**Chromium – Niobium – Titanium**

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**Literature Data**

A fairly large number of experimental studies have been carried out to establish the ternary phase equilibria [1962Sha, 1962Sve1, 1962Sve2, 1963Sha1, 1963Kor, 1964Koc, 1964Sve, 1965Kor, 2002Tho]. Some of these results were reviewed by [1973Bud]. [1962Sha] determined three partial isothermal sections at 600, 800 and 1000°C. [1962Sve1] determined and isothermal section at 1250°C, and an isopleth along NbCr$_2$-TiCr$_2$ and another isopleth at 10 mass% Ti. The first comprehensive study of phase equilibria was carried out by [1965Kor]. They prepared a large number of alloys using iodide grade Ti, 99.27% Nb and 99.98% Cr. The alloys were prepared by both arc-melting in an argon atmosphere and levitation melting in a helium atmosphere. The alloys were homogenized in the temperature range 1300 to 1500°C for up to 240 h depending on the alloy composition. For determining isothermal sections in the temperature range of 600 to 1000°C, the alloys were annealed further for up to 550 h. Conventional metallography and X-ray diffraction were used to establish the phase equilibria. The results were presented in terms seven isothermal sections, from 1900 to 1300°C, and four vertical sections. [2001Yos] determined the phase equilibria of the Cr corner at 1250°C using optical microscopy, X-ray diffraction and analytical electron microscopy. They prepared ten ternary alloys using 99.9% Cr, 99.5% Nb and 99.9% Ti by arc melting, and subsequently they were annealed at 1250°C for 24 h. The tie lines between the phases were established by quantitative analytical electron microscopy. Besides experimental phase equilibria studies, there are two reports on thermodynamic calculation of phase equilibria using CALPHAD (Calculation of Phase Diagrams) methodology [1975Kau, 2000Lee, 2001Kau]. [2004Zha] investigated solid-solid phase equilibria at 1000, 1150 and 1200°C using diffusion multiples. They also reported three vertical sections along Nb:Ti=1:3, Nb:Ti=1:1 and Nb:Ti=3:1 showing the solubility of Cr in β(Nb,Ti), with respect to C15 Laves phase, in the temperature range of 800 to 1600°C. The diffusion multiples were prepared using high purity Cr, Nb and Ti which were subjected to hot isostatic pressing at 1204°C and 200 MPa for 4 h. The entire assembly was then encapsulated in quartz tubes, containing yttrium in tantalum foil as getters for interstitials (C, N and O), backfilled with pure Ar. The encapsulated samples were then annealed at 1000°C (for 4000 h), 1150°C (for 2000 h) and 1200°C (for 1000 h). The composition of phases in the interdiffusion zone was measured by quantitative electron probe microanalysis technique, and the structural information of the phases was obtained by electron backscattered diffraction analysis.

**Binary Systems**

The Cr-Nb, Cr-Ti and Nb-Ti binary phase diagrams are accepted from [2004Iva1], [2004Iva2] and [2001Zha], respectively. In the Cr-Nb equilibrium diagram there are two Laves phases βNbCr$_2$ (C36) and αNbCr$_2$ (C15), while all three Laves phases γTiCr$_2$ (C14), βTiCr$_2$ (C36) and αTiCr$_2$ (C15) are stable in the Cr-Ti equilibrium phase diagram. In the case of NbCr$_2$, the polymorphic transformation C15 → C36 was assumed to be a first-order. In the ternary system, the polymorphic transformations of the Laves phases are also assumed to be first-order.

**Solid Phases**

There is no ternary phase in this system. The details of crystal structures and lattice parameters of the solid phases are listed in Table 1. The stability of Laves phases has been discussed a number of times [1997Zhu, 1998Tak, 2002Tho]. [1997Zhu] suggested that the average valence electron concentration (e/a) is a dominant factor in controlling the stability of NbCr$_2$-based transition-metal Laves phases. They proposed the following
empirical rule: C14 is stabilized in the e/a range of 5.88 to 7.53; C15 is stabilized when e/a ≤ 5.76 and e/a ≥ 7.65; C36 is stabilized when 5.88 > e/a > 5.76 and 7.65 > e/a > 7.53.

The site occupancy of Ti in C15-$\alpha$NbCr$_2$ has been studied in detail [1998Kot, 1999Oka] using ALCHEMI (Atom Location by CHanneling Enhanced MIcroanalysis) technique in a transmission electron microscope. [1998Kot] used Cr$_{68}$Nb$_{15}$Ti$_{17}$ alloy while [1999Oka] used Cr$_{66.7-x}$Nb$_{33.3-x}$Ti$_x$ and Cr$_{66.7}$Nb$_{33.3}$Ti$_1$ alloys. In all cases Ti prefers to occupy Nb sublattice, while Nb partitions to both sublattices. These results has been discussed both in terms of size effect [1998Kot] and electronic structure viewpoint [2002Tho].

At 1200°C, $\alpha$NbCr$_2$ and $\alpha$TiCr$_2$ phases form a continuous solid solution. The lattice parameter of (Nb$_{33-x}$Ti$_x$)Cr$_{67}$ shows a significant negative departure from a linear rule of mixtures suggesting tighter binding than binary alloys [2002Tho]. The authors [1998Che, 2002Tho] reported the lattice parameter of C15-(Nb$_{33-x}$Ti$_x$)Cr$_{67}$ as a function of composition. The upper and lower limits are given in Table 1. The variation of lattice parameter of the solid solution between $\alpha$NbCr$_2$ and $\alpha$TiCr$_2$ was also reported by [1962Sha] in alloys quenched from 600°C corresponding to the two-phase field C15+bcc. They agree fairly well with more recent lattice parameter data of $\alpha$Nb$_{1-x}$Ti$_x$Cr$_2$ [1998Che, 2002Tho]; however, [1962Sha] did not determine the composition of $\alpha$Nb$_{1-x}$Ti$_x$Cr$_2$ phase.

[1995Tho] obtained a metastable bcc phase in alloys along NbCr$_2$-TiCr$_2$ and Ti-NbCr$_2$ sections where the formation of Laves phases were suppressed by splat quenching. The lattice parameter of bcc phase is shown to obey Vegard’s law.

**Liquidus and Solidus Surfaces**

[1962Sve1] reported approximate liquidus and solidus isotherms for the composition range Cr-NbCr$_2$-TiCr$_2$. [1963Sha2] determined the solidification temperature of several ternary alloys. They reported the solidification temperature in both tabulated and graphical forms; however, it is not clear if the solidification temperature referred to liquidus or solidus. Their graphical plot “solidification temperature” showed significant discrepancy with the accepted binary phase diagrams. [1964Koc] also reported liquidus and solidus isotherms for the entire composition range. Once again, these isotherms also show significant discrepancy with the accepted binary phase diagrams.

**Isothermal Sections**

Figures 1 to 7 show the isothermal sections from 1900 to 1300°C, at 100°C interval [1965Kor]. Most of these are constructed from the results of vertical sections. The isothermal section at 1600°C proposed by [1965Kor] is inconsistent with thermodynamic principles. Consequently, the liquidus shape has been changed (see Fig. 4). Recently, [1992Tho] calculated the phase diagram at 1400°C which is in good agreement with the experimental isothermal section reported by [1965Kor]. The isothermal section shown in Fig. 6 is a compilation of phase diagrams reported by [1965Kor] and [1992Tho]. In Fig. 7, $\gamma$TiCr$_2$ Laves phase should be stable at the Cr-Ti binary edge at 1300°C. However, the composition trajectory for $\gamma$TiCr$_2$ → $\beta$TiCr$_2$ transformation is not known, and hence it is shown dotted. Furthermore, additional phase fields, such as ($\beta$Ti)$+\gamma$TiCr$_2$ and ($\beta$Ti)$+\gamma$TiCr$_2$ → $\beta$TiCr$_2$ are expected to be present very close to the Cr-Ti edge. Figure 8 shows the isothermal section at 1250°C adopted from [1962Sve1]; however, the phase equilibria involving (Cr), $\beta$TiCr$_2$ and $\alpha$NbCr$_2$ are taken from recent results of [2001Yos]. Results of [1965Kor] and [2001Yos] show that Nb stabilizes $\alpha$NbCr$_2$ phase. Figures 9, 10, 11, 12, 13 and 14 show the isothermal sections at 1200°C [2004Zha], 1150°C [2004Zha], 1000°C [1962Sha, 2004Zha], 950°C [2002Tho], 800°C [1962Sha] and 600°C [1962Sha], respectively. Both $\alpha$Nb$_{1-x}$Ti$_x$Cr$_2$ and $\beta$TiCr$_2$ Laves phases are stable at the Cr-Ti binary edge in the temperature range of 950 to 1200°C as seen in Figs. 9 to 12. This inevitably causes the presence of a three-phase field (Cr)+$\alpha$Nb$_{1-x}$Ti$_x$Cr$_2$+$\beta$TiCr$_2$ shown with dashed lines, as it has not been experimentally verified. However, it is important to note that this situation is similar to the case of Cr-Ti-V system [2002Gho]. In Figs. 1 to 14, several adjustments were made to comply with the accepted binary phase diagrams.
Temperature – Composition Sections

Several temperature-composition sections were determined [1962Sve1, 1964Koc, 1964Sve, 1965Kor]. It is interesting to note that NbCr$_2$ and TiCr$_2$ do not form a pseudobinary section. Due to the disagreement between the vertical section at a constant Cr-content of 66.7 at.% and the accepted Cr-Ti binary phase diagram, the isopleth proposed by [1962Sve1] and [1964Sve] is not considered in this evaluation. Figure 15 shows the polythermal section along Ti-NbCr$_2$ [1964Sve]. Isopleths at constant mass ratios of 1:4, 2:3, 3:2 and 4:1 were reported by [1965Kor]. [1964Koc] determined eight isopleths at a constant Ti-content of 5, 10, 15, 20, 25, 30, 35, 40 and 70 mass%. [2004Zha] reported three vertical sections along Nb:Ti=1:3, Nb:Ti=1:1 and Nb:Ti=3:1 (atomic ratios) showing the solubility of Cr in $\beta$(Nb,Ti) in the temperature range of 800 to 1600°C. Their measured solubility agrees fairly well with those reported by [1962Sha]. Selected isopleths are shown in Figs. 15, 16, 17, 18, 19, 20, and 21. Like isothermal sections, adjustments were made in the temperature-composition sections to comply with the accepted binary phase diagrams.

Thermodynamics

There is no measured thermodynamic data for the ternary alloys. [1975Kau] employed the CALPHAD technique to calculate isothermal sections at 1300, 1500, 1700 and 1900°C which were in good agreement with the experimental results of [1965Kor]. [1975Kau] used only the binary interaction parameters. Later, [2001Kau] calculated isothermal sections at 1300, 1500, 1600 and 1800°C by considering ternary solubility of the Laves phases. [2000Lee] also employed the CALPHAD technique to derive an optimized set of ternary interaction parameters for the bcc phase using experimental phase diagram of [1962Sha]. They also reported calculated isothermal sections at 800 and 1000°C which were in good accord with the experimental data.

Notes on Materials Properties and Applications

The ambient temperature elastic properties (bulk, shear and Young’s moduli, and Poisson’s ratio), hardness and indentation fracture toughness of the C15 Laves phase ($\alpha$NbCr$_2$-$\alpha$TiCr$_2$) were measured by [2002Tho]. [1998Che] also reported hardness and fracture toughness of single phase (C15) (Nb,Ti)Cr$_2$ alloys. The elastic moduli and hardness generally decreases along the constant Nb/Ti ratio [2002Tho]. With the substitution of Nb by Ti in $\alpha$NbCr$_2$, the shear moduli and hardness showed a positive deviation with respect to a linear rule of mixture between $\alpha$NbCr$_2$ and $\alpha$TiCr$_2$. However, the toughness increased only along the constant Nb/Ti ratio. [1998Che] found that the substitution of Ti by Nb causes an increase in hardness and a decrease in fracture toughness of the C15 phase. The Vickers hardness values range from 871 to 914 kg:mm$^{-2}$ [1998Che], and 840 to 890 kg:mm$^{-2}$ [2002Tho], while the indentation fracture toughness values range from 0.69 to 0.82 MPa$m^{0.5}$ [1998Che] and 1.1 to 1.24 MPa$m^{0.5}$ [2002Tho]. [1965Sha] determined the elastic (Young’s and shear moduli) and plastic (hardness) properties of single- and two-phase alloys as a function heat treatment. The composition of single-phase alloys range from Ti-rich to Nb-rich. They found that Cr is a better solid solution strengthener than Ti. [1962Sve2] measured hardness of Cr-rich and Ti-rich alloys as a function of temperature (from 20 to 1000°C); however, the alloys were single phase (bcc, hcp, C15), two-phase (bcc+C15) and three-phase (bcc+hcp+C15). Fracture toughness and fatigue crack growth resistance were measured by [1996Dav] where Ti was found to increase the toughness of solid solution of Cr-Nb alloys. [1997Cha] studied the fracture and fatigue behavior of in situ composites based on the Cr-Nb-Ti ternary system and showed an increase in fracture resistance with a decreasing volume fraction of NbCr$_2$ particles.
References


Cr–Nb–Ti


### Table 1: Crystallographic Data of Solid Phases

<table>
<thead>
<tr>
<th>Phase/ Temperature Range[^°C]</th>
<th>Pearson Symbol/ Space Group/ Prototype</th>
<th>Lattice Parameters [pm]</th>
<th>Comments/References</th>
</tr>
</thead>
<tbody>
<tr>
<td>(β, (Cr,Nb,βTi)) ≤ 1863</td>
<td>cf2 (\text{Im3m})</td>
<td>(a = 288.4)</td>
<td>pure Cr at 27°C [V-C2]</td>
</tr>
<tr>
<td>(Cr) ≤ 1455</td>
<td>W</td>
<td>(a = 330.04)</td>
<td>pure Nb at 25°C [V-C2]</td>
</tr>
<tr>
<td>(βTi)(h) 1670 - 882</td>
<td>(hP2\ \ P6_3/mmc)</td>
<td>(a = 330.65)</td>
<td>pure Ti [Mas2]</td>
</tr>
<tr>
<td>(Cr) ≤ 882</td>
<td>(hP2\ \ P6_3/mmc)</td>
<td>(a = 295.06)</td>
<td>pure Ti at 25°C [Mas2]</td>
</tr>
<tr>
<td>(αTi)(r) 1370 - 1270</td>
<td>(hP12\ \ P6_3/mmc)</td>
<td>(a = 493.1)</td>
<td>C36 Laves phase.</td>
</tr>
<tr>
<td>(βNb1-xTi_xCr_2(h) 1730 - 1585</td>
<td>(hP12\ \ P6_3/mmc)</td>
<td>(a = 493.1)</td>
<td>at 66.7 at.% Cr and 25°C [2004Iva1]; solid solubility 62.2 to 70 at.% Cr.</td>
</tr>
<tr>
<td>(βNbCr_2(h) 1270 - 800</td>
<td>(hP12\ \ P6_3/mmc)</td>
<td>(a = 493.1)</td>
<td>at 25°C [V-C2].</td>
</tr>
<tr>
<td>(αNb1-xTi_xCr_2(r) ≤ 1625</td>
<td>(cF24\ \ \text{Fd3m})</td>
<td>(a = 693.88)</td>
<td>0 ≤ (x) ≤ 1; C15 Laves phase.</td>
</tr>
<tr>
<td>(αNbCr_2(r)  ≤ 1625</td>
<td>(cF24\ \ \text{Fd3m})</td>
<td>(a = 693.82)</td>
<td>at Nb_5Ti_28Cr_67 and 25°C [1998Che]</td>
</tr>
<tr>
<td>(αTiCr_2(r) ≤ 1220</td>
<td>(cF24\ \ \text{Fd3m})</td>
<td>(a = 693.2)</td>
<td>at TiCr_1.9 and 25°C [V-C2].</td>
</tr>
<tr>
<td>(γTiCr_2(h) 1370 - 1270</td>
<td>(hP24\ \ P6_3/mmc)</td>
<td>(a = 493.2 ± 0.2)</td>
<td>C14 Laves phase.</td>
</tr>
<tr>
<td>(γTiCr_2(h) 1370 - 1270</td>
<td>(hP24\ \ P6_3/mmc)</td>
<td>(c = 1601.0 ± 0.1)</td>
<td>at Ti_{1.12}Cr_2 and 25°C [V-C2].</td>
</tr>
</tbody>
</table>
**Fig. 1: Cr-Nb-Ti.**
Isothermal section at 1900°C

**Fig. 2: Cr-Nb-Ti.**
Isothermal section at 1800°C
Fig. 3: Cr-Nb-Ti. Isothermal section at 1700°C

Fig. 4: Cr-Nb-Ti. Isothermal section at 1600°C
Fig. 5: Cr–Nb–Ti. Isothermal section at 1500°C

Fig. 6: Cr–Nb–Ti. Isothermal section at 1400°C
**Fig. 7: Cr-Nb-Ti.**
Isothermal section at 1300°C

**Fig. 8: Cr-Nb-Ti.**
Isothermal section at 1250°C
**Fig. 9: Cr-Nb-Ti.**
Isothermal section at 1200°C

**Fig. 10: Cr-Nb-Ti.**
Isothermal section at 1150°C
Fig. 11: Cr-Nb-Ti.
Isothermal section at 1000°C

Fig. 12: Cr-Nb-Ti.
Isothermal section at 950°C
Fig. 13: Cr-Nb-Ti.
Isothermal section at 800°C

Fig. 14: Cr-Nb-Ti.
Partial isothermal section at 600°C
Fig. 15: Cr-Nb-Ti.
Polythermal section Ti-NbCr$_2$

Fig. 16: Cr-Nb-Ti.
An isopleth at a constant mass ratio of Nb:Ti=1:4
**Fig. 17: Cr-Nb-Ti.**
An isopleth at a constant atomic ratio of Nb:Ti=1:3

**Fig. 18: Cr-Nb-Ti.**
An isopleth at a constant mass ratio of Nb:Ti=2:3
Fig. 19: Cr-Nb-Ti.
An isopleth at a constant atomic ratio of Nb:Ti=1:1

Fig. 20: Cr-Nb-Ti.
An isopleth at a constant atomic ratio of Nb:Ti=3:1
Fig. 21: Cr-Nb-Ti.
An isopleth at a constant Ti content of 5 mass%