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The Co-Sn-Zr (Cobalt-Tin-Zircoium) System

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Introduction

The Co-Sn-Zr system has been studied and one isothermal section has been established at reasonably low temperature and is reported here.

Binary Systems

The Co-Sn binary system [1983Nis, Massalski2] (Fig. 1) has three intermediate phases: Co_3Sn_2 in two allotropic forms Co_3Sn_2 (η) above ~500 °C and Co_3Sn_2 (η_1) below 500 °C, CoSn (π) and $CoSn_2$ (ζ). The η phase melts congruently at ~1170 °C and the other two phases form through peritectic reactions: $L + \eta \leftrightarrow \pi$ at 936 °C and $L + \pi \leftrightarrow \zeta$ at 525 °C. Two eutectic reactions $L \leftrightarrow \gamma + \eta$ and $L \leftrightarrow \zeta + \beta$ occur at 1112 °C and 229 °C, respectively. The γ and β phases are the terminal solid solutions of fcc αCo and of tetragonal βSn, respectively. The $\gamma \leftrightarrow \varepsilon$ transformation possibly occurs through a eutectoid type reaction at ~420 °C where ε is the terminal solid solution of close packed hexagonal (cph) εCo.

The Co-Zr system [Massalski2] (Fig. 2) shows the presence of five intermediate phases $Co_{11}Zr_2$ (ψ), Co_4Zr (ι), Co_2Zr (λ_2), CoZr (β_1), and $CoZr_2$ (ξ). The probable presence of another phase $CoZr_3$ (ν) was reported but requires further confirmation. With the Co_2Zr phase being an exception, all other phases are stoichiometric compounds. The Co_2Zr, CoZr, and $CoZr_2$ phase are believed to melt congruently at approximately 1620, 1420, and 1125 °C, respectively. The ψ and ι phases form through peritectic reactions: $L + \lambda_2 \leftrightarrow L$ at 1452 °C and $L + \iota \leftrightarrow \psi$ at 1272 °C. Four eutectic reactions occur in the Co-Zr system: $L \leftrightarrow \gamma + \psi$ at 1222 °C, $L \leftrightarrow \lambda_2 + \beta_1$ at 1312 °C, $L \leftrightarrow \beta_1 + \xi$ at 1061 °C, and $L \leftrightarrow \xi + \alpha$ at 981 °C where α is the body centered cubic (bcc) terminal solid solution of βZr. A eutectoid reaction $\alpha \leftrightarrow \xi + \varepsilon_2$ occurs at 834 °C where ε_2 is the cph terminal solid solution of αZr. In the Co-rich region possibly a eutectoid reaction $\gamma \leftrightarrow \psi + \varepsilon_1$ occurs at ~422 °C.

The Sn-Zr system [Massalski2] (Fig. 3) has three intermediate phases, $SnZr_4$ (θ), Sn_3Zr_5 (ω), and Sn_2Zr (ϕ) of which the ω phase melts congruently at 1988 °C. The probable existence of another phase Sn_4Zr_5 (T) has been suggested in the SnZr system. The θ and ϕ phases form through peritectoid and peritectic reactions: $\omega + \alpha \leftrightarrow \theta$ at 1327 °C and $L + \omega \leftrightarrow \phi$ at 1142 °C.

The reaction through which the T phase forms is not known. Two eutectic reactions $L \leftrightarrow \alpha + \omega$ and $L \leftrightarrow \phi + \beta$ occur at 1592 and ~232 °C, respectively. The cph ε_2 phase forms through a peritectoid reaction $\alpha + \theta \leftrightarrow \varepsilon_2$ at 982 °C where ε_2 is the cph terminal solid solution αZr.

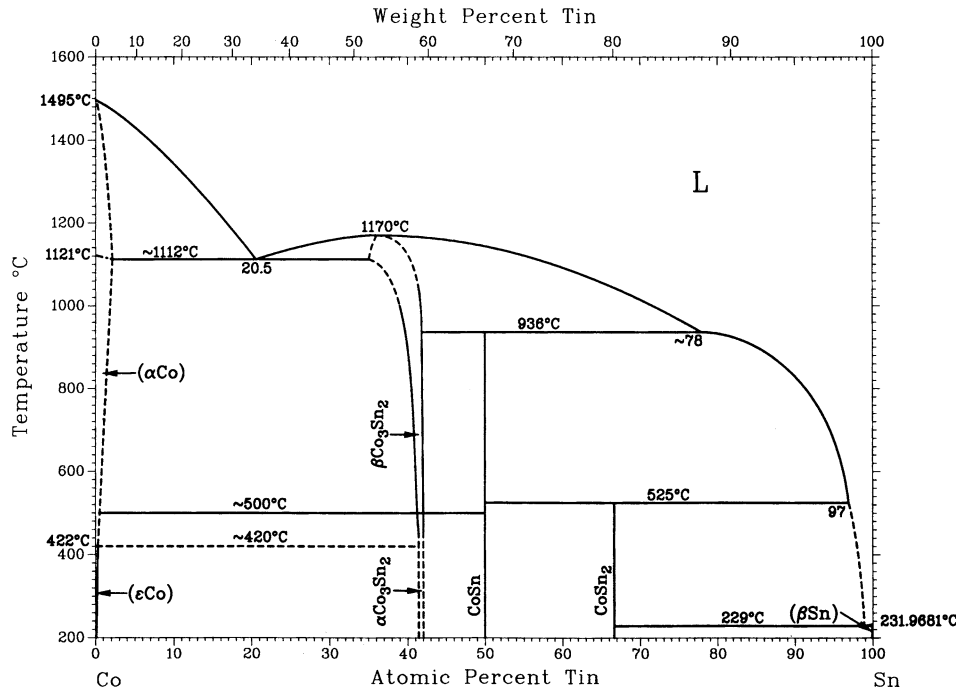

Fig. 1 The Co-Sn binary system [Massalski2]

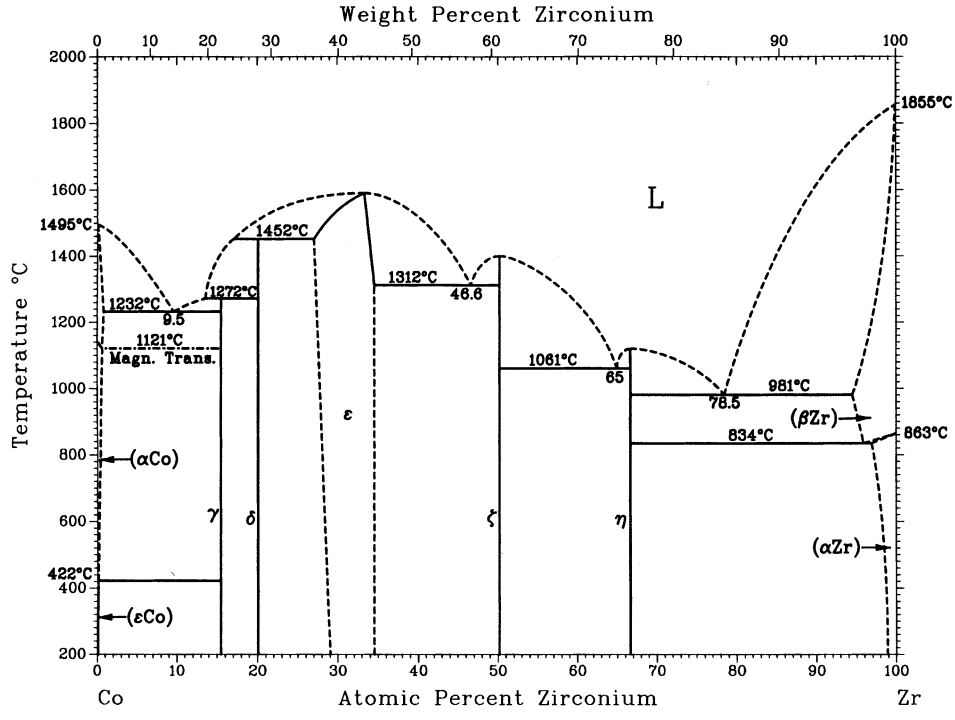

Fig. 2 The Co-Zr binary system [Massalski2]

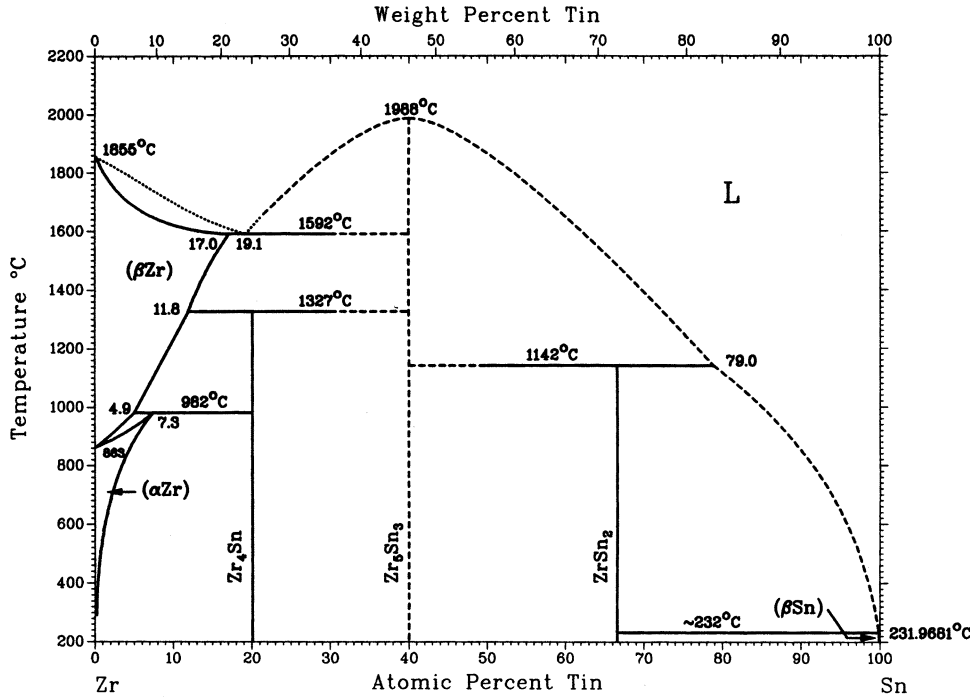

Fig. 3 The Sn-Zr binary system [Massalski2]

Binary and Ternary Phases

In the three binary systems Co-Sn, Co-Zr, and Sn-Zr given by [Massalski2] 11 intermediate phases form. Two more phases, one is the Co-Zr system and the other is the Sn-Zr system, have been reported but possibly require further confirmation. In the Co-Sn-Zr system four ternary intermediate phases form. The binary and ternary phases of

Table 1 Binary and ternary phases of the Co-Sn-Zr system and their structure data

Phase designation	Composition	Pearson's symbol	Space group	Type	Lattice parameters, nm		
					a	*b*	*c*
γ	(αCo)	*cF*4	$Fm\bar{3}m$	Cu	...	...	...
ε_1	(εCo)	*hP*2	$P6_3/mmc$	Mg	...	...	...
α	(βZr)	*Cl*2	$Im\bar{3}m$	W	...	...	...
ε_2	(αZr)	*hP*2	$P6_3/mmc$	Mg	...	...	...
β	(βSn)	*tl*4	$I4_1/amd$	βSn	...	...	...
η	Co_3Sn_2(HT)	*hP*4	$P6_3/mmc$	AsNi	0.411	...	0.5183
η_1	Co_3Sn_2(LT)	*oP*20	*Pnma*	Ni_3Sn_2	...	...	...
π	CoSn	*hP*6	*P6/mmc*	CoSn	0.5279	...	0.4259
ζ	$CoSn_2$	*tl*112	*I4/m*	Al_2Cu	0.6361	...	0.5452
ψ	$Co_{11}Zr_2$	...	...	...	...	...	...
ι	Co_4Zr	*cF*116	$Fm\bar{3}m$	$Mn_{23}Th_6$	1.1516	...	...
λ_2	Co_2Zr	*cF*24	$Fd\bar{3}m$	Cu_2Mg	0.69512	...	...
β_1	CoZr	*cP*2	$Pm\bar{3}m$	CsCl	0.3197	...	...
ξ	$CoZr_2$	*tl*12	*I4/mcm*	Al_2Cu	0.6364	...	0.5518
ν	$CoZr_3$ (a)	*oC*16 *hP*8	*Cmcm* $P6_3/mmc$	Re_2BNi_3Sn	...	...	...
ϕ	$SnZr_2$	*oF*24	*Fddd*	$TiSi_2$	0.957	0.564	0.992
T	Sn_4Zr_5 (a)	*hP*18	...	$GaTi_5$	...	...	...
ω	Sn_3Zr_5	*hP*16	$P6_3/mcm$	Mn_5Si_3	0.8461	...	0.5795
θ	$SnZr_4$	*cP*8	$Pm\bar{3}m$	Cr_3Si	0.565	...	...
ψ	CoSnZr	...	$P\bar{6}2m$	AlNiZr	0.7133	...	0.3571
Ω	Co_2SnZr	...	$Fm\bar{3}m$	$AlCu_2Mn$	0.6227	...	...
Δ	$Co_{1.65}Sn_{1.35}Zr_6$	...	$P\bar{6}2m$	...	0.7971	...	0.3453
Φ	$Co_6Sn_{18}Zr_5$	...	...	...	1.3268	...	...

(a) Probably exists

the Co-Sn-Zr system and their structure data are given in Table 1.

Ternary System

The Co-Sn-Zr system has been studied by [1995Sta] using 125 alloys, arc melted under purified argon atmosphere. High purity component elements, electrolytic Co of 99.6 mass% purity, Sn of 99.99 mass% purity, and iodide Zr of 99.9 mass% purity, were used to prepare the alloys. For annealing, the alloys were sealed in evacuated quartz capsules. The alloys containing ≤40 at.% Sn were first annealed at 797 °C for 240 h and subsequently annealed at 497 °C for 240 h. The alloys with >40 at.% Sn were directly annealed at 497 °C for 240 h. The alloys after annealing were quenched in cold water. For phase analysis and phase identification, a Dehye Scherrer x-ray powder diffraction camera was used. For a few ternary intermediate phases structure analysis was done by using Laue and rotating crystal techniques and for structure refinement a diffractometer was used.

The 497 °C isothermal section of Co-Sn-Zr system established by [1995Sta] is given in Fig. 4. Four ternary intermediate phases were found of which two of the phases Co-Sn-Zr (ψ) and CoSnZr (Ω) were reported earlier by [1986Sko] and [1976Sob], respectively. The two new ternary intermediate phases were found to exist with approximate compositions of $CoSn_3Zr$ (ϕ) and $CoSnZr_4$ (Δ). The binary intermediate phases were found to have very limited solubility ~1 at.% of a third element. Even though the binary diagrams of Co-Zr and Sn-Zr systems do not include the $CoZr_3$ (ν) and Sn_4Zr_5 (γ) phases, the 497 °C isothermal section by [1995Sta] show these two phases. These two phases were found in equilibrium with the ternary intermediate phases Δ and ψ, respectively. The CoSnZr (Ω) phase region is a small elongated region extending along a line joining Co and $Sn_{50}Zr_{50}$ composition, extending from ~40% ~50 at.% Co. The Ω phase was found in equilibrium with the λ_2, η_1, π, ζ, ϕ, ψ, and ω phases. The ψ phase was found in equilibrium with the Φ, ϕ, T, Ω, and ω phases. The Φ phase was reported to be in equilibrium with the Ω, ψ, ζ, Sn, and ϕ phases. Since at 497 °C Sn is in liquid form the Φ phase should be in equilibrium with liquid Sn. The Δ phase was found in equilibrium with the β_1, ξ, ν, θ, and ω phases. The $Co_{11}Zr_2$ (ψ) phases exists in the Co-Zr binary system but the investigation by [1995Sta] does not show this phase in the isothermal section at 497 °C. The Co-corner of the Co-Sn-Zr thus appears to be incomplete and should be reinvestigated. The binaries Co-Zr system and Sn-Zr system also should be carefully studied to establish the existence as well as the mode of formation of the $CoZr_3$ and Sn_4Zr_5 phases.

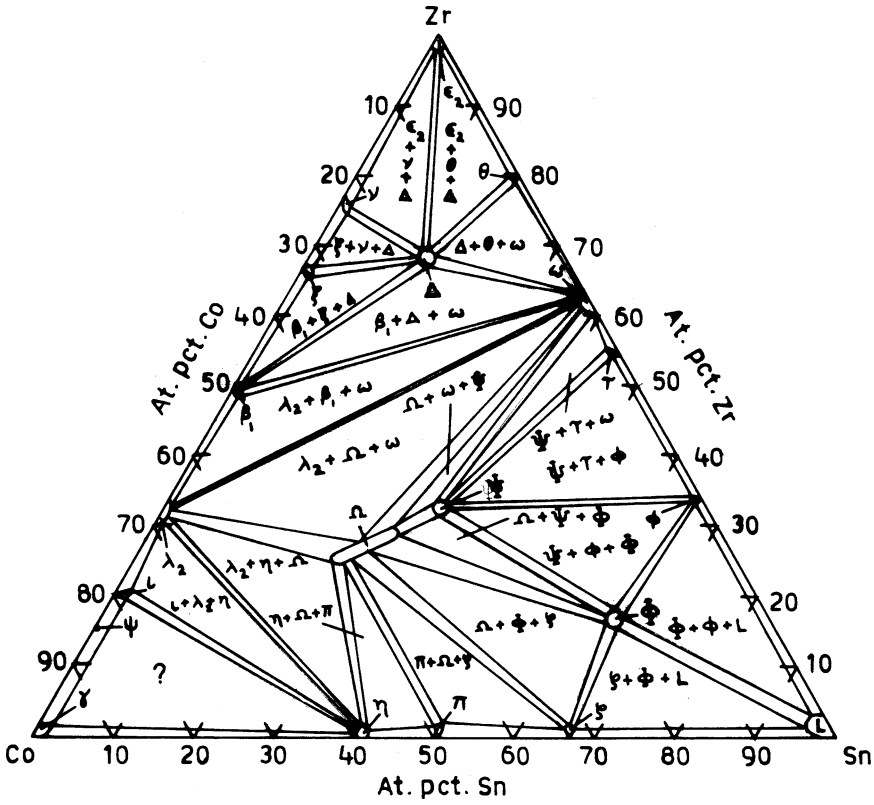

Fig. 4 Isothermal section of the Co-Sn-Zr system at 497 °C [1995Sta]

Of the four ternary intermediate phases found in the Co-Sn-Zr system, two intermediate phases CoSnZr and Co_2SnZr were reported earlier by [1974Dwi] and [1976Sob], respectively. The CoSnZr phase was reported to be of Fe_2P type with lattice parameters a = 0.7156 nm and c = 0.3563 nm and the Co_2SnZr phase was reported to be of BiF_3 type with lattice parameter a = 0.6285 nm. [1986Sko], however, reported the CoSnZr phase to be of AlNiZr type, a superstructure of Fe_2P type structure, with lattice parameters a = 0.7133 nm, c = 0.3571 nm, and γ = 120°. [1986Sko] also showed that the Co_2SnZr phase to be of $AlCu_2Mn$ type with lattice parameter a = 0.6234 nm. Laue and rotation x-ray diffraction patterns taken with a single crystal extracted from the $CoSnZr_4$ alloy showed that this phase is of Fe_2P type with lattice parameter a = 0.7971 nm and c = 0.3453 nm. Structure refinement was done using a diffractometer. The structure was found to be a superstructure of Fe_2P type structure and the ideal composition was reported to be $Co_{1.65}Sn_{1.35}Zr_6$. An x-ray diffraction pattern of $CoSn_3Zr$ phase was found to closely resemble the diffraction pattern of a phase found in the Er-Rh-Sn system having a composition $Sn_{1-x}(Sn_{1-x}Zr_x)Zr_4Rh_6Sn_{18}$ which has a cubic structure. The diffraction pattern of an alloy with composition $Co_{20}Sn_{65}Zr_{15}$could be indexed reasonably well with a cubic cell with lattice parameter a = 1.3682 nm. On the basis of similarity of this diffraction pattern of the $Co_{20}Sn_{65}Zr_{15}$ alloy with that of the Er-Rh-Sn phase, the composition for the $CoSn_2Zr$ phase has been given a tentative composition identification of $Co_6Sn_{18}Zr_5$ phase. Further work has to be done to identify the $Co_6Sn_{18}Zr_5$ phase.

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