Nb-Al Binary System: Reevaluation of the Solubility Limits of the (Nb), Nb₃Al, Nb₂Al and Nb₃Al₃ Phases at High Temperatures

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In this work a re-investigation of the solubility limits of the (Nb), Nb₃Al, Nb₂Al and the Nb-rich side of the Nb₃Al₃ phases on the Nb-Al system is presented. Alloys in the binary fields ((Nb)+Nb₃Al, Nb₃Al+Nb₂Al and Nb₂Al+Nb₃Al₃) were arc-melted, and then equilibrated at 1000, 1200 and 1400 °C. The phases were confirmed via X-ray powder diffractometry, and their compositions were determined via EPMA measurements. The results showed agreement with the literature concerning the solubility limits of (Nb), Nb₃Al and Nb₃Al₃ phases, while important differences in the values were found for the Nb₂Al phase. In addition, the lattice parameters of the Nb₂Al phase were determined via Rietveld refinement. This new set of more accurate experimental information indicates that a thermodynamic reassessment is necessary to precisely describe this system.

Keywords: intermetallics, phase diagrams, Nb-Al system.

1. Introduction

Accurate description of binaries and ternaries phase diagrams is of fundamental importance for the development of thermodynamic databases, useful to predict phase relations, and to define processing conditions for multicomponent alloys. Investigations carried out in our group have contributed to better description of phase diagrams for several binaries systems. Based on inconsistencies between the most recent assessments as well as data from heat-treated ternary alloys containing Nb and Al, new investigations on the solubility limits of the intermetallic phases of the Nb-Al system are necessary. Thus, in this work, the solubility limits of the (Nb), Nb₃Al, Nb₂Al and the Nb-rich side of the Nb₃Al₃ phase were reevaluated via Electron Probe Microanalysis – Wavelength dispersive spectrometry (EPMA – WDS) from equilibrated alloys.

2. Literature Review

Table 1 summarizes the experimental information available for the Nb-Al system concerning solidus/liquidus temperatures, phase solubility range, activity data and enthalpy of formation.

2.1 Phase equilibria data

Due to its importance for the development of superconductors and high-temperature materials, many authors have investigated the Nb-Al phase diagram. The early studies of this system are all in relatively good agreement in terms of phase stability. Besides the terminal compounds, the Nb₃Al (A15), Nb₂Al (σ) and Nb₃Al₃ (D0₂₂) phases are reported as stable (see Table 2 for crystallographic structural information), however, Richards indicates the presence of 2 extra high temperature phases (Nb₇Al₃ and Nb₁₇Al₃) which have not been reported by other authors. The congruent formation of Nb₃Al₃ is well established, however, there have been some discrepancies in terms of the nature of formation of the other phases. For example, Nb₃Al is reported to be formed either peritectoidically or peritectically. The Al-rich side of this system is characterized by a degenerated equilibrium in which the Liquid, Nb₃Al₃ and (Al) phases are involved. This invariant reaction has been reported either as eutectic or peritectic.

The most complete experimental work on the Nb-Al system was carried out by Jorda et al. In this paper, the authors determined the phases’ solubilities ranges via metallography, XRD and EPMA analysis of samples heat-treated from 24 hours up to 1 month according to the temperature of heat treatment. The authors also used levitation thermal analysis (LTA) and differential thermal analysis (DTA) to determine the temperature of the invariant reactions, solidus and liquidus, and the peritectic nature for the Nb₃Al and Nb₂Al formation.

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Table 1. Summary of Experimental information available for the Nb-Al System.

| Information                        | Reference                          | Technique  |
|------------------------------------|------------------------------------|------------|
| Temperatures (Solidus/Liquidus)    | Jorda et al. 20                     | DTA/LTA    |
|                                   | Stein et al. 21                     | DTA        |
|                                   | Wicker et al. 18                    | DTA        |
|                                   | Witusiewicz et al. 7               | DTA        |
|                                   | Zhu et al. 24                       | DSC        |
|                                   | Lundin and Yamamoto 16             | DTA        |
|                                   | Baron and Savitskii 14              | TA         |
|                                   | Svechnikov et al. 17               | TA         |
| Phase solubility Range            | This work                           | EPMA       |
|                                   | Menon et al. 22                     | EPMA       |
|                                   | Kokot et al. 21                     | XRD        |
|                                   | Shilo et al. 23                     | Knudsen Effusion |
|                                   | Jorda et al. 20                     | MA         |
|                                   | Menon et al. 22                     | XRD        |
|                                   | Lundin and Yamamoto 16 (a)          | XRD        |
|                                   | Svechnikov et al. 17(a)             | XRD        |
|                                   | Glazov et al. 12,13                 | Hardness(b) |
| Enthalpy of Formation of Intermetallic Phases | Colinet et al. 27                  | LMTO-FP    |
|                                   | De Boer et al. 28                   | Miedema Model |
|                                   | Meschel et al. 29                   | DRC        |
|                                   | Shilo et al. 23                     | Knudsen Effusion |
|                                   | George et al. 31                    | EMF        |
|                                   | Mahdouk et al. 30                   | DRC        |

(a) apud Jorda et al. 20; (b) Solubility of Nb in (Al); DTA: Differential Thermal Analysis; LTA: Levitation Thermal Analysis; PA: Pirani-Alterthum Method; TA: Thermal Analysis; DSC: Differential Scanning Calorimetry; EPMA: Electron Probe Microanalysis; XRD: X-ray Diffractometry; MA: Metallographic Analysis; LMTO: full potential Linear Muffin tin orbital; DRC: Direct Reaction Calorimetry; EMF: Electromotive Force.

Table 2. Crystallographic information of stable solid phases of the Nb-Al system.

| Phase | Strukturbericht Designation | Pearson Symbol | Space Group | Prototype | Occupation | Wyckoff | x   | y   | z   |
|-------|-----------------------------|----------------|-------------|-----------|------------|---------|-----|-----|-----|
| (Nb)  | A2                          | cl2            | Im3m        | W         | Nb         | 2a      | 0   | 0   | 0   |
| Nb3Al | A15                         | cP8            | Pm3n        | Cr3Si     | Nb (1)     | 2a      | 0   | 0   | 0   |
|       |                             |                |             |           | Nb (1)     | 0.25    | 0   | 0.5 |     |
|       |                             |                |             |           | Al (1)     | 2a      | 0   | 0   | 0   |
|       |                             |                |             |           | Al (2)     | 0.0665  | 0.2615| 0   |     |
| Nb2Al | D8h                         | tP30           | P42/mmm     | CrFe      | Nb (1)     | 8i      | 0.535| 0.128| 0   |
|       |                             |                |             |           | Nb (2)     | 0.3965  | 0.6035| 0   |     |
|       |                             |                |             |           | Nb (3)     | 0.318   | 0.318| 0.252|     |
|       |                             |                |             |           | Al (1)     | 2b      | 0    | 0.5 | 0.25|
|       |                             |                |             |           | Al (2)     | 0       | 0    | 0   |     |
| NbAl3 | D022                        | tI8            | I4/mmm      | TiAl3     | Nb (1)     | 2a      | 0   | 0   | 0   |
| (Al)  | A1                          | cF4            | Fm3m        | Cu        | Al         | 2a      | 0   | 0   | 0   |
was confirmed. The solubility limits of the phases were also indirectly determined by Kokot et al. 21 via XRD analysis of arc-melted samples heat-treated for 14 days at 1100 °C and Menon et al. 22 via EPMA measurements of arc-melted alloys heat-treated at 1650 °C/50 h and subsequently heat treated at 1200 °C/14 days or 1000 °C/30 days. Shilo et al. 23 measured the variation of vapor pressure of Al according to the composition from binary alloys and indirectly determined the solubility limits of the phases. Their samples were previously heat-treated at 1297 °C for 12 hours and then the vapor pressures were measured at 1571, 1607, 1672, 1721 °C with different times and heating/cooling cycles.

Zhu et al. 24 performed Differential Scanning Calorimetry (DSC) measurements with different scanning rates from heat treated samples in order to determine the nature of the Al-rich equilibrium involving Liquid, NbAl3, and (Al). The suggested temperature was 661.44 °C, leading to a peritectic type reaction because it is higher than the melting point of pure Al (660.3 °C). Witusiewicz et al. 7 performed new experiments (DTA and Pirani-Alterthum method) aiming at the determination of the high temperature solidus and liquidus lines. In general, their results are in good agreement with previous information 20. Witusiewicz et al. 7 also measured the temperature of the degenerated Al-rich reaction as 657 °C ± 5 (DTA), despite this, they modeled the reaction as peritectic. More recently, Stein et al. 25 measured the NbAl3 (D022) phase congruent melting temperature via DTA.

2.2 Thermodynamic data and CALPHAD modeling

Several studies present estimated data for enthalpies of formation of the Nb-Al compounds based both in calculations as well as on experimental results. Gelashvili and Dzneladze 26 estimated the enthalpies of formation calculating the changes in the free energy of the process of reduction of Al and Nb oxides with CaH2. Colinet et al. 27 reported the enthalpies of formation of the intermetallic phases via direct principle calculations (Full Potential Linear Muffin Tin Orbital, FP-LMTO) and de Boer et al. 28 via Miedema Model. Shilo et al. 23 carried out vapor pressure measurements in the high-temperature range 1844-2146 °K using the Knudsen Effusion Method aiming the determination of enthalpy of formation of the intermetallic compounds. Meschel and Kleppa 29 and Mahdouk et al. 30 conducted experiments of Direct Reaction Calorimetry (DRC). George et al. 34 performed Electromotive Force (EMF) measurements in the intermediate temperature (973 to 1078 K) range by using solid-state electrochemical cells and CaF2 as solid electrolyte. George et al. 31 and Shilo et al. 23 have also measured the activities of Al in the Nb-Al system.

The Nb-Al system was firstly described according to the CALPHAD methodology by Kaufman and Nesor 32, considering all compounds as stoichiometric. Latter, it was reassessed by Kaufman 33 where the NbAl phase was modeled as a substitutional solid solution. Subsequent studies have modeled the NbAl phase either as (Nb)3(Al,Nb) 8,24,33 or (Al,Nb)1(Al,Nb) 2,7,8,36. Joubert 37 investigated the Nb2Al site occupancy via Rietveld refinement of X-ray diffraction data and Mathieu et al. 38 investigated simplifications for the σ phase sublattice models, evaluating the best agreement with the experimental phase diagram. The model type (Al,Nb)1(Al,Nb)1(Al,Nb)3 should be used in order to respect the crystal structure and the nature of the defects in this phase. Table 3 summarizes the sublattices models applied for the description of these intermetallic phases from assessments of different authors.

3. Experiments Procedure

Alloys with initial masses between 1 and 2 g were weighed on an analytical balance with accuracy of 0.1 mg from high purity raw materials, Al (min. 99.999 wt. %) and Nb (min. 99.8 wt. %)

3.1 Arc-melting

The alloys were arc-melted in a water-cooled copper crucible under argon atmosphere (min. 99.995%) and non-consumable tungsten electrode. Five melting steps were carried out for each alloy to ensure chemical homogeneity, turning the ingots upside-down from one melting step to the next. Before each melting step a piece of pure Ti (getter) was melted to remove residual gas impurities from the furnace atmosphere. After melting, the ingots were weighed to evaluate possible mass losses during arc-melting.

| Sublattice model | NbAl (A15) | NbAl (σ) | NbAl1 (D022) |
|------------------|------------|-----------|---------------|
| Reference        |            |           |               |
| He et al. 8      | (Nb)3(Al,Nb) | (Al,Nb)1(Al,Nb) | (Al,Nb) | (Al,Nb) |
| Witusiewicz et al. 7 | (Al,Nb)3(Al,Nb) | (Al,Nb)1(Al,Nb) | (Al,Nb) | (Al,Nb) |
| Zhu et al. 24    | (Nb)3(Al,Nb) | (Al,Nb)1(Al,Nb) | (Al,Nb) | (Al,Nb) |
| Shao 34          | (Al,Nb) | (Al,Nb)1(Al,Nb) | (Al,Nb) | (Al,Nb) |
| Servant and Ansara 6 | (Al,Nb)3(Al,Nb) | (Al,Nb)1(Al,Nb) | (Al,Nb) | (Al,Nb) |
| Kattner and Boettinger 25 | (Al,Nb) | (Al,Nb)1(Al,Nb) | (Al,Nb) | (Al,Nb) |
| Kaufman 33       | Stoichiometric | (Al,Nb) | Stoichiometric |
| Kaufman and Nesor 32 | Stoichiometric | (Al,Nb) | Stoichiometric |
3.2 Heat treatments

Aiming to reach thermodynamic equilibrium conditions, all alloys where heat treated at 1400 °C for 75 h in a resistive (Ta heating element) furnace under argon. The temperature was measured by an optical pyrometer calibrated against the melting point of pure elements. Subsequently, samples of each alloy were wrapped in thin Ta foil, encapsulated in quartz tubes (under argon) and heat treated at 1200 °C for 200 h or 1000 °C for 600 h using tubular resistive furnaces.

3.3 X-ray diffractometry (XRD)

For the X-ray diffraction experiments, the samples were analyzed in powder form, with powder size below 80 mesh (178 µm). The following conditions were adopted: Cu-Kα radiation, 40 kV voltage, 30 mA current, 0.02º angular step, 15s per step, and angle (2θ) ranging from 10 to 90°. The phases present in the samples were identified by comparison between experimental and simulated diffractograms, using PowderCell Software with crystallographic information reported by Villars and Calvert. The lattice parameters for the Nb₂Al phase were obtained via Rietveld refinement using the software FullProf.

3.4 Scanning electron microscopy and electron probe micro-analysis

The samples were prepared according to the following route: (1) hot mounting; (2) manual grinding with SiC sand paper, in the sequence: 220, 400, 600, 1200, 2400, 4000; (3) Final polishing with a colloidal silica suspension (OP-S); (4) ultrasonic cleaning for 15 minutes; (5) coating with carbon. Initial images were obtained in the backscattered electron mode in conventional SEM microscopes (TM3000, Hitachi), equipped with Energy Dispersive Spectrometers (EDS). The determination of alloys’ global composition was made via EDS measurement in representative area (at least 0.15 mm²) skipping possible cracks and pores. Wavelength X-ray Spectroscopy (WDS) analyses were performed in a SX100 (CAMECA) instrument equipped with 5 spectrometers. The standards were Pure Nb (min. 99.8 wt.%) and Pure Al (min. 99.999 wt.%). The compositions proposed for the phases are the average values of at least 7 measurements in different regions of the sample.

4. Results and Discussion

4.1 Solubility range

Table 4 shows the chemical composition of the prepared alloys, the mass losses associated with the melting steps, and the calculated composition interval for each alloy assuming that all mass losses were either from Nb or Al volatilization. Alloy Nb₆₀Al presented an important mass variation, however, EDS analysis indicated that the global composition of the sample was kept. Thus, it should have occurred due to macroscopic pieces of the alloy that were thrown out of the crucible during cooling inside the arc-melter.

Table 4. Compositions of the Nb-Al alloys prepared in this work, after arc-melting.

| Alloy Id | Composition (at.% Al) | Mass Variation (%) | Possible Composition Interval* (at.% Al) |
|----------|-----------------------|--------------------|----------------------------------------|
| Nb₁₂Al   | 12.0                  | 0.92               | 9.4  12.1                               |
| Nb₂₃Al   | 25.1                  | 0.87               | 23.1 25.2                               |
| Nb₆₀Al   | 59.9                  | 7.33               | 53.1 62.5                               |

*calculated composition attributing mass loss to either (a) Al or (b) Nb.

Figure 1 presents the X-ray diffractograms of the alloys equilibrated at 1000, 1200 and 1400 °C. All peaks were identified and only the expected phases are present in the alloys: (Nb) + Nb₃Al (Nb₁₂Al); Nb₃Al + Nb₂Al (Nb₂₃Al); Nb₂Al+NbAl₃ (Nb₆₀Al).

Figure 2 presents SEM micrographs of the heat-treated alloys, with significant microstructural differences from the as-cast condition, indicating that significant diffusion process occurred, and the equilibria was achieved. Alloy Nb₁₂Al in all conditions presented grains of (Nb) and intergranular Nb₃Al. In the interior of the (Nb) grains, precipitates of Nb₃Al are observed in the samples equilibrated at 1000 and 1200 °C, but not in the sample equilibrated at 1400 °C. The formation of
these precipitates is due to a solid state precipitation of Nb₃Al that came from a supersaturated (Nb). No significant change is observed in the microstructures of the Alloy Nb23Al with the heat treatment conditions. These samples show Nb₃Al matrix and a fraction of distributed Nb₂Al. Micrographs of Alloy Nb60Al present a microstructure with alternate plates of Nb₃Al and NbAl₃.

Table 5 shows the composition of the alloys measured via EDS and the phases measured via EPMA along with the error which is calculated based on the standard deviation of the measured values. The presence of precipitates in the interior of the (Nb) phase equilibrated at 1000 °C did not allow reliable EMPA measurements. Results of EPMA measurements are also plotted in Figure 3 along with selected experimental data available in the literature as well as the calculated phase diagrams with the parameters optimized by Witusiewicz et al. and He et al. The measurements in the (Nb), Nb₃Al and NbAl₃ phases are in agreement with the literature experimental data as well as the Nb-rich limit of the NbAl₃ phase. The Al-rich limit of the NbAl₃ phase exhibits important discrepancies with the most recent assessment.

![Microstructure Images](image)

**Figure 2.** Evolution of the microstructure of the Alloys Nb12Al, Nb23Al and Nb60Al equilibrated at 1000, 1200 and 1400 °C.

**Table 5.** Composition limits of the phases of the Nb-Al system measured via EPMA.

| Alloy   | Equilibrated Temperature (°C) | Global Composition - EDS (at. % Al) | Phase Composition - EPMA (at. % Al) |
|---------|-------------------------------|-------------------------------------|-------------------------------------|
| Nb12Al  | 1400                          | 10.3                                | Nb₃Al (A15) 19.3 ± 0.2              |
|         | 1200                          | 11.3                                | -                                    |
|         | 1000                          | 11.1                                | 6.5 ± 0.7 18.6 ± 0.4                 |
| Nb23Al  | 1400                          | 21.9                                | Nb₂Al (A15) 3.1 ± 0.2 31.5 ± 0.3     |
|         | 1200                          | 21.7                                | 2.0 ± 0.1 31.7 ± 0.1                 |
|         | 1000                          | 21.6                                | 2.0 ± 0.1 31.9 ± 0.2                 |
| Nb60Al  | 1400                          | 57.7                                | Nb₂Al (A15) 42.4 ± 0.2 74.4 ± 0.1    |
|         | 1200                          | 58.7                                | -                                    |
|         | 1000                          | 59.3                                | 36.7 ± 0.9 74.7 ± 0.1                |
Figure 3. Nb-Al phase diagram calculated with the parameters optimized by Witusiewicz et al. \(^7\) (solid lines) and He et al. \(^6\) (dashed lines) along with experimental data from: This work (EPMA), Jorda et al. \(^20\) (▲ XRD; △ DTA/LTA; ● EPMA), Kokot et al. \(^21\) (◆ XRD), Menon et al. \(^22\) (● EPMA), Shilo et al. \(^23\) (♦ Knudsen Effusion), Witusiewicz et al. \(^7\) (○ DTA), Wicker et al. \(^18\) (□ DTA) and Zhu et al. \(^24\) (◇ DSC). Note: (Nb) phase’s composition measurement in Nb12Al alloy equilibrated at 1000 °C was removed from the figure because of its low reliability.

Figure 4 shows details of the Nb-Al phase diagram in the Nb$_2$Al region along with the EPMA composition measurements for this phase. The square symbols are from the present work while the stars are from measurements in ternary samples (Al-Co-Nb \(^{11}\) or Al-Fe-Nb \(^{9,10}\) ) positioned in three phase field equilibria in which the third component (Co or Fe) solubility is lower than 1 at.% in the Nb$_2$Al phase. Our results are in agreement with the results from Silva \(^{10}\) (alloy heat treated at 1400 °C/75h) and Stein et al. \(^{9}\) (alloys heat treated at 1450 °C/50 h, 1150 °C/168 h and 1000 °C/1000 h). However, the alloy heat treated at 1300 °C/100 h in the work of Stein et al. \(^9\) presented a slightly lower Al solubility. Compared with the results from Dovbenko et al. \(^{11}\), our results are in agreement with the measurement obtained from the alloy heat treated at 1250 °C/72 h. However, the results at 1200 °C/96 h and 1150 °C/136 h presented significantly lower Al contents while for the samples 1000 °C/236 h and 800 °C/1000 h the contents were higher than the expected.

4.2 XRD rietveld refinement

Figure 5 shows the lattice parameters “a” and “c” for the Nb$_2$Al phase in function of temperature, along with the results from Kokot et al. \(^{21}\) and Joubert \(^{37}\). The symbols in black (◆ and □) represent the parameters obtained for the Nb-rich side of the Nb$_2$Al phase (results from alloys in Nb$_3$Al+Nb$_2$Al field), while the gray symbols (◄ and ■) the parameters obtained for the Al-rich side of the phase (results from alloys in Nb$_2$Al+NbAl$_3$ field). It should be stated that Joubert \(^{37}\) results (symbol ●) is from a Nb$_2$Al single phase alloy with composition 34.2 at.% of Al. In general, our results are in agreement with Kokot et al. \(^{21}\) as well as results from Joubert \(^{37}\). The presence of excess Al in the structure of Nb$_2$Al promoted the decreasing of the parameter “a” and increasing of the parameter “c” of the crystal structure. This can be noted both in a fixed temperature, comparing the Al-rich side with the Nb-rich side as well as the lattices parameters change when the solubility of Al increases with the temperature (Al-rich side).
5. Conclusions

Experiments aiming to determine the solubility limits of the intermetallic phases in the Nb-Al system confirmed the solubility range for the phases (Nb) and Nb₃Al. The Nb-rich sides of the phases NbAl₃, Nb₂Al were also in agreement with the previous data. Different values from those reported in the literature were found for the Al-rich border of the NbAl₃ phase. The present experimental results are consistent with the experimental data in the ternary alloy systems containing Nb and Al\(^{8–11}\), suggesting necessary changes in the currently accepted Nb-Al phase diagram and the thermodynamic description of this system, specially concerning the Nb-Al phase.

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