The Co-Ni-Sn (Cobalt-Nickel-Tin) System

K.P. Gupta, The Indian Institute of Metals

Introduction

Very little work has been done in the Co-Ni-Sn system. Only one pseudobinary has been established and reported here.

Binary Systems

The Co-Ni system [1991Nas] (Fig. 1) is a simple isomorphous system. In the fcc α solid solution, there are indications of formation of short range order near the CoNi₃ composition.

The Co-Sn system [1983Nis, Massalski2] (Fig. 2) has three intermediate phases, Co_3Sn_2 in two allotropic forms, $Co_3Sn_2(HT)$ and $Co_3Sn_2(LT)$; CoSn; and CoSn₂. The Co_3Sn_2 phase melts congruently at ~1170 °C and the other two phases form through peritectic reactions L + $Co_3Sn_2(HT) \leftrightarrow CoSn$ at 936 °C and L + CoSn \leftrightarrow CoSn₂ at 525 °C. $Co_3Sn_2(HT) \rightarrow Co_3Sn_2(LT)$ transformation occurs at ~500 °C. Two eutectic reactions L \leftrightarrow (α Co) + $Co_3Sn_2(HT)$ and L \leftrightarrow CoSn₂ + (β Sn) occur at ~1112 and ~229 °C, respectively. The fcc (α Co) \rightarrow hcp (ϵ Co) reaction, possibly a eutectoid type reaction, occurs at ~420 °C.

The Ni-Sn system [1991Nas, Massalski2] (Fig. 3) has three intermediate phases, Ni₃Sn and Ni₃Sn₂, both of which exist in two allotropic forms, and Ni₃Sn₄. Both Ni₃Sn₂ and Ni₃Sn phases melt congruently at 1264 and 1174 °C, respectively, and the Ni₃Sn₄ phase forms through a peritectic reaction L + Ni₃Sn₂ \leftrightarrow Ni₃Sn₄ at 795 °C. Three eutectic reactions L \leftrightarrow (Ni) + Ni₃Sn(HT), L \leftrightarrow Ni₃Sn(HT) + Ni₃Sn₂(HT), and L \leftrightarrow Ni₃Sn₄ + (β Sn) occur respectively at 1130, 1160, and 231 °C. The Ni₃Sn(LT) phase forms through a congruent transformation at 977 °C. The Ni₃Sn₂(HT) \rightarrow Ni₃Sn₂(LT) transformation occurs at ~ 600 °C.

Binary and Ternary Phases

In the Co-Ni-Sn system, six intermediate phases form, of which three phases exist in two allotropic forms. No ternary intermediate phase has been reported in the Co-Ni-Sn system. The binary phases and their structure data are given in Table 1.



Fig. 1 Co-Ni binary phase diagram [1991Nas]



Fig. 2 Co-Sn binary phase diagram [Massalski2]



Fig. 3 Ni-Sn binary phase diagram [1991Nas]

Ternary System

In the Co-Ni-Sn system a pseudobinary section $Co-Ni_3Sn_2$ has been established by [1973Pan]. The alloys

were prepared using 99.99 mass% pure Co and Ni and 99.999 mass% pure Sn powder, pressed and sintered under an inert atmosphere. Differential thermal analysis of alloys was used to determine the phase transformation temperatures.

Phase designation	Composition	Pearson's symbol	Space group	Туре	Lattice parameters, nm		
					а	b	с
α	(αCo), (Ni), (αCo, Ni)	cF4	$Fm\overline{3}m$	Cu			
3	(eCo)	hP2	$P6_3/mmc$	Mg			
β	(βSn)	tI4	$I4_1/amd$	βSn			
η	Co ₃ Sn ₂ (HT)	hP4	$P6_3/mmc$	AsNi	0.411		0.5183
η′	$Co_3Sn_2(LT)$	oP20	Pnma	Ni ₃ Sn ₂			
π	CoSn	hP6	P6/mmm	CoSn	0.5279		0.4259
ζ	CoSn ₂	<i>tI</i> 12	I4/m	Al ₂ Cu	0.6361		0.5452
γ	Ni ₃ Sn(HT)	<i>cF</i> 16	$Fm\overline{3}m$	BiF ₃	0.598		
γ	Ni ₃ Sn(LT)	hP8	$P6_3/mmc$	CdMg ₃	0.5286		0.4243
η′	$Ni_3Sn_2(HT)$	oP20	Pnma	Ni ₃ Sn ₂	0.711	0.521	0.823
η_1	$Ni_3Sn_2(LT)$	hP4	$P6_3/mmc$	AsNi	0.4125		0.5198
ξ	Ni ₃ Sn ₄	<i>mC</i> 14	C2/m		1.2223	0.4061	0.5187
						$\alpha = 103.5^{\circ}$	

 Table 1
 Binary phases and their structure data

(HT) and (LT) indicate high temperature and low temperature, respectively



Fig. 4 Pseudobinary Ni₃S₂-Co [1973Pan]

The other methods that were used to characterize the alloys are microscopic analysis, hardness, and magnetic susceptibility measurements. The Co-Ni₃Sn₂ pseudobinary section, as determined by [1973Pan] is given in Fig. 4. It shows a simple eutectic system with a eutectic reaction $L \leftrightarrow$ (γ Co) + Ni₃Sn₂(HT) occurring at 1075 °C. The eutectic composition is with 40 at.% Co in Ni₃Sn₂(HT). At lower temperature, a thermal effect was observed at ~470 °C. Since the accepted (γ Co) \leftrightarrow (ϵ Co) transformation temperature is 422 °C, a eutectoid reaction is not possible. A peritectoid reaction (γ Co) + Ni₃Sn₂ \leftrightarrow (ϵ Co) with peritectic temperature ~470 °C is more probable and is shown in Fig. 4. At the Ni₃Sn₂ end of the pseudobinary the allotropic transformation of the Ni₃Sn₂ phase should occur but has not been determined. The pseudobinary section is thus incomplete at lower temperatures.

Even though no other information is available for the Co-Ni-Sn system, it may be possible to suggest what kinds of reactions involving the liquid phase are to be expected. The Co-Ni system is a simple isomorphous system and no ternary intermediate phases have been reported in the Co-Ni-Sn system. In the low Sn side of the Co-Ni₃Sn₂ pseudobinary, only two eutectic reactions, e1 and e2, occur in the Ni-Sn binary. On the basis of this information, the probable liquidus projection for the Co-Ni-Ni₃Sn₂ region is expected to have a U-type reaction U1, and the resulting three phase equilibrium triangle. $L + \alpha + \eta'$ should terminate at the eutectic line of the Co-Ni₃Sn₂ pseudobinary at 1075 °C (Fig. 5 and 6). On the higher Sn side of the Co-Ni₃Sn₂ pseudobinary, one eutectic reaction e₃ occurs in the Co-Sn binary which is close to the pseudobinary. The liquid composition from the three phase equilibrium in the Co-Sn binary, however, cannot terminate at e4 at 1075 °C because the Co₃Sn₂(HT) and Ni₃Sn₂(HT) phases have different crystal structures. Both Co3Sn2 and Ni3Sn2 phases melt congruently and it may be possible that a Co₃Sn₂-Ni₃Sn₂ eutectic type pseudobinary exists. In such a case a U-type reaction U2 may occur in the composition region Co-Co₃Sn₂-Ni₃Sn₂ and the resulting three phase equilibrium triangle $L + \alpha + \eta'$ finally terminates at the Co-Ni₃Sn₂ eutectic line at 1075 °C (Fig. 5 and 6a). If, on the other hand, no Co₃Sn₂-Ni₃Sn₂ pseudobinary exists, the liquid composition coming down from e₃ and e₄ may give a





Fig. 6 (a) Probable reaction scheme for the Co-Ni-Sn system with Co_3Sn_2 -Ni $_3Sn_2$ pseudobinary. (b) Change in the probable reaction scheme if Co_3Sn_2 -Ni $_3Sn_2$ pseudobinary does not exist

Section II: Phase Diagram Evaluations

U-type reaction U'_{2} (see Fig. 3b). On the higher Sn side of the Co_3Sn_2 -Ni_3Sn_2 line, the possible reactions are indicated in Fig. 5 and 6(a). For either of the two possibilities mentioned above, the reactions at the higher Sn side of the Co-Ni-Sn system will remain the same as indicated in Fig. 5 and 6(a, b). The above suggested liquidus projection and reaction schemes for the Co-Ni-Sn system (Fig. 5 and 6a, b) requires experimental verification to know whether the Co_3Sn_2 -Ni₃Sn_2 pseudobinary exists and to know which of the two reaction schemes is actually applicable for the Co-Ni-Sn system.

References

- **1973Pan:** L.A. Panteleimonov and I.A. Babanskaya, Alloys of Ni₃Sn₂ with Fe and Co, *Vestn. Moskov. Univ. (Khim)*, 1973, **14**, p 486-487, in Russian (Phase Equilibria, #)
- 1983Nis: T. Nishizawa and K. Ishida, Bull. Alloy Phase Diagrams, 1983, 4(4), p 387-390 (Evaluation)
- **1991Nas:** P. Nash, *Phase Diagrams of Binary Nickel Alloys*, ASM International, Materials Park, OH, USA (Review)

indicates presence of phase diagram.

Co-Ni-Sn 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.