Chromium – Nickel – Silicon

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Introduction

A summary of experimental studies of phase equilibria is given in Table 1. [1960Gua] determined a partial isothermal section at 1050°C, in the composition range of Ni-NiCr-NiSi, by means of metallography and XRD techniques. [1960Gup] determined the homogeneity range of σ phase at 1175°C using XRD technique. Later, [1963Gla1] investigated the phase equilibria of the entire system at 850°C. In addition, selected phase boundaries were also determined at 1050 and 1175°C. They prepared 185 alloys using 99.9% Cr, 99.95% Ni and silane Si (99.9% Si). The alloys were prepared in a high-frequency induction furnace under hydrogen atmosphere, and subsequently heat treated at 850°C for 200 to 1000 h under vacuum. The phase equilibria were determined by metallography and XRD techniques. [1963Gla1] reported the existence of five ternary phases.
[1980Cha] calculated partial isothermal sections, in the composition range Cr-Cr_3Si-$Ni_{31}Si_{12}$-Ni, at 427, 527, 627, 800 and 827°C by CALPHAD method.
[1993Kod] determined an isothermal section at 900°C employing both diffusion couple data and phase analysis of bulk ternary alloys. They prepared several diffusion couples involving Ni silicides (Ni_3Si, Ni_5Si_2 and Ni_2Si), pure Si (99.99 at.%), pure Cr (99.9 at.%) and Cr-Ni alloys. Bulk ternary alloys were prepared by arc melting, and they were subsequently annealed at 900°C under a He atmosphere for 300 to 700 h. The phase relations were established using SEM and EPMA techniques. [1995Cec] reported two isothermal sections at 1050 and 1125°C. Both studies confirmed the existence of four of the five ternary phases reported earlier [1963Gla1].
Very recently, [2000Sch] reported the results of a very comprehensive study of phase equilibria. They prepared 35 ternary alloys using powders of Cr (99.95%), Ni (99.9%) and Si (99.9%). The as-cast alloys were encapsulated in quartz tubes under vacuum and then annealed at 900°C for 25 d. The solid phases were characterized by XRD, while the presence of invariant reactions involving the liquid phase was established by DTA. These experimental results were then used to derive a set of thermodynamic model parameters optimized by CALPHAD method. [2000Sch] summarized their results in terms of two isothermal sections (900 and 1050°C), two isopleths (10 and 40 at.% Cr), the liquidus surface and a reaction scheme.
Atomic transport kinetics of Cr and Si in (Ni) was determined by [1982Joh].

Binary Systems

The Cr-Ni and Ni-Si binary phase diagrams are accepted from [Mas2], the latter is based on the assessment of [1987Nas]. The Cr-Si binary system is accepted from [2006Leb].

Solid Phases

The crystallographic data of the solid phases are listed in Table 2.
The solubility of Cr in all Ni-Si intermetallics is less than 5 at.% at 850°C [1963Gla1]. However, at higher temperature the solubility of Cr in γ ($Ni_{31}Si_{12}$) and δ (Ni_2Si) are much higher: 9.4 and 15.5 at.% at 900°C [1993Kod], 12.8 and 16.2 at.% at 1050°C [1995Cec], and 14.1 and 23.5 at.% at 1125°C [1995Cec], respectively. [1998Lan] carried out XRD of as-solidified (after levitation melting) δ (Ni_2Si) alloyed with Cr, and their results suggest that δ (Ni_2Si) dissolves about 33.3 at.% Cr. [1990Li] and [1991Zha] investigated the substitution behavior of Cr in β_1 (Ni_3Si) (*cP*4 or $L1_2$) at 900°C, but their results are rather confusing. [1990Li] reported that Cr atoms reside primarily in the Si-site, while [1991Zha] reported that Cr atoms reside in both Ni- and Si-site. A first-principles calculation of effective pair interaction (EPI) demonstrates that Cr has EPI with Ni and Si of nearly equal strength, suggesting that Cr does not have a particular preference for the sublattice occupancy [1995Slu]. These theoretical results seem to support the experimental results of [1991Zha].

The solubility of Ni in Cr_3Si, α (Cr_5Si_3) and $CrSi_2$ is less than 5 at.% at 850°C [1963Gla1]. On the other hand, the solubility of Ni in CrSi is about 30 at.% at 850 [1963Gla1] and 900°C [1993Kod], but it decreases to 17.8 at.% at 1050°C [1995Cec] and 10 at.% at 1125°C [1995Cec]. Furthermore, the dissolution of Ni in CrSi is associated with a decrease in its lattice parameter [1963Gla1, 1962Bur].

Five ternary phases have been reported: σ (≈$Cr_{13}Ni_5Si_2$) [1957Aro, 1960Gup, 1962Gla1, 1962Gla2, 1962Gla3, 1963Gla1, 1993Kod, 1995Cec, 2000Sch], π (≈$Cr_3Ni_5Si_2$) [1962Gla2, 1962Gla3, 1963Gla1, 1993Kod, 1995Cec, 2000Sch], τ_1 (≈Cr_2Ni_2Si) [1963Gla1, 1993Kod, 1995Cec, 2000Sch] and τ_2 (≈$Cr_3Ni_3Si_4$) [1963Gla1, 1993Kod, 1995Cec, 2000Sch], T (≈$Cr_6Ni_{16}Si_7$) [1961Gla2, 1963Gla1].

While the σ phase is not stable in binary Cr-Ni alloys, it is stabilized by the addition of about 6 at.% Si in Cr-Ni alloys, particularly at high temperatures [1957Aro, 1960Gup]. At 1175°C, the homogeneity range of σ phase extends from 35.5 to 43.5 at.% Ni and from 58 to 66.4 at.% Cr [1960Gup]. However, the homogeneity range is reduced considerably at lower temperatures [1963Gla1, 1993Kod, 1995Cec]. At 600°C, the σ phase is reported to decompose into γ ($Ni_{31}Si_{12}$) and (Cr) [1963Gla1]. [1962Gla3] calculated X-ray diffraction patterns of σ phase, at $Cr_{19.5}Ni_{7.5}Si_3$, assuming two different site occupancy models. In Model-1, it was assumed that the atomic species are randomly distributed in five Wyckoff positions. In Model-2, it was assumed that all Cr and 16.7% of Si atoms reside in 4*f*, 8*i*(1) and 8*j* sites while all Ni and 83% of Si atoms reside in 2*a* and 8*i*(2) sites. Both models gave the same level of agreement between calculated and observed X-ray diffraction patterns.

The Ni content in π phase lies in the range of 46 to 52 at.% at 800°C [1962Gla3] and 46 to 54 at.% at 1050°C [1995Cec] with an average Si content of 20 at.%. The π phase was not observed at 1125°C [1995Cec], and also it is not stable below 800°C [1963Gla1]. A comparison between calculated and observed X-ray diffraction patterns of π phase suggests a random mixing of Cr and Ni atoms in 12*b* and 4*a* sites [1962Gla3].

The composition of τ_1 phase may be approximated as Cr_2Ni_2Si, and it does not change appreciably with temperature. [1963Gla1] reported that τ_1 phase might have been stabilized by carbon; however, the presence of this phase was confirmed in all subsequent investigations [1993Kod, 1995Cec, 2000Sch]. The composition τ_2 phase may be approximated as $Cr_3Ni_3Si_4$, but its crystal structure is not known. Even though the Si content in τ_2 remains around 42 at.%, the Cr content varies significantly with temperature. The following values of Cr content in τ_2 phase are extracted from the reported isothermal sections: 25.7 to 42.3 at.% at 900°C [1993Kod], 76.3 to 87.7 at.% at 1050°C [1995Cec] and 84.5 to 87.2 at.% at 1125°C [1995Cec].

The T phase was reported by Gladyshevsky *et al* [1961Gla1, 1961Gla2, 1962Gla2, 1962Gla4, 1963Gla1], but was not confirmed in the subsequent investigations [1993Kod, 1995Cec, 2000Sch]. Therefore, it is not considered to be an equilibrium phase in this assessment.

Invariant Equilibria

Based on thermal analysis of thirty-five ternary alloys, [2000Sch] established the presence of twenty invariant reactions involving the liquid phase; however, the compositions of participating phases were not reported. Twenty invariant reactions experimentally observed are listed in Table 3. In addition, [2000Sch] also detected two three-phase equilibria, L ⇌ NiSi+CrSi (e_{13}, max) and L ⇌ NiSi+$CrSi_2$ (e_{14}, max). The observed invariant reactions are listed in Table 3. Despite the presence of four ternary eutectics, [1978Hao] did not observe any eutectic in this system; however, they did not report the composition range of investigation. The experimental values of the temperature, 1084 ± 2°C [2000Sch] and 1077°C [1979Lug], for the eutectic reaction, L ⇌ (Ni) + γ ($Ni_{31}Si_{12}$) + π, agree well with each other.

A reaction scheme based on thermodynamic calculations [2000Sch] and valid up to 800°C is shown in Fig. 1. Here, it is important to note that the temperature of binary invariant reactions are slightly different from those in the accepted binaries as Fig.1 is based on CALPHAD modeling. In Fig.1, twenty-one invariant reactions (thirteen U type, four E type, two P type and two D type) participate in the primary solidification. Four ternary phases (σ, π, τ_1 and τ_2) were considered in thermodynamic calculations, and all are shown to participate in the primary crystallization during solidification. The homogeneity ranges of σ and τ_2 phases were considered in the thermodynamic modeling, but π and τ_1 phases were treated as stoichiometric with composition $Cr_3Ni_5Si_2$ and $Cr_5Ni_5Si_3$, respectively [2000Sch]. The thermodynamic

calculations can reproduce the temperature of all experimentally observed invariant reactions within 13°C. However, an invariant reaction L + βCr_5Si_3 ⇌ αCr_5Si_3 + Cr_3Si was predicted to occur at 1489°C, but it was not experimentally verified. The experimentally determined composition of the liquid phase in invariant reaction L ⇌ (Ni) + γ-$Ni_{31}Si_{12}$ + π is 20 at.% Cr and 21 at.% Si [1979Lug], which agree well with the corresponding values obtained from thermodynamic calculations 19 at.% Cr and 22 at.% Si [2000Sch].
[1979Lug] proposed a partial reaction scheme, with four invariant reactions, for the solidification of Ni rich alloys. The invariant reactions P_{II}, P_{III} and E_{III} of [1979Lug] correspond to D_1, U_2, E_2, respectively, of [2000Sch]. Another invariant reaction P_{IV} (L + σ ⇌ (Ni) + π) postulated by [1979Lug] was not predicted in thermodynamic calculations.

Liquidus Surface

The liquidus temperature of several ternary alloys has been determined by DTA [1979Lug, 1990Kag, 1995Cec, 2000Sch]. The liquidus surface shown in Fig. 2 is based on thermodynamic calculations of [2000Sch]. In an earlier study, [1979Lug] reported the liquidus surface of Ni corner only showing the presence of two invariant reactions. The calculated liquidus surface in Fig. 2 shows melting grooves separating eighteen different areas of primary crystallization, including four ternary phases. The melting groove defining the composition range for the primary crystallization of π phase is very narrow. Selected liquidus isotherms are shown in Fig. 2.

Isothermal Sections

Figure 3 shows the isothermal section of Cr corner at 1175°C [1960Gup]. This study clearly established the homogeneity range of σ phase. Even though the adjoining two- and three-phase boundaries were not determined, the reported phase fields are consistent with the reaction scheme shown in Fig. 1. At 1175°C, the three-phase fields L+(Ni)+σ and (Cr)+(Ni)+σ originate from the invariant reaction U_2, while L+σ+Cr_3Si and (Cr)+σ+Cr_3Si originate from the invariant reaction U_3.
Figures 4 and 5 show the isothermal section at 1125 and 1050°C [1995Cec], respectively. [1960Gua] also reported an isothermal section at 1050°C, but only in the Ni corner. The phase relations in [1960Gua] differ significantly from [1995Cec] due to following reasons: (i) [1960Gua] observed only one ternary phase τ_1, and (ii) [1960Gua] reported negligible solubilities of Cr in γ ($Ni_{31}Si_{12}$) and δ (Ni_2Si), but they are found to be significant [1995Cec].
The π phase was not observed at 1125°C [1995Cec]. Thermodynamic calculations show that the π phase forms via a peritectic reaction (P_2 in Fig. 1) at 1108°C [2000Sch], and it is not stable below 843°C due to the eutectoid reaction E_5 (in Fig. 1). The latter temperature is in reasonably good agreement with an earlier report that π phase is not stable below 800°C [1963Gla1]. Similarly, thermodynamic calculations indicate that the σ phase is not stable below 525°C [2000Sch], while an experimental investigation found that it decomposes into γ ($Ni_{31}Si_{12}$) and (Cr) at 600°C.
Figure 6 shows the isothermal section at 900°C [1993Kod], while Fig. 7 shows the isothermal section at 850°C [1963Gla1]. The isothermal section at 850°C reported by [1963Gla1] suffers from the following drawbacks: (i) the reported ternary phase T was not confirmed in any subsequent investigations, (ii) they did not establish the phase relations involving T and τ_1, and (iii) the reported three phase field π+σ+(Ni) is inconsistent with the thermodynamic calculations. Due to these reasons, the following amendments are made in Fig. 7: (i) the T phase is not shown, and (ii) the phase fields involving π, τ_1 and σ are redrawn to make them consistent with the expected phase relations based on the reaction scheme in Fig. 1. For example, the three-phase field π+σ+(Ni) reported by [1963Gla1] has been replaced by two three-phase fields, τ_1+σ+(Ni) and π+τ_1+(Ni). The amended two- and three-phase fields involving π, τ_1 and σ are shown dashed in Fig. 7.
[1980Cha] reported partial isothermal sections at 427, 527, 627 and 827°C based on thermodynamic calculations where only one ternary phase, σ, was considered. The presence of a three phase (Cr)+(Ni)+σ is predicted at all temperatures.
In Fig. 3 to 7, adjustments are made along the binary edges to comply with the corresponding phase diagrams accepted in this assessment.

Temperature – Composition Sections

Figures 8a and 9a show calculated isopleths along $Cr_{0.1}Ni_{0.9}$-$Cr_{0.1}Si_{0.9}$ and $Cr_{0.4}Ni_{0.6}$-$Cr_{0.4}Si_{0.6}$ section, respectively, based on thermodynamic calculations [2000Sch]. These authors also determined liquidus and solidus of several ternary alloys using DTA, and these results were used in the optimization of thermodynamic model parameters. To delineate the phase boundaries clearly in certain composition ranges, enlarged parts are shown in Figs. 8b and 9b.

Thermodynamics

[1977Ost] determined the enthalpy of solution of Si (up to 0.4 at.%) in a Ni-30Cr (at.%) alloy in the temperature range of 1550 to 1600°C by means of calorimetry. The experimental value of ΔH_{Si}^{∞} (in Ni-30Cr (at.%)) is –102.1 ± 5.9 kJ·atom^{-1}. [1968Che] determined the activity of Si (up to 2 mass%) in liquid Cr-Ni alloys at 1600°C by the emf method. Their results show that Cr has a strong tendency to increase the activity of Si.
Thermodynamic modeling of the ternary system by [1980Cha] was restricted to the composition range of Cr-Cr_3Si-$Ni_{31}Si_{12}$-Ni. More recently, [2000Sch] carried out a comprehensive thermodynamic assessment, and reported a set of self-consistent thermodynamic model parameters.

Notes on Materials Properties and Applications

A summary of experimental investigation of properties is given in Table 4. Both Cr-Ni and Cr-Ni-Si alloys are potential candidates for joining of Si_3N_4 ceramic parts by brazing and solid state bonding [1990Nak, 1991McD, 1993Kod, 1995Cec, 1996Tun, 2001Lin]. Consequently, these studies have investigated various physico-chemical and mechanical properties of Si_3N_4/Cr-Ni-Si system, such the contact angle [1995Cec], interfacial microstructure [1993Kod, 1995Cec, 1996Tun, 2001Lin], and the joint strength [1990Nak].
Mechanical, oxidation and electrochemical properties of three-phase alloys (Ni)+β_1(Ni_3Si)+γ($Ni_{31}Si_{12}$) were reported by [2002Tak]. The high-temperature mechanical properties and oxidation resistance of these alloys are better then β_1 (Ni_3Si) while the corrosion resistance in sulphuric acid is comparable to β_1 (Ni_3Si).
The wear resistance of $Cr_{13}Ni_5Si_2$ (σ phase) was evaluated under dry sliding condition at room temperature [2004Tan]. The results show it has excellent wear resistance under dry sliding condition due to high hardness and strong atomic bonds. Also, due to same reasons, a two phase microstructure, Cr_3Si+$Cr_{13}Ni_5Si_2$, also exhibits good high temperature sliding wear resistance at 400, 500 and 600°C [2004Zha2]. When used as a coating on titanium alloys, $Cr_{13}Ni_5Si_2$ based alloys exhibit excellent wear resistance under dry-sliding wear test conditions [2005Jia1, 2005Jia2]. The laser cladding of Cr-alloyed nickel silicide coating (Ni-22.6 mass% Si-5.6 mass% Cr) on 0.2% C steel has a rapidly solidified microstructure consisting of the Ni_2Si primary cellular-dendrites and minor amount of interdendritic Ni_2Si/NiSi eutectics [2003Cai]. The intermetallic coating has good wear resistance under dry sliding wear test conditions due to the high hardness, refined microstructure and strong intermetallic atomic bonds [2003Cai].
Alloying of Ni_2Si/NiSi coatings (on 0.2% C steel) with 1.5% Cr and 5.6% Cr considerably enhanced the corrosion resistance under both anodic polarization and immersion corrosion test conditions [2004Cai].
[2001Don] and [2004Zha1] studied the electrical properties of amorphous thin films of $Cr_{17}Si_{80}Ni_3$, on glass and n type Si (100) surface, in the temperature range 250 to 750°C. Crystallization leads to the formation of $CrSi_2$ phase, and with its increasing fraction leads to the decrease in conductivity of the films. A proper mixture of amorphous and crystalline phases could result in a final zero temperature coefficient of resistance.

Miscellaneous

Atomic transport kinetics of Cr and Si in γ solid solutions has been studied by [1982Joh] at 1250°C. Eight diffusion couples, made of either Ni-Cr/Ni-Si or Ni-Cr-Si/Ni or Ni-Cr-Si/Ni-Si alloys, were prepared and then annealed at 1250°C for up to 180.5 h, and then the composition profiles were measured by EPMA.

Using the experimental composition profiles, [1982Joh] evaluated four interdiffusion coefficients, D^{Ni}_{CrCr}, D^{Ni}_{CrSi}, D^{Ni}_{SiCr} and D^{Ni}_{SiSi}, in the composition range of 2.1 to 13.5 at.% Cr and 0.79 to 4.04 at.% Si. Their results show that the indirect diffusion coefficients, D^{Ni}_{CrSi} and D^{Ni}_{SiCr}, follow a dilute solution model where both are proportional to x_{Cr} and x_{Si}, respectively, and approach zero as the respective concentrations approach zero. The direct diffusion coefficient, D^{Ni}_{SiSi}, was found to be consistent with the diffusion coefficient of Si in binary Ni-Si alloys, both in magnitude and Si concentration dependence. In contrast, D^{Ni}_{CrCr} was found to be greater than the diffusion coefficient of Cr in binary Cr-Ni alloys and also a function of Si concentration. The diffusivity data of [1982Joh] data was used to derive a set of optimized mobility parameters of Cr, Ni and Si in fcc solid solution within CALPHAD formalism [2001Du].
In a Ni-3.2Cr-4.91Si (mass%) alloy, the Cr and Si partitioning ratios (concentration in solid/ concentration in solid) at 1336°C were reported to be 1.13 and 0.59, respectively.
Solid state reactions in Cr/Ni/Si thin films have been studied using a variety of techniques [1982Nau, 1984App, 1993Pim]. These results were reviewed by [1995Set]. The reaction products in thin film multilayers, though only binary silicides, depend primarily on the temperature. For example, [1984App] reported that Cr/Ni/Si layers react independently with Si to form the following products after 30 min anneal: Cr/Ni_2Si/Si at 300°C, Cr/NiSi/Si at 400°C, $CrSi_2$/NiSi/Si at 500°C, $CrSi_2$/$NiSi_2$/Si at 850°C. The formation of an amorphous NiSi around 320°C has also been reported [1993Pim]. No ternary phase was observed in any of these studies.
Rapid solidification of $Cr_5Ni_3Si_2$ by piston-and-anvil method leads to the formation of octagonal quasicrystals, which is closely related to the βMn structure [1987Wan, 1990Wan].

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Table 1: Investigations of the Cr-Ni-Si Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1960Gua]	Metallography and XRD	900-1050°C; 20-50 mass% Cr, 30 mass% Si, bal. Ni
[1960Gup]	Metallography and XRD	1175°C; 50-80 at.% Cr, 8-20 at.% Si, bal. Ni
[1961Gla1, 1961Gla2]	XRD	$Cr_6Ni_{16}Si_7$
[1962Gla1]	XRD	$Cr_{13}Ni_5Si_2$
[1962Gla2]	XRD	$Cr_3Ni_5Si_2$
[1962Gla3]	Metallography and XRD	800-1100°C; 5-30 at.% Ni, 5-25 at.% Si, bal. Cr
[1963Gla1]	Metallography and XRD	850°C; entire composition range
[1963Gla2]	XRD	Cr_3Ni_2Si
[1968Che]	EMF	1600°C; 20 mass% Cr, 2 mass% Si, bal. Ni
[1977Ost]	EMF	1600°C; Cr: 0.1-1.3 mass%, Ni: 0.35-1.45 mass%, Cu: bal.
[1979Lug]	Thermal analysis	Up to 27 at.% Cr and up to 21 at.% Si
[1980Cha]	Thermodynamic modeling	427-827°C; up to 20 at.% Si
[1987Wan, 1990Wan]	TEM and HREM	$Cr_5Ni_3Si_2$

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1993Kod]	Diffusion couple, thermodynamic modelling	900°C; entire composition range
[1995Cec]	-	1050°C and 1125°C; entire composition range
[2000Sch]	DTA, XRD and thermodynamic modelling	900-1200°C; entire composition range

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Cr) < 1863	*cI*2 $Im\bar{3}m$ W	a = 288.48	pure Cr at 25°C [Mas2]
(Ni) < 1455	*cF*4 $Fm\bar{3}m$ Cu	a = 352.40	pure Ni at 25°C [Mas2]
(Si) < 1414	*cF*8 $Fd\bar{3}m$ C (diamond)	a = 543.06	pure Si at 25°C [Mas2]
$CrNi_2$	*oP*6 *Immm* $MoPt_2$	a = 252.4 b = 757.1 c = 356.8	[V-C2], 60 to 76.5 at.% Ni [V-C2]
Cr_3Si < 1780	*cP*8 $Pm\bar{3}m$ Cr_3Si	a = 456.27 ± 0.04 a = 456.67 ± 0.02	20.8 - 25.3 at.% Si [2006Leb] at 22.5 ± 0.4 at.% Si [2006Leb] at 1200°C at 20.8 ± 0.4 at.% Si [2006Leb] at 1600°C
βCr_5Si_3 1666 - 1488	-	-	37.5 - 37.7 at.% Si [2006Leb]
αCr_5Si_3 < 1519	*tI*32 *I*4*mcm* W_5Si_3	a = 917.0 c = 463.6	[V-C2] at 37.5 at.% Si
$(Cr_{1-x}Ni_x)Si$ < 1424	*cF*8 $P2_13$ FeSi	a = 462.2 ± 0.01 a = 459.24 a = 458.64 a = 456.92	[V-C2], $0 \le x \le 0.3$ [1962Bur] at CrSi at $Cr_{40}Ni_{10}Si_{50}$ [1962Bur] at $Cr_{37.7}Ni_{12.3}Si_{50}$ [1962Bur] at $Cr_{30}Ni_{20}Si_{50}$ [1962Bur]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
$CrSi_2$ < 1439	*hP*9 $P6_422$ $CrSi_2$	 $a = 442.83 \pm 0.01$ $c = 636.80 \pm 0.09$	[V-C2], 66.3 - 68 at.% Si at 66.7 at.% Si
β_1, Ni_3Si < 1035	*cP*4 $Pm\bar{3}m$ $AuCu_3$	 $a = 350.6$	[V-C2], 22.8 - 24.5 at.% Si at $Ni_{3.04}Si_{0.96}$
β_2, Ni_3Si 1115 - 990	*mC*16 *C*2/*m* $GePt_3$(?)	 $a = 697 \pm 2$ $b = 625 \pm 4$ $c = 507 \pm 8$ $\beta = 48.74°$	[Mas2], 24.5 - 25.5 at.% Si [1987Nas]
β_3, Ni_3Si 1170 - 1115	*mC*16 *C*2/*m* $GePt_3$(?)	 $a = 704 \pm 7$ $b = 626 \pm 4$ $c = 508 \pm 4$ $\beta = 48.74°$	[Mas2], 24.5 - 25.5 at.% Si [1987Nas]
γ, $Ni_{31}Si_{12}$ < 1242	*hP*43 *P*321 $Ni_{31}Si_{12}$	$a = 667.1$ $c = 1228$	[V-C2]
θ, Ni_2Si 1306 - 825	*hP*6 $P6_322$ Ni_2Si	$a = 383.6$ to 380.2 $c = 494.8$ to 486.3 $a = 383.6$ $c = 494.8$	37.5 - 43 at.% Si [V-C2] at $Ni_{1.86}Si_{1.14}$ [V-C2]
δ, Ni_2Si < 1255	*oP*12 *Pnma* Co_2Si	$a = 502.2$ $b = 374.1$ $c = 708.8$ $a = 566.72$ $b = 361.31$ $c = 688.72$	at 33.3 at.% Si [V-C2] [1998Lan], at equiatomic CrNiSi
ε, Ni_3Si_2 < 830	*oC*80 $Cmc2_1$ Ni_3Si_2	 $a = 1222.9$ $b = 1080.5$ $c = 692.4$	39.2 - 41 at.% Si [Mas2] at 33.3 at.% Si [V-C2]
$(Ni_{1-x}Cr_x)Si$ < 992	*oP*8 *Pnma* MnP	 $a = 519.0$ $b = 333.0$ $c = 562.8$ $a = 518.0$ $b = 336.0$ $c = 561.0$	$0 \le x \le 0.05$ [1962Bur] at NiSi [V-C2] at $Ni_{48}Cr_2Si_{50}$ [1962Bur]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
βNiSi$_2$ 993 - 981	-	-	[Mas2]
αNiSi$_2$ < 981	*cF*12 *Fm*$\bar{3}$*m* CaF$_2$	*a* = 540.6	[V-C2]
* σ, Cr$_{13}$Ni$_5$Si$_2$	*tP*30 *P*4$_2$/*mnm* CrFe	*a* = 878.67 *c* = 457.02	[1962Gla1, 1962Gla2, 1962Gla3]
* π, Cr$_3$Ni$_5$Si$_2$	*cP*20 *P*2$_1$3 AlAu$_4$	 *a* = 611.83	[1962Gla2, 1962Gla3], 46 - 52 at.% Ni and 18 - 22 at.% Si at 800°C at Cr$_3$Ni$_5$Si$_2$
* τ$_1$, Cr$_3$Ni$_2$Si	*cF*96 *Fd*$\bar{3}$*m* NiTi$_2$	 *a* = 1062.0	[1963Gla2]
* τ$_2$, Cr$_3$Ni$_3$Si$_4$	-	-	[1963Gla1]
T, Cr$_6$Ni$_{16}$Si$_7$	*cF*116 *Fm*$\bar{3}$*m* Mn$_{23}$Th$_6$ or Mg$_6$Cu$_{16}$Si$_7$	*a* = 1111.0	[1961Gla1, 1961Gla2, 1962Gla2, 1963Gla1] not accepted in this assessment as a stable ternary phase

Table 3: Experimentally Observed Invariant Equilibria

Reaction	*T* [°C]	Type
L + (Cr) ⇌ Cr$_3$Si + σ	1294 ± 2	U
L + (Cr) ⇌ (Ni) + σ	≈1294	U
L + Cr$_3$Si ⇌ δ(Ni$_2$Si) + αCr$_5$Si$_2$	1210 ± 2	U
L + CrSi + αCr$_5$Si$_2$ ⇌ τ$_2$	1174 ± 2	P
L ⇌ Ni$_5$Si$_2$ + δ(Ni$_2$Si)+αCr$_5$Si$_2$	1141 ± 2	E
L + Cr$_3$Si ⇌ τ$_1$ + σ	1140 ± 2	U
L + σ ⇌ (Ni) + τ$_1$	1122 ± 4	U
L + Cr$_3$Si ⇌ γ(Ni$_{31}$Si$_{12}$) + σ	1121 ± 2	U
L + (Ni) + τ$_1$ ⇌ π	1105 ± 2	P
L + τ$_1$ ⇌ γ(Ni$_{31}$Si$_{12}$) + π	1095 ± 2	U
L ⇌ (Ni) + γ(Ni$_{31}$Si$_{12}$) + π	1084 ± 2	E
L + αCr$_5$Si$_2$ ⇌ δ(Ni$_2$Si) + τ$_2$	1063 ± 2	U
L + δ(Ni$_2$Si) ⇌ θ(Ni$_2$Si) + τ$_2$	≈964	U
L + (Si) ⇌ CrSi$_2$ + NiSi$_2$	962 ± 2	U

Reaction	T [°C]	Type
$L \rightleftharpoons CrSi_2 + NiSi + NiSi_2$	946 ± 2	E
$L + \tau_2 \rightleftharpoons \theta(Ni_2Si) + CrSi$	944 ± 2	U
$L \rightleftharpoons CrSi + NiSi, CrSi_2$	943 ± 2	D
$L \rightleftharpoons \theta(Ni_2Si) + NiSi + CrSi$	927 ± 2	E

Table 4: Investigations of the Cr-Ni-Si Materials Properties

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[2001Don, 2004Zha1]	XRD, resistivity	250-750°C; $Cr_{17}Si_{80}Ni_3$
[2003Cai]	Wear test	RT; Ni-22.6Si-5.6Cr (mass%) coatings on 0.2% C steel
[2004Cai]	Corrosion test	RT; Ni_2Si/NiSi coatings (on 0.2% C steel) containing 1.5% and 5.6% Cr
[2004Tan]	Wear test	RT; $Cr_{13}Ni_5Si_2$
[2004Zha1]	XRD	$Cr_{13}Ni_5Si_2$
[2004Zha2]	Wear test	400-600°C; Cr_3Si+$Cr_{13}Ni_5Si_2$
[2005Jia1, 2005Jia2]	Wear test	RT; $Cr_{13}Ni_5Si_2$ based coatings on Ti base alloys

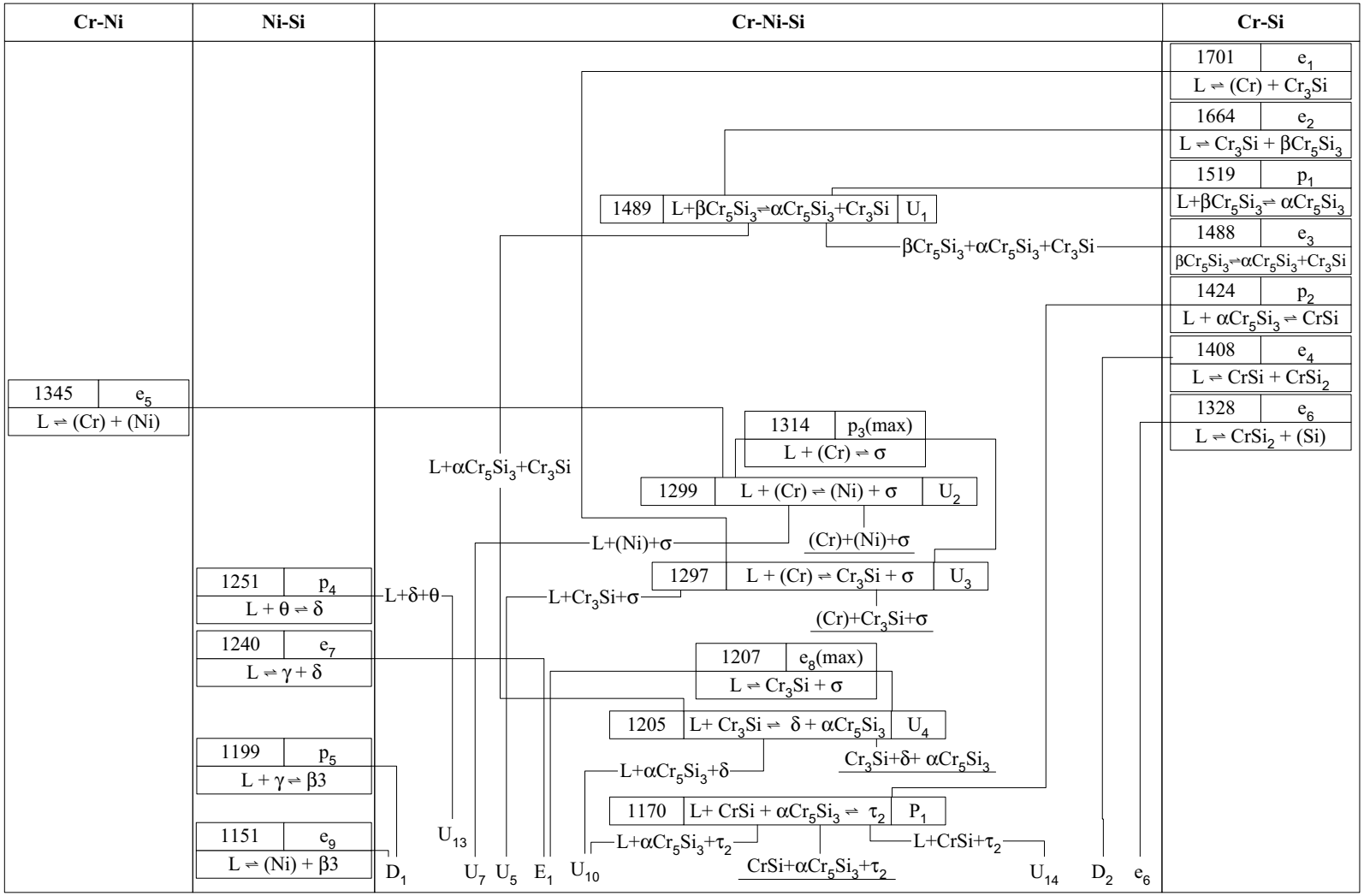


Fig. 1a: Cr-Ni-Si. Reaction scheme, part 1

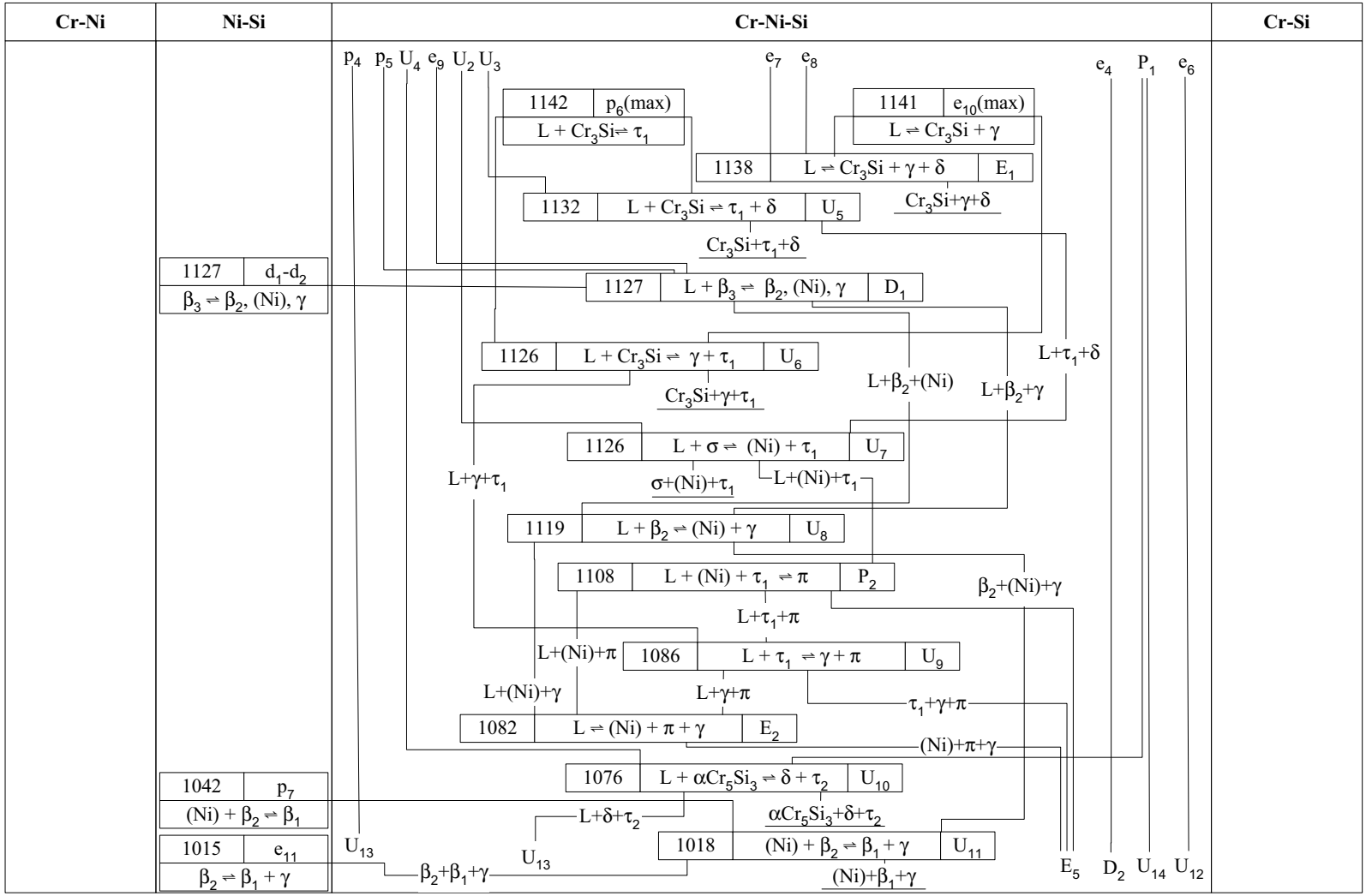


Fig. 1b: Cr-Ni-Si. Reaction scheme, part 2

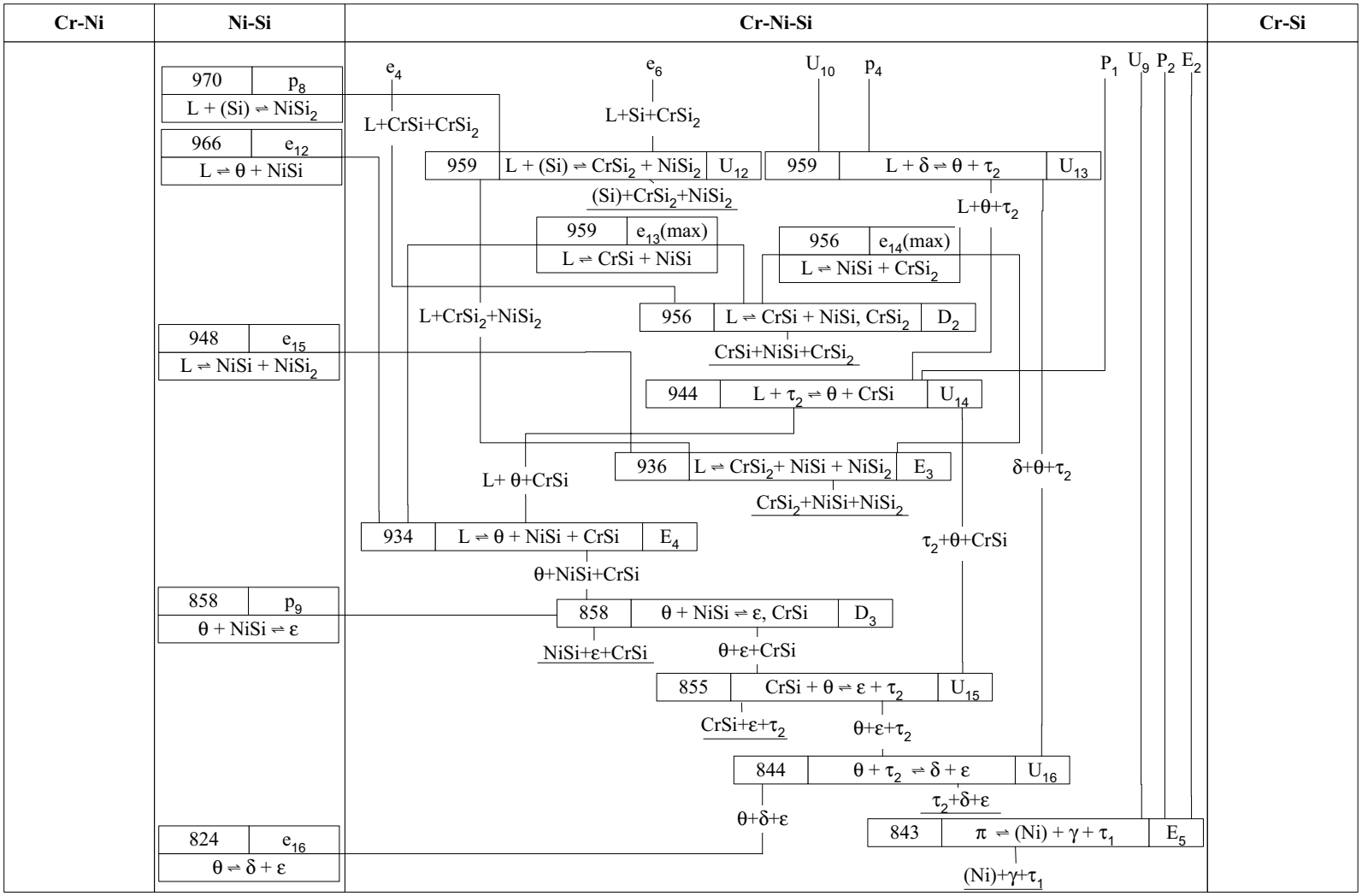


Fig. 1c: Cr-Ni-Si. Reaction scheme, part 3

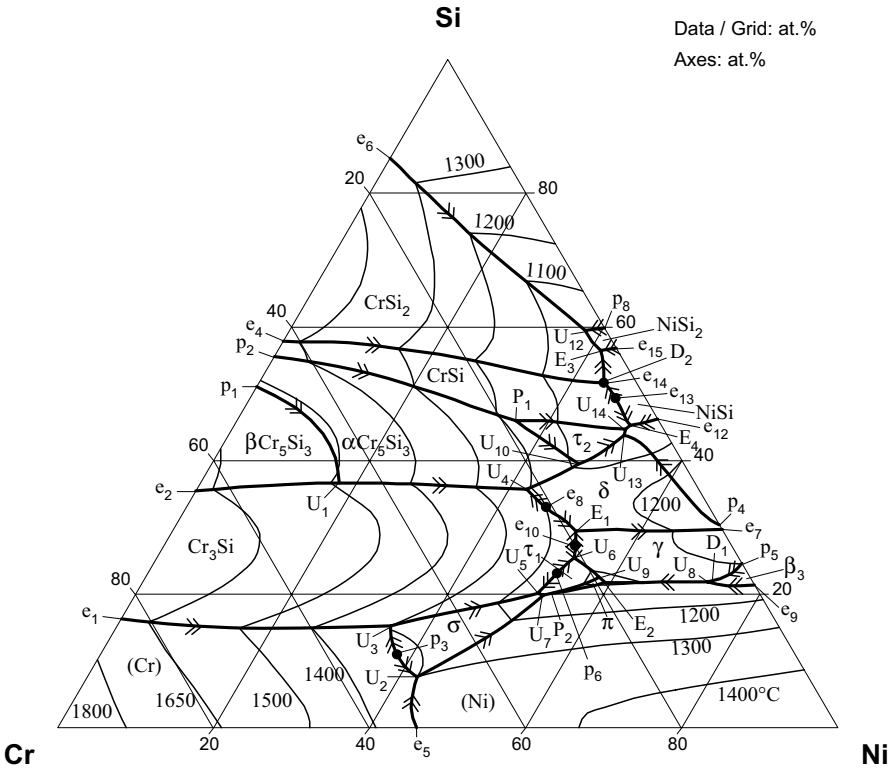


Fig. 2: Cr-Ni-Si. Calculated liquidus surface projection

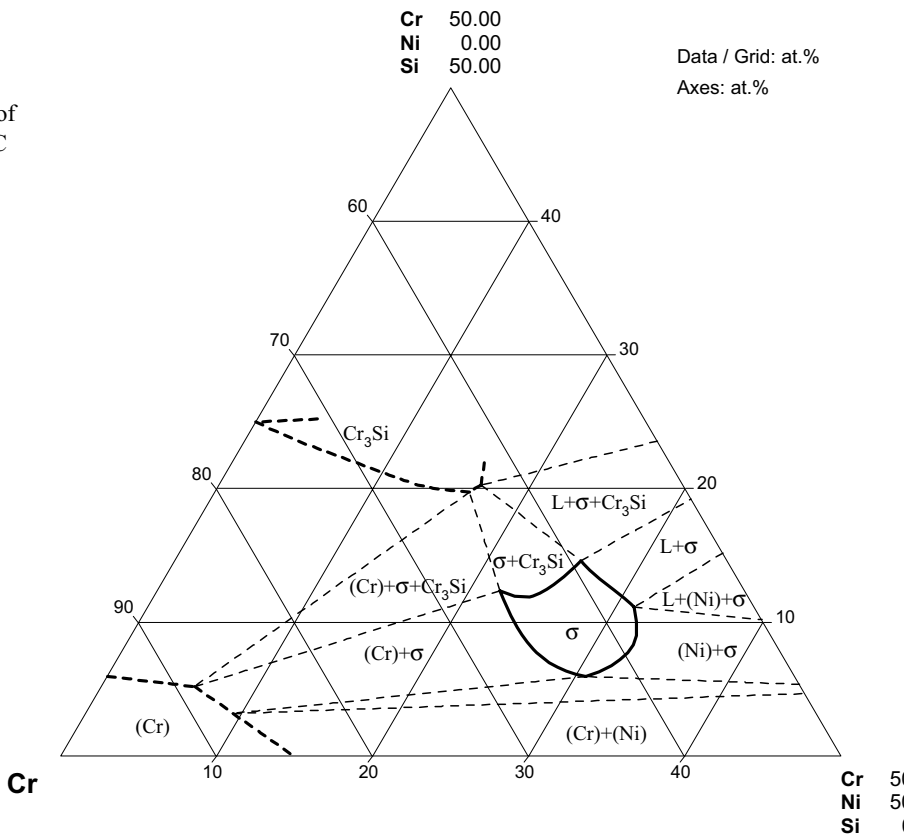


Fig. 3: Cr-Ni-Si. Isothermal section of Cr corner at 1175°C

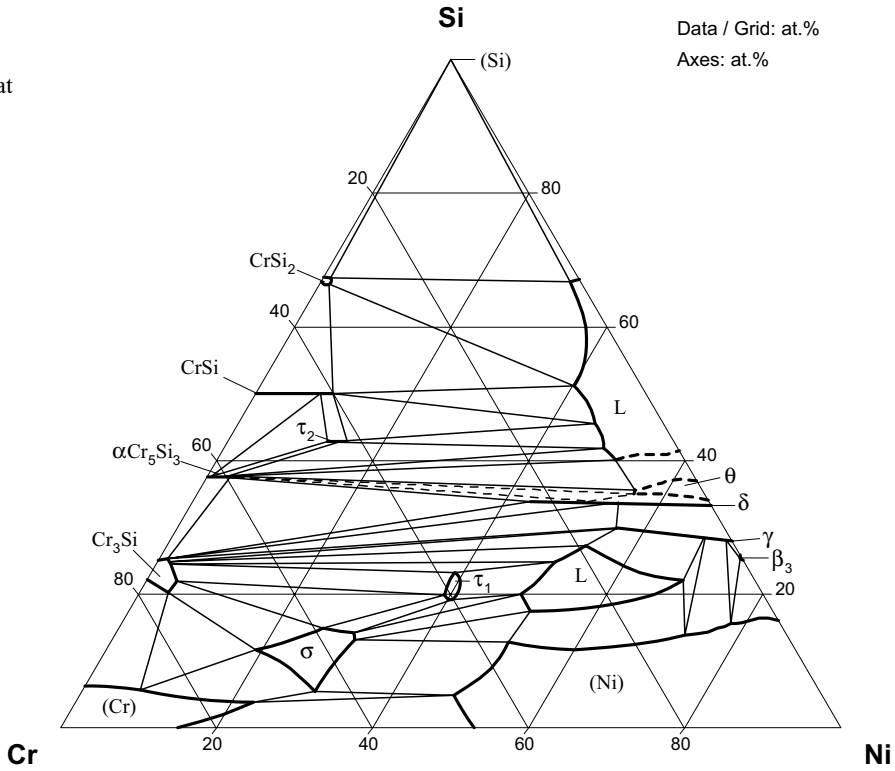


Fig. 4: Cr-Ni-Si. Isothermal section at 1125°C

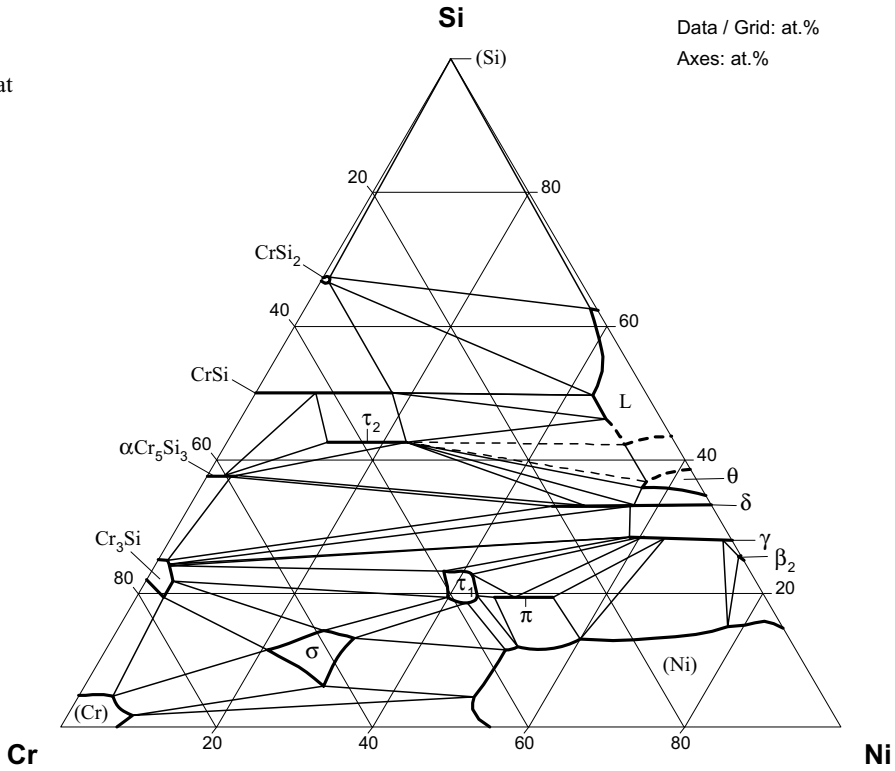


Fig. 5: Cr-Ni-Si. Isothermal section at 1050°C

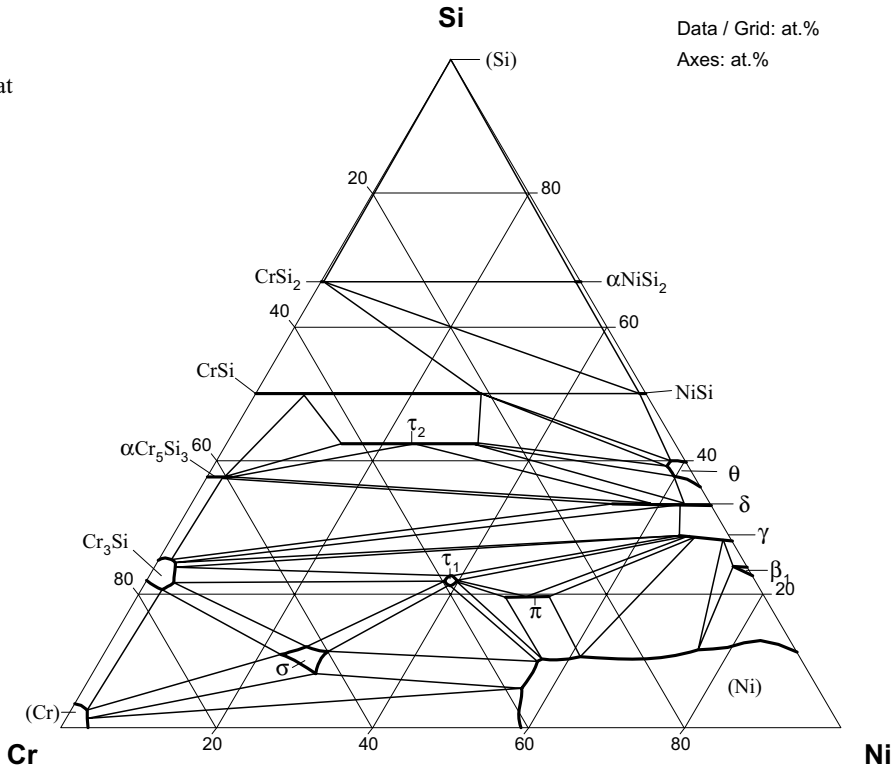


Fig. 6: Cr-Ni-Si. Isothermal section at 900°C

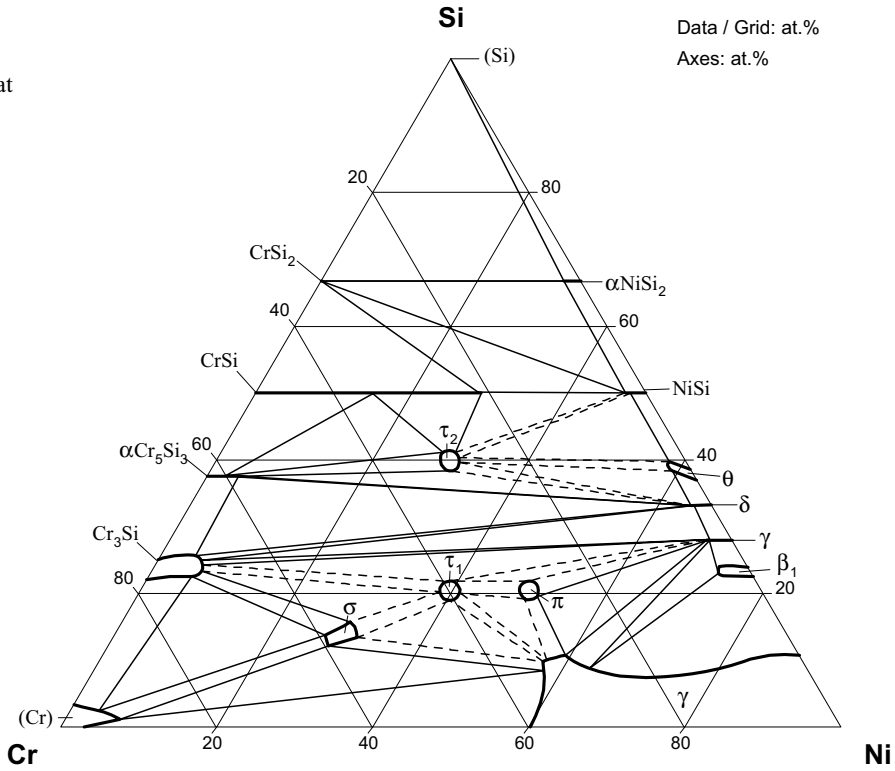


Fig. 7: Cr-Ni-Si. Isothermal section at 850°C

Fig. 8a: Cr-Ni-Si. Calculated vertical section at a constant Cr content of 10 at.%

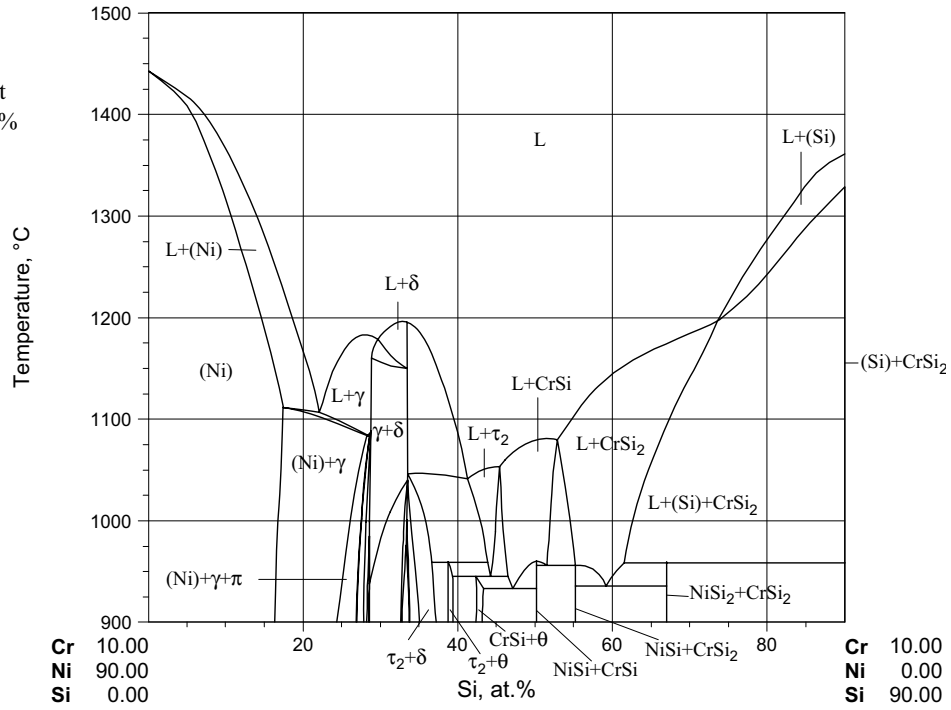
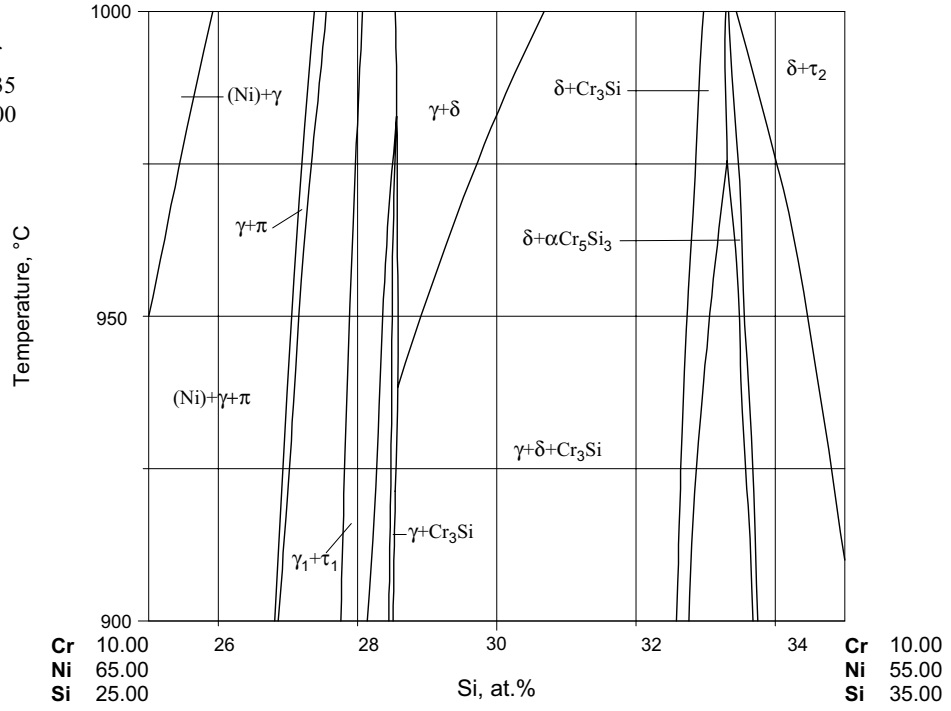


Fig. 8b: Cr-Ni-Si. An enlarged part of Fig. 8a from 25 to 35 at.% Si and from 900 to 1000°C



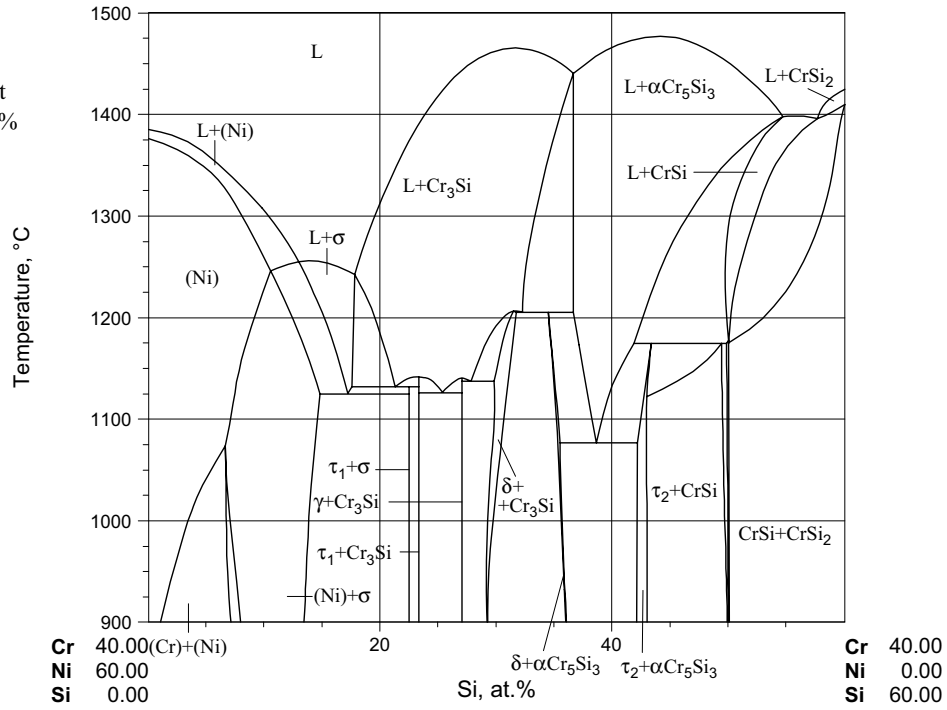


Fig. 9a: Cr-Ni-Si. Calculated vertical section at a constant Cr content of 40 at.%

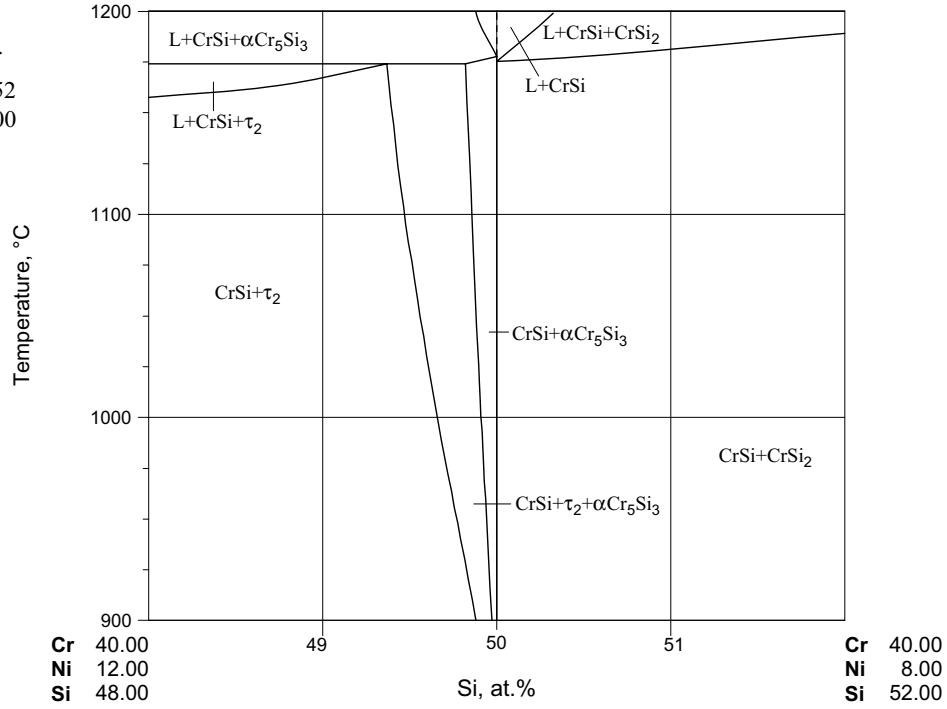


Fig. 9b: Cr-Ni-Si. An enlarged part of Fig. 8a from 48 to 52 at.% Si and from 900 to 1200°C