

Boron – Chromium – Nickel

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Introduction

This ternary system is of interest because the Cr–Ni brazing alloys are used for joining silicon nitride ceramic bodies as well as for joining silicon nitride to Ni based superalloys, and small additions of B depresses the melting temperatures to below 1100°C. Data on the phase equilibria were presented as isothermal sections at 800°C [1972Che] and 1000°C [1960Kol, 1962Kol, 1974Lug], a partial liquidus surface projection within the composition region bounded by Cr, CrB, Ni₂B and Ni [1985Omo], and a portion of the vertical section from Ni to CrB₂ [1992Yan] (Table 1). By means of X-ray diffraction (XRD) and microstructural observation, [1972Che] determined the isothermal section at 800°C and established the existence of two ternary compounds, Cr₃NiB₆ and Cr₂Ni₃B₆. The samples were prepared from powdered metals of electrolytic Cr (99.5%), Ni (99.9%) and B (99.3%), placed in Al₂O₃ crucibles, heated in a vacuum furnace to 1400°C, and then annealed at 800°C for at least 300 h. [1962Kol] determined the partial isothermal section for the field Cr–CrB–Ni₂B–Ni at 1000°C using XRD, metallography, measurements of microhardness and chemical analysis. The alloys were prepared from pure elements and were then annealed at 1000°C for 250 h. [1974Lug] established the isothermal section at 1000°C by a combination of XRD and metallographic examinations. The samples were prepared from powders of Ni (purity of 99.97 or 99.5%) and Cr borides (purity of 99.8%) by induction melting in Al₂O₃ crucibles and then annealing at 1000°C for 200 h. At this temperature, two ternary compounds, Cr₃NiB₆ and Ni₃Cr₂B₆ were confirmed. [1999Ohs] performed a numerical modeling for the transient liquid phase (TLP) bonding process of Ni using a B–Cr–Ni filler by combining thermodynamic calculation with diffusion analysis. Their calculated results agree well with their own experimental data. [1992Yan] constructed the Ni–CrB₂ vertical section by using metallography, XRD, measurements of hardness and microhardness, and abrasive wear tests. The samples were prepared from powders of electrolytic Ni and CrB₂ in ceramic crucibles under vacuum (0.1 - ~0.01 Pa) with the furnace temperature kept at 1250°C for 10 min.

A thermodynamic assessment of the B–Cr–Ni system was performed by [2002Cam], who used the experimental phase equilibrium data at 1000°C [1974Lug] and 800°C [1972Che] for the optimization of the model parameters.

Binary Systems

The B–Cr phase diagram is based mainly on the experimental data of [1969Por, 1972Por]. The phase diagram from [1972Por] was accepted in the present work (Fig. 1). Subsequently, this binary system was reviewed by [1986Lia], and a thermodynamic assessment was conducted by [2002Cam]. [1969Por] reported that Cr₂B and CrB₂ possess remarkable homogeneity ranges with the characteristics of B and Cr deficiency, respectively. Such a spread could be expected for the homogeneity range of CrB also, as it is analogous to other borides with the same crystal structure and showing noticeable homogeneity ranges. Furthermore, a Cr₂B₃ boride was separated from the Al–B–Cr solid-liquid sample kept at 1500°C for 10 h [1987Oka]. Although the Cr₂B₃ crystals contained 3.2 mass% Al, EPMA measurement showed the Al solubility to be about the detection threshold estimated as 0.05 mass%. So, the Cr₂B₃ boride should be inserted in the phase diagram, as was the CrB₄ boride, found after annealing at 1350 and 1400°C in [1968And] (after annealing at 1600°C it was absent).

The B–Ni phase diagram is accepted after [1965Sch] who obtained detailed experimental data. In [1965Sch], as well as in later thermodynamic assessments [1993Tep, 1999Cam], all the nickel borides were presented as practically stoichiometric compounds, and Ni₃B₄ was treated as two phases Ni_{3+x}B_{4-x} (orthorhombic) and Ni_{3-x}B_{4+x} (monoclinic) with composition 41.4 and 43.6 at.% B (*i.e.* Ni_{3.1}B_{2.9} and Ni_{2.95}B_{4.05}), respectively. Nevertheless, the lattice parameters of Ni_{3+x}B_{4-x}(o) reported in [1969Lun] are different for the Ni rich and B rich compositions, and [1965Sch] proposed its homogeneity field extension to be about 0.2 at.%.

The Cr–Ni phase diagram was taken from [1995Udo], where a number of experimental data were carefully evaluated. The version of [1995Udo] nearly coincides with the phase diagram in [Mas2].

Solid Phases

All the unary, binary and ternary phases are presented in Table 2. It seems that the “Cr₂NiB₄” ternary phase reported in [1956Pos] corresponds to the ternary compound Cr₂Ni₃B₆ found in [1972Che, 1974Lug]. It is not impossible that all the ternary phases found are terminal solid solutions based on isostructural binary Cr₅B₆ and Cr₂B₃, taking into account the closeness of their lattice parameters and compositions.

The solubilities of the third element in the chromium and nickel borides were accepted as negligibly small in [1960Kol, 1962Kol, 1972Che, 1974Lug]. Wet chemical analyses of extracted borides showed that the mutual solubility between Cr and Ni borides (Cr₂B, Cr₅B₃, CrB, Ni₃B, and Ni₂B) is negligible, not exceeding 0.2 at.% [1960Kol]. However, [1977Spr] claimed that EPMA reveals 5 at.% Ni solubility in Cr₂B, resulting in no change in the lattice parameters.

[1960Kol, 1962Kol] reported that the solubility of B in the Ni based phase is about 0.02 to 0.04 at.% at 1000°C, which coincides with the computed solubility of 0.023 at.% B [1993Tep].

Quasibinary Systems

Two quasibinary eutectic reactions should be added, based on the four-phase invariant equilibria shown in the liquidus given by [1985Omo] (Figs. 2 and 3). The first of them (e₅(max)) is $L \rightleftharpoons (\text{Ni}) + \text{Cr}_2\text{B}$ at a temperature between 1258°C (E₁), and ~1390°C, which is the melting temperature of Cr₃₅Ni₆₅. The temperature for the second reaction (e₆(max)), $L \rightleftharpoons \text{Ni}_2\text{B} + \text{CrB}$, is estimated to be about 1110°C based on the liquidus isotherms [1985Omo] (higher than 1096°C for E₂ and lower than the melting point of Ni₂B at 1156°C).

Invariant Equilibria

Invariant equilibria in the composition range bounded by Cr, CrB, Ni₂B and Ni are presented in Table 3 [1985Omo].

Liquidus Surface

Figure 3 presents the partial liquidus surface projection taken from [1985Omo]. The alternative version calculated in [2002Cam] for the whole concentration range proposes extended regions of primary separation of chromium borides Cr₅B₃, CrB, Cr₃B₄, and CrB₂ up to less than 1 at.% Cr for Cr₃B₄ and CrB₂. In the present assessment, this version was not adopted because it is in contradiction with the phase constituents of the Ni rich eutectic alloys. The widely used commercial alloys are well known to contain the three-phase eutectic (Ni) + Ni₃B + CrB, rather than (Ni) + Ni₃B + Cr₅B₃ suggested by [2002Cam]. The liquidus surface calculated in [2002Cam] also disagrees with the experimental liquidus temperatures [1974Lug] and results in an essentially larger extension of the primary regions of Ni₃B and Ni₂B as compared with [1985Omo].

Isothermal Sections

Isothermal sections in the Ni rich region for temperatures from 1012 to 1200°C (Figs. 4a - 4e), calculated in [1999Ohs], show phase equilibria involving the melt, Ni₃B and the (Ni) phase, which are of interest for treatment of brazing processes. The isothermal sections likely reflect the phase equilibria between the above mentioned phases. However, other phases are not included and the melt was presented as stable at 1012°C, which is noticeably lower than the most low-melting eutectic (Ni) + Ni₃B + CrB, 1050°C after [1985Omo]. Figures 5 and 6 present isothermal sections at 1000 [1962Kol, 1974Lug] and 800°C [1972Che]. It is necessary to note that the data of the three studies are in good agreement with each other. For the 1000°C section, the results of [1974Lug] were proffered for high B contents. While in [1960Kol, 1962Kol], the equilibria with the (Ni) phase were studied more carefully using the extraction of borides by electrochemical dissolution of the metal matrix followed by XRD and wet chemical analyses. Phase equilibria with the

participation of $\text{Ni}_{4+x}\text{B}_{3-x}(\text{o})$ and CrB_4 were added as they are present in [1972Che] for 800°C, as well as equilibria with Cr_2B_3 (just in the $\text{Cr}_2\text{B}_3 + \text{Cr}_3\text{NiB}_6$ phase field there is a two-phase sample in [1974Lug]).

Temperature – Composition Sections

The Ni–CrB₂ vertical section from 100 to 40 at.% Ni is presented in Fig. 7 after [1992Yan].

Thermodynamics

Gibbs energies of the ternary phases Cr_3NiB_6 and $\text{Cr}_2\text{Ni}_3\text{B}_6$ were optimized in [2002Cam] as (in J·mol^{−1}):

$$G_{\text{Cr}_3\text{NiB}_6} = -37450 + 3.45 \cdot T + 0.3 \cdot G_{\text{Cr}} + 0.1 \cdot G_{\text{Ni}} + 0.6 \cdot G_{\text{B}};$$

$$G_{\text{Cr}_2\text{Ni}_3\text{B}_6} = -34150 + 4.08575 \cdot T + 0.18 \cdot G_{\text{Cr}} + 0.27 \cdot G_{\text{Ni}} + 0.54 \cdot G_{\text{B}}.$$

Notes on Materials Properties and Applications

A summary of studies of the materials properties and applications related to the B–Cr–Ni based brazing alloys is presented in Table 4.

Miscellaneous

[1991Har] studied reversible structural relaxation in amorphous alloys of compositions $\text{Cr}_{14}\text{Ni}_{68}\text{B}_{18}$ and $\text{Cr}_{14}\text{Ni}_{68}\text{B}_{18}$ using differential scanning calorimetry (DSC) and electrical resistance.

[1966Yas] investigated the wetting of CrB₂ by molten Ni under vacuum and Ar. The contact angle was measured to be 40°C at the temperature close to the Ni melting point.

In [1997Hyo], an aluminium oxide intermediate layer was applied as a diffusion barrier to the brazing of a stainless steel using a filler of evaporated B–Cr–Ni film. It was found that the intermediate layer was effective in reducing the diffusion of Ni and B in the filler into the substrate.

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Table 1: Investigations of the B-Cr-Ni Phase Relations and Structures

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[2002Cam]	Thermodynamic calculation (Thermocalc software) using a regular solution model for melt and sublattice model for solid phases. The B-Cr-Ni parameters determined by the PARROT optimization and trial-and-error method.	The B-Cr-Ni liquidus surface and isothermal sections at 1000 and 800°C were calculated for the whole concentration region.
[1999Ohs]	Diffusion analysis and thermodynamic calculation with Thermocalc software. A join of Ni blocks bonded with a Ni-15.2Cr-4.0B (mass%) filler metal of 30 µm thick was studied by SEM/EPMA.	Isothermal sections in Ni rich region showed phase equilibria of melt, Ni ₃ B and (Ni) phase were presented.
[1992Yan]	Optical metallography, XRD, measurements of hardness (HRC), microhardness and relative wear were applied for alloys melted in resistance furnace at 1250°C in vacuum using ceramic crucibles from powders of electrolytic Ni and CrB ₂ .	Morphology and properties for alloys of the Ni-CrB ₂ section from 3 to 23 mass% CrB ₂ , the Ni-CrB ₂ vertical section from 100 to 40 at.% Ni were presented.
[1985Omo]	As-cast and annealed (at 1000°C for 556 h) alloys were studied by optical metallography, XRD and DTA.	The liquidus surface projection was presented for the field Cr-CrB-Ni ₂ B-Ni.
[1977Spr]	Samples melted in arc furnace and zone smelted were studied by DTA, XRD and metallography (optical microscopy and SEM/EPMA).	Search of eutectics was carried out in sections from Ni to chromium borides Cr ₂ B, Cr ₃ B ₅ and CrB.
[1974Lug]	Optical metallography, XRD and DTA were applied for alloys melted in an induction furnace at 1700°C in Al ₂ O ₃ crucibles and then annealed at 1000°C 20 to 200 h.	The isothermal section at 1000°C in the whole concentration range and temperatures of melting for alloys up to 35 at.% B and ~85 at.% Ni.
[1972Che]	XRD and optical metallography were applied for alloys melted in an arc furnace, heated to 1400°C in a resistance furnace (in Al ₂ O ₃ crucibles) and then annealed at 800°C not less than 300 h.	The isothermal section at 800°C was presented for the whole concentration range.

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1962Kol]	XRD, optical metallography and measurements of microhardness were applied for alloys melted from pure elements and then annealed at 1000°C 250 h. Borides extracted by electrochemical solution of metal matrix were examined by XRD and wet chemical analysis.	The isothermal section at 1000°C was presented for the Cr–CrB–Ni ₂ B–Ni field.
[1960Kol]	The same as [1962Kol]	The isothermal section at 1000°C was presented for the Ni rich portion (not exceeding 30 mass% Cr and 5 mass% B).
[1956Pos]	Powder XRD of samples hot pressed at 1500–1700°C or sintered at 1650°C in purified hydrogen.	Cr ₃ B ₄ and new ternary phase Cr ₂ NiB ₄ were identified.

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(αCr) < 1863	<i>cI2</i> <i>Im$\bar{3}m$</i> W	<i>a</i> = 288.48	at 25°C [Mas2]
(Ni) < 1455	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	<i>a</i> = 352.3	at 25°C [Mas2]
(βB) < 2092	<i>hR105</i> or <i>hR111</i> βB	<i>a</i> = 1093.02 <i>c</i> = 2381.66 <i>a</i> = 1092.65 ± 0.04 <i>c</i> = 2380.96 ± 0.13	pure B (99.9999%) [1976Lun] arc melted crystalline B [1981Cre]
Cr ₂ B < 1850	<i>oF40</i> <i>Fddd</i> Mn ₄ B	<i>a</i> = 146.92 <i>b</i> = 739.9 <i>c</i> = 426.6	[1974Lug]
Cr ₅ B ₃ < 1890	<i>tI32</i> <i>I4/mcm</i> Cr ₅ B ₃	<i>a</i> = 546.8 <i>c</i> = 1008.9	[1974Lug]
CrB < 2090	<i>oC8</i> <i>Cmcm</i> CrB	<i>a</i> = 297.5 <i>b</i> = 786.6 <i>c</i> = 293.4	[1974Lug]
Cr ₃ B ₄ < 2080	<i>oI14</i> <i>Immm</i> Ta ₃ B ₄	<i>a</i> = 294.6 <i>b</i> = 1301.8 <i>c</i> = 296.4	[1974Lug]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
Cr ₂ B ₃ ≤ 1500	<i>oC20</i> <i>Cmcm</i> V ₂ B ₃	$a = 302.64 \pm 0.05$ $b = 1811.5 \pm 0.4$ $c = 295.42 \pm 0.04$	[1987Oka]
CrB ₂ < 2200	<i>hP3</i> <i>P6/mmm</i> AlB ₂	$a = 297.3$ $c = 307.0$	[1974Lug]
CrB ₄ ≤ 1400	<i>oI10</i> <i>Immm</i> CrB ₄	$a = 474.4$ $b = 547.7$ $c = 286.6$	[1968And]
Ni ₃ B < 1156	<i>oP16</i> <i>Pnma</i> Fe ₃ C	$a = 521.95 \pm 0.05$ $b = 661.64 \pm 0.06$ $c = 439.12 \pm 0.04$	[1996Kay]
Ni ₂ B < 1125	<i>tI12</i> <i>I4/mcm</i> Al ₂ Cu	$a = 499.1$ $c = 424.6$	[Mas2, V-C2]
Ni _{4+x} B _{3-x} (o) < 1025	<i>oP28</i> <i>Pnma</i> Ni ₄ B ₃	$a = 1195.3$ $b = 298.1$ $c = 656.9$	$x \approx 0.1$ Ni rich
		$a = 1197.3$ $b = 298.5$ $c = 658.4$	B rich [1969Lun]
Ni _{4-x} B _{3+x} (m) < 1031	<i>mC28</i> <i>C2/c</i> Ni ₄ B ₃	$a = 642.8$ $b = 488.0$ $c = 781.9$ $\beta = 103.32^\circ$	$x \approx 0.05$ [1969Lun]
NiB < 1035	<i>oC8</i> <i>Cmcm</i> CrB	$a = 292.9$ $b = 739.2$ $c = 296.1$	[Mas2, V-C2]
* τ_1 , Cr ₃ NiB ₆ ≤ 1000	<i>oC20</i> <i>Cmcm</i> V ₂ B ₃	$a = 303.4 \pm 0.3$ $b = 1811 \pm 2$ $c = 295.6 \pm 0.3$	[1972Che]
		$a = 300.8$ $b = 1770.5$ $c = 295.6$	[1974Lug]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
* τ_2 , $\text{Cr}_2\text{Ni}_3\text{B}_6$ ≤ 1000	<i>oI14</i> <i>Immm</i> Ta_3B_4	$a = 297.1 \pm 0.3$ $b = 2034 \pm 2$ $c = 301.1 \pm 0.3$	[1972Che]
		$a = 293.1$ $b = 2063.1$ $c = 297.7$	[1974Lug]
* τ_3 , Cr_2NiB_4 ≤ 1700	<i>o**</i> ordered Ta_3B_4 type	$a = 596$ $b = 1267$ $c = 605$	[1956Pos]

Table 3: Invariant Equilibria

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				B	Cr	Ni
$\text{L} \rightleftharpoons (\text{Ni}) + \text{Cr}_2\text{B}$	1258 - 1390	$e_5(\text{max})$	L^*	8.6	43.2	48.2
$\text{L} \rightleftharpoons (\text{Ni}) + (\text{Cr}) + \text{Cr}_2\text{B}$	1258	E_1	L	4.3	57.9	37.8
$\text{L} + \text{Cr}_2\text{B} \rightleftharpoons (\text{Ni}) + \text{Cr}_5\text{B}_3$	1220	U_1	L	12.3	35.3	52.4
$\text{L} \rightleftharpoons \text{Ni}_3\text{B} + \text{CrB}$	~ 1110	$e_6(\text{max})$	L^*	32.5	15.5	52
$\text{L} + \text{Cr}_5\text{B}_3 \rightleftharpoons (\text{Ni}) + \text{CrB}$	1096	U_2	L	17.3	21.2	61.5
$\text{L} \rightleftharpoons \text{Ni}_3\text{B} + \text{Ni}_2\text{B} + \text{CrB}$	1096	E_2	L	35.6	14.7	49.7
$\text{L} \rightleftharpoons (\text{Ni}) + \text{Ni}_3\text{B} + \text{CrB}$	1050	E_3	L	18.3	16.1	65.6

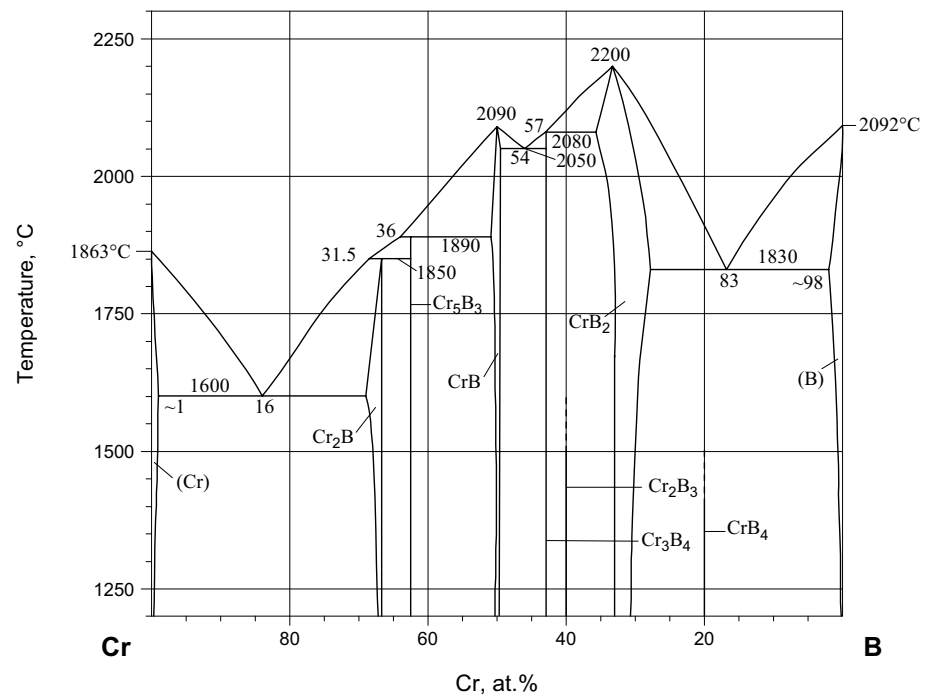
* - compositions are estimated from Fig. 3

Table 4: Investigations of the B–Cr–Ni Materials Properties

Reference	Method/Experimental Technique	Type of Property
[2003Lia]	XRD and SEM/EDX	A commercially available alloy foil Ni-14.2Cr-3.6B (mass%) named Ni-Flex95 (USA), consisting of (Ni) + $\text{Ni}_3\text{B} + \text{CrB}$, was successfully used for joining a Si_3N_4 ceramic.
[1997Hyo]	SEM	An alloy Ni-15Cr-4B (mass%) exhibits increase in the tensile strength of brazed join of stainless steel as the filler thickness increases from 7 to 10 μm . An intermediate Al_2O_3 coating the steel was found to be effective in increasing the tensile strength of the brazed join.

Reference	Method/Experimental Technique	Type of Property
[1996Tun]	SEM/EDS	A join of pure nickel plates brazed with an alloy Microbraz 150, Ni-15Cr-3.5B (mass%) contains the three-phase eutectic of nickel, nickel boride and chromium boride phases.
[1992Yan]	Optic metallography, XRD, measurements of hardness (HRC), microhardness and relative wear.	Morphology, Rockwell hardness and relative wear were studied for alloys the Ni-CrB ₂ section from 3 to 23 mass% CrB ₂ .

Fig. 1: B–Cr–Ni.
The B–Cr phase diagram



Cr-Ni	B-Cr	B-Cr-Ni	B-Ni
	<div>2080 p₁</div> <div>l + CrB₂ ⇌ Cr₃B₄</div> <div>2050 e₁</div> <div>l ⇌ CrB + Cr₃B₄</div> <div>1890 p₂</div> <div>l + CrB ⇌ Cr₅B₃</div> <div>1850 p₃</div> <div>l + Cr₅B₃ ⇌ Cr₂B</div> <div>1830 e₂</div> <div>l ⇌ CrB₂ + (B)</div> <div>1600 e₃</div> <div>l ⇌ (Cr) + Cr₂B</div>	<div>1258-1390 e₅(max)</div> <div>L ⇌ (Ni) + Cr₂B</div> <div>1258 L ⇌ (Ni) + (Cr) + Cr₂B E₁</div> <div>(Cr)+(Ni)+Cr₅B₃</div> <div>1220 L + Cr₂B ⇌ (Ni) + Cr₅B₃ U₁</div> <div>Cr₂B+(Ni)+Cr₅B₃</div> <div>L+(Ni)+Cr₅B₃</div> <div>1096 L + Cr₅B₃ ⇌ (Ni) + CrB U₂</div> <div>Cr₅B₃+(Ni)+CrB</div> <div>L+(Ni)+CrB</div> <div>1096 L ⇌ Ni₃B + Ni₂B + CrB E₂</div> <div>Ni₃B+Ni₂B+CrB</div> <div>1050 L ⇌ (Ni) + Ni₃B + CrB E₃</div> <div>(Ni)+Ni₃B+CrB</div> <div>~1110 e₆(max)</div> <div>L ⇌ Ni₃B + CrB</div> <div>?</div> <div>?</div> <div>?</div> <div>?</div>	<div>1111 e₇</div> <div>l ⇌ Ni₃B + Ni₂B</div> <div>1093 e₈</div> <div>l ⇌ Ni₃B + Ni₂B</div> <div>1035 p₄</div> <div>l + (B) ⇌ NiB</div> <div>1025 p₅</div> <div>l + Ni_{4-x}B_{3+x} ⇌ Ni_{4+x}B_{3-x}</div> <div>1018 e₉</div> <div>l ⇌ Ni₂B + Ni_{4+x}B_{3-x}</div> <div>1018 e₁₀</div> <div>l ⇌ Ni_{4-x}B_{3+x} + NiB</div>
<div>1336 e₄</div> <div>l ⇌ (Ni) + (Cr)</div>			

Fig. 2: B-Cr-Ni. Partial reaction scheme

Fig. 3: B-Cr-Ni.
Partial liquidus
surface projection

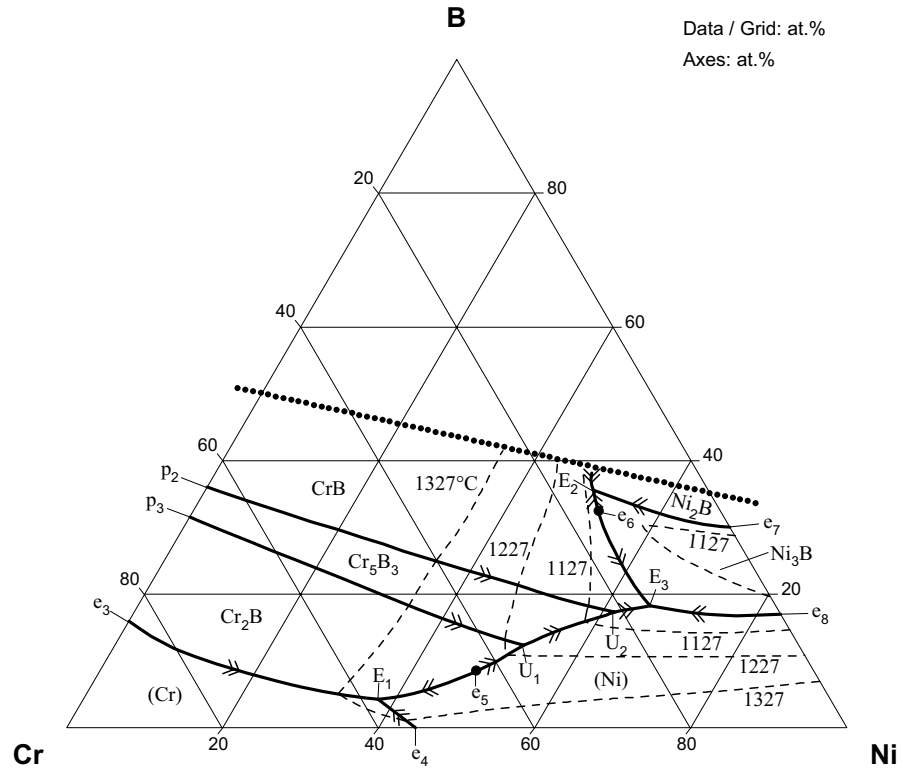


Fig. 4a: B-Cr-Ni.
Phase equilibria of
melt with (Ni), Ni₃B
and some other
phases at 1200°C

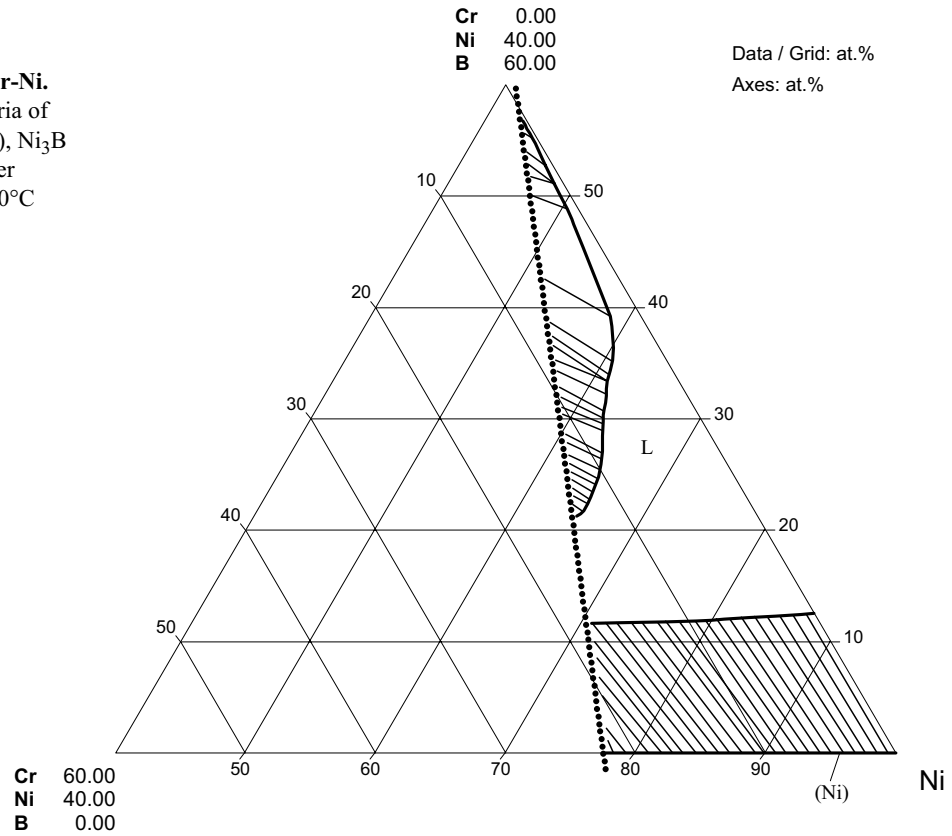


Fig. 4b: B-Cr-Ni.
Phase equilibria of
melt with (Ni), Ni_3B
and some other
phases at 1100°C

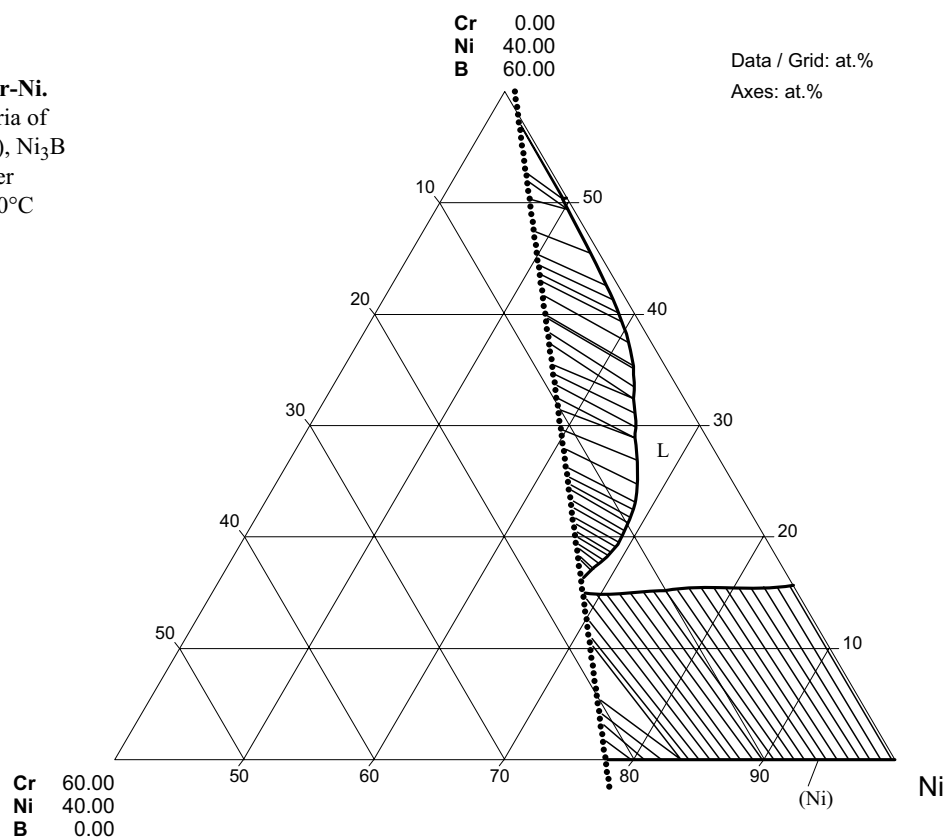


Fig. 4c: B-Cr-Ni.
Phase equilibria of
melt with (Ni), Ni_3B
and some other
phases at 1077°C

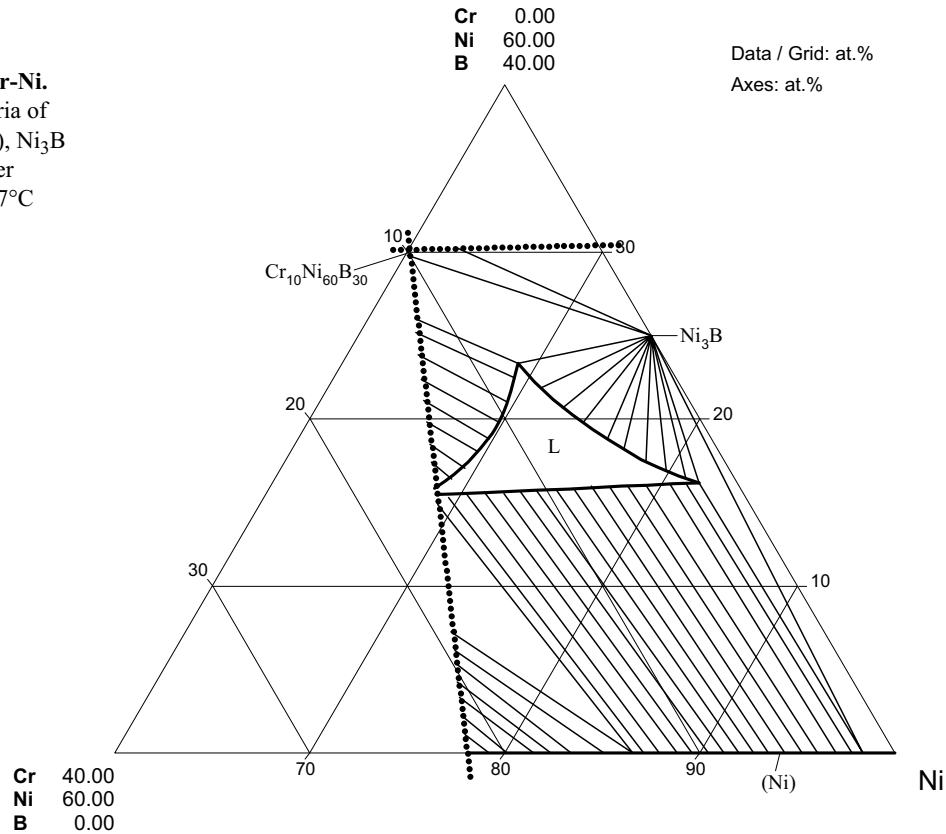


Fig. 4d: B-Cr-Ni.
Phase equilibria of
melt with (Ni), Ni_3B
and some other
phases at 1027°C

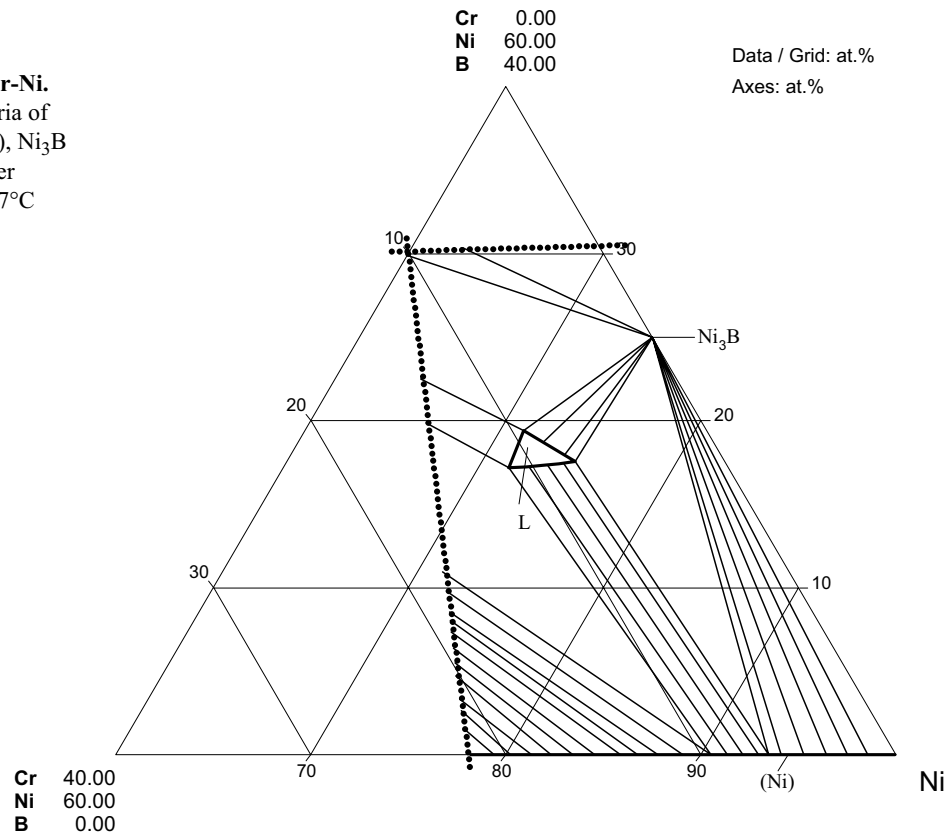


Fig. 4e: B-Cr-Ni.
Phase equilibria of
melt with (Ni), Ni_3B
and some other
phases at 1012°C

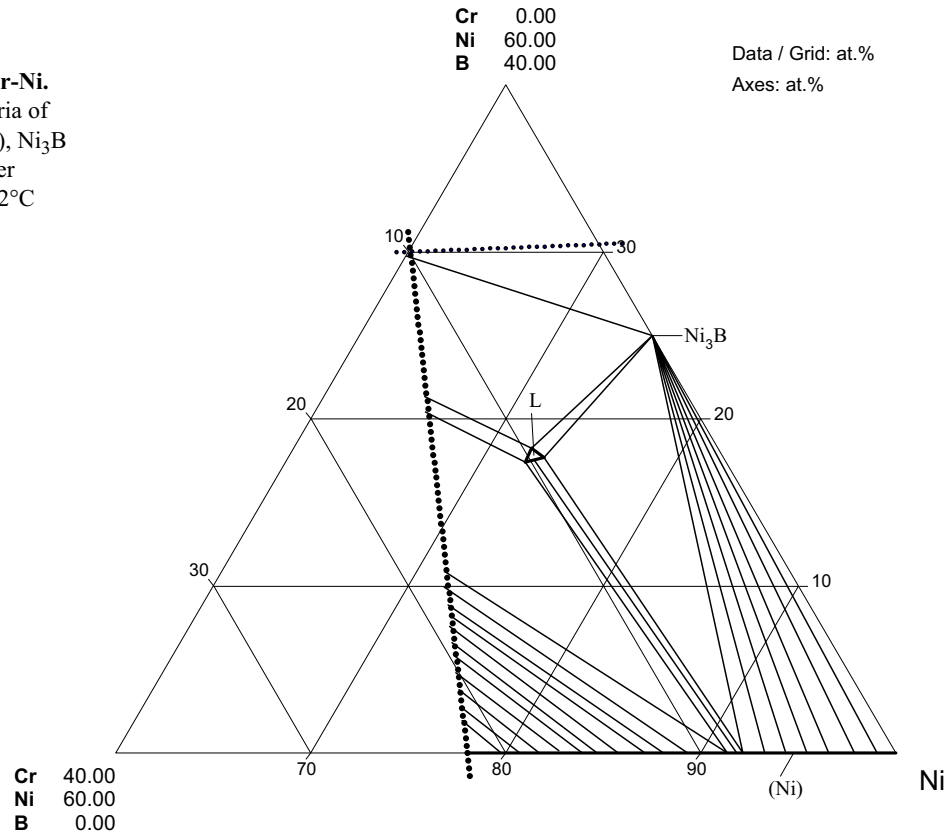


Fig. 5: B-Cr-Ni.
Isothermal section at
1000°C

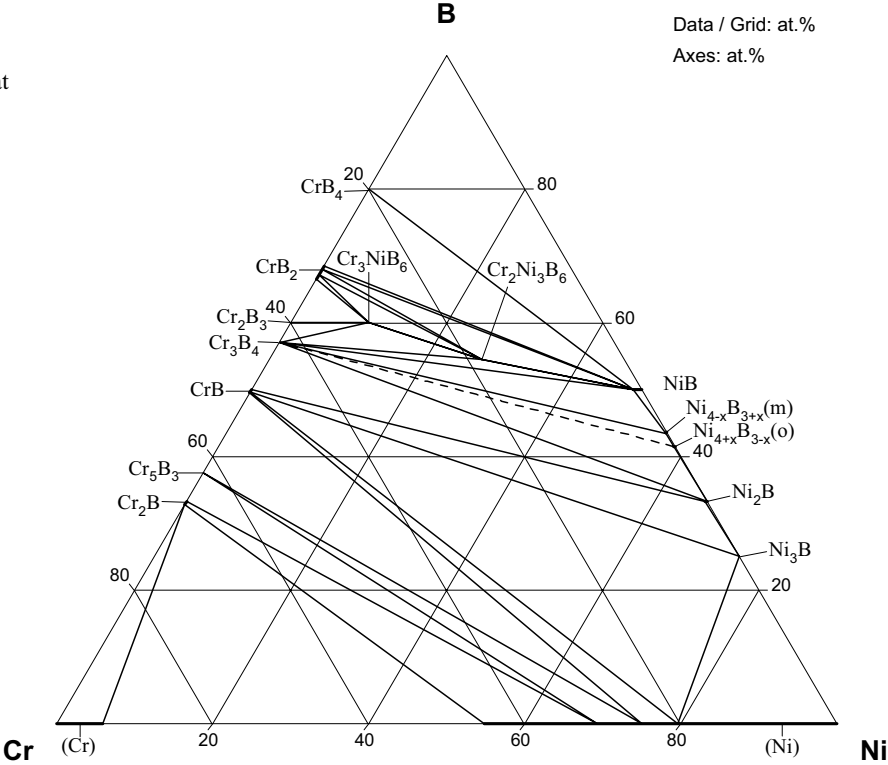


Fig. 6: B-Cr-Ni.
Isothermal section at
800°C

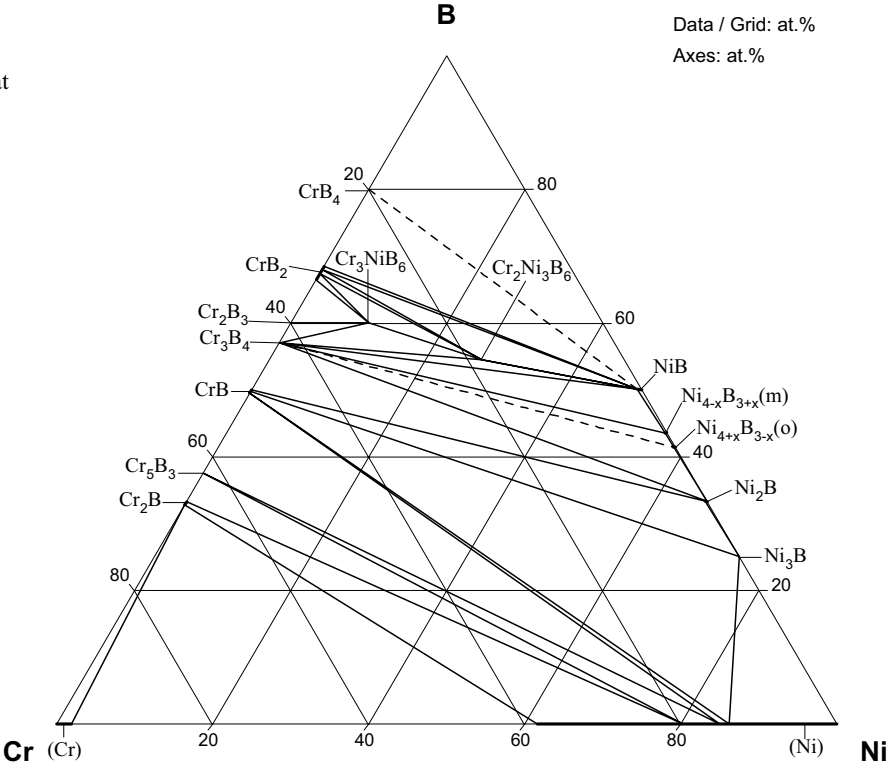


Fig. 7: B-Cr-Ni.
Vertical section
Ni-CrB₂ from 100 to
40 at.% Ni

