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The Ni-Si-V (Nickel-Silicon-Vanadium) System

K.P. Gupta, The Indian Institute of Metals

Introduction

Phase equilibria in the Ni-Si-V system has been established in the composition region up to ~50 at.% Si. The existence at a large number of ternary intermediate phases has been reported in the investigated composition region.

Binary Systems

The Ni-Si system [1991Nas] (Fig. 1) has eight intermediate phases, Ni_3Si (β_1), Ni_3Si (β_2 and β_3), $Ni_{31}Si_{12}$ (γ'), Ni_2Si (δ'), Ni_2Si (θ), Ni_3Si_2 (ϵ and ϵ'), NiSi (ξ), and $NiSi_2$ (ζ and ζ'), of which several phases β_2 and β_3, ϵ and ϵ', and ζ and ζ', exist in polymorphic forms with polymorphic transition temperatures of ~1165, 830, and 981 °C, respectively. The γ', θ, and ξ phases melt congruently at 1242, 1306, and 992 °C, respectively. The β_1, β_3, δ', ϵ', and ζ' phases form through peritectic or peritectoid reactions: L + γ' ↔ β_3 at 1178 °C; L + θ ↔ δ' at 1255 °C; L + (Si) ↔ ζ' at 113 °C; (Ni) + β_2 ↔ β_1 at 1035 °C; and θ + ξ ↔ ϵ' at 845 °C. There are eight eutectic and eutectoid reactions in the Ni-Si system: L ↔ (Ni) + β_3 at 1145 °C; L ↔ γ' + δ' at 1215 °C, L ↔ θ + ξ at 964 °C; L ↔ ξ + ζ at 966 °C; β_2 ↔ β_1 + γ' at 990 °C; θ ↔ δ' + ϵ at 825 °C, ϵ' ↔ δ + ϵ at 820 °C; ϵ ↔ ϵ' + ξ at 800 °C; and ϵ ↔ ϵ' + δ' at 820 °C. The γ', δ, ξ, and ζ phases are single-composition phases.

The Ni-V system [Massalski 2] (Fig. 2) has five intermediate phases: Ni_8V, Ni_3V, Ni_2V, σ, and NiV_3. The Ni_8V, Ni_3V, and Ni_2V phases form from the face-centered cubic (fcc) (Ni) solid solution through congruent transformations; the transformation temperatures are 406, 1045, and 992 °C, respectively. There is some controversy regarding the two suggested forms of the σ phase with σ' at the higher temperatures and σ at the lower temperature. X-ray diffraction (XRD) does not show any difference between the two forms of the σ phase. The σ' phase and the NiV_3 phases form through peritectic and peritectoid reactions L + (V) ↔ σ' and σ' + (V) ↔ NiV_3 at 1280 and 900 °C, respectively. Only one eutectic reaction, L ↔ (Ni) + (V), occurs at 1202 °C.

The Si-V system [Massalski2] (Fig. 3) has four intermediate phases, SiV_3, Si_3V_5, Si_5V_6, and Si_2V. The SiV_3, Si_3V_5, and Si_2V phases melt congruently at 1925, 2010, and 1677 °C, respectively. Except for the SiV_3 phase, all of the other intermediate phases are single-composition phases. The Si_5V_6 phase occurs through a peritectic reaction L + Si_3V_5 ↔ Si_5V_6 at 1670 °C, and it undergoes a eutectoid transformation Si_5V_6 ↔ Si_3V_5 + Si_2V at ~1160 °C. Four eutectic reactions L ↔ (V) + SiV_3, L ↔ SiV_3 + Si_3V_5, L ↔ Si_5V_6 + Si_2V, and L ↔ Si_2V + (Si) occur at 1870, 1875, 1640, and 1400 °C, respectively.

Binary and Ternary Phases

In the three binary systems of the Ni-Si-V system, 17 binary intermediate phases exist. In the investigated com-

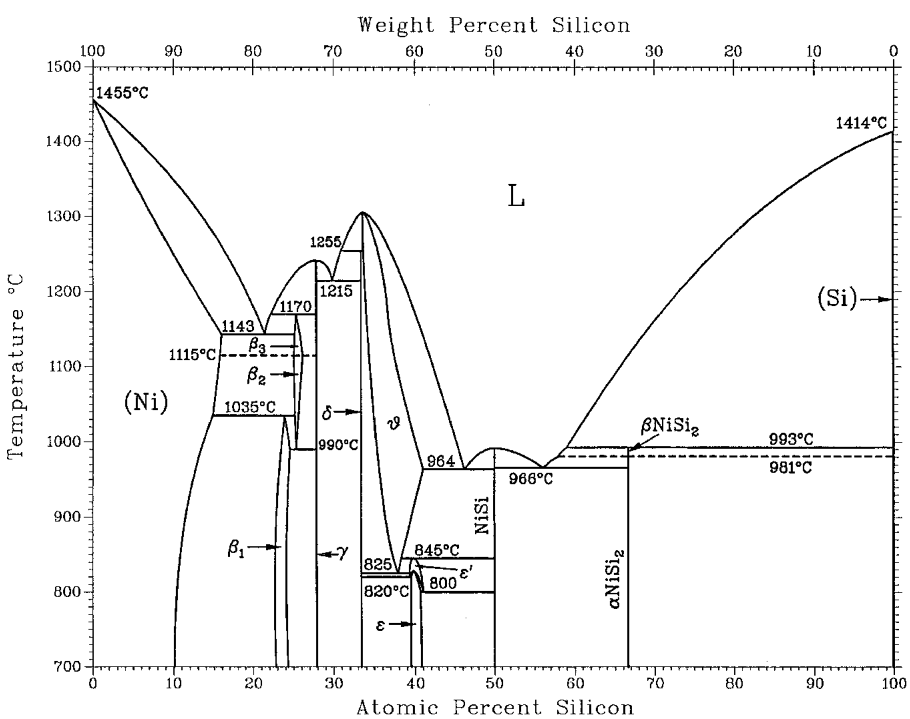

Fig. 1 Ni-Si phase diagram [1991Nas]

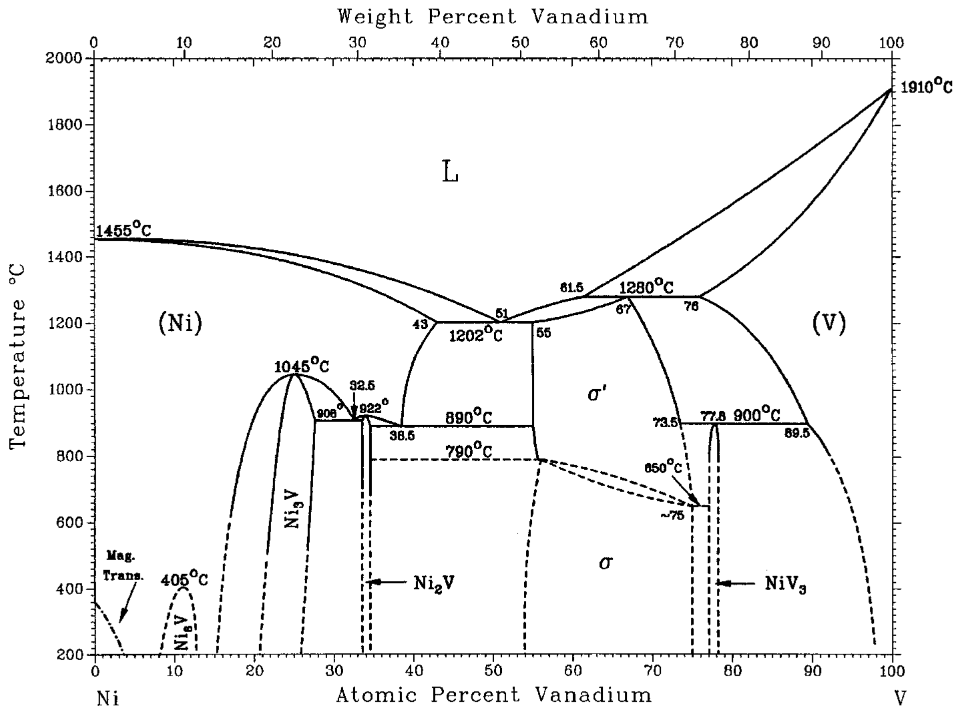

Fig. 2 Ni-V phase diagram [Massalski2]

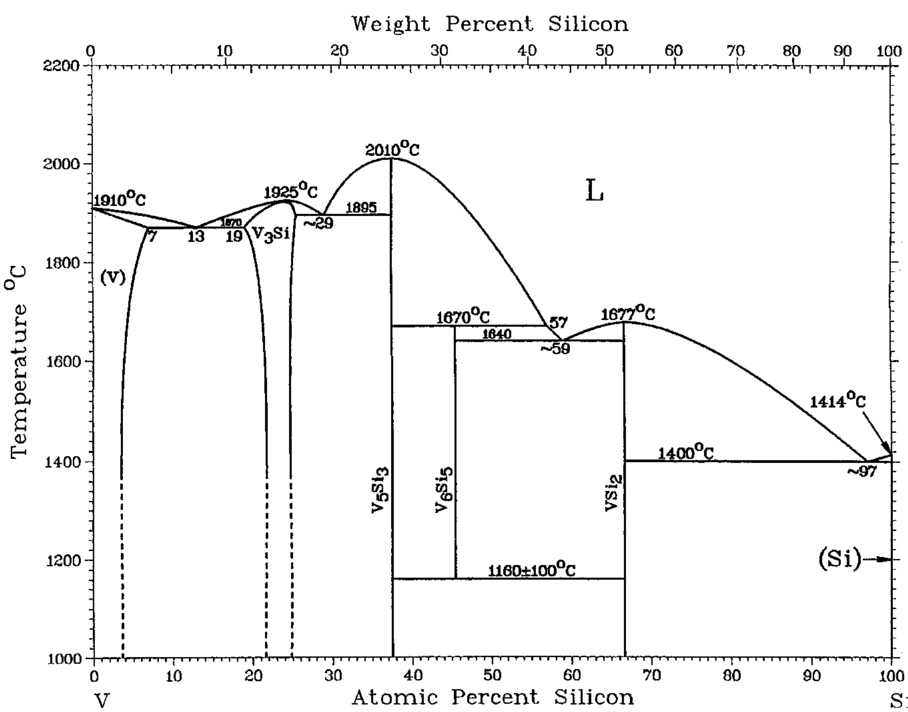

Fig. 3 Si-V phase diagram [Massalski2]

position region of the Ni-Si-V system, six ternary intermediate phases, R, χ, I, G, and E, and two regions of an $MgZn_2$-type Laves phase, Γ_1 and Γ_1', were found. The phases and their structure data are given in Table 1.

Ternary System

The Ni-Si-V system was studied by [1960Gup] with a limited goal of finding the extension of the σ phase region

Table 1 Binary and ternary phases in the Ni-Si-V system

Phase designation	Composition(a)	Pearson symbol	Space group	Type	Lattice parameter, nm *a*	*b*	*c*
α	(V)	*cI*2	$Im\bar{3}m$	W	…	…	…
γ	(Ni)	*cF*4	$Fm\bar{3}m$	Cu	…	…	…
Si	(Si)	*cF*8	$Fd\bar{3}m$	C (diamond)	…	…	…
β_1	Ni_3Si(22.8-25.4)	*cP*4	$Pm\bar{3}m$	$AuCu_3$	0.350	…	…
β_2	Ni_3Si(24.5-25.5)	*mC*16	…	$GePt_3$	0.697	0.625 β = 48.74°	0.507
β_3	Ni_3Si(24.5-25.5)	*mC*16	…	…	0.704	0.626 β = 48.84°	0.508
γ′	$Ni_{31}Si_{12}$	*hP*43	*P*321	$Ni_{31}Si_{12}$	0.667	…	1.228
δ′	Ni_2Si(33.3)	*oP*12	*Pnma*	Co_2Si	0.706	0.499	0.372
θ	Ni_2Si(33.4-41.0)	*hP*6	$P6_3/m$	Ni_2Si	0.3805	…	0.489
ϵ	Ni_3Si_2	*oP*8	…	…	…	…	…
ϵ′	Ni_3Si_2	…	…	…	…	…	…
ξ	NiSi	*oP*8	*Pnma*	MnP	0.562	0.518	0.334
ζ	$NiSi_2$	*cF*12	$Fm\bar{3}m$	CaF_2	0.5406	…	…
ζ′	$NiSi_2$	…	…	…	…	…	…
ν	Ni_8V	*tI*18	…	$NbNi_8$	1.08	…	0.36(b)
ς	Ni_3V	*tI*8	*I*4/*mmm*	Al_3Ti	0.35424	…	0.71731
Π	Ni_2V	*oI*6	*Immm*	$MoPt_2$	0.2559	0.7641	0.3549
σ	57.5-~75	*tP*30	$P4_2/mnm$	σ(CrFe)	0.8980	…	0.4640
β	NiV_3	*cP*8	$Pm\bar{3}m$	Cr_3Si	0.4710	…	…
β	SiV_3	…	…	…	0.4721	…	…
ξ′	Si_3V_5	*tI*32	*I*4/*mcm*	Si_3W_5	0.943	…	0.476
θ′	Si_5V_6	*oI*44	*Immm*	Nb_6Sn_5	…	…	…
ϕ	Si_2V	*hP*99	$P6_222$	$CrSi_2$	0.4571	…	0.6372
R	$Ni_{40}Si_{15}V_{45}$	*hR*53	$R\bar{3}$	R(Mo,Co,Cr)	1.082	…	1.910
χ	$Ni_{52.5}Si_{12.5}V_{35}$	*cI*58	$I\bar{4}3m$	αMn	0.8828	…	…
I	$Ni_{36.5}Si_{22.5}V_{41}$	*m*	…	I(Mn,Co,Si)	1.332	2.353 β = 98.9°	0.911
Γ_1,Γ_1′	$Ni_5Si_3V_4$	*hP*12	$P6_3/mnc$	$MgZn_2$	0.471	…	0.735
E	NiSiV	*oP*12	*Pnma*	$PbC1_2$	0.5970	0.3580	0.6922(c)
G	$Ni_{16}Si_7V_6$	*c*	…	$Mg_6Cu_{16}Si_7$	1.1153	…	…

(a) Composition limits in at.%. (b) Lattice parameter of face-centered tetragonal cell with 36 atoms/cell. (c) Lattice parameters from [1969 Jei]

into the ternary. Electrolytic grade component elements were arc-melted under a He atmosphere. The alloys, which were sealed in evacuated fused silica capsules, were annealed at 1175 °C for 72 h and quenched in water. Metallography and XRD were used for phase identification and phase boundary determination. The σ phase region was found to extend up to ~9 at.% Si and was found in equilibrium with the body-centered cubic (bcc) (V), fcc (Ni), and SiV_3 phases, and with another unidentified phase designated as phase V (Fig. 4).

In an exploratory study of the existence of the R phase stabilized by Si in transition metal systems, [1961Bar1] reported the existence of an R phase in the Ni-Si-V system at the composition $Ni_{40}Si_{15}V_{45}$ at 1100 °C. In this investigation, the unidentified phase V of [1960Gup] was identified as the R phase. The lattice parameter of the $Ni_{36}Si_{25}V_{39}$ R phase was found to be $a = 1.082$ nm and $c = 1.910$ nm. The composition of the R phase alloy is indicated in Fig. 4.

In another exploratory work to find the existence of Si-stabilized Laves phases in the transition metal systems, [1961Bar2] reported the existence of a $MgZn_2$-type Laves phase, Γ_1, in the Ni-Si-V system at the $Ni_5Si_3V_4$ composition at 1100 °C. The lattice parameter of the Laves phase was reported to be $a = 0.471$ nm and $c = 0.735$ nm. The composition of the $Ni_5Si_3V_4$ alloy is also indicated in Fig. 4.

The existence of a αMn-type χ phase was reported by [1963Nev] at the composition $Ni_{55}Si_{15}V_{30}$. The presence of a G phase in the Ni-Si-V system was reported at the $Ni_{16}Si_7V_6$ composition by [1963Spi]. The compositions of the χ and G phases are shown in Fig. 4.

A more detailed study of the phase equilibria in the Ni-Si-V system was made by [1966Bar] in the composition region up to 50 at.% Si. The alloys were arc-melted from pure component elements (Ni and V of 99.9^+ mass% and Si of 99.98 mass% purity) under a He atmosphere. The alloys wrapped in Mo foil were annealed at 1100 °C (the time of annealing was not mentioned) in evacuated and sealed fused silica capsules and was quenched water. Alloys were characterized by metallography and x-ray diffraction.

The 1100 °C isothermal section of the Ni-Si-V system by

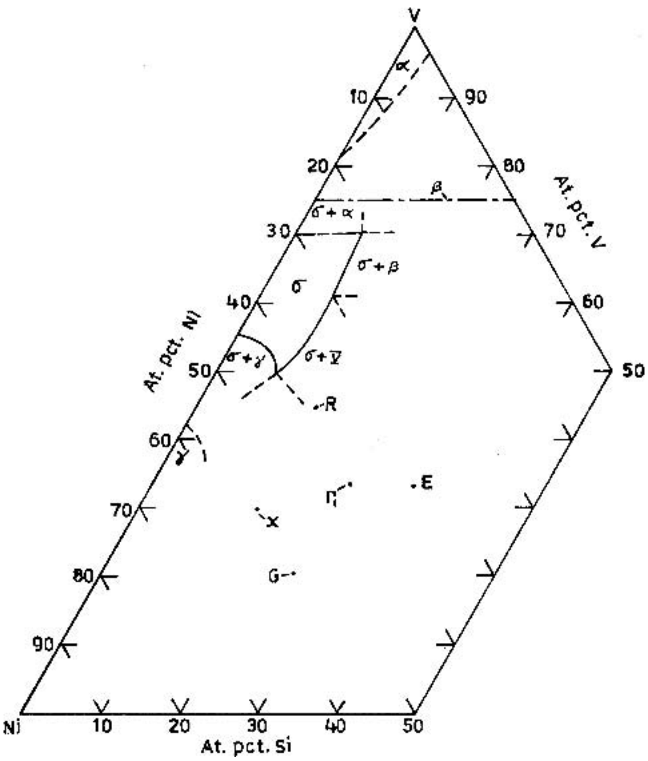

Fig. 4 Isothermal section of Ni-Si-V system at 1175 °C [1960Gup]. The compositions of the χ, R, Γ_1, G, and E phases reported by various investigators are also indicated. The probable pseudobinary line between NiV_3-SiV_3 is indicated by a dash-dot line.

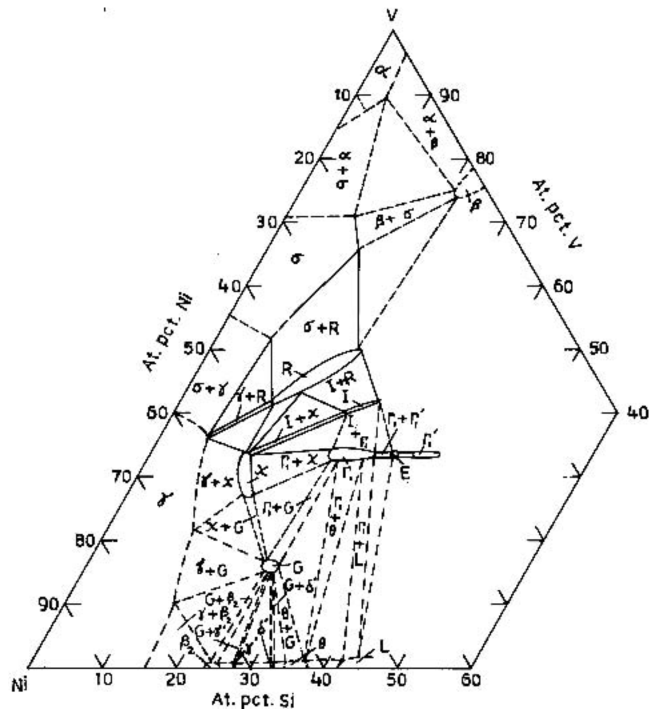

Fig. 5 Isothermal section of the Ni-Si-V system at 1100 °C [1966Bar]

[1966Bar] is given in Fig. 5. In this study, the phase boundaries of all of the ternary intermediate phases were determined accurately, and the phase equilibria between the intermediate phase were determined. The phase equilibrium involving these ternary intermediate phases and the binary phases were not well determined and hence are shown in Fig. 5 in dashed lines. While the Γ_1 phase was found to occur around the composition given by [1961Bar2], a second $MgZn_2$-type Laves phase region, $\Gamma_1{}'$ was found at a slightly higher Si content of ~37 at.% Si along the 33.3 at.% V line. Figure 5 shows, like the Co-Si-V system, the presence of an E phase at an NiSiV composition between the two Laves phase regions Γ_1 and $\Gamma_1{}'$. The E phase region at 1100 °C is very small, approximately ~1 at.% wide. The existence of the E phase in the Ni-Si-V system was confirmed by [1969Jei], and the lattice parameters of the E phase are given as $a = 0.5970$ nm, $b = 0.3580$ nm, and $c = 0.6922$ nm. The existence of a very small E phase region between the two Laves phase regions Γ_1 and $\Gamma_1{}'$ suggests that at a temperature slightly higher or lower than 1100 °C the two Laves phase regions may exist as a single extended phase region. This possibility should be experimentally verified. Besides the earlier reported R, χ, Γ, G, and E ternary intermediate phases, another ternary intermediate phase I was found to occur in the Ni-Si-V system as a small elongated region at approximately the $Ni_{36.5}Si_{22.5}V_{41}$ composition. The lattice parameters of the I phase are reported to be $a = 1.332$ nm, $b = 2.353$ nm, $c = 0.911$ nm, and $\beta = 98.9$ °C. The R phase region is an elongated region, ~2 at.% Si wide, extending from about 30 to 46 at.% Ni and 42 to 50 at.% V, and is found in equilibrium with the σ, χ, Γ_1, I, and β phases. The G phase is found to be in equilibrium with the χ, Γ_1, and γ phases, as well as with the Ni-Si binary phases β_2, γ′, δ′, and θ. The E phase is found to be in equilibrium with the I, Γ_1, $\Gamma_1{}'$ phases, and a liquid phase existing at the Ni-Si binary. The phase boundaries of the fcc γ and bcc γ terminal solutions were not determined and are shown schematically in Fig. 5. The phase boundary at the high V side of the σ phase region has been slightly adjusted to conform to the accepted binary data.

The NiV_3 and SiV_3 phases are isostructural. It is probable that a pseudobinary between the two β phases exists in the Ni-Si-V system. The probable pseudobinary line is shown in Fig. 4. Whether a pseudobinary exists between the two β phases should be experimentally determined.

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Ni-Si-V 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 Program Co-Category Editor for ternary nickel alloys.