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Phase Equilibria of the Cu-Co-Nb system at 1198 K

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Abstract

The isothermal section of the Cu-Co-Nb ternary system at 1198 K has been investigated by means of diffusion triple together with electron probe microanalysis technique. Series of tie lines and tie-triangles have been determined and the isothermal section at 1198 K has been established, and four three-phase fields have been figured out. Namely, (Nb)+(Cu)+Co_7Nb_6, (Cu)+Co_2Nb+Co_7Nb_6, Co_2Nb+Co_3Nb+(Cu) and Co_3Nb+(Co)+(Cu) existing in the present isothermal section. In present work Co_3Nb and Co_7Nb_2 were disposed as only one phase Co_3Nb. It is found that the solubility of Cu in Co_3Nb, Co_2Nb and Co_7Nb_6 are only up to 5.70, 5.80 and 4.20 at.% Cu, respectively. The range of homogeneity of Co_7Nb_6 and Co_2Nb is 44.7 to 48.0 at.% and 25.0 to 29.6 at.% Nb, respectively. The Co_3Nb is line compounds.

Keywords*: Electron probe micro-analyze; Alloys; Diffusion couples; Equilibrium diagram*

Introduction

The Cu-Co system displays a metastable liquid phase separation in the undercooled melt below the liquidus temperature and its binary phase diagram is characterized by a metastable liquid miscibility gap [1]. A considerable amount of works has been published on this alloy system to study the position of the liquid miscibility gap and the mechanism of liquid phase separation as well as the related solidification microstructures [2-11]. In addition, to control the formation of macroscopic and microscopic morphologies, addition of elements such as Cr, Zr and Fe etc. were added to the Cu-Co [12-14] alloy samples to enhance or reduce the extent of liquid phase separation. In rapidly solidified Cu-Fe alloy samples, the addition of Nb was found to stabilize the liquid miscibility gap and increase its critical temperature [15]. Thus, the Cu-Co-Nb ternary alloys may also display metastable liquid demixing, however, no information is available in the literature on this system. Therefore, it is important and necessary to investigate the effect of Nb addition on the liquid phase separation of Cu-Co.

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To obtain more details about the liquid phase separation in the Cu-Co-Nb system, the information concerning the phase equilibria in this ternary system is necessary. The Cu-Nb system [16] is a simple system without any intermediate compounds as shown in FIG. 1. In the Cu-Co system as shown in FIG. 2, only terminal solutions α-(Co), ε-(Co) and (Cu) exist as stable solid phases [17]. The binary Co-Nb system as shown in FIG. 3 belongs to the few examples where different polytypes of the Laves phase occur as stable phase [18,19]. There are five binary compounds, Co_7Nb_2, αCo_2Nb, βCo_2Nb, γCo_2Nb and Co_6Nb_7. The previous, sparse knowledge of the binary systems is studied in ref. [20]. There are five intermediate phases in of Co_7Nb_6, $Co_{16}Nb_9$, Co_2Nb, Co_3Nb and Co_7Nb_2, of which the phases Co_7Nb_6 and Co_2Nb melt congruently at 1697K and 1748K, respectively.

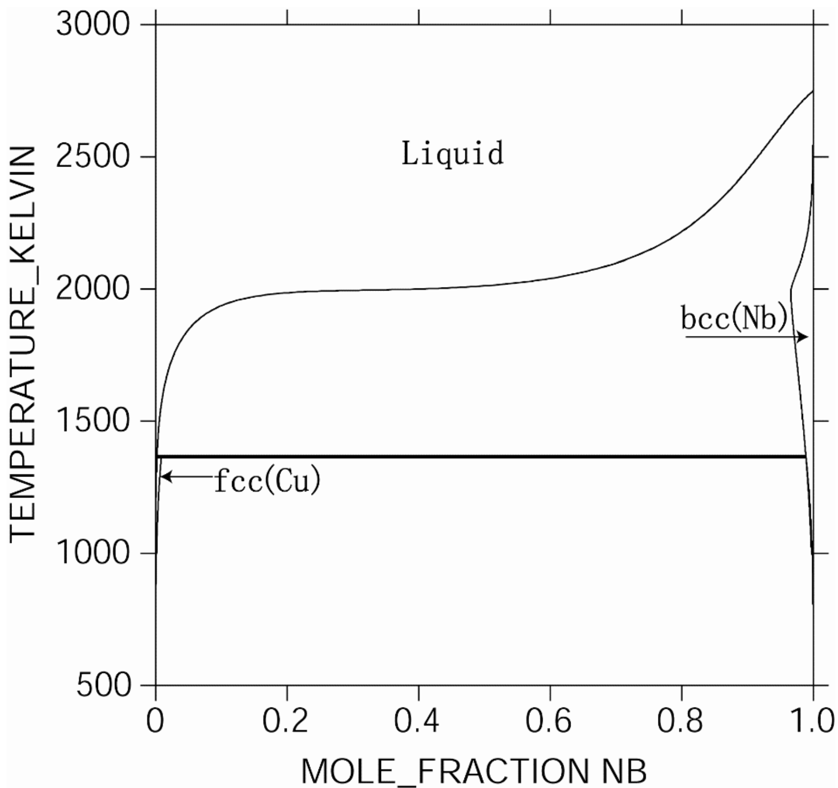

FIG.1. **Cu-Nb binary phase diagram.**

Up to now, to the best of our knowledge, very little work [21] has been done about the phase equilibria in the Cu-Co-Nb ternary system. In order to deeply understand this ternary system, more information about phase relations is desirable. The high-efficiency diffusion-multiple approach [22,23] is ideally suited for determining phase diagrams of these ternary systems. It would take thousands of alloys to determine these systems using the traditional one-alloy-at-a-time (equilibrated alloy) approach. Apart from possible deleterious effects, interstitial elements are well known to stabilize binary and ternary intermetallic phases that would otherwise not form. In contrast, the diffusion-multiple approach needs no or only a few cast alloys. Samples are easy to make, and safe-guarding against interstitial contamination can be very easily implemented. The general diffusion-multiple approach has been discussed in detail previously and has been successfully applied to many alloy systems [22]. In present work, the phase equilibria in the Cu-Co-Nb system at 1198K were investigated by means of diffusion-triple approach.

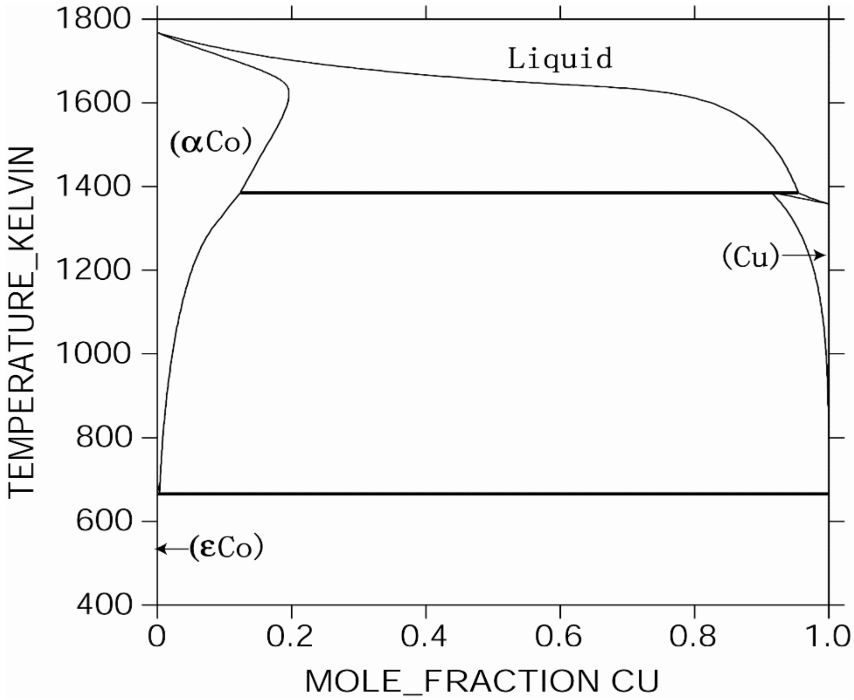

FIG. 2. **Phase diagram of Cu-Co binary system.**

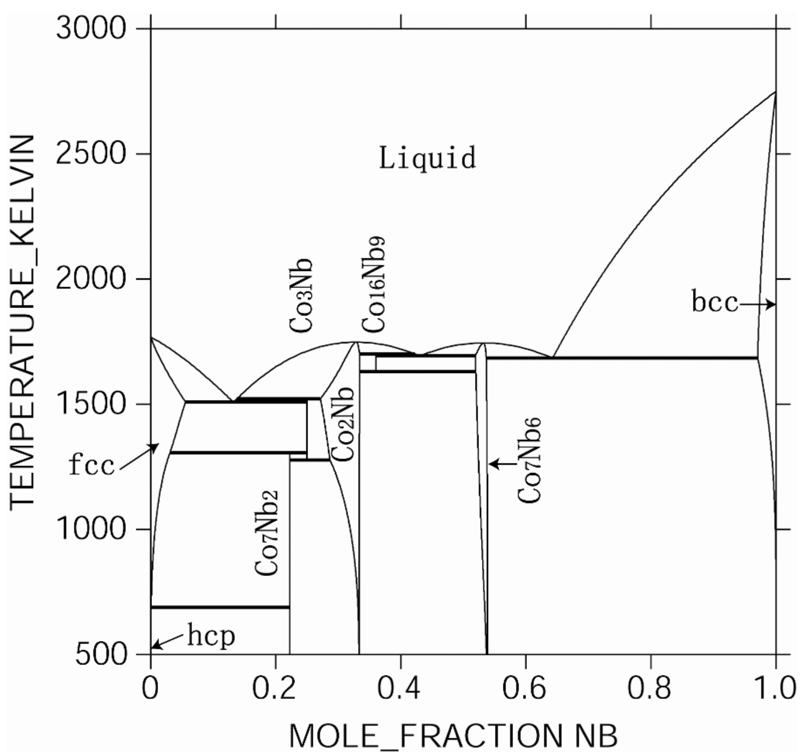

FIG. 3. **Phase diagram of Co-Nb binary system.**

Experimental

The Cu-Co-Nb diffusion triple specimens were prepared from blocks of copper, cobalt and niobium (99.9 wt% purity each. Firstly, Co-Cu diffusion couples were welded together by diffusion under 4.5MPa pressure in Ar atmosphere at 1198 K for 15 min then cooled to ambient temperature. Secondly, the Cu-Co-Nb diffusion couples were assembled from the Co-Cu couples and the pure Nb blocks at 1198 K under Ar flow for 15 min. The Cu-Co-Nb diffusion couples, which were sealed in a silica capsule back-filled with high purity argon, were annealed in an L4514-type diffusion furnace at 1198 ± 2K (Qingdao Instrument & Equipment Co. Ltd., China) for 1440 hours and quenched in water. Thirdly, the annealed diffusion couples were ground and polished along a face parallel to the direction of interatomic diffusion. The flow chart for making the Cu-Co-Nb diffusion triple is shown in FIG. 4.

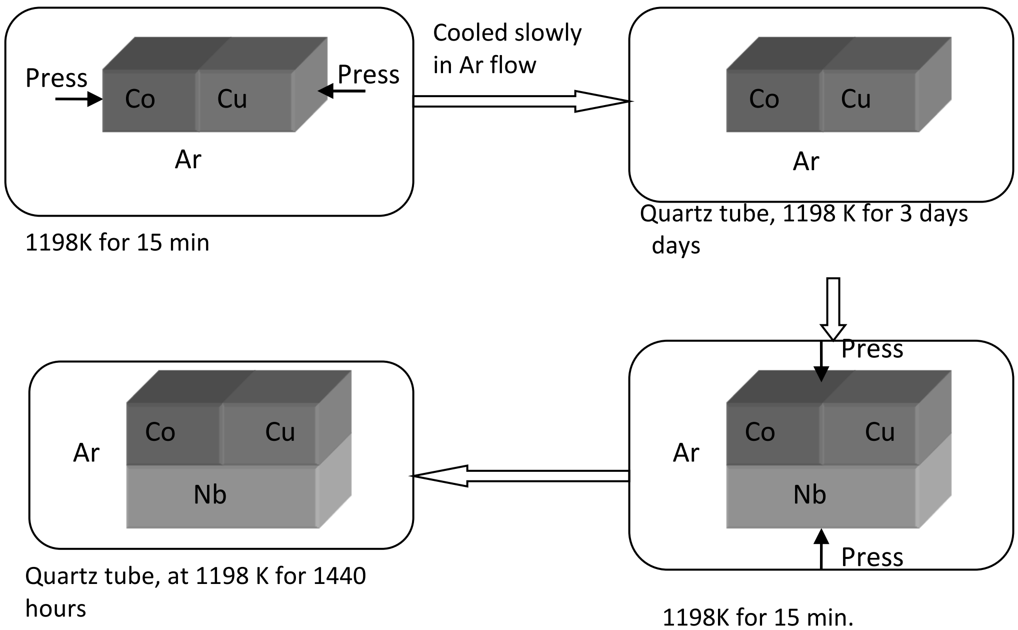

FIG. 4. **Fabrication flow chart of the Cu-Co-Nb diffusion triple.**

Microstructure and phase compositions of the diffusion triple were examined by electron probe microanalysis (EPMA) (JX-8800 R, Japan, electron Optics Ltd., Tokyo) under the operation condition of 20 kV voltage, 2×10^{-8} A current and a 40° take-off angle.

Results and Discussion

Binary system

The backscattered electron (BSE) image of the Cu-Co-Nb diffusion triple annealed at 1198 K for 1440 h is shown in FIG. 5a and 5b. A schematic diagram of phase distribution in the triple is illustrated in FIG. 5c. During the long-term diffusion treatment, extensive inter diffusion among Co, Cu and Nb blocks has been occurred. The equilibrium binary phases along interface are clear identifiable in the triple. There are three layers of compounds formed along blocks of Co and Nb. These compounds have been determined by EPMA to be Co_3Nb, Co_2Nb and Co_7Nb_6, respectively. Comparison on the ref. [18], an interesting feature of this phase diagram is that Co_2Nb is exists in three forms side by side. αCo_2Nb and βCo_2Nb were shown as line compounds and named Co_3Nb and $Co_{16}Nb_9$ respectively [20]. It should be point out that the phases Co_7Nb_2 and Co_3Nb, which are very close to each other are just one phase. Note, Co_7Nb_2 and Co_3Nb are treated as Co_3Nb in present work for they are very close to each other and just one phase. However, there are no intermetallic compounds formed between blocks Cu-Co and Cu-Nb, which is in good agreement with binary phase diagrams of the Cu-Co [16], Cu-Nb [17] and Co-Nb [20] binary phase diagrams.

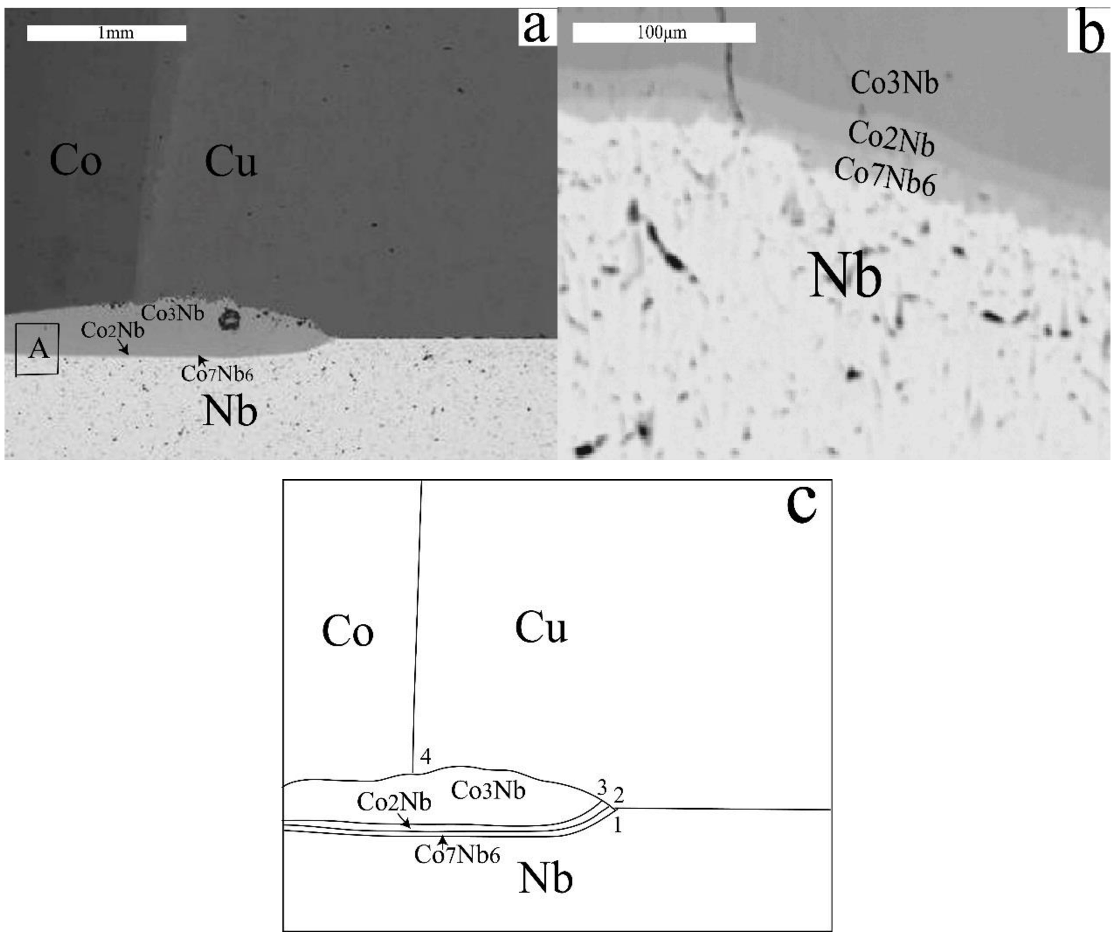

FIG. 5. **The Cu-Co-Nb diffusion triple heated at 1198 K for 1440 h; (a) Back-scattered electronic image; (b) Back-scattered electron images of the A area; (c) Schematic diagram of the 1198 K diffusion triple.**

Solid solution

TABLE 1 lists the tie-lines data obtained by EPMA, all the experiment data were taken from the couple cross-section along the phase boundary. As shown in TABLE 1, the solubility of Cu in Co_3Nb, Co_2Nb and Co_7Nb_6 are only up to 5.70, 5.80 and 4.20 at.% Cu, respectively.

TABLE 1. **Extrapolated compositions of the phases in equilibrium at 1198 K.**

Co	Nb	Co	Nb	Co	Nb	Co	Nb
Co/Co_3Nb				**Co_3Nb/Co_2Nb**			
0.976	0.015	0.781	0.201	0.775	0.208	0.733	0.25
0.966	0.017	0.779	0.187	0.772	0.203	0.735	0.232
0.951	0.021	0.771	0.181	0.77	0.182	0.715	0.233
Co_2Nb/ Co_7Nb_6				**Co_7Nb_6/Nb**			
0.685	0.296	0.545	0.447	0.509	0.48	0.028	0.963
0.689	0.283	0.528	0.441				
0.686	0.267	0.522	0.438	0.511	0.469	0.027	0.956
Co_3Nb/Cu				**Co_2Nb/Cu**			
				0.711	0.231	0.02	0.031
0.767	0.176	0.033	0.018	0.675	0.269	0.02	0.038
Co_7Nb_6/Cu				**Nb/Cu**			
0.499	0.459	0.019	0.045				
Co/Cu							
0.953	0.013	0.031	0.008	0.017	0.951	0.011	0.044

The experimental results may contain errors directly attributable to the nature of the sample [22]. Another source of error is in the experimental measurements themselves. The difficulties connected with the accurate determination of the boundary concentrations in the reaction zone are a problem for both semi-infinite and finite diffusion couple of techniques. Several items concerning the electron-beam microanalytical techniques used are to be noted here. Thirdly, the determination of a chemical composition with EPMA has an inherent experimental error associated with data counting statistics and data correction procedures [22].

Of course we can't neglect the solubility limit in this work. Through EPMA we found that Cu can replace Nb in Co_3Nb, Co_2Nb and Co_7Nb_6. However, the solubility limit is small in all these compounds. So, all these binary phases are no longer maintained as stoichiometric compounds as their names may suggested, but instead they have developed into solution phases (with certain solubility limit) in ternary system. The range of homogeneity of Co_7Nb_6 and Co_2Nb is 44.7-48.0 at.% and 25.0-29.6 at.% Nb, respectively. The Co_3Nb is line compounds.

Isothermal section

Based on the experimental data in TABLE 1 and FIG. 5c, the 1198 K isothermal section of the Cu-Co-Nb system is constructed as shown in FIG. 6. Each line represents one interface between two phases, and each tri-junction point represents one three-phase equilibrium. In principle, we can define as many tie-triangles in the isothermal section as possible by measuring the compositions of the phases near triple points. However, due to the effect of the electron scattering plus the very thin layers of the phases presented near the triple points, it is difficult to measure the three-phase equilibrium compositions by EPMA. Instead, tie-lines of two-phase equilibrium have been determined in this study and the EPMA measurements were carried out at a short distance with small interval along lines perpendicular to and across the interfaces.

Extrapolation of the concentration profiles to the interfaces is used to present approximately the phase compositions in equilibrium. This isothermal section consists of four three-phase fields, namely (1) (Nb)+(Cu)+Co_7Nb_6, (2) (Cu)+Co_2Nb+Co_7Nb_6, (3) Co_2Nb+Co_3Nb+(Cu) and (4) Co_3Nb+(Co)+(Cu). The tie-lines are defined from the EPMA line profiles by taking advantage of the local equilibrium at interfaces formed among the phases. Note, at this phase diagram, the three-phase equilibrium concentrations are just estimated values, hence the corresponding tie-triangles are drawn as dashed lines.

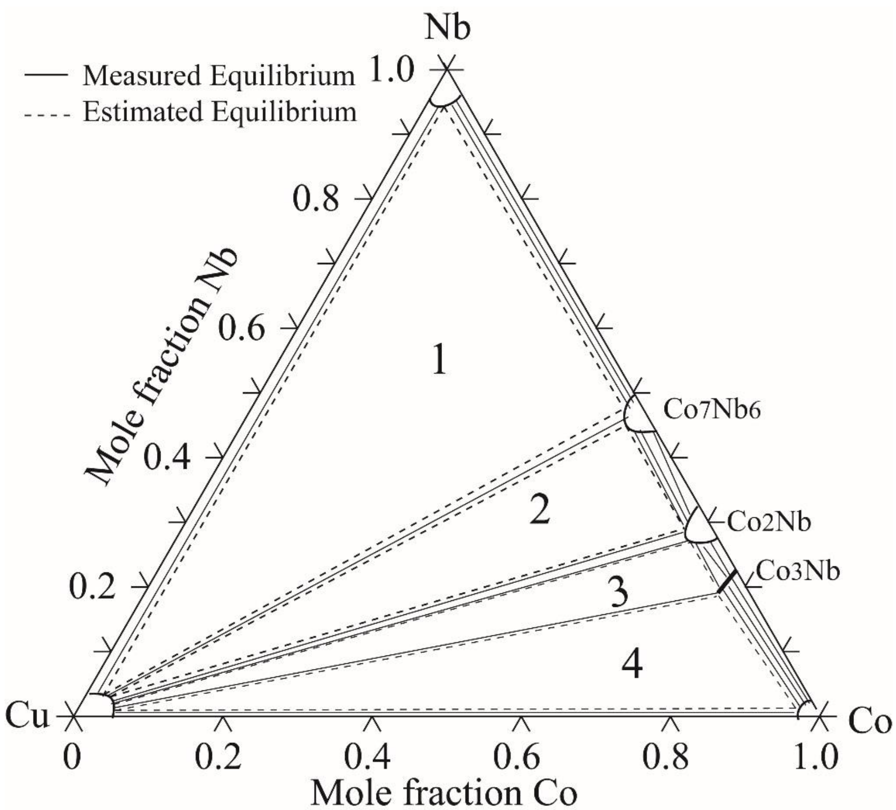

FIG. 6. **The measured isothermal section of the Cu-Co-Nb ternary system at 1198 K.**

Conclusion

The isothermal section of the Cu-Co-Nb ternary system at 1198 K has been investigated by means of diffusion triple together with electron probe microanalysis technique. Series of tie lines and tie-triangles have been determined and the isothermal section at 1198 K has been established and four three-phase fields have been figured out. It is found that the solubility of Cu in Co_3Nb, Co_2Nb and Co_7Nb_6 are only up to 5.70, 5.80 and 4.20 at.% Cu, respectively. The range of homogeneity of Co_7Nb_6 and Co_2Nb is 44.7-48.0 at.% and 25.0-29.6 at.% Nb, respectively. The Co_3Nb is line compounds.

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