at the higher temperatures and transform through eu-

tectoid reactions: Co₃Ge ↔ (εCo) + βCo₅Ge₃ at temperatures above 836 °C and Co₅Ge₂ ↔ (εCo) + βCo₅Ge₃ at temperatures 382 °C. Two eutectic reactions, L ↔ (εCo) + βCo₅Ge₃ and L ↔ CoGe₂ + (Ge), occur at 1108 and 817 °C, respectively.

The Co-Mo system [Massalski2] (Fig. 2) shows the presence of four intermediate phases: Co₉Mo₂, Co₃Mo, Co₇Mo₆ (μ); and σ. The σ and μ phases form through the peritectic reactions L + (Mo) ↔ σ at 1620 °C and L + σ ↔ μ at ~1510 °C. A eutectic reaction, L ↔ μ + (αCo), occurs at 1335 °C. Three peritectoid reactions, μ + (αCo) ↔ Co₉Mo₂, Co₉Mo₂ + μ ↔ Co₃Mo, and probably (αCo) + Co₃Mo ↔ (εCo), occur at 1200, 1025, and ~700 °C, respectively. The Co₉Mo₂ and σ phases transform through eutectoid reactions Co₉Mo₂ ↔ (αCo) + Co₃Mo and σ ↔ (Mo) + μ at 1018 and ~1000 °C, respectively.

The Ge-Mo system [1987Ole, Massalski2] (Fig. 3) has four intermediate phases: αGe₂Mo; Ge₂₃Mo₁₃; Ge₃Mo; and GeMo₃. A metastable βGe₂Mo phase forms on rapid quenching of alloys containing <40 at.% Mo from 1350 °C. The βGe₂Mo phase, however, is a stable phase above 20 kbar pressure, and only after annealing in a vacuum at 1000 °C for 5 h does the βGe₂Mo phase transform into the αGe₂Mo phase. All of the intermediate phases form through peritectic reactions: L + (Mo) ↔ GeMo₃ at 1800 °C;

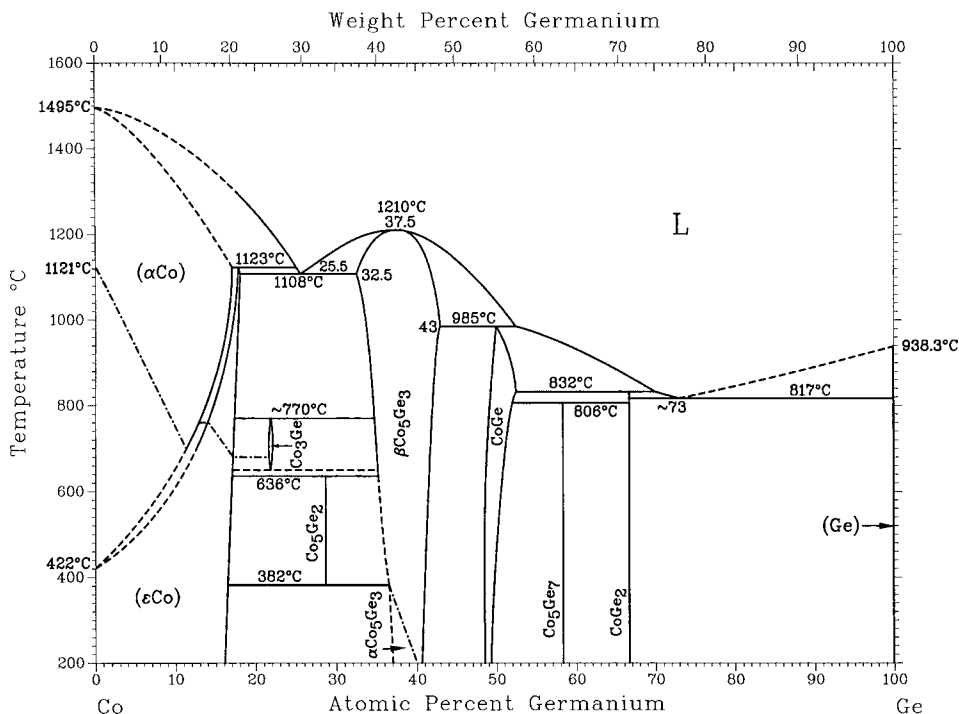


Fig. 1 The binary Co-Ge diagram [Massalski2]

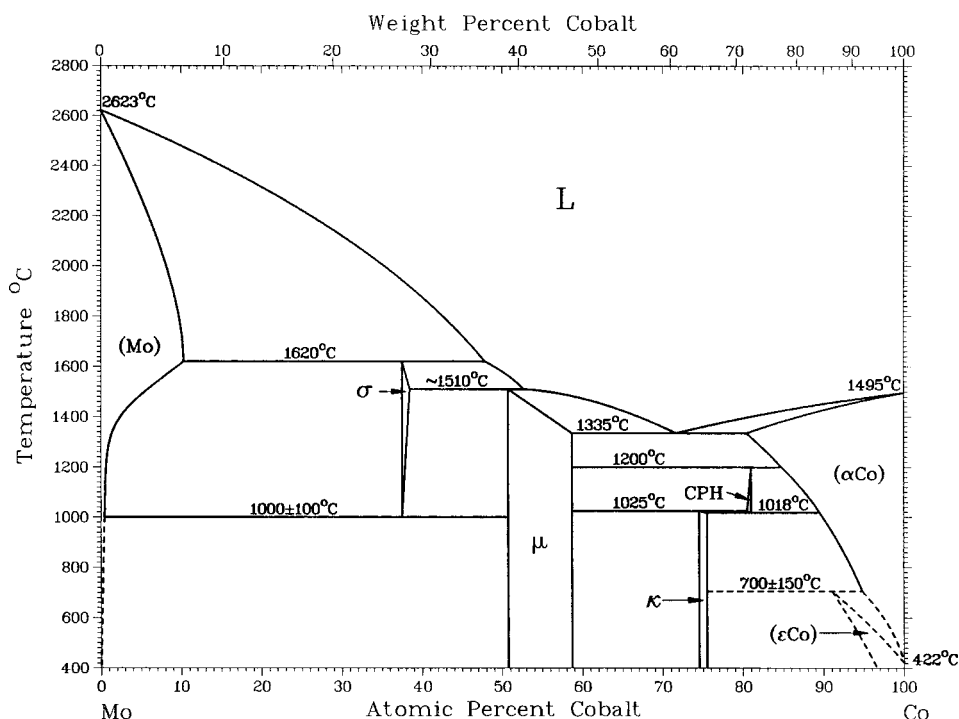


Fig. 2 The binary Co-Mo diagram [Massalski2]

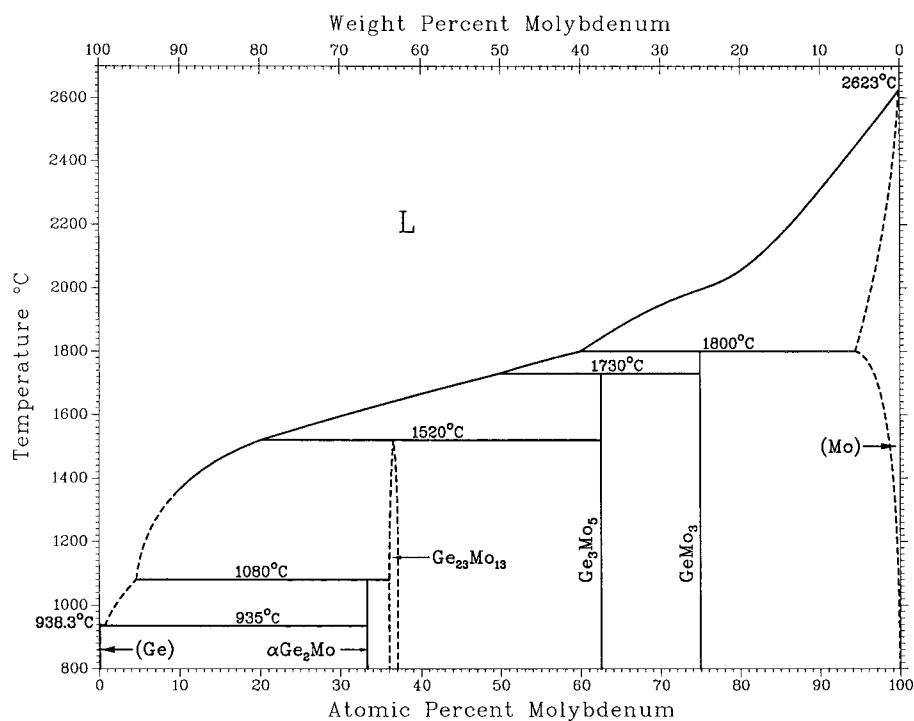


Fig. 3 The binary Ge-Mo diagram [Massalski2]

$L + \text{GeMo}_3 \leftrightarrow \text{Ge}_3\text{Mo}_5$ at 1730°C ; $L + \text{Ge}_3\text{Mo}_5 \leftrightarrow \text{Ge}_{23}\text{Mo}_{13}$ at 1520°C ; and $L + \text{Ge}_{23}\text{Mo}_{13} \leftrightarrow \alpha\text{Ge}_2\text{Mo}$ at 1080°C . A eutectic reaction, $L \leftrightarrow (\text{Ge}) + \alpha\text{Ge}_2\text{Mo}$, occurs at 935°C .

Binary and Ternary Phases

In the three binary systems of the Co-Ge-Mo system, 14 intermediate phases form. In the Co-Ge-Mo system, the

Section II: Phase Diagram Evaluations

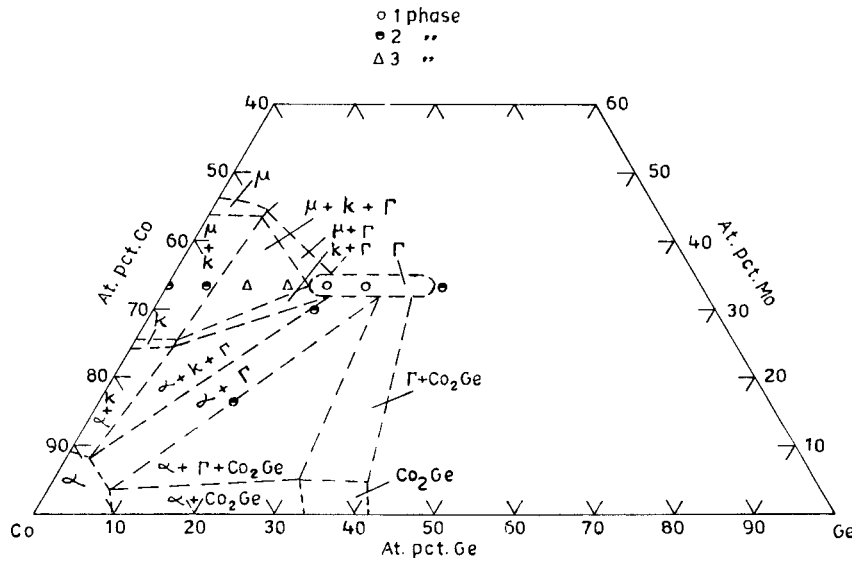


Fig. 4 A partial isothermal section of Co-Ge-Mo system at 600 °C [1964Bor]

Table 1 Binary and ternary phases in the Co-Ge-Mo system

Phase designation	Composition	Pearson symbol	Space group	Type	Lattice parameter, nm		
					<i>a</i>	<i>b</i>	<i>c</i>
(α Co)	(α Co)	<i>cF4</i>	$Fm\bar{3}m$	Cu
(ϵ Co)	(ϵ Co)	<i>hP2</i>	$P6_3/mmc$	Mg
(Mo)	(Mo)	<i>cI2</i>	$Im\bar{3}m$	W
(Ge)	(Ge)	<i>cF8</i>	$Fd\bar{3}m$	C(diamond)
δ_1	Co ₃ Ge	<i>cP8(?)</i>	$Pm\bar{3}n(?)$	Cr ₃ Si(?)
θ	Co ₅ Ge ₂
α_1	α Co ₅ Ge ₃	<i>oP12</i>	$Pnma$	Co ₂ Si	0.502	0.382	0.726
β_1	β Co ₅ Ge ₃	<i>hP6</i>	$P6_3/mmc$	InNi ₂	0.3876	...	0.4995
η	CoGe	<i>mC16</i>	$c2m$...	1.1648	0.3807	0.4945
		<i>cP8</i>	$P2_13$	FeSi
ρ	Co ₅ Ge ₇	<i>tI24</i>	$I4mm$...	0.764	...	0.581
τ	CoGe ₂	<i>oC24</i>	$Aba2$...	0.5681	0.5681	1.0818
α^1	α Ge ₂ Mo	<i>oP12</i>	$Pnma$	PbCl ₂	0.6343	0.3451	0.8582
β^1	β Ge ₂ Mo(HP)(a)	<i>tI8</i>	$I4/mmm$	MoSi ₂	0.3322	...	0.8219
i	Ge ₂₃ Mo ₁₃	<i>tP144</i>	$P\bar{4}n2$	Ge ₂₃ Mo ₁₃	0.599	...	6.354
ν	Ge ₃ Mo ₅	<i>hP16</i>	$P6_3/mcm$	Mn ₅ Si ₃	0.9837	...	0.4973
δ_2	GeMo ₃	<i>cP8</i>	$Pm\bar{3}n$	Cr ₃ Si	0.49330
π	Co ₉ Mo ₂	<i>h</i>	0.25973	...	0.42123
κ	Co ₃ Mo	<i>hP8</i>	$P6_3/mcm$	Ni ₃ Sn	0.51245	...	0.41125
μ	Co ₇ Mo ₆	<i>hR13</i>	$R\bar{3}m$	Fe ₇ W ₆	0.4726	...	2.5015
σ	Co ₉ Mo ₁₅	<i>tP30</i>	$P4_2/mnm$	σ (CrFe)	0.92287	...	0.48269
Γ	Co _{1.4} Ge _{0.6} Mo	<i>hP12</i>	$P6_3/mmc$	MgZn ₂	0.4790	...	0.7688

(a) Lattice parameters for the Co-Ge and Co-Mo systems are from [Pearson3]; lattice parameters for the Ge-Mo system are from [1987Ole]. (b) β Ge₂Mo is metastable at ordinary pressures but is stable above 20 kbar pressure

existence of a ternary intermediate phase has been reported. The phases and their structural data are given in Table 1.

Ternary System

The Co-Ge-Mo system was investigated at the Co end by [1964Bor] around the (Co,Ge)₂Mo composition up to ~34

at.% Ge. Nine alloys were melted, using pure metals Mo (99.93 mass%), Co (99.98 mass%), and Ge (99.99 mass%), in corundum crucibles under an argon atmosphere. Samples were annealed in sealed quartz capsules (time of annealing and annealing temperature were not mentioned) and water-quenched. The characterization of the annealed alloys was done by metallography and x-ray diffraction. The

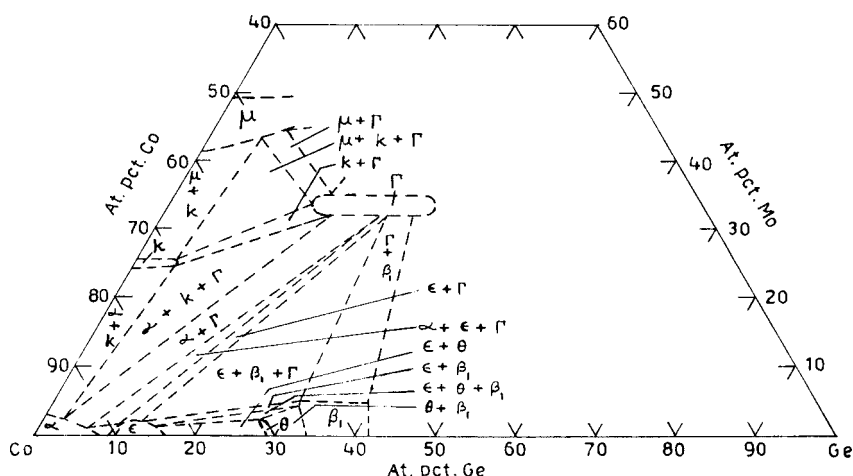


Fig. 5 A probable isothermal section (schematic) of Co-Ge-Mo system at 600 °C

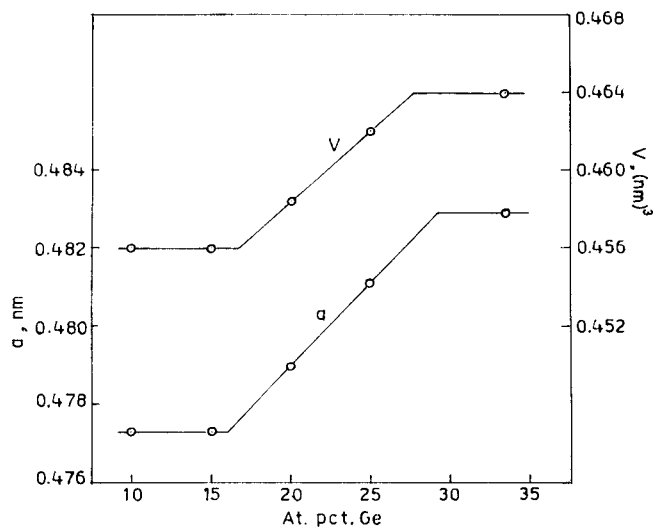


Fig. 6 Variation of lattice parameter a and lattice volume V of the phase as a function of Ge content [1964Bor]

existence of a ternary phase, Γ , was established along the $(\text{Co,Ge})_2\text{Mo}$ composition line. The Γ phase region was shown to be very narrow and was reported to be in equilibrium with the (αCo) , Co_3Mo , Co_7Mo_6 (μ), and Co_2Ge phases. Among the alloys along the $(\text{Co}_x\text{Ge}_{1-x})\text{Mo}$ line, the alloy with 5 at.% Ge had two phases ($\mu + \kappa$), the alloy with 15 at.% Ge had three phases ($\mu + \kappa + \Gamma$), and the alloy with 20 at.% Ge had a single phase Γ , whereas the alloy with 33.4 at.% Ge was found to have two phases, the Γ phase and a second phase that was not identified. Two alloys containing 16.7 at.% Ge and 16.7 at.% Mo and 20 at.% Ge and 30 at.% Mo were found to have two phases, (αCo) and Γ ; the latter alloy contained only traces of the (αCo) phase.

On the basis of these data, the possible phase equilibria for the Co corner of the Co-Ge-Mo system was drawn and is given in Fig. 4. Because only a few alloys were used and

for most of the two-phase and three phase regions no experimental data are available, the phase equilibria given in Fig. 4 should be treated as a schematic representation of phase equilibria of the Co-Ge-Mo system at 600 °C. The phase equilibria given in Fig. 4 also does not agree with the accepted data of Co-Ge and Co-Mo systems. According to the accepted Co-Mo binary diagram, the μ phase region is much wider than that given in Fig. 4. In the accepted Co-Ge binary system, the sequence of phases at 600 °C is (αCo) , (ϵCo) , Co_5Ge_2 , and $\beta\text{Co}_5\text{Ge}_3$ as Ge content increases. There is no Co_2Ge phase in the Co-Ge system, but the composition region of the Co_2Ge phase in Fig. 4 agrees well with the $\beta\text{Co}_5\text{Ge}_3$ phase in the Co-Ge system. The solubility of Mo in αCo at 600 °C is ~3 at.% Mo and that of Ge in αCo in the Co-Ge system is ~8 at.% Ge. Thus, the (αCo) phase region will be smaller than that given in Fig. 4. Moreover, the presence of the (ϵCo) and Co_5Ge_2 phases in the Co-Ge system should show additional phase boundaries related to the equilibrium of the Γ phase with the (ϵCo) phase, and the equilibrium of the Co_5Ge_2 phase with the (ϵCo) and $\beta\text{Co}_5\text{Ge}_3$ phases. The probable phase equilibria at the Co corner of the Co-Ge-Mo system is schematically shown in Fig. 5.

The Γ phase was identified as an MgZn_2 -type Laves phase. For the alloy with composition $\text{Co}_{1.4}\text{Ge}_{0.6}\text{Mo}$, the lattice parameter was reported to be $a = 0.4790 \pm 0.0003$ nm and $c = 0.7665 \pm 0.0004$ nm. With the increase in Ge content the variation of lattice parameter a and lattice volume V (Fig. 6) indicates that the Γ phase region extends from ~16 at.% Ge to ~28 at.% Ge.

References

- 1964Bor:** L.K. Borusevich, Crystal Structure of Phases in (Mo,Fe) - (Co,Ni) -Ge, 1964, p 78-82, in Russian (Phase Equilibria, #)
1987Ole: R.W. Olesinski and G.J. Abbaschian, *Bull. Alloy Phase Diagram*, 1978, **8**, p 53-56 (Evaluation)

Indicates presence of phase diagram.

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