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# The Co-Mn-Si (Cobalt-Manganese-Silicon) System

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The Co-Mn-Si system has been studied at three different temperatures, and two isothermal sections were established. A large number of ternary intermediate phases exist in the Co-Mn-Si system.

## Binary Systems

The Co-Mn system [Massalski2] (Fig. 1) has only one intermediate phase, CoMn, which forms through a peritectoid reaction, (γCo) + (βMn) ↔ CoMn at 545 °C. Two peritectic reactions occur in the Co-Mn-Si system: L + (δMn) ↔ (βMn) at ~1185 °C and L + (γCo) ↔ (βMn) at 1161 °C. A solidus / liquidus minimum of ~1123 °C also occurs at ~72 at.% Mn. The (γMn) phase forms through a peritectoid reaction, (δMn) + (βMn) ↔ (γMn) at 1154 °C. A wide (βMn) phase field occurs from Mn to about the middle of the phase diagram. At the Mn end, the (βMn) → (αMn) transformation occurs at ≤727 °C. At the Co end the fcc (γCo) → cph (εCo) transformation occurs at ≤422 °C.

The Mn-Si system [Massalski2] (Fig. 2) has seven intermediate phases $Mn_6Si$ (R), ν, $Mn_3Si$, $Mn_5Si_2$, $Mn_5Si_3$, MnSi, and $MnSi_{1.75-x}$, of which the $Mn_5Si_3$ and MnSi phases melt congruently at 1300 and 1276 °C, respectively. The $Mn_3Si$ phase exists in two polymorphic forms, high-temperature $\beta Mn_3Si$ and low-temperature $\alpha Mn_3Si$ with the transformation occurring at ~677 °C. The ν, $\beta Mn_3Si$, and $MnSi_{1.75-x}$ phases form through peritectic reactions: L + (βMn) ↔ ν at 1060 °C, L + $Mn_5Si_3$ ↔ $\beta Mn_3Si$ at 1070 °C, and L + MnS ↔ $MnSi_{1.75-x}$ at 1155 °C. The R and $Mn_5Si_2$ phases form through peritectoid reactions: (βMn) + ν ↔ R at 880 °C and $\beta Mn_3Si$ + $Mn_5Si_3$ ↔ $Mn_5Si_2$ at ~850 °C. At the Mn-end of the system, the (γMn) and (βMn) phases form through peritectic reactions: L + (δMn) ↔ (γMn) at 1205 °C and L + (γMn) ↔ (βMn) at 1155 °C. The (βMn) phase transforms through a eutectoid reaction, (βMn) ↔ (αMn) + R at ~635 °C.

The Co-Si system [Massalski2] (Fig. 3) has five intermediate phases: $Co_3Si$ (ι), $\alpha Co_2Si$ ($\rho_1$), $\beta Co_2Si$ ($\rho_2$), CoSi (ζ), and $CoSi_2$ (π) of which the $\beta Co_2Si$, CoSi, and $CoSi_2$ phases melt congruently at 1334, 1460, and 1326 °C, respectively. The $Co_3Si$ and $\alpha Co_2Si$ phases form through peritectic reactions: L + $\rho_1$ ↔ ι at 1214 °C and L + $\rho_2$ ↔ $\rho_1$ at ~1370 °C. Addition of Si to Co stabilizes the cph (εCo) phase to high temperatures and a peritectic reaction L +

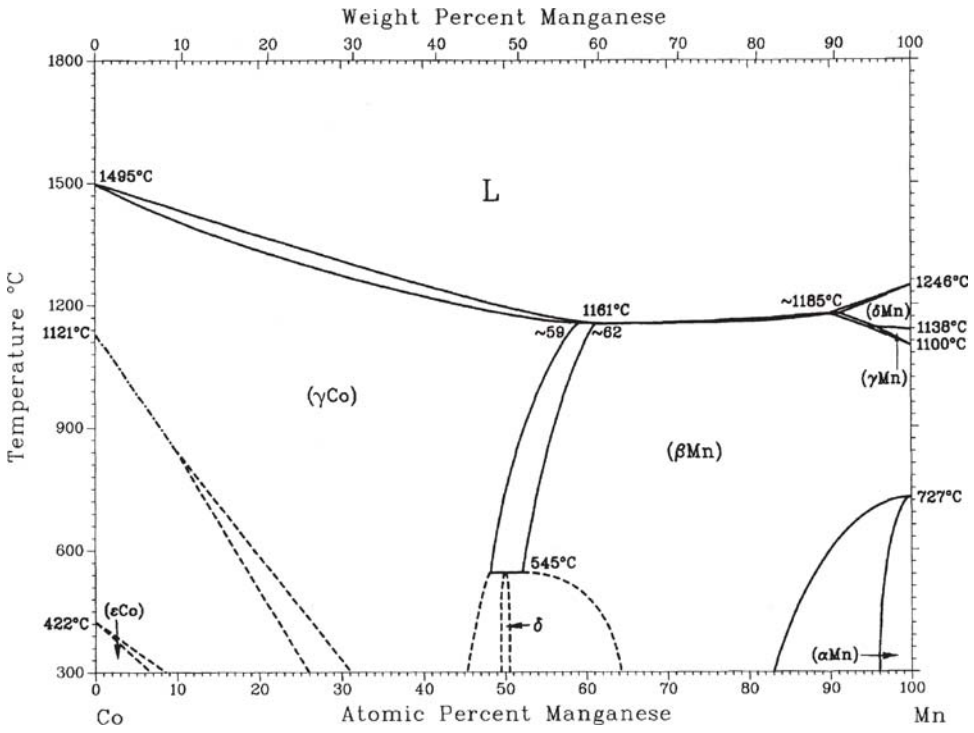


**Fig. 1** Binary Co-Mn diagram [Massalski2]

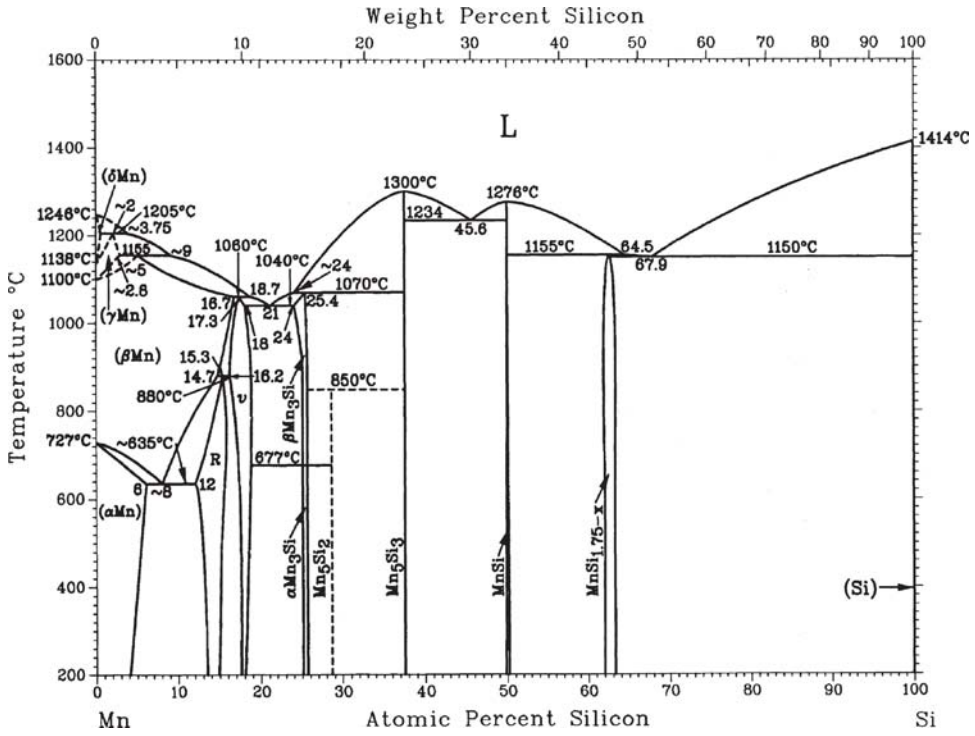


**Fig. 2** Binary Mn-Si diagram [Massalski2]

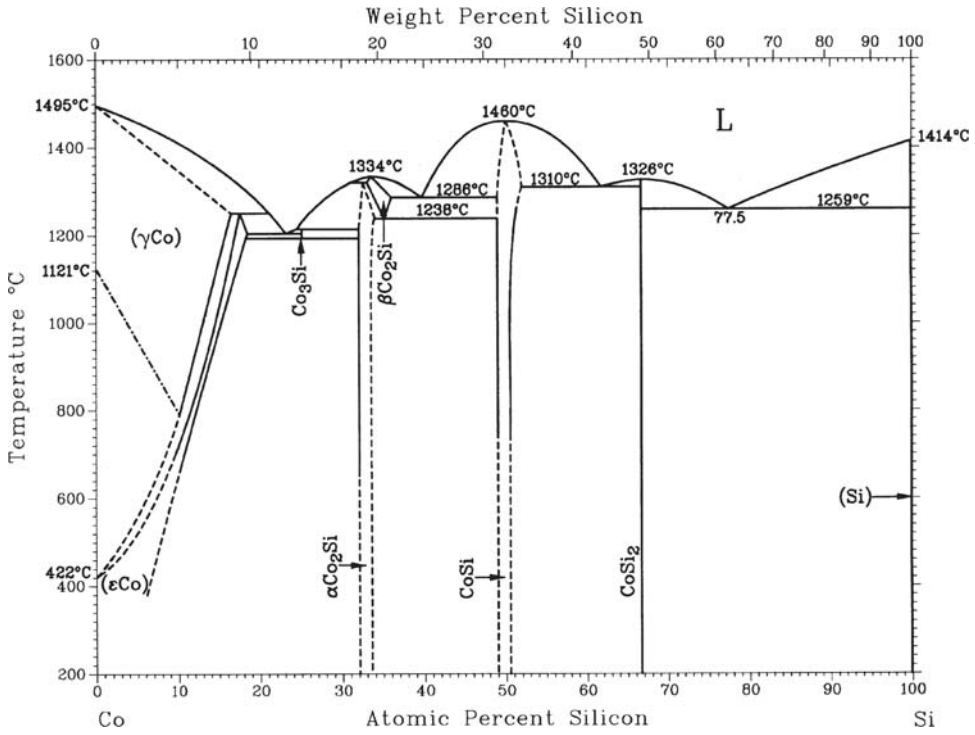


**Fig. 3** Binary Co-Si diagram [Massalski2]

($\gamma$Co) $\leftrightarrow$ ($\epsilon$Co) occurs at 1250 °C. The $Co_3Si$ and $\beta Co_2Si$ phases exist only at high temperatures and decompose through eutectoid reactions, $\iota \leftrightarrow (\epsilon Co) + \rho_1$ at 1193 °C and $\rho_2 \leftrightarrow \rho_1 + \zeta$ at 1286 °C. Four eutectic reactions, $L \leftrightarrow (\epsilon Co) + \iota$, $L \leftrightarrow \rho_2 + \zeta$, $L \leftrightarrow \zeta + \pi$, and $L \leftrightarrow \pi +$ (Si), occur at 1204, 1286, 1310, and 1259 °C, respectively.

**Table 1 Binary and ternary phases of the Co-Mn-Si system and their structure data**

| Phase designation | Composition | Pearsons symbol | Space group | Type | Lattice parameters, nm | | |
|---|---|---|---|---|---|---|---|
| | | | | | *a* | *b* | *c* |
| γ | (γCo) | *cF*4 | $Fm\bar{3}m$ | Cu | … | … | … |
| ϵ | (ϵCo) | *hP*2 | $P6_3/mmc$ | Mg | … | … | … |
| δMn | (δMn) | *cI*2 | $Im\bar{3}m$ | W | … | … | … |
| γMn | (γMn) | *cF*4 | $Fm\bar{3}m$ | Cu | … | … | … |
| βMn | (βMn) | *cP*20 | *P*4, 32 | βMn | … | … | … |
| αMn | (αMn) | *cI*58 | $I4\bar{3}m$ | αMn | … | … | … |
| Si | (Si) | *cF*8 | $Fd\bar{3}m$ | C(diamond) | … | … | … |
| δ | CoMn | … | … | (a) | … | … | … |
| ι | $Co_3Si$ | … | … | … | … | … | … |
| $\rho_1$ | $\alpha Co_2Si$ (32-34Si) | *oP*12 | *Pnma* | $Co_2Si$ | 0.7109 | 0.4918 | 0.3738 |
| $\rho_2$ | $\beta Co_2Si$(~32-35.8Si) | … | … | … | … | … | … |
| ζ | CoSi | *cP*8 | $P2_13$ | FeSi | 0.4447 | … | … |
| π | $CoSi_2$ | *cF*12 | $Pm\bar{3}m$ | $CaF_2$ | 0.5376 | … | … |
| R | $Mn_6Si$ | *hR*53 | $R\bar{3}$ | R(Co, Cr, Mo) | 1.0874 | … | 1.9177 |
| ν | $Mn_{4.5}Si$ | *oI*186 | *Immm* | … | … | … | … |
| $\beta_1$ | $\beta Mn_3Si$(25-25.6Si) | *cF*16 | $Fm\bar{3}m$ | $BiF_3$ | … | … | … |
| $\beta_2$ | $\alpha Mn_3Si$(25-25.6Si) | … | … | … | … | … | … |
| ξ | $Mn_5Si_2$ | *tP*56 | $P4_12_12$ | … | … | … | … |
| ϕ | $Mn_5Si_3$ | *hP*16 | $P6_3/mcm$ | $Mn_5Si_3$ | 0.6912 | … | 0.4812 |
| τ | MnSi | *cP*8 | $P2_13$ | FeSi | 0.4557 | … | … |
| θ | $MnSi_{1.75-x}$ | *tP*120 | $P\bar{4}n2$ | … | … | … | … |
| H | $Co_2MnSi$ | *cF*16 | $Fm\bar{3}m$ | $Fe_3Al$ (ordered) | 0.5670 | … | … |
| $\Gamma_1$ | $Co_3Mn_3Si_2$ | *hP*12 | $P6_3/mmc$ | $MgZn_2$ | 0.4738 | … | 0.7452 |
| X | $Co_3Mn_3Si$(b) | … | … | … | … | … | … |
| S | $CoMn_2Si$ | *cF*16 | $Fm\bar{3}m$ | $BiF_3$ | 0.5670 | … | … |
| ω(E) | CoMnSi | *oP*12 | *Pnma* | $Pbc1_2$ | 0.58543(c) | 0.36853(c) | 0.68526(c) |
| R | $Co_{20}Mn_{33}Si_{27}$ | *hR*53 | $R\bar{3}$ | R(Co,Cr,Mo) | 1.0755 | … | 1.9126 |
| U | $Co_8Mn_{64}Si_{28}$ | … | … | … | … | … | … |
| I | $Co_{32.5}Mn_{42.5}Si_{25}$ | *m* | … | I(V,Ni,Si) | … | … | … |
| Y | $Co_{42}Mn_{39}Si_{19}$(b) | … | … | … | … | … | … |
| Q | $Co_4Mn_{43}Si_{14}$ | *oP*74 | *Pnnm* | $Co_8Mn_9Si_3$ | 1.247 | 1.550 | 0.476 |

(a) Reported to be σ type. (b) X-ray diffraction patterns of X and Y phases have similarity. Possibly they are the same phase. (c) Lattice parameters from [1969 Jei]

## Binary and Ternary Phases

In the three binary systems 13 intermediate phases form. In the Co-Mn-Si system 10 ternary intermediate phases form. The structure data for the binary and ternary phases are given in Table 1.

## Ternary System

Early investigations of the Co-Mn-Si system were exploratory in nature with an aim to find intermediate phases that may form in the ternary system. In the earliest investigation of the Co-Mn-Si system by [1956Gla], the presence of a $MgZn_2$-type Laves phase $\Gamma_1$ was reported at the $Co_3Mn_3Si_2$ composition. The lattice parameter of the Laves phase was reported to be $a = 0.4747$ nm and $c = 0.7467$ nm.

The Co-Mn-Si system was studied in a somewhat detailed way by [1958Che]. Electrolytic grade Mn and Co and Si (purity not specified) were used to prepare about 100 alloys in porcelain crucibles under a layer of KCl + NaCl. The alloys were annealed at 400 °C for 10 days and quenched. X-ray diffraction (XRD) was used for phase identification. Four ternary intermediate phases were reported to be present at compositions of $Co_2MnSi$, $Co_3Mn_3Si_2$ ($\Gamma_1$), CoMnSi, and $Co_3Mn_{12}Si_5$. Besides these, the MnSi phase was reported to extend to ~30 at.% Co and the $Mn_5Si_3$ phase was found to extend to ~25 at.% Co at constant Si contents of 50 at.% Si and ~38% Si, respectively. The (βMn) phase was reported to extend to ~50 at.% Co and to ~15 at.% Si. The $Co_3Mn_{12}Si_5$ phase was reported to be related to the σ type phases. The $\Gamma_1$ phase is an $MgZn_2$-type Laves phase, reported earlier by [1956Gla]. The $Co_2MnSi$ phase was reported to be of CsCl type with lattice parameter $a = 0.2833$ nm. On the other hand, [1961Gla] reported the presence of a ternary intermediate phase at a composition of $Co_2MnSi$ at 800 °C with lattice parameter $a = 0.5670$ nm, and at 1000 °C it was reported to be a body-centered cubic (bcc) αFe-type structure with lattice parameter $a = 0.283$ nm.

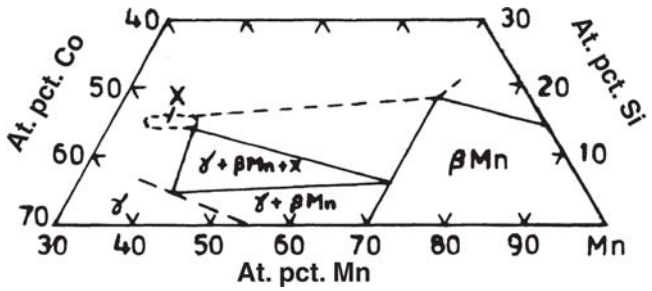


**Fig. 4** Partial isothermal section of the Co-Mn-Si system at 800 °C [1962Kuz]

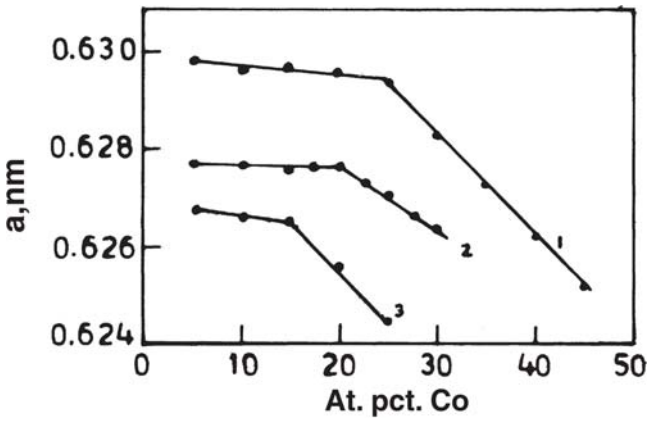


**Fig. 5** Lattice parameter of βMn phase as a function of Co content at 1-5 at.% Si, 2-10 at.% Si, and 3-15 at.% Si [1962Kuz]

A further exploratory study of the Co-Mn-Si system was made at the Mn corner by [1962Kuz]. Thirty-nine alloys with 5, 10, 15, and 20 at.% Si were melted in porcelain crucibles in an induction furnace under hydrogen. Purities of elemental components were indicated as electrolytic Mn, 99.9 mass% Co, and 99.5 mass% Si. The alloys were annealed in sealed quartz capsules at 800 °C for 120 h. Metallography and XRD methods were used for phase analysis and phase identification. Phase equilibria at the Mn corner were determined by [1962Kuz] as shown in Fig. 4. For the βMn phase, alloys containing 5, 10, 15 at.% Si, lattice parameter measurements as a function of Co content (Fig. 5) were used to determine the βMn phase boundary. The 800 °C βMn phase boundary was reported to be at 25 at.% Co for 5 at.% Si, at 20 at.% Co for 10 at.% Si, and at 15 at.% Co for 15 at.% Si. A ternary intermediate phase X was detected and found to be homogeneous in the composition region 45 to 50 at.% Co, 40 to 35 at.% Mn, and 15 at.% Si. The alloys with >32 at.% Co and 10 at.% Si were found to be in a three-phase region βMn + γCo + X, whereas the alloys with 5 at.% Si and >25 at.% Co were found to be in a two-phase region of γ + βMn. At 20 at.% Si and 5 at.% Co, the alloy was found to be in a different two-phase region, βMn + $Mn_3Si$.

A detailed investigation of the Co-Mn-Si system was done by [1964Kuz] to establish phase equilibria at 800 °C. One hundred eighty-five alloys were used in this investigation covering the entire composition region of the Co-Mn-Si ternary. Alloy preparation and characterization of alloys was done as given by [1962Kuz]. The 800 °C isothermal section by [1964Kuz] is given in Fig. 6. Seven ternary intermediate phases were found to exist at Si contents less than 40 at.%. Above 40 at.% Si, the binary phase CoSi was found in equilibrium with the MnSi phase, and the $CoSi_2$ phase was found in equilibrium with the $MnSi_{1.75-x}$ phase. The four binary phases $Co_2Si$, CoSi, MnSi, and $Mn_5Si_3$ phases were found to extend more or less along stoichiometric lines to ~13 at.% Mn, ~7 at.% Mn, ~25. at.% Co, and ~10 at.% Co, respectively. The solubilities of Co in MnSi and $Mn_5Si_3$ at 800 °C were found somewhat smaller than those at 400 °C [1958Gla]. Solubilities of Mn or Co in all other binary phases, namely the εCo, $CoSi_2$, $MnSi_{1.75-x}$, $Mn_3Si$, ν, and $Mn_6Si$ (R) phases were found to be ≤2 at.%. The βMn phase dissolves up to ~15 at.% Si. At the Co-end, the alloys with 5 at.% Si showed the presence of both (γCo) and (εCo) phases indicating the presence of an elongated γ + ε two-phase region surrounded by a γ phase region. In Fig. 6, the binary phase compositions have been adjusted to conform to the accepted binary data.

Seven ternary intermediate phases have been reported for the Co-Mn-Si system and are designated ω, H, $\Gamma_1$, S, R, U, and X. Five out of these seven intermediate phases, namely H, $\Gamma_1$, S, R, and U phases, were found at silicon content of ~25 at.%. A small, ~2 at.% wide, ω phase region exists around the CoMnSi composition and extends along the 33 at.% Co line from 32 to 36 at.% Si. The ω phase has been identified as isostructural with the orthorhombic TiNiSi E phase [1969Jei] with lattice parameters $a = 0.58543$ nm, $b = 0.36853$ nm, and $c = 0.68526$ nm. The ω phase was found in equilibrium with the $Co_2Si$, CoSi, $Mn_5Si_3$, H, $\Gamma_1$, S, and the ternary R phases.

The $Co_2MnSi$ phase, designated as the H phase, extends along the 25 at.% Si line from about 16 to 28 at.% Mn. The H phase is related to the $Fe_3Al$-type (ordered) structure with lattice parameter of $a = 0.5670$ nm. The H phase was found in equilibrium with the γ, $Co_2Si$, ω, and $\Gamma_1$ phases. The $\Gamma_1$ phase ($MgZn_2$-type Laves phase) extends along the 33 at.% Mn line from ~22 to 25 at.% Si. The lattice parameters for the $\Gamma_1$ phase have been reported to be $a = 0.474$ nm and $c = 0.7514$ nm at 22.5 at.% Si and $a = 0.4735$ nm and $c = 0.7491$ nm at 25 at.% Si. The $\Gamma_1$ phase was found in equilibrium with the γ, H, ω, S, and X phases. The S phase ($CoMn_2Si$ phase) occurs at ~25 at.% Si and extends from ~44 to 52 at.% Mn and is ~3 at.% Si wide. Microstructure observations of the as-cast as well as the annealed (1000, 800, and 400 °C) S phase alloys suggest the S phase forms from liquid and is stable down to room temperature. The S phase has been found in equilibrium with the $\Gamma_1$, ω, R, βMn, and X phases.

The ternary R phase occurs near the composition $Co_{20}Mn_{53}Si_{27}$, has a small region of homogeneity, ~3 at.% Si wide and extends from 52 to 57 at.% Mn. The ternary R phase is structurally similar to the binary $Mn_6Si$ (R) phase. It is surprising that even though the $Mn_6Si$ (R) phase exists at 800 °C, it does not extend toward the ternary R phase region. Whether the ternary R phase is an extension of the binary R phase is not known and merits investigation. The

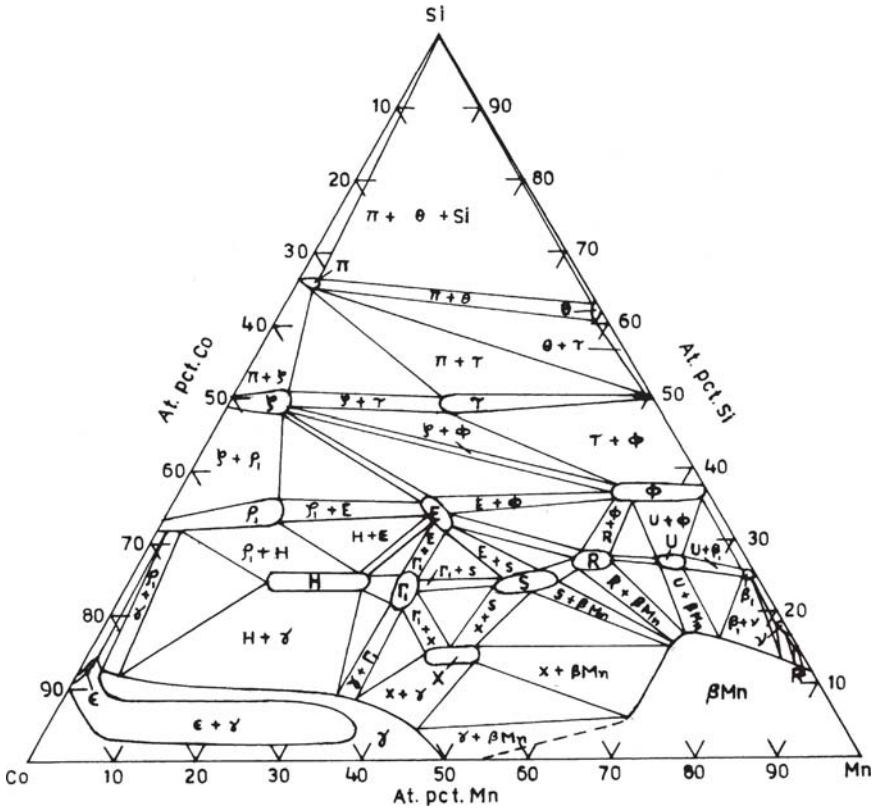


**Fig. 6** The 800 °C isothermal section of the Co-Mn-Si system [1964Kuz]

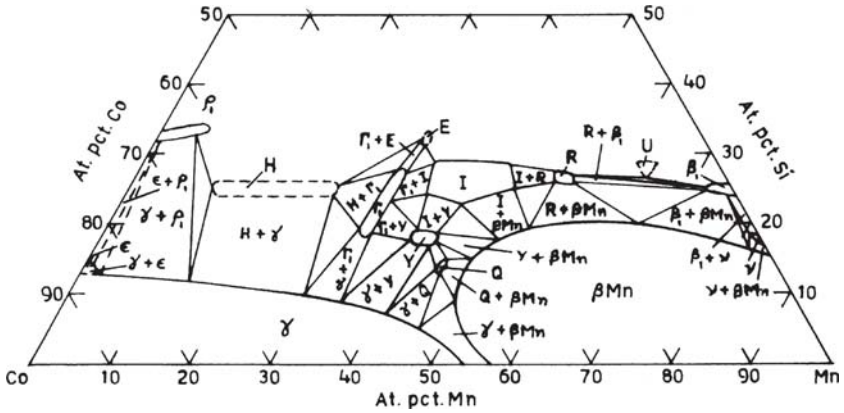


**Fig. 7** Partial isothermal section of the Co-Mn-Si system at 1000 °C [1966Bar]

R phase lattice parameters are given as $a = 1.0755$ nm and $c = 1.9126$ nm, which are reasonably close to the lattice parameters of the $Mn_6Si$ (R) phase $a = 1.0874$ nm and $c = 1.9177$ nm [1964Kuz]. The R phase was found in equilibrium with the ω. $Mn_3Si_3$, U, βMn, and S phases.

The U phase occurs around the composition $Co_8Mn_{64}Si_{28}$. The XRD pattern of the U phase resembles that of the δ(MoNi) phase. The U phase was found in equilibrium with the βMn, $Mn_5Si_3$, $Mn_3Si$, and R phases. The X phase ($Mn_3Co_3Si$) exists at ~15 at.% Si and extends from 40 to 45 at.% Mn. The X phase was found in equilibrium with the γ, $\Gamma_1$, S, and βMn phases.

The Co-Mn-Si system was studied at 1000 °C by [1966Bar] up to ~35 at.% Si. The alloys were melted in recrystallized alumina crucibles in a high-frequency induction furnace under argon gas using Co and Mn of at least 99.7 mass% purity and Si of 99.98 mass% purity. The alloys were annealed at 1000 °C in evacuated and sealed silica capsules. The duration of annealing, however, was not mentioned. XRD and metallographic methods were used for phase identification and phase-boundary determination. The partial isothermal section of the Co-Mn-Si, determined by [1966Bar], is given in Fig. 7. In the investigated composition region, binary phases $Co_2Si$, $Mn_3Si$, and ν were only

found in equilibrium with other phases. The ϵCo phase, which is stable at 1000 °C in the Co-Si system, has not been indicated in the isothermal section. Hence, the phase equilibria at the Co end of the diagram is incomplete. Further work will be required to establish phase equilibria involving the ϵCo phase. The existence of eight ternary intermediate phases—U, R, I, ω, Y, Q, and the H phase—were reported in the investigated composition region of the Co-Mn-Si system. Unlike [1964Kuz], the U phase region was found to have a smaller composition range than at 800 °C and was found not to be in equilibrium with the βMn phase. The U phase was found in equilibrium with the $Mn_3Si$ and R phases. The R phase region is also found to have a somewhat smaller composition range than at 800 °C. The I phase of [1966Bar] exists at about the same composition region as does the S phase of [1964Kuz], but the XRD patterns of the I and S phases differ. The (Co,Mn,Si) I phase has been found [1966Bar] to be isotypic with the I phase of the V-Ni-Si system. The Y phase of [1966Bar] occurs at ~18 at.% Si and ~41 at.% Mn. The XRD patterns of the Y phase and the X phase of [1984Kuz] are somewhat similar except that a much larger number of diffraction lines occur in the diffraction pattern of the Y phase. Whether the X and Y phases are the same phase should be further verified. [1966Bar] found the $MgZn_2$-type Laves phase to ($\Gamma_1$) to have a composition range extending from ~18 to 28 at.% Si, thus somewhat larger than the range found by [1964Kuz]. The ω phase was found at the CoMnSi composition, but its phase boundary was not determined. A new ternary intermediate phase, the Q phase, was found to occur between the Y phase and the βMn phase at about the composition of $Co_{39}Mn_{46}Si_{15}$. The βMn phase region was found to extend to ~20 at.% Si and to ~43 at.% Co. The Q phase was found in equilibrium with the βMn, Y, and γ phases. Unlike what has been reported by [1963Kuz], at 1000 °C the H phase was reported to extend from ~11 to 27 at.% Mn at 25 at.% Si. The phase boundary of the H phase was not determined accurately by [1966Bar].

## References


**1956Gla:** E.I. Gladyshevskii, P.I. Kripyakevich, and Yu.B. Kuzma, *Dopovidi Akad. Nauk. Ukrain, RSR,* 1956, No. 1, p 67. (Quoted by [1964Kuz])

**1958Che:** E.E. Cherkashin, E.I. Gladyshevskii, P.I. Kripyakevich, and Yu. B. Kuzma, X-Ray Structural Analysis of Certain Systems of Transition Metals, *Russ. J. Inorg. Chem.,* 1958, **3**(3), p 650-653. (Phase equilibria)

**1961Gla:** E.I. Gladyshevskii, P.I. Kripyakevich, M.Yu. Teslyuk, O.S. Zarechnyuk, and Yu. B. Kuzma, *Kristallografiya,* 1961, **6,** p. 267. (Quoted by [1964Kuz])

**1962Kuz:** Yu.B. Kuzma, βMn Based Solid Solutions in the Mn-(Co, Ni)-Si Ternary Systems, *Russ. J. Inorg. Chem.,* 1962, **7**(6), p 691-694. (Phase equilibria, #)

**1963Kuz:** Yu.B. Kuzma, E.I. Gladyshevskii, and V.Ya. Markev, *Khim. Visnik. L'viv. Derzh. Univ.,* 1963, No. 7. (Quoted by [1964Kuz])

**1964Kuz:** Yu.B. Kuz and E.I. Gladyshevskii, The Co-Mn-Si System, *Russ. J. Inorg. Chem.,* 1964, **9**(3), p 373-377. (Phase equilibria, #)

**1966Bar:** D.I. Bardos, R.K. Malik, F.X. Spiegel, and P.A. Beck, Beta-Manganese Phases in Ternary Systems of Transition Elements with Silicon, Germanium, or Tin, *Trans. TMS-AIME,* 1966, **236,** p 40-48. (Phase equilibria, #)

**1969Jei:** W. Jeitschko, A.G. Jordan, and P.A. Beck, V and E Phases in Ternary Systems with Transition Metals and Silicon or Germanium, *Trans. TMS-AIME,* 1969, **245,** p 335-39. (Crys Structure)


*indicates key paper.
#indicates presence of a phase diagram.

Co-Mn-Si 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 1997. Dr. Gupta is the Alloy Phase Diagram Co-Category Program Editor for ternary alloys.