

# STRUCTURE AND DIFFUSION PROCESSES IN LAMINATED COMPOSITES OF A Cu–Ti SYSTEM

B. S. Bokstein,<sup>1</sup> V. I. Vnukov,<sup>3</sup> E. V. Golosov,<sup>2</sup>  
M. I. Karpov,<sup>3</sup> Yu. R. Kolobov,<sup>2</sup> D. A. Kolesnikov,<sup>2</sup>  
V. P. Korzhov,<sup>3</sup> and A. O. Rodin<sup>1</sup>

UDC 621.763:620.18

*Characteristics of diffusion transformations in a multi-layer composite of a Cu–Ti system, which was produced by high-temperature diffusion welding followed by rolling at room temperature, are reported. It is shown that phase-formation at the layer boundaries in this system at the temperature below 823 K is determined by diffusion along the inner surfaces of these boundaries; while above this temperature it is controlled by bulk diffusion.*

**Keywords:** copper–titanium system, diffusion-controlled processes, phase formation, intermetallic compounds.

## INTRODUCTION

Multi-layer laminates serve a typical example of composite materials consisting of two or more layers of heterogeneous metals and alloys [1–5]. The use of these materials provides for a combination of mechanical and physical properties of their constituent components [1–8]. On the other hand, in the course of their manufacture and during their further service we are often faced with the problems of interaction of heterogeneous materials. This can give rise to degradation of structure and changes in phase composition of the multi-layer composite [8]. The main interaction between metallic materials at phase boundaries at elevated temperatures is diffusion and diffusion-controlled processes, such as formation of intermetallic phases on the interfaces between heterogeneous materials. In view of these circumstances, it appears critically important to investigate diffusion-controlled processes of phase- and structure transformations in the systems with different degree of solubility of the constituent components and the character of their interaction. The processes of interdiffusion acquire a special significance when it concerns layer thicknesses of nanoscale range. This is associated with a higher volume fraction and degree of non-equilibrium of grain and phase boundaries, where the diffusion coefficients exceed those for polycrystals [9].

A typical example of a multi-layer composite is a Cu–Nb system [1–4, 7, 8]. Its characteristics consists in the fact the there is virtually no mutual solubility of components (according to the phase diagram). In this case one would expect the structural transformations (recovery, polygonization, and recrystallization) in the laminated composite to occur within every layer and not to be controlled by the diffusion flows in the bulk. Grain-boundary diffusion flows, however, cannot be ruled out [8, 9]; these might give rise to structure degradation at the temperatures where the bulk diffusion is “frozen”.

A different scenario can take place in a Cu–Ti system [6]. A characteristic feature of interaction between copper and titanium is a limited mutual solubility and a possibility (according to the equilibrium phase diagram) of forming intermetallic compounds [10]. It is common knowledge that formation of intermetallic phases can result in lower ductility and render these laminated composites brittle.

---

<sup>1</sup>State Technological University, Moscow Institute of Steel and Alloys, Moscow, Russia, <sup>2</sup>Research and Innovation Center for Nanostructured Materials and Nanotechnologies, Belgorod State University, Belgorod, Russia, <sup>3</sup>Institute of Solid-State Physics of the Russian Academy of Sciences, Chernogolovka, Russia, e-mail: gev501@mail.ru. Translated from *Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika*, No. 8, pp. 40–44, August, 2009. Original article submitted October 24, 2008.

The present work deals with investigation of phase transformations and diffusion-controlled processes at the layer interfaces (in strained state and upon vacuum annealing) in the Cu–Ti system. To study the diffusion-controlled processes at the layer interfaces we selected laminated composites with a sufficiently large layer thickness (which allowed us to rule out reciprocal influence of the neighboring layer interfaces on the diffusion kinetics). These layers were, however, subjected to cold straining to achieve a straining degree of the layer comparable to that of nanostructured laminates.

## MATERIAL AND EXPERIMENTAL TECHNIQUES

The samples investigated were made from a composite of the Cu–Ti system consisting of 13 layers: 7 layers of copper and 6 layers of titanium. The laminate was formed by making a stack of 13 plates followed by hot pressing of the stack in vacuum and subsequent cold rolling in air to achieve a thickness of 0.25 mm.

The initial plates measuring 50×100 mm with the thickness 0.25 mm were assembled into a stack of 13 alternating copper and titanium layers that were fixed at the corners by clamps. Before assembly, the plate surface was ground with abrasive paper to remove oxides from the surface and to produce the required roughness. Rolling in vacuum was performed at the temperature 1123 K, with the tempering time at this temperature being 15 min. The rolling was performed within a single run to achieve a reduction of 30 %. Further on, the samples were rolled in air at 20 °C with a reduction of 10% per one run. The final thickness of the rolled stack was 0.25 mm.

The resulting laminates were annealed in vacuum at the temperatures 723, 823, 923 and 1023 K for 1 hour.

The laminate structure was examined using a Quanta 200 3D scanning electron-ion microscope equipped with a Genesis 2000 energy-dispersion analyzer manufactured by EDAX Co. and a Quanta 600 FEG scanning electron microscope with field emission and a Trident integrated elemental analyzer manufactured by EDAX Co., which provided the energy dispersion and low-energy wave (WDS – LEXS) microanalyses. The sample surfaces for the electron microscopy were prepared using a TegraPol-31 grinding/polishing machine manufactured by Struers Co., with the samples preliminary fixed by cold-sealed epoxy.

## EXPERIMENTAL

A special feature of the binary Cu–Ti system is the presence of both solid solutions and a large number of intermetallic phases such as  $Ti_2Cu$ ,  $TiCu$ ,  $Ti_3Cu_4$ ,  $Ti_2Cu_3$ ,  $TiCu_2$  and  $TiCu_4$  with the melting and decomposition temperature below 1273 K. Given this, intermetallic layers can form at the interfaces in the course of diffusion interaction, vacuum high-temperature welding and subsequent high-temperature treatments.

From a theoretical standpoint, in the Cu–Ti system at the temperatures below 1123 K, according to the Fick's equation

$$j = -D\nabla C, \quad (1)$$

where  $j$  is the diffusion flow,  $\nabla C$  is the concentration gradient, and  $D$  is the bulk diffusion coefficient; in other words, if the driving force of diffusion is ensured by the concentration gradient, not all of the above-enumerated phases would be formed via diffusion. Three of the above –  $Ti_2Cu$ ,  $Ti_3Cu_4$  and  $Ti_2Cu_3$  – are stoichiometric phases, and, according to the first Fick's law (1), they cannot be formed by diffusion.

Actually, the diffusion flow is not determined by the concentration gradient but rather by the chemical potential gradient  $\nabla\mu$  as follows:

$$j = -L\nabla\mu, \quad (2)$$

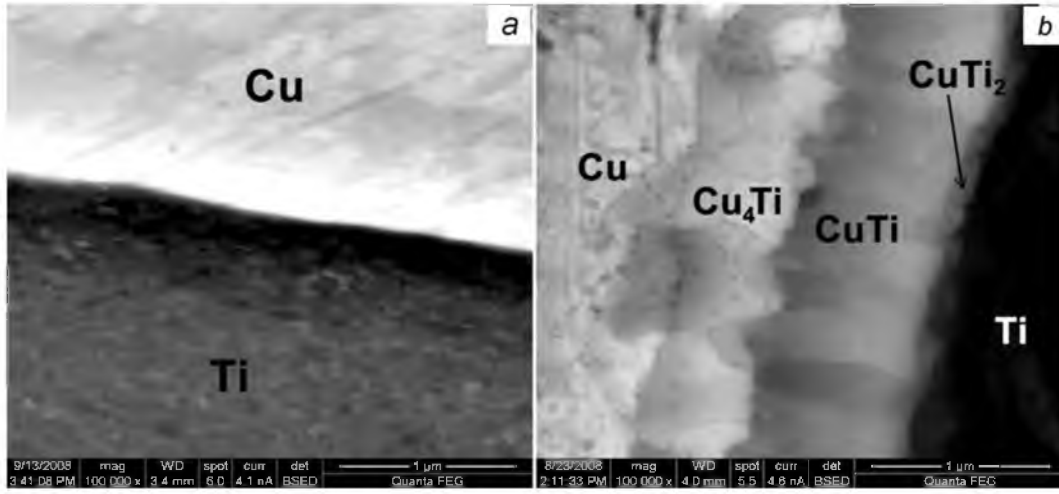


Fig. 1. Layer interface in the Cu–Ti system in strained state (a) and the structure of the interface between the layers of titanium and copper upon annealing at 723 K (b).

where  $L$  is the kinetic coefficient proportional to the diffusion coefficient, and  $\nabla\mu$  . in addition to the concentration difference, also includes certain other thermodynamic forces, such as the stress gradient  $\nabla\sigma$  , related to the atomic volume difference of intermetallic compounds and solid solutions

$$j = -D \left( \nabla C - \frac{CV}{3RT} \nabla \sigma \right), \quad (3)$$

where  $V$ ,  $C$ , and  $T$  are the diffusant mole volume, concentration and temperature, respectively.

These considerations reasonably account for formation of intermetallic compounds during thermal treatment.

**Strained state.** In a strained state (after diffusion welding by rolling followed by cold rolling), no formation of intermetallic phases was found at the layer interfaces. An examination of the structure state of the composite layers demonstrated that there is a considerable refinement of the structure elements in titanium and copper layers (Fig. 1). The average size of the grain-subgrain structure elements was found to be  $d^{\text{Cu}} \sim 0.3 \mu\text{m}$  for copper and  $d^{\text{Ti}} \sim 0.12 \mu\text{m}$  for titanium. Under these conditions, the processes of mutual diffusion followed by formation of intermetallic phases can significantly exceed those estimated by calculations, as it is well known that in submicro- and nanostructured materials the grain-boundary diffusion can by 2–3 orders exceed that in the coarse-grained state [11, 12].

**Annealed state.** The investigations have shown that diffusion interaction between copper and titanium is intensively developed already at the temperatures just above 723 K.

At the annealing temperature up to 723 K (1 h), we have revealed formation of an intermetallic layer consisting of three intermetallic compounds:  $\text{Cu}_4\text{Ti}$ ,  $\text{CuTi}$ ,  $\text{CuTi}_2$  (Fig. 1b) and recrystallization of copper, while in titanium there is no significant grain-size growth is observed. The overall thickness of the diffusion zone was found to be 1.2–1.5  $\mu\text{m}$ .

The bulk diffusion coefficient for copper and titanium can be estimated according to the formula reported in [13]  $D_{\text{Ti-Cu}} = 0.693 \cdot 10^{-4} \exp\left(-\frac{196000}{RT}\right) \text{m}^2/\text{s}$ , which for 723 K was found to be  $D_{\text{Ti-Cu}} = 4.7 \cdot 10^{-19} \text{m}^2/\text{s}$ , while according to the formula for root-mean-square atomic displacement given by

$$X = 2\sqrt{D^v t}, \quad (4)$$

where  $t$  is the diffusion annealing time, the value of  $X$  for  $t = 1 \text{ h}$  and  $T = 723 \text{ K}$  should be as small as  $\sim 0.1 \mu\text{m}$ . On the other hand, we have shown above that the intermetallic layer thickness is  $\sim 1.2\text{--}1.5 \mu\text{m}$ . This is due to the structure state

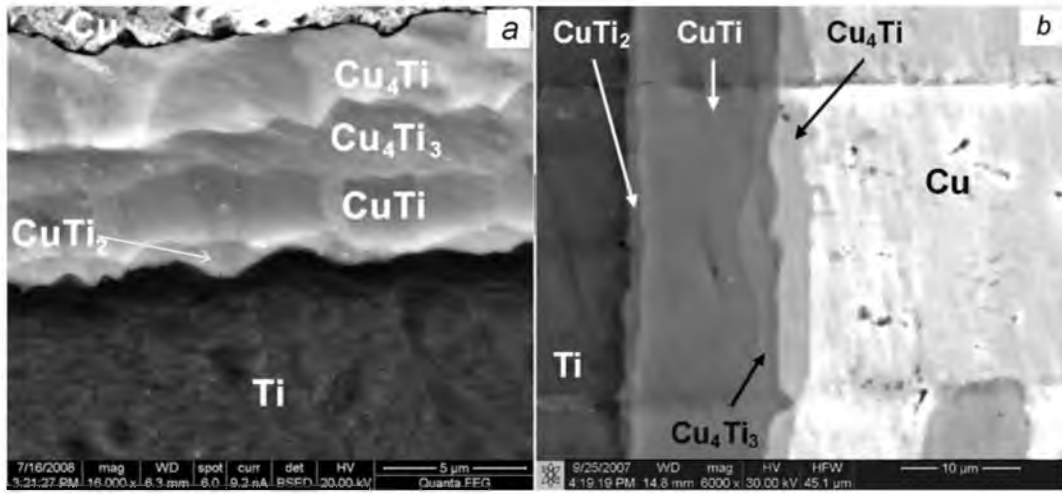


Fig. 2. Microstructure of the intermetallic layer at the copper–titanium interface following annealing at the temperature 923 K for 1 h. (a) and 1023 K for 3 hours (b).

of the composite after straining and is related to the high dislocation density and high overall grain- and subgrain-boundary length, which serve as pathways for fast diffusion in materials.

According to Fisher's model [14], the diffusion path in a grain boundary disregarding adsorption is given by

$$L = \sqrt{\frac{\delta D^{\text{gb}} \sqrt{\pi t}}{2\sqrt{D^{\text{v}}}}}, \quad (5)$$

where  $\delta$  is the grain-boundary width (commonly taken to be  $5 \cdot 10^{-10}$  m),  $D^{\text{gb}}$  is the grain-boundary diffusion coefficient, and  $t$  is the time. There is no literature data on the grain-boundary diffusion coefficient in this system. Let us assume, according to the correlations available, that pre-exponential factors in the equation for grain-boundary diffusion  $D_0^{\text{gb}}$  and bulk diffusion  $D_0^{\text{v}}$  are equal ( $D_0^{\text{gb}} = D_0^{\text{v}}$ ), and the grain-boundary diffusion activation energy  $E^{\text{gb}} = 1/2E$  ( $E$  – bulk diffusion activation energy). Hence  $D_{\text{Ti-Cu}} = 10^{-4} \exp\left(-\frac{98000}{RT}\right)$  m<sup>2</sup>/s, and for the temperature 723 K we obtain

$D^{\text{gb}} = 8 \cdot 10^{-12}$  m<sup>2</sup>/s and  $\delta D^{\text{gb}} = 4 \cdot 10^{-21}$  m<sup>3</sup>/s. Then  $L = \sqrt{\frac{4 \cdot 10^{-21} \sqrt{\pi} \cdot 3600}{2\sqrt{4.7 \cdot 10^{-19}}}} = 16 \mu\text{m}$  for  $t = 1$  h, which is in a satisfactory

agreement with the experiment and demonstrates that phase-formation at interfaces of a multi-layer composite is controlled by grain-boundary diffusion.

An increase in the annealing temperature to as high as 823 K results in an increase in the intermetallic layer thickness up to 3–4  $\mu\text{m}$ , with the phase composition of the intermetallic layer remaining unchanged though (Fig. 2). Formation of one more intermetallic compound  $\text{Cu}_4\text{Ti}_3$  is observed after annealing at the temperature 923 K (Fig. 2a).

A further increase in the temperature to as high as 1023 K does not give rise to any significant changes in the diffusion zone and no peculiarities related to this temperature increase have been revealed. On the other hand, there is a significant growth in the titanium grain size, which results in larger grain-boundary length. In this connection, the diffusion-zone thickness at these temperatures is controlled by the bulk diffusion. At 1023 K for 1 and 3 hours, the diffusion path calculated as  $2\sqrt{D^{\text{v}}t}$ , was found to be approximately 10 and 16  $\mu\text{m}$ , which is consistent with the experimental data (Fig. 2b).

## SUMMARY

It has been shown in this work that in strongly strained composite materials based on copper and titanium, intermetallic compounds such as  $\text{Cu}_4\text{Ti}$ ,  $\text{CuTi}$  and  $\text{CuTi}_2\text{Ti}$  are formed at their layer interfaces at the annealing temperatures within the range from 723 to 823 K. The overall diffusion zone thickness has been found to be 1.5  $\mu\text{m}$ , which after annealing at 823 K it increases to as high as 3–4  $\mu\text{m}$ . Following annealing at the temperature 923 K, formation of intermetallic  $\text{Cu}_4\text{Ti}_3$  was observed.

The estimates made in this work demonstrate that below 823 K phase formation is controlled by grain-boundary diffusion, while above this temperature – by bulk diffusion.

The work has been funded within an FTP grant 02.513.11.3198.

## REFERENCES

1. N. A. Mara, T. Tamayo, A. V. Sergueeva, *et al.*, *Thin Solid Films*, **515**, 3241–3245 (2007).
2. M. I. Karpov, V. I. Vnukov, K. G. Volkov, *et al.*, *Materialovedeniye*, No. 1, 48–53 (2004).
3. B. Z. Cui, Y. Xin, and K. Han, *Scripta Mater.*, **56**, 879–882 (2007).
4. Y.-C. Wang, A. Misra, and R. G. Hoagland, *Ibid.*, **54**, 1593–1598 (2006).
5. Yang Chengtao, Zhang Shuren, Luo Jiahui, *et al.*, *Vacuum*, **80**, 317–323 (2005).
6. S. Lee, H. T. Son, I. H. Oh, *et al.*, *J. Mater. Processing Technol.*, **187–188**, 653–656 (2007).
7. S. V. Lempitskii, *Physica C*, **167**, 168–176 (1990).
8. M. I. Karpov, V. I. Vnukov, K. G. Volkov, *et al.*, *Materialovedeniye*, No. 2, 47–52 (2004).
9. Yu. R. Kolobov, *Diffusion-Controlled Processes at Grain-Boundaries and Plasticity of Metal Polycrystals* [in Russian], Novosibirsk, Nauka (1998).
10. *Phase Diagrams of Binary Metallic Systems: A Handbook* (Ed. N. P. Lyakishev) [in Russian], Volumes 1–3 (2001).
11. Yu. R. Kolobov, R. Z. Valiev, *et al.*, *Grain Boundary Diffusion and Properties of Nanostructured Materials*, Cambridge International Science Publishing (2007).
12. G. P. Grabovetskaya, I. P. Mishin, I. V. Ratochka, *et al.*, *Pis'ma Zh. Techn. Phys.*, No. 4 (**34**), 1–7 (2008).
13. *Numerical Data and Functional Relationships in Science and Technology. Gr. III*, **26**, *Diffusion in Solid Metals and Alloys* (Ed. H. Mehrer), Berlin, Germany, Springer Verlag (1990).
14. J. C. Fisher, *J. Appl. Phys.*, **22**, 74 (1951).