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Reaction diffusion in the Nb–Ge system

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Reaction diffusion in the Nb–Ge system was studied in the temperature range 1243 to 1723 K for diffusion couples of (pure solid Nb)–(pure liquid Ge) and (pure solid Nb)–(Ge–37.5 wt% Nb liquid alloy). Growth of the $NbGe_2$, Nb_3Ge_2, Nb_5Ge_3 and Nb_3Ge layers was observed, and the growth rates of all except the Nb_3Ge layer were found to conform to the parabolic law. Growth of the Nb_3Ge layer was observed only along the grain boundaries in the Nb_5Ge_3 layer. Interdiffusion coefficients ($\tilde{D}$) in the $NbGe_2$, Nb_3Ge_2 and Nb_5Ge_3 phases were determined by Heumann's method, and the temperature dependence of these was expressed by the Arrhenius equations as follows:

$$\tilde{D}_{NbGe_2} = (6.40^{+2.25}_{-1.66}) \times 10^{-6} \exp\,[-(161 \pm 4)\,\mathrm{kJ\,mol^{-1}}/RT]\ \mathrm{m^2\,sec^{-1}},$$

$$\tilde{D}_{Nb_3Ge_2} = (2.27^{+0.82}_{-0.60}) \times 10^{-4} \exp\,[-(282 \pm 4)\,\mathrm{kJ\,mol^{-1}}/RT]\ \mathrm{m^2\,sec^{-1}}$$

and

$$\tilde{D}_{Nb_5Ge_3} = (6.28^{+2.78}_{-1.93}) \times 10^{-5} \exp\,[-(238 \pm 5)\,\mathrm{kJ\,mol^{-1}}/RT]\ \mathrm{m^2\,sec^{-1}}.$$

In addition to the binary Nb–Ge system, the reaction diffusion of (pure solid Nb)–(Cu–13 wt% Ge liquid alloy) couples was also studied. In this case, only growth of the Nb_5Ge_3 layer containing negligible copper content was observed.

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1. Introduction

The intermetallic compound Nb_3Ge has an A-15 structure and the highest critical temperature among many superconducting materials discovered. Up to now, Nb_3Ge film has been made by evaporation or sputtering techniques and has not yet been put into practical use, because it is difficult to produce wire or tape in large quantities. Today, development in the production process of a Nb_3Ge–metal composite is hoped for, and in this context experimental data on the growth kinetics of layers in the Nb–Ge diffusion couple are very useful as in the cases of the development of Nb_3Sn– and V_3Ga–copper composites [1, 2]. No systematic study of diffusion and the growth kinetics of the layers of the intermetallic compounds in the Nb–Ge system has been made, although diffusion coefficients in the intermetallic phases have been obtained by Ronami *et al.* [3].

The equilibrium phase diagram of the Nb–Ge system has not been established; only a rough phase diagram of the Nb-rich side has been proposed by Müller [4], and the existence of four intermetallic compounds, $NbGe_2$, Nb_3Ge_2, Nb_5Ge_3 and Nb_3Ge, has been recognized by Wallbaum [5] and by Carpenter and Searcy [6]. Addition of copper to the V–Ga diffusion system considerably enhances the growth of the superconducting V_3Ga layer [2, 7, 8], therefore it may be interesting to study the effect of the addition of copper to the layer growth in the Nb–Ge diffusion system.

In the present work, reaction diffusion in the Nb–Ge and Nb–(Cu–Ge) systems has been studied in the temperature range 1243 to 1723 K. The temperature dependence of the rate constant for the growth of the layers of the intermetallic phases and the diffusion coefficient in each phase has been examined.

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2. Experimental procedure

A niobium rod, >99.96% purity, was made by electron-beam melting and zone-refining a raw material of 99.5% purity. The rod was machined to produce disc specimens 8 mm diameter and 4 mm thick. The average grain size was about 3 mm. Flat faces of the specimens were ground on waterproof abrasive papers and polished on a lap with fine chromium oxide powder. Finally, the faces were electropolished in a solution of containing HF (46%, 10 cm^3) and H_2SO_4 (sp. gr. 1.84, 90 cm^3). Small pieces of 99.999% pure germanium were polished chemically in a solution containing HF (46%, 17 cm^3), H_2O_2 (30%, 17 cm^3) and H_2O (66 cm^3). To form (pure solid Nb)–(pure liquid Ge) couples the niobium disc and small pieces of germanium were sealed in an evacuated quartz tube at 2 mPa and annealed in the temperature range 1243 to 1723 K. For diffusion above 1603 K, the quartz tube was again sealed in a larger quartz tube at 0.2 Pa to prevent devitrification and fracture. The furnace temperature was controlled within ±2 K during the run. Below 1423 K, niobium dissolved rapidly into the liquid phase, and above 1473 K, layers of intermetallic phases were formed on the solid niobium. The growth kinetics of the layers was then studied on the specimens diffused above 1473 K. To ensure that initially the liquid phase was saturated with niobium at the diffusion temperature, (pure solid Nb)–(Ge–37.5 wt% Nb liquid alloy) couples were also used for the diffusion runs above 1473 K. Ge–37.5 wt% Nb alloy contains a little less than 39.02 wt% niobium which corresponds to the stoichiometric concentration in the $NbGe_2$ phase.

In addition to the binary Nb–Ge system, reaction diffusion in (pure solid Nb)–(Cu–13 wt% Ge liquid alloy) couples was studied. Cu–13 wt% Ge alloy was prepared previously by vacuum-melting chips of oxygen-free 99.99% pure copper and small pieces of 99.999% pure germanium. The niobium specimen and Cu–13 wt% Ge alloy pieces were sealed in an evacuated quartz tube at 2 mPa and annealed in the temperature range 1273 to 1473 K.

After diffusion annealing, the couple was cut parallel to the diffusion direction, and the section was polished using the usual metallographic method and finished by polishing on a lap with diamond paste. Electron probe microanalysers (Hitachi XMA-5B type or Shimazu ARL-II type) were used to determine the concentration distribution in the diffused specimen. The operating conditions of the microanalyser were as follows: accelerating voltage, 20 kV; take-off angle of radiation, 38° (XMA-5B) or 52.5° (ARL-II); specimen current for pure Ge, 0.03 μA; analysing X-rays, GeK_α and NbL_α. The line scanning by XMA-5B was done at scanning speed of 5 or 10 μm min^{-1}. The point-counting method by ARL-II at intervals of 3 μm was also used. The relationship between the relative intensity I_{Ge} of GeK_α X-ray and the mole fraction of germanium N_{Ge} conformed to the Ziebold–Ogilvie expression [9] $(1 - I_{Ge})/I_{Ge} = \alpha(1 - N_{Ge})/N_{Ge}$, where the constant α was found experimentally to be 0.86 under the given conditions. No important difference in the results from the two types of the microanalyser was found. The layers of the intermetallic phases were also identified using an optical microscope after anodic etching in NH_4OH (sp. gr. 0.90) with a stainless steel cathode at 30 V. Anodic etching coloured the phases as follows: Nb, blue; Nb_3Ge, light blue; Nb_5Ge_3, purple; Nb_3Ge_2, light purple; $NbGe_2$, light brown. The interdiffusion coefficient in each phase was determined by Heumann's method assuming that the interdiffusion coefficient in intermetallic phases formed by diffusion was independent of the concentration in each phase.

3. Results and discussion

3.1. Metallography

Fig. 1a and b shows optical micrographs of the diffusion zone of the Nb–Ge couple diffused at 1723 K for 16 h. All four intermetallic phase layers shown by the metallographic studies on the Nb–Ge system [4–6] are also identified in the diffused couples by electron probe microanalysis. The dark areas in the $NbGe_2$ layer observed in Fig. 1a are vacant holes caused by breakage of the brittle layer during polishing. It is noted that the Nb_3Ge layer is formed only at 1723 K, the highest temperature in the present diffusion experiment. In Fig. 1a, needle-shaped Nb_3Ge layer is observed along the grain boundaries parallel to the diffusion direction in the Nb_5Ge_3 layer. Chains of circles observed in Fig. 1b are traces of contamination by the electron probe microanalysis. Such growth behaviour along the grain boundaries has also been observed in reaction diffusion in the V–Ga system [7].

Table I shows the composition ranges of

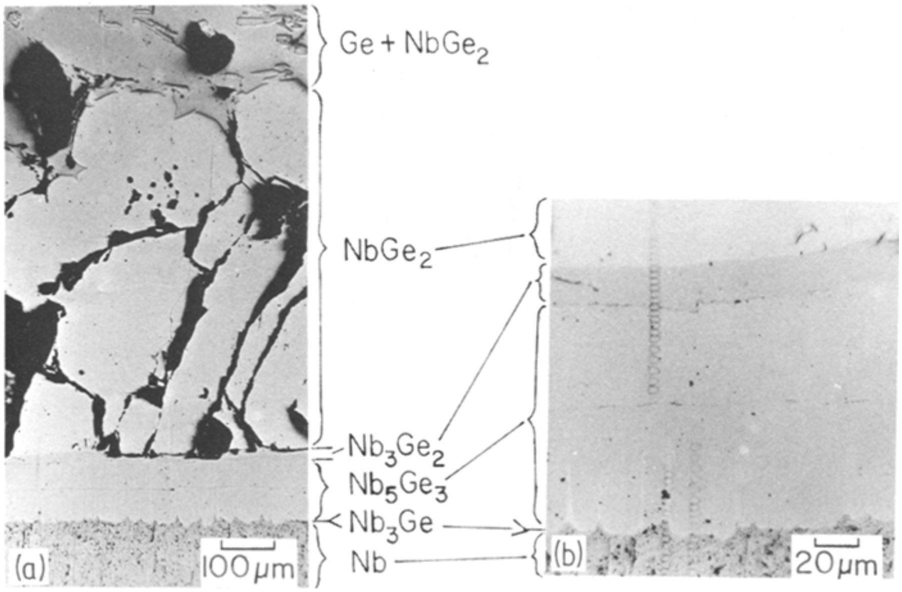

Figure 1 Optical micrograph of an Nb–Ge couple diffused at 1723 K for 16 h.

germanium in the primary solid solution of niobium and intermetallic phases determined by the electron probe microanalysis of the diffusion couples. These composition ranges have been found to be narrow and almost independent of temperature from 1473 to 1723 K. The concentration of germanium in the Nb_3Ge phase, formed as a very thin layer along the grain boundaries of the Nb_5Ge_3 layer, is found to be 26 at.% Ge. The Nb_3Ge_2 phase contains more germanium than the stoichiometric compound.

In the experiments below 1423 K, it is found that niobium dissolves rapidly into the liquid phase, in which isolated areas of Nb_3Ge_2 and Nb_5Ge_3 as well as $NbGe_2$ are observed. The fact that indentation is observed on the interface between Nb and the Nb_5Ge_3 phases suggests that grain-boundary diffusion dominates the growth of the Nb_5Ge_3 layer. It appears that at the interface, conditions for one-dimensional diffusion are no longer satisfied due to a large lateral diffusion, and the layers of Nb_5Ge_3 and also other phases are floated out into the liquid phase.

TABLE I Composition ranges of germanium in the primary solid solution of niobium and intermetallic phases

Phase	Composition range determined from diffusion couples (at.% Ge)	Stoichiometric composition (at.% Ge)
Primary solid solution of Nb containing Ge	0 to 1.8	–
Nb_3Ge	26	25.0
Nb_5Ge_3	37.3 to 39.3	37.5
Nb_3Ge_2	41.8 to 43.7	40.0
$NbGe_2$	66.4 to 67.2	66.7

3.2. Growth kinetics of intermetallic compounds

Thickness (d_i) of the $NbGe_2$, Nb_3Ge_2 and Nb_5Ge_3 layers versus square root of diffusion time (t) is

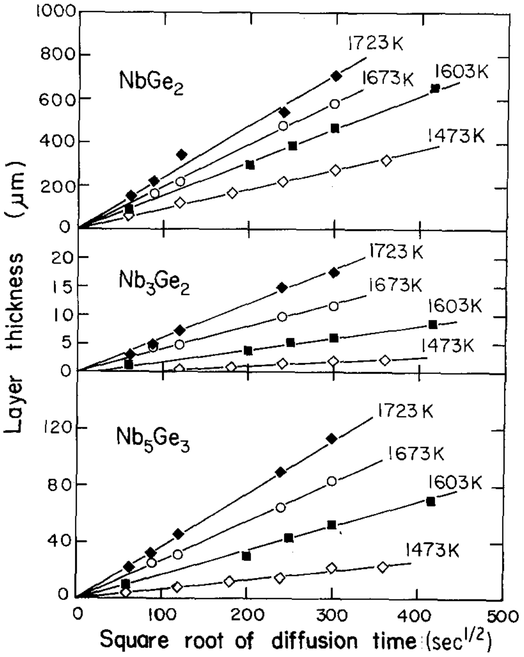

Figure 2 Growth of $NbGe_2$, Nb_3Ge_2 and Nb_5Ge_3 layers in an Nb–Ge diffusion couple by reaction diffusion.

plotted in Fig. 2, where a linear relationship is observed for all the phases at each temperature:

$$d_i = k_i t^{1/2}, \qquad (1)$$

where k_i is the rate constant for the growth of compound i. No difference in the thickness of the layers is observed between (pure solid Nb)–(pure liquid Ge) and (pure solid Nb)–(Ge–37.5 wt% Nb liquid alloy) couples. The temperature dependence of k_i is shown in Fig. 3 for each layer. From the linearity between $\ln k_i$ and $1/T$, the Arrhenius equations are obtained:

$$k^2_{\mathrm{NbGe_2}} = (2.99^{+1.77}_{-1.11}) \times 10^{-7}$$

$$\exp\,[-161 \pm 6)\,\mathrm{kJ\,mol^{-1}}/RT]\ \mathrm{m^2\,sec^{-1}}, \qquad (2)$$

$$k^2_{\mathrm{Nb_3Ge_2}} = (3.18^{+4.05}_{-1.78}) \times 10^{-5}$$

$$\exp\,[-(330 \pm 11)\,\mathrm{kJ\,mol^{-1}}/RT]\ \mathrm{m^2\,sec^{-1}} \qquad (3)$$

and

$$k^2_{\mathrm{Nb_5Ge_3}} = (8.24^{+3.76}_{-2.58}) \times 10^{-5}$$

$$\exp\,[-(290 \pm 5)\,\mathrm{kJ\,mol^{-1}}/RT]\ \mathrm{m^2\,sec^{-1}} \qquad (4)$$

The activation energy for the layer growth is the largest in Nb_3Ge_2, while the pre-exponential factor for this compound has middle value, and the growth rate of this layer is very slow, as shown in Fig. 2. Furthermore, Fig. 2 also shows that the straight lines of the $NbGe_2$ and Nb_5Ge_3 layers for all temperatures pass through the origin, indicating that the incubation time for the growth of these layers is negligible. However, incubation time was observed only for the growth of the Nb_3Ge_2 layer at lower temperatures, 1473 and 1603 K. For the reaction diffusion of the Fe–Zn system, Onishi *et al.* [10] have shown that incubation time (t_0) for layer growth is denoted by $A \exp(B/T)$, where A and B are constants. Assuming a similar relationship for the Nb_3Ge_2 layer, we have

$$t_0 = 4 \times 10^{-8} \exp(6 \times 10^4/T)\ \mathrm{h}. \qquad (5)$$

Using this equation, incubation times at 1673 and 1723 K are estimated to be 1.7×10^{-2} and 6×10^{-3} h, respectively, which are too short to be measured in the present experiment. The origin of incubation time in the Nb_3Ge_2 layer is unknown as in the case of the Fe–Zn system.

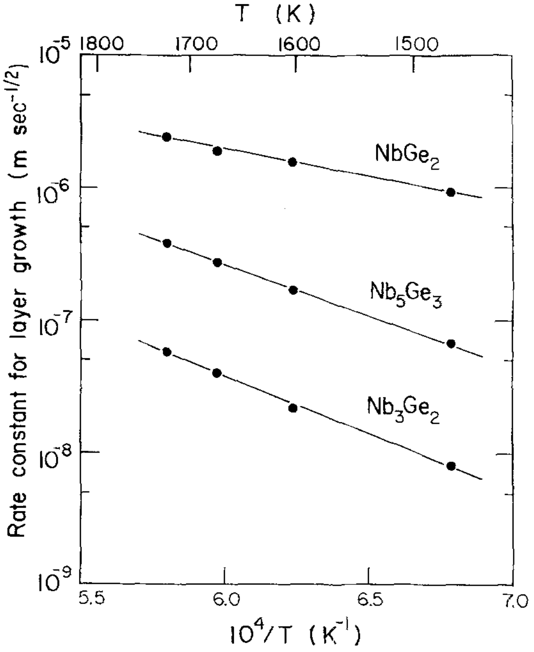

Figure 3 Temperature dependence of the rate constant for layer growth of $NbGe_2$, Nb_3Ge_2 and Nb_5Ge_3 phases in the Nb–Ge system.

3.3. Interdiffusion coefficients for intermetallic phases

The concentration–penetration curve of the diffused couple obtained by the electron probe microanalysis shows that the mole fraction of germanium varies linearly with distance in each intermetallic phase. Thus, Heumann's method is applicable to determine the interdiffusion coefficient in the intermetallic phases formed by diffusion is independent of concentration in each phase. According to Heumann [11], the interdiffusion coefficient ($\tilde{D}_i$) in a phase i is given by

$$\tilde{D}_i = -\frac{d_i}{2t\,\Delta C_i}\int_0^{C_i^{1/2}} x\,\mathrm{d}C \qquad (6)$$

where ΔC_i is the difference in concentrations for the both ends of the i layer in the concentration–penetration curve, $C_i^{1/2}$ the average concentration within the layer, and x is the distance from the origin determined by the condition $\int_{C(-)}^{C(+)} x\,\mathrm{d}C = 0$. $C(-)$ and $C(+)$ are the concentrations at the both ends of the diffusion zone, respectively. In the Nb–Ge system, the molar volume varies almost linearly with composition [12], thus, "1 mol germanium per m^3" should be used as the unit of concentration for Heumann's method. However, in this system, dependence of the molar volume on concentration is small, and a "mole fraction" can be used in place of "1 mol m^{-3}" without correction. As shown in Fig. 4, in all the phases, the temperature depen-

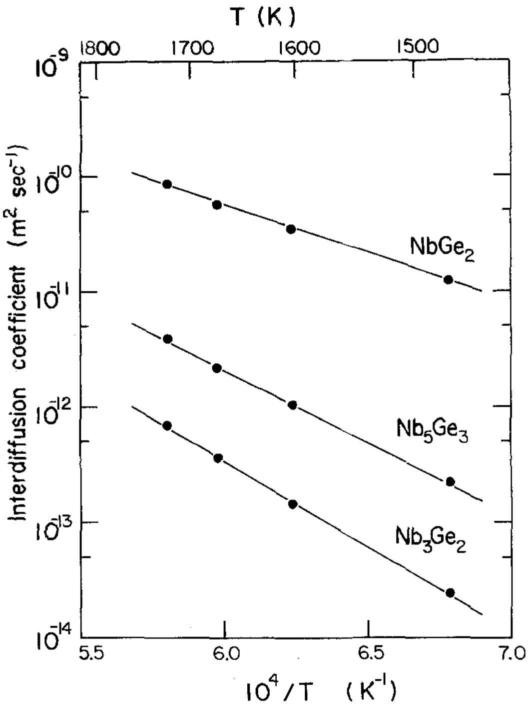

Figure 4 Temperature dependence of the interdiffusion coefficient in the $NbGe_2$, Nb_3Ge_2 and Nb_5Ge_3 phases in the Nb–Ge system.

dence of $\tilde{D}_i$ fits each Arrhenius equation well, and the following expressions are obtained:

$$\tilde{D}_{NbGe_2} = (6.40^{+2.25}_{-1.66}) \times 10^{-6}$$

$$\exp\,[-(161 \pm 4)\,\mathrm{kJ\,mol^{-1}}/RT]\ \mathrm{m^2\,sec^{-1}} \quad (7)$$

$$\tilde{D}_{Nb_3Ge_2} = (2.27^{+0.82}_{-0.60}) \times 10^{-4}$$

$$\exp\,[-(282 \pm 4)\,\mathrm{kJ\,mol^{-1}}/RT]\ \mathrm{m^2\,sec^{-1}} \quad (8)$$

and

$$\tilde{D}_{Nb_5Ge_3} = (6.28^{+2.78}_{-1.93}) \times 10^{-5}$$

$$\exp\,[-(238 \pm 5)\,\mathrm{kJ\,mol^{-1}}/RT]\ \mathrm{m^2\,sec^{-1}}. \quad (9)$$

The activation energy for interdiffusion is the largest in the Nb_3Ge_2 phase, as in the case of layer growth. It is noted that the values of the activation energies and the pre-exponential factors for interdiffusion in the Nb–Ge system are of the same order of magnitude as those for the Nb–Al system [13].

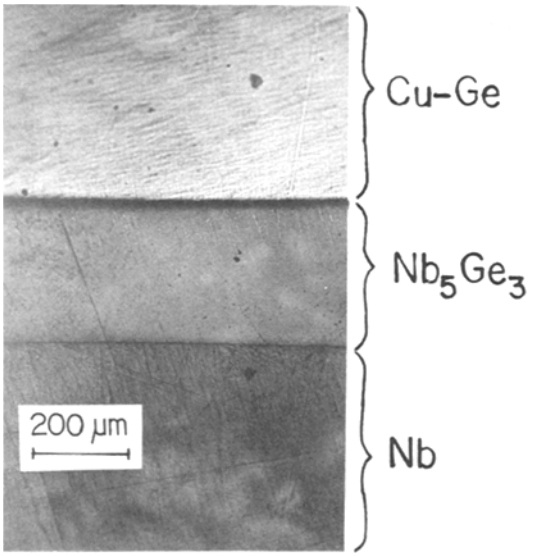

Figure 5 Optical micrograph of an Nb–(Cu–Ge) couple diffused at 1273 K for 31 h.

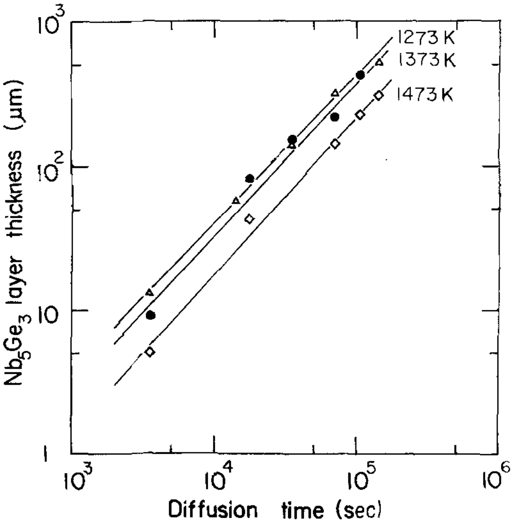

Figure 6 Growth of an Nb_5Ge_3 layer in the Nb–(Cu–Ge) diffusion couple.

3.4. Reaction diffusion in Nb–(Cu–13 wt% Ge alloy) couple

To examine the effect of the addition of the copper on the growth kinetics of the intermetallic phase layers in the Nb–Ge system, reaction diffusion on (pure solid Nb)–(Cu–13 wt% Ge liquid alloy) couples has been carried out in the temperature range 1273 to 1473 K. Fig. 5 shows an optical micrograph of the diffusion zone in the couple diffused at 1273 K for 31 h. The electron probe microanalysis shows that only the Nb_5Ge_3 phase is formed and the concentration of copper in it is negligible. Fig. 6 shows that log layer thickness of the Nb_5Ge_3 phase increases linearly with log diffusion time, and we obtain

$$d_{Nb_5Ge_3} = k_{Nb_5Ge_3}\, t^{1/n} \quad (10)$$

when *n* is a constant, which is nearly equal to 1, independent of temperature. This suggests that the growth of the Nb_5Ge_3 layer is controlled by an interface reation [14].

For the superconducting Nb_3Ge phase, it is concluded that a thick layer cannot be produced by reaction diffusion in the binary Nb–Ge system. Only a very thin layer was produced at 1723 K as shown in Fig. 1b. In contrast to the fact that addition of copper to the V–Ga diffusion system [2, 7, 8] enhances the growth of the superconducting layer at relatively low temperatures, ternary diffusion in the Nb–(Cu–Ge) couples yields only the Nb_5Ge_3 layer. Lack of growth of the Nb_3Ge layer in the diffusion zone can be explained by the fact that the diffusion path in the ternary Nb–(Cu–Ge) system does not pass the Nb_3Ge phase field in the ternary isothermal phase diagram, as shown by Hopkins *et al.* [15].

4. Conclusions

(1) In the reaction diffusion of the Nb–Ge system in the temperature range 1243 to 1723 K, growth of the $NbGe_2$, Nb_3Ge_2 and Nb_5Ge_3 layers is observed. A very thin Nb_3Ge layer grows at 1723 K along the grain boundaries in the Nb_5Ge_3 layer.

(2) In the reaction diffusion of Nb–(Cu–13 wt % Ge alloy) couple in the temperature range 1273 to 1473 K, only the Nb_5Ge_3 layer grows.

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