

Phase relations in the Nb–Ni–Cr system at 1,100 °C

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Abstract The isothermal cross section through the ternary phase diagram Nb–Ni–Cr at 1,100 °C was constructed by means of diffusion couples and equilibrated alloys. It was found that nearly 28 at.% of Cr can be dissolved in the μ phase (Nb_7Ni_6) at this temperature, and the solubility of chromium in NbNi_3 is approximately 5 at.%. Under these circumstances the low-temperature (cubic) modification of the NbCr_2 Laves phase can dissolve up to 6 at.% of nickel, but further increase of the Ni content (up to approximately 10 at.%) stabilizes the hexagonal (high-temperature) modification of the Laves phase. The presence of this pseudo-ternary compound which is in equilibrium with all binary intermetallics and body-centred cubic (BCC) Nb- and Cr-based solid solutions largely determines the topology of the isotherm at 1,100 °C. The formation of this phase was also observed in the reaction zone between Nb and Ni–Cr solid solution when chromium concentration exceeded 15 at.%.

Keywords Solid state · Alloys · Phase diagrams · Transition metals compounds

Introduction

The practical interest in the Nb–Ni–Cr system is generated mainly by the fact that Ni–Cr-based alloys are important corrosion-resistant high-temperature materials. Their application in combination with the Nb-based alloys having a very high specific strength at elevated temperatures might lead to a significant improvement in the high-temperature performance of various structural components. To optimize the fabrication procedure of such composite structures, it is paramount to be able to predict (and control) the phases which are formed at the interfaces between niobium and Ni–Cr alloys upon solid-state bonding and under service conditions. It was repeatedly demonstrated that the optimal starting point for research on any metal–metal interactions is the investigation of the phase equilibria and reactive phase formation in relevant materials systems.

The Nb–Ni–Cr system has been studied extensively within a limited composition domain bounded by the binary NbNi_3 and NbCr_2 intermetallics and Ni- and Cr-based solid solutions [1–7]. Most of the cited work was performed almost 50 years ago. In the investigated composition region the partial liquidus projections, several isothermal sections (in the temperature range 1,100–1,200 °C) and several isopleths have been established. For more details and more complete bibliography the reader should access a rather exhaustive compilation by Gupta [8].

On the contrary, for the higher Nb-containing regions of this system only very limited experimental information about phase relations is available [9]. Therefore the present investigation was designed to establish the phase relations in the Nb–Ni–Cr system at 1,100 °C (below the liquidus temperature [4]) and to gain insight into the morphological evolution of the interfacial region between niobium and Ni–Cr solid solution during the reaction at this temperature.

Dedicated to Professor H. Ipsen on the occasion of his 65th birthday.

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Results and discussion

Phase equilibria in the Nb–Ni–Cr system at 1,100 °C

The isothermal cross section through the ternary diagram was constructed by the traditional method of equilibrated alloys and diffusion couple technique. Diffusion couples with two-phase end-members were used. The efficiency of this technique in constructing isothermal cross sections through ternary phase diagrams is higher compared with that when single-phase alloys are used as end-members of the couples because in this case, the chance to “hit” interfaces at which three phases are in equilibrium is much larger. Further details concerning the use of diffusion couple techniques in studying phase diagrams can be found in Ref. [10].

The microstructure of the reaction zone developed after annealing (1,100 °C, 196 h) in the diffusion couple based on pure Cr and two-phase alloy with nominal composition $\text{Ni}_{60}\text{Nb}_{40}$ consisting of (after the equilibration) $\mu\text{-Nb}_7\text{Ni}_6$ intermetallic and NbNi_3 is given in Fig. 1. From the micrograph one can notice that a continuous layer of pseudo-ternary phase (henceforth designated as “T”) is a dominant reaction product in this diffusion couple. The

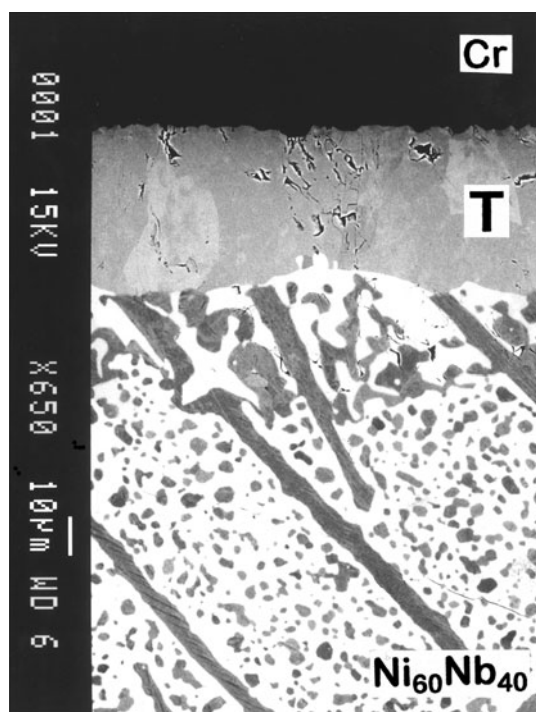


Fig. 1 Back-scattered electron image (BEI) showing the morphology of the diffusion zone developed between chromium and two-phase alloy with the nominal composition $\text{Ni}_{60}\text{Nb}_{40}$ after annealing in vacuum at 1,100 °C for 196 h. Note that the NbNi_3 domains within the microstructure of the two-phase end-member exhibit a white contrast

product ternary compound appears to be in equilibrium with Cr-based solid solution as well as with both constituents of the initial two-phase alloy. The latter indicates a three-phase equilibrium $\text{NbNi}_3 + \mu\text{-Nb}_7\text{Ni}_6 + \text{T}$ in the Nb–Ni–Cr system at this temperature.

When another two-phase material with the nominal composition $\text{Ni}_{50}\text{Cr}_{50}$, which after equilibration at 1,100 °C and quenching in water is a mixture of face-centred cubic (FCC) Ni-based and body-centred cubic (BCC) Cr-based solid solutions [8], was used as the end-member of the diffusion couple, the interfacial reaction with the $\text{Ni}_{60}\text{Nb}_{40}$ alloy also resulted in the formation of a continuous layer of the pseudo-ternary intermetallic (Fig. 2a). An interesting feature here is that the product layer of the T phase is not in

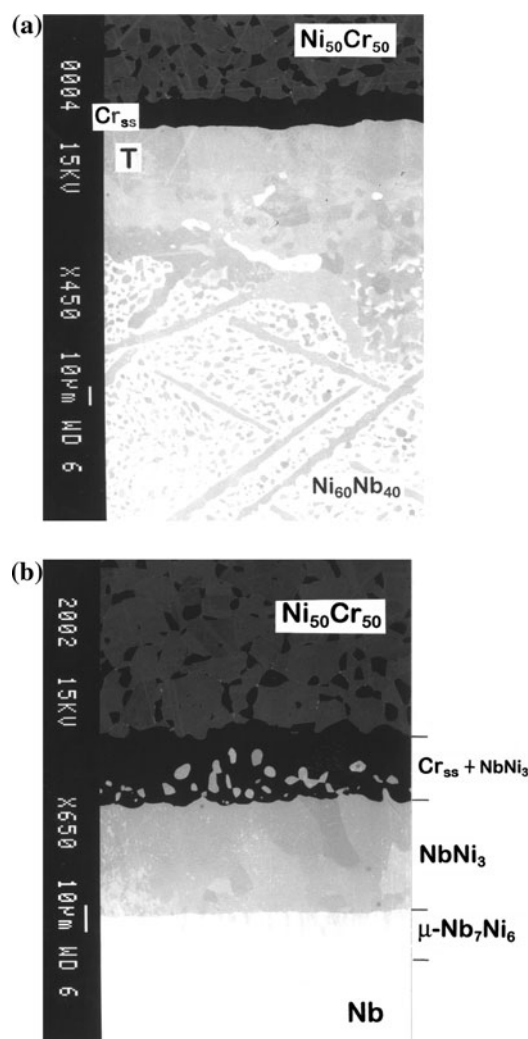


Fig. 2 BEIs of the reaction zones developed in the annealed (1,100 °C, 196 h) diffusion couples based on two-phase alloy with the nominal composition $\text{Ni}_{50}\text{Cr}_{50}$ and **a** the two-phase alloy $\text{Ni}_{60}\text{Nb}_{40}$ and **b** pure Nb. Note that domains of the Cr-based solid solution (Cr_{ss}) present within the microstructure of the $\text{Ni}_{50}\text{Cr}_{50}$ alloy exhibit a dark contrast (the various phases on the micrographs are denoted by their binary formulae, and T is the pseudo-ternary phase)

direct contact with the initial two-phase substrate, but separated from it by the layer of Cr-based solid solution. This implies that in the Nb–Ni–Cr system the pseudo-ternary compound *T* is not in equilibrium with the Ni-based solid solution at 1,100 °C.

There also exists an equilibrium between Cr-based solid solution and NbNi₃ compound on the Nb–Ni–Cr isotherm. This can be appreciated from the diffusion zone morphology developed in a Ni₅₀Cr₅₀/Nb couple after reaction at 1,100 °C for 196 h (Fig. 2b).

From the diffusion couple experiments described above, it may be suggested that on the Nb–Ni–Cr isotherm at 1,100 °C the Cr-based solid solution is involved in three-phase equilibria Cr_{ss} + NbNi₃ + *T* and Cr_{ss} + NbNi₃ + Ni_{ss}. Moreover, information obtained with the diffusion technique was used as a guide for selecting the compositions of the alloys used to verify the provisionally found equilibria and to determine the boundaries of the phase fields in this ternary system.

As it was expected, after equilibrating at 1,100 °C for 400 h and quenching ternary alloys with nominal composition Ni₅₀Cr₄₀Nb₁₀, Ni₄₀Cr₄₀Nb₂₀, Ni₅₅Cr₅Nb₄₀, and Ni₁₅Cr₃₅Nb₅₀, they indeed exhibited a three-phase morphology (Fig. 3). The composition of the phases present in the alloys after heat treatment was measured with electron probe microanalysis (EPMA) and the corresponding three-phase equilibria were plotted on the isotherm. It was found that nearly 28 at.% of Cr can be dissolved in the μ phase (Nb₇Ni₆) at this temperature, and the solubility of chromium in the NbNi₃ is approximately 5 at.%.

In order to determine more precisely the phase boundaries on this isotherm a number of equilibrated two- (and single-) phase alloys were studied with optical microscopy, EPMA, and X-ray diffraction (XRD). Results of this investigation are summarized in Table 1.

With respect to the last three alloys listed in the table some comments concerning the phase determination have to be made. It turned out to be extremely difficult to draw a

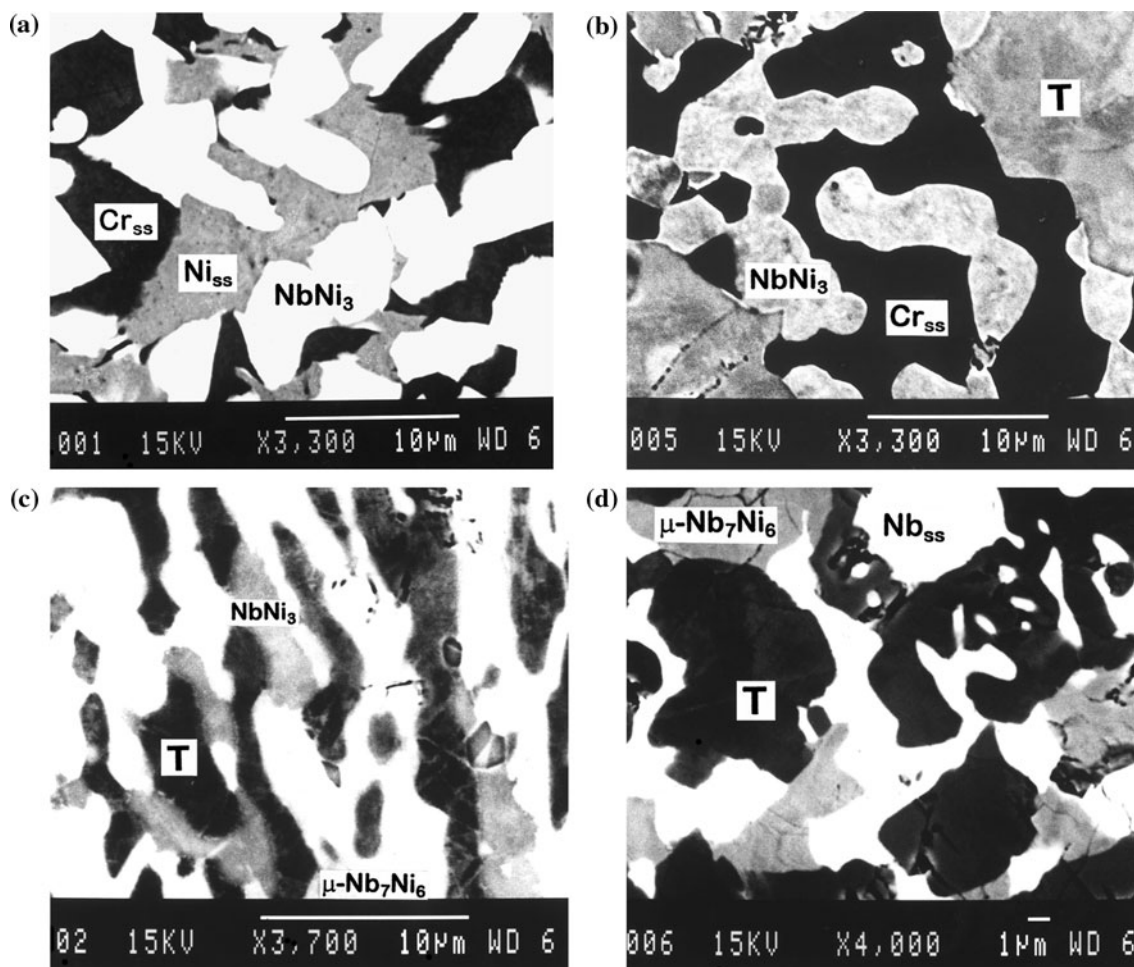


Fig. 3 Microstructure of the three-phase alloys of the Nb–Ni–Cr system after equilibrating at 1,100 °C in vacuum for 196 h and quenching **a** Ni₅₀Cr₄₀Nb₁₀, **b** Ni₄₀Cr₄₀Nb₂₀, **c** Ni₅₅Cr₅Nb₄₀, and

d Ni₁₅Cr₃₅Nb₅₀ (the various phases on the micrographs are denoted by their binary formulae. *T* is the pseudo-ternary phase, and Ni_{ss}, Cr_{ss}, and Nb_{ss} are the Ni-, Cr-, and Nb-based solid solution, respectively)

Table 1 Phases present in equilibrated alloys after annealing at 1,100 °C for 400 h and quenching

Alloy	Phases ^a present at 1,100 °C
Ni ₇₅ Cr ₁₀ Nb ₁₅	Ni _{ss} + NbNi ₃
Ni ₅₅ Cr ₁₅ Nb ₃₀	T + NbNi ₃
Ni ₃₀ Cr ₅ Nb ₆₅	μ-Nb ₇ Ni ₆ + Nb _{ss}
Ni ₂₅ Cr ₁₅ Nb ₆₀	μ-Nb ₇ Ni ₆ + Nb _{ss}
Ni ₃₀ Cr ₂₅ Nb ₄₅	μ-Nb ₇ Ni ₆ + T
Ni ₃₀ Cr ₄₅ Nb ₂₅	Cr _{ss} + T
Ni ₁₅ Cr ₆₀ Nb ₂₅	Cr _{ss} + T
Ni ₃ Cr ₇₇ Nb ₂₀	Cr _{ss} + NbCr ₂ (LT)
Ni ₃ Cr ₅₇ Nb ₄₀	Nb _{ss} + NbCr ₂ (LT)
Ni ₆ Cr ₆₀ Nb ₃₄	NbCr ₂ (LT)
Ni ₈ Cr ₅₈ Nb ₃₄	NbCr ₂ (LT) + T
Ni ₁₀ Cr ₅₀ Nb ₃₄	T

T pseudo-ternary phase, Ni_{ss}, Cr_{ss}, and Nb_{ss} Ni-, Cr-, and Nb-based solid solution, respectively

^a The various phases are denoted by their binary formulae

definite conclusion about the stability region of the pseudo-ternary phase in the Nb–Ni–Cr system at 1,100 °C on the basis of the results of XRD analysis. Attempts to discriminate between the XRD patterns produced by these intermetallics were inconclusive. Therefore, a thorough investigation using polarized light microscopy has been performed. Three ternary alloys with a fixed Nb content of 34 at.%, namely Ni₆Cr₆₀Nb₃₄, Ni₈Cr₅₈Nb₃₄, and Ni₁₀Cr₅₀Nb₃₄, were annealed at 1,100 °C and examined with EPMA, XRD, and polarized light microscopy. The alloy with the nominal composition Ni₆Cr₆₀Nb₃₄ turned out to be a single-phase material and does not show any polarization effect, which is not a surprising finding given the fact that the low-temperature modification of the NbCr₂ Laves phase of the binary Nb–Cr system possesses a cubic structure of the MgCu₂ type (C15, *cF24*) [8]. On the other hand, the Ni₈Cr₅₈Nb₃₄ alloy after equilibration and quenching exhibits two-phase morphology. It was observed that some domains within the microstructure corresponding to the pseudo-ternary phase show a distinct polarization effect, which indicates a crystal symmetry lower than cubic.

The third alloy Ni₁₀Cr₅₀Nb₃₄ also appears to be a single-phase material, but contrary to the Ni₆Cr₆₀Nb₃₄ alloy, differently oriented grains of the optically anisotropic T phase within the microstructure show distinctly different colours in white polarized light due to reflection pleochroism.

As to the nature of the phase T in the Nb–Ni–Cr system at this temperature, it is well known that in some instances the crystal structure of a Laves phase is dependent on electron concentration [11] and in the case of the Nb–Ni–Cr system it was conjectured that nickel can stabilize the

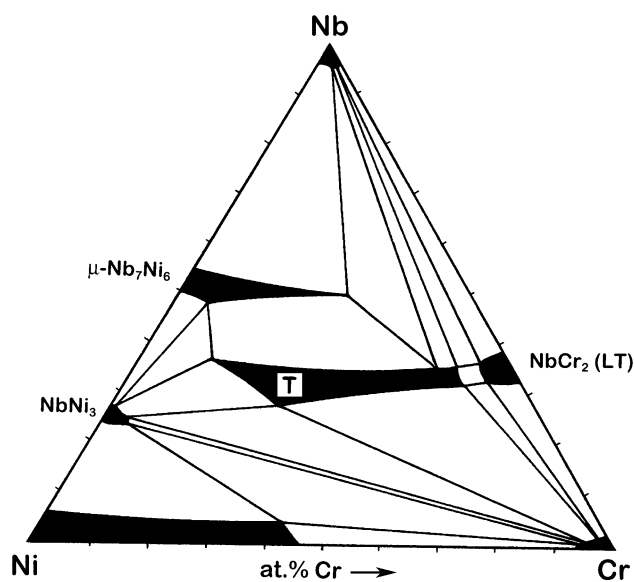


Fig. 4 Isothermal cross section through the ternary phase diagram of Nb–Ni–Cr at 1,100 °C determined in the present study

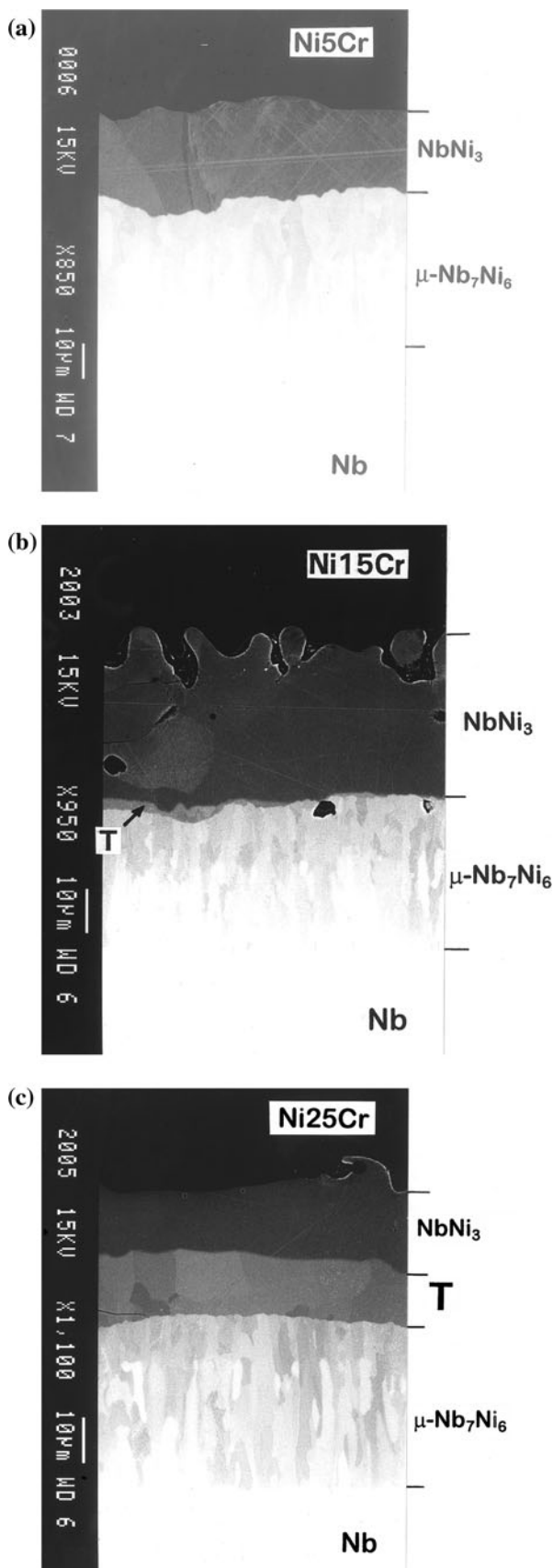
high-temperature (HT) modification of NbCr₂. This is consistent with the results of the present work; at 1,100 °C the low-temperature (LT) cubic modification of the NbCr₂ Laves phase can dissolve up to 6 at.% of nickel, whereas further increase of the Ni-content (up to approximately 10 at.%) stabilizes the HT (hexagonal MgZn₂ type, C14, *hP12*) modification of the Laves phase.

Finally, the results from phase analysis and concentration measurements in diffusion couples and equilibrated alloys lead to the cross section of the Nb–Ni–Cr phase diagram at 1,100 °C represented in Fig. 4.

Reactions at the interfaces between Nb and Ni–Cr solid solution alloys at 1,100 °C

The microstructure of the reaction zones in the diffusion couples based on niobium and various Ni–Cr solid solution alloys are shown in Fig. 5. Solid-state reaction of Ni–5 at.% Cr solid solution with Nb at 1,100 °C results in reaction products somewhat similar to those that would be expected (from the phase diagram) in a binary Nb/Ni couple [8]. Two binary intermetallic compounds, viz. NbNi₃ and μ-Nb₇Ni₆ with very low chromium content (<0.3 at.%), are formed in the transition zone (Fig. 5a). It was found that the reaction layer growth follows a parabolic kinetics profile which is indicative of a diffusion-controlled process.

However, when 15 at.% of Cr was introduced into nickel, interaction in the diffusion couple with Nb led to a different morphology. A new feature here is the formation of a continuous (very thin) layer of pseudo-ternary compound T between the NbNi₃ and μ-Nb₇Ni₆ product phases



◀ **Fig. 5** BEIs of the reaction zones developed in the diffusion couples based on Nb and Ni–Cr solid solution alloys with different Cr content **a** 5 at.%, **b** 15 at.%, and **c** 25 at.%

(Fig. 5b). It was observed that at this temperature, diffusion zones of the Ni–Cr/Nb couples containing from 15 to 25 at.% of Ni exhibit similar reaction pattern, although the relative volume of the pseudo-ternary compound within the reaction product increases with increasing the Cr content in the initial end-member (Fig. 5c). Another characteristic feature of the diffusion zones developed in these samples is a significant enrichment of chromium in the Ni-based solution in the vicinity of the alloy–reaction product interface. This implies that in the phase field of the Ni-based solid solution on the ternary Nb–Ni–Cr isotherm the diffusion paths proceed in the direction of increasing chromium concentration before entering the single-phase region of NbNi₃. This is connected with the higher affinity of Ni towards niobium as compared to that for chromium and mass balance requirements.

Experimental

Nickel (99.98 %), chromium (99.95 %), and niobium (99.98 %) supplied by Goodfellow (Huntingdon, UK) were used as initial materials. Ni–Cr alloys (5–50 at.% of Cr) were melted in an arc furnace under argon atmosphere using a non-consumable tungsten electrode. The ingots were cold-rolled to a thickness of 1.5 mm. Slices of 8 × 8 mm² were cut from the sheets and homogenized under 1 bar of gas mixture Ar + 10 vol% of H₂ (H₂O ≤ 5 ppm) at 1,100 °C for 100 h.

The various Ni–Cr–Nb alloys were also made in an arc furnace. The ingots of ternary alloys were re-melted five times to improve their homogeneity. The weight loss of the alloys after melting was less than 1 wt% relative. The specimens were annealed in an electro-resistance tube furnace in evacuated quartz ampoules at 1,100 °C. The temperature was controlled within ±3 °C. After annealing the samples were quenched in water.

The diffusion couples were prepared and heat-treated in a vacuum furnace (ca. 5 × 10^{−6} mbar) under an external load of approximately 2 MPa. Temperature control was carried out within ±2 °C accuracy. For a typical experiment, the cooling rate of the sample in the vacuum furnace was about 600 °C/h.

After annealing and standard metallographic preparation the diffusion couples and equilibrated alloys were examined by optical microscopy, scanning electron microscopy (SEM), and EPMA. Owing to the coarse structure of the annealed alloys, XRD analysis was performed with a cylindrical texture camera using nickel-filtered K_αCu radiation.

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