UDC 620.186:546.07

Employing Atomic Force Microscopy for Studying the Structure and Morphology of Mechanocomposites and Metal Cements Based on Them

S. A. KOVALEVA[1], P. A. VITYAZ[1], A. I. ANCHAROV[2] and T. F. GRIGORIEVA[2]

[1]*Joint Institute of Mechanical Engineering, National Academy of Sciences of Belarus, Ul. Akademicheskaya 12, Minsk 220072 (Belarus)*

E-mail: sveta_kovaleva@tut.by

[2]*Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, Ul. Kutateladze 18, Novosibirsk 630128 (Russia)*

E-mail: grig@solid.nsc.ru

Abstract

The scope of using the atomic force microscopy (AFM) technique for studies concerning the morphological features and structural parameters of mechanochemicaly synthesized alloys and metal cements based on them are presented. It is noted that in the studies on diffusion-hardening alloys whose structure formation process is of long duration nature, the application of AFM allows one to investigate intermediate states of surface. A comparative analysis has been performed concerning atomic force microscopy and scanning electron microscopy data.

Key words: atomic force microscopy, mechanocomposite, morphology

INTRODUCTION

It is commonly known that nanosized solid solutions, intermetallic compounds and nanocomposites can be synthesized in a mechanochemical manner. Employing them in the development of diffusion-hardening compositions changes to a considerable extent the kinetics of interactions between solid and liquid phases, exerts an influence upon morphological and dimensional characteristics of products formed as well as upon the process of structure formation as a whole [1–3].

The investigation of such samples has revealed a number of features, in particular a low-dimension level of structural components, low hardness and low melting point. The most of existing analytical methods for studying surfaces with the submicron resolution is based on the interaction between a beam of elementary particles (electrons, ions, *etc.)* and surface layers of a material, which could be possible only under high vacuum conditions (10^{-5} Pa). In the case under consideration, a thorough sample preparation is required including mechanical operation, sample surface polishing, applying a conducting metal coating, which often results in a considerable deformation of the surface of obtained diffusion-hardening alloys.

In order to perform monitoring the condition of surface and registering the properties of thin surface layer, it is promising to apply an atomic force microscope belonging to the class of scanning probe microscopes and allows researchers to carry out the measurement and analysis of surface micro- and submicrorelief as well as the objects of micro- and nanorange with high resolution. The method of atomic force microscopy (AFM) is based on interaction (in this case Van der Waals interaction) between a cantilever needle (probe) with the surface of a sample under investigation. The AFM technique belongs to non-destructive methods of investigation [4] and allows researchers to study both conducting and non-conducting surfaces. The spatial resolution of an atomic force mi-

croscope depends on the needle rounding-radius. For the majority of commercial probes the rounding radius of probe amounts to less than 10 nm, which allows one to display surface elements with the size about 1 nm.

The purpose of the present work consisted in studies concerning the application of AFM for investigation of the morphology of mechanochemically synthesized alloys and metal cements obtained on their basis, with the visualization of phase topography on the surfaces, as well as studying the features of crystallization processes in diffusion-hardening alloys.

EXPERIMENTAL

As samples, we used powder mechanocomposite Cu/Bi, Cu/Fe systems, solid Cu/In solutions obtained *via* mechanical activation during 15 min using AGO-2 high-energy spherical planetary mill with water cooling in an argon atmosphere, and their products of interaction with gallium melt and GaIn eutectic. In order to prepare powder samples for the investigation and fixing particles we used cold pressing. The investigation of the surface was carried out with the help of NT-206 atomic force microscope (Microtest-machines, Belarus), standard commercial NSC11 V-shaped probes (Mikromasch, Estonia) in the contact mode and MIRA high resolution scanning electron microscope (Tescan, Czechia) with a an attachment for micro-X-ray spectral analysis.

Employing a four-section photodetector in an atomic force microscope allows researchers to register simultaneously the variations of interaction forces (normal and lateral) between the end of a cantilever needle and the surface under investigation, from point to point. Normal deviations of a probe form a topographical contrast of a surface (topography), whereas lateral (torsion) deviations are caused mainly by difference in tribological properties of structural elements of the surface.

The method of lateral forces allows one to distinguish areas with different action of friction forces those arise owing to elasticity, adhesion, viscosity, capillary forces, chemical features, *etc*. In some cases, simultaneous obtaining of topography, torsion and deflection images (a mismatch signal formed owing to the delay of a feedback signal being a peculiar display of the surface topography) allows one to find out even insignificant features of the relief.

The identification of phases on AFM images was carried out basing on indirect data obtained employing XRD structural and X-ray spectral analytical methods.

RESULTS AND DISCUSSION

Figure 1 presents AFM data concerning the topography for the powders of initial copper and copper/bismuth mechanocomposites with the mass fractions of bismuth amounting to 3 and 10 %, as well as for mechanoactivated Cu/In powders (indium mass fraction being of 12 and 20 %). Using a cross section profile it is demonstrated that with the increase in the content of bismuth (Fig. 2, *b*, *c*) in the Cu/Bi system the size of particles decreases from 3–1 to 120–250 μm with improving their size uniformity. Also it should be noted that as opposed to the particles of Fe/Bi mechanocomposite particles, the Cu/Bi powder particles exhibit an equiaxial rather than deformed shape (see Fig. 1, *d*).

The mechanical activation of Cu/12 % In system results in the formation of locally clustering fine particles of solid indium solution in copper with particle size amounting to 150–230 nm, as well as in recrystallizing the solid solution of copper and the formation of grains with particle size higher than 15 μm. With the content of indium amounting to 20 mass % (see Fig. 1, *e*) the particle size scatter decreases being equal to about 100–150 nm, in this case scaly aggregates are formed with the size ranging within 1–1.5 μm.

The simultaneously obtained torsion and deflection images for the powders of the solid solution of Cu/In system demonstrate the features of the surface topography for large crystals of an indium-in-copper Cu (In) solid solution (see Fig. 2). So, on the deflection image it is seen that local radial areas are formed on copper crystal faces. To all appearance, it could be caused by local melting of indium particles due to mechanoactivation, as well as by colliding melt drops with a crystal face. The use of other methods does not allow us to find out

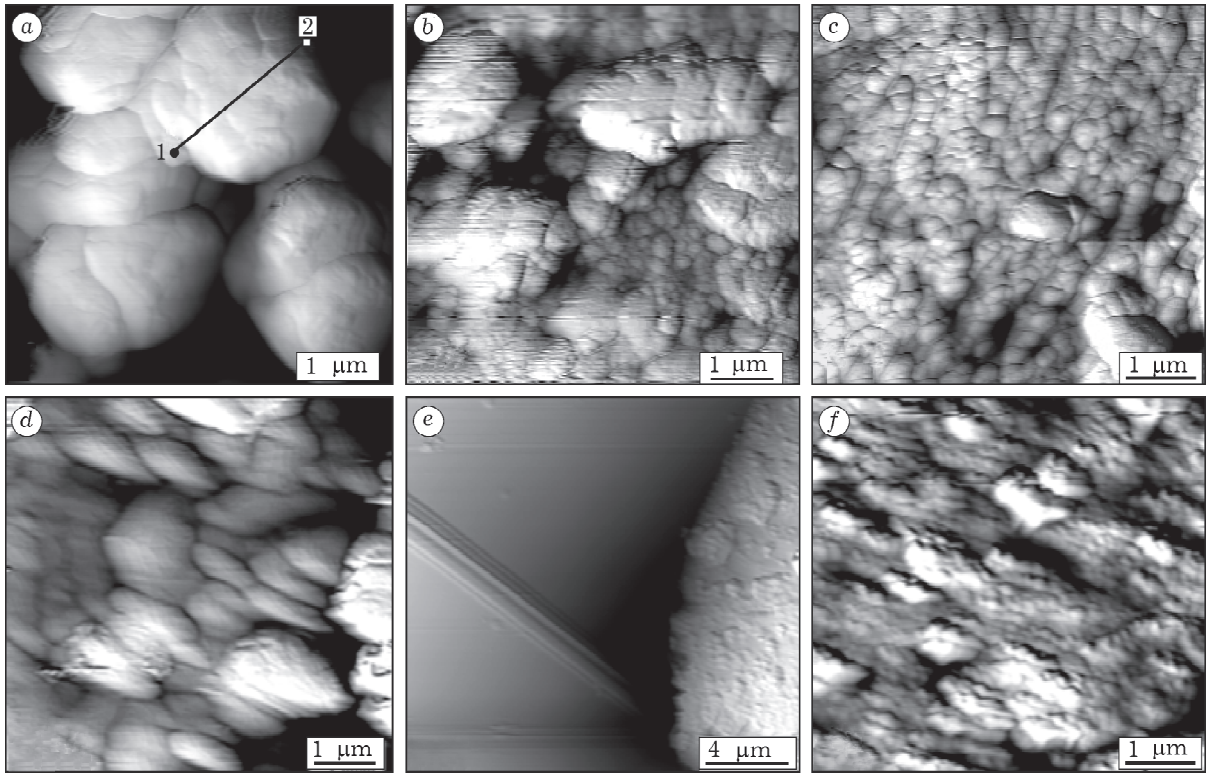

Fig. 1. AFM topography for powder mechanocomposites: Cu (*a*), Cu/3 % Bi (*b*), Cu/10 % Bi (*c*), Fe/10 % Bi (*d*), Cu/12 % In (*e*), Cu/20 % In (*f*).

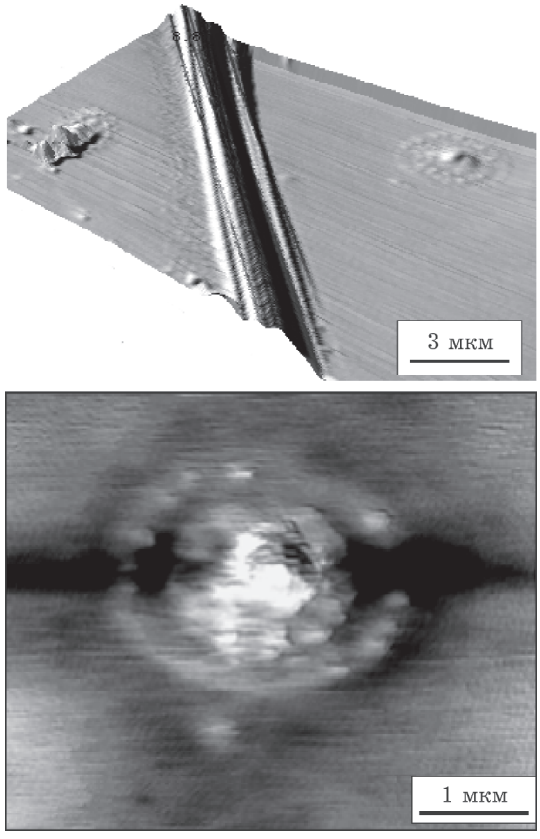

Fig. 2. 3D topography of a particle of Cu/12 % In solid solution powder after mechanical activation with local formations of indium melt.

such structures due to their small height (about 22 nm in the central part and 0.5–1.7 nm at the edges). The data obtained indicate that during the mechanical activation there is a local increase in the temperature resulting in this case in the melting of indium (m. p. = 156 °C).

We have undertaken attempts to apply the AFM method for studying the dynamics of changing the surface of the alloy under the interaction between mechanocomposites and metal melt. The process of image formation in a scanning microscope longs within 5–30 min, therefore the method of AFM cannot be used for studying any rapid processes. However, in studies concerning long processes of structure formation (several hours) the application of the method allows researchers to reveal changes in the surface topography. On the AFM image for the topography for the surface of Cu/10 % Bi + Ga alloy in 30 min and in 2 h after mixing, one can observe an increase in the amount of intermetallic compound $CuGa_2$ as well as the development of surface topography (Fig. 3). After 2 h, the topography of the surface and the morphology of the crystals obtained did not change. According to XRD studies *in situ*

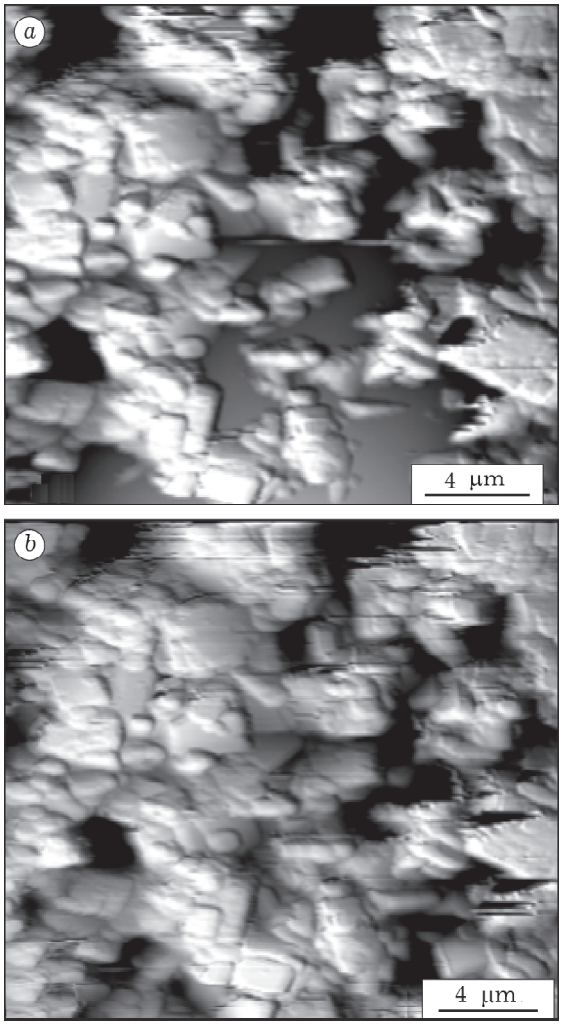

Fig. 3. Surface of Cu/10 % Bi + Ga alloy in 30 (*a*) and 120 min (*b*) after mixing.

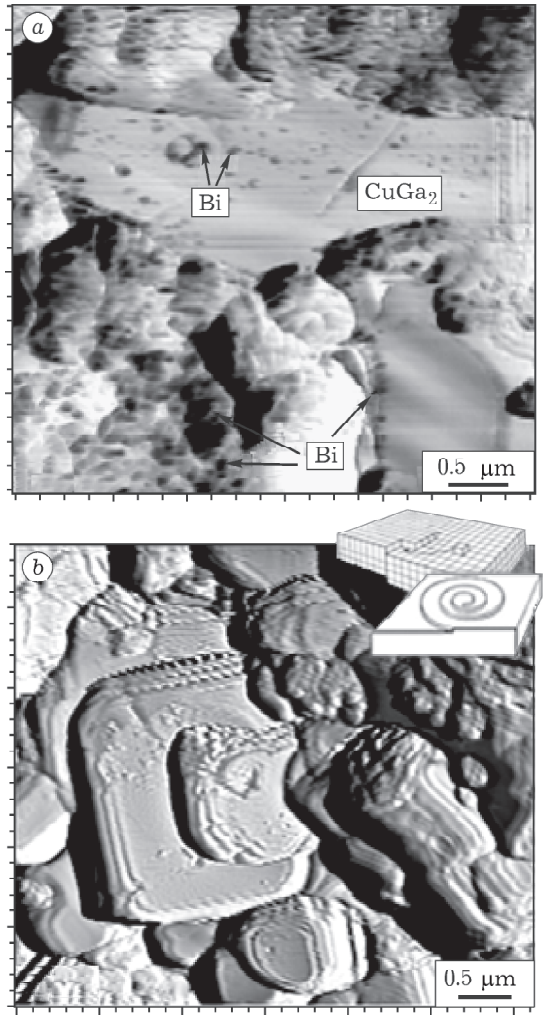

Fig. 4. AFM images of the surface of Cu/Bi + 2Ga → $CuGa_2$ + Bi alloy obtained: *a* – torsion image of bismuth on the faces and growth steps of $CuGa_2$ (the contrast is caused by the difference in tribological properties of intermetallide and bismuth phases); *b* – layered spiral growth of $CuGa_2$ crystals along a screw dislocation (pointed by arrows). Upward there are schemes of crystal growth *via* a screw dislocation mechanism and the shape a step in the course of spiral growth depicted [6].

concerning the dynamics of phase formation [1, 5], the segregation of intermetallide $CuGa_2$ and bismuth is registered simultaneously, and the duration of the alloy formation up to complete gallium consumption has amounted to 4 h. One could assume that crystallization processes of longer duration occur in the bulk of the alloy; therefore the morphology of the crystals on the surface remains constant. Only the height of the relief is changed, which could be connected with an increase in the volume of intermetallic compound $CuGa_2$ with crystallization.

On the AFM images obtained for the surface $CuGa_2$ one could observe crystal face microstructure, crystal geometric parameters and defects. It is seen that the growth of crystallographic faces occurs layer-by-layer, the edges of uncompleted layers move along the face side in the growth process. The step height ranges up to 200 nm. The occurrence of high steps could result in capturing the droplets of mother solution as well as in precipitating an insoluble impurity on the surface of the steps of growing crystals. Bismuth is adsorbed onto the faces, growth steps as well as onto the grain interface in the form of disperse formations with the size up to 250 nm (Fig. 4, *a*).

The application of the AFM method has allowed us to establish the presence of screw dislocations in growing crystals of $CuGa_2$ intermetallide. As a result, the crystal layer grows, con-

tinuously wrapping on itself, overbuilding the dislocation, whereas the step in the course of the growth forms a spiral shape (see Fig. 4, *b*). As it is commonly known, the presence of screw dislocations provides a square-law dependence of face growth rate on the supersaturation level, *i. e.* a considerable growth rate can be observed already at a small deviation from equilibrium [6]. Thus, one could note a layered spiral mechanism for the growth of these crystals.

After completing the processes of structure formation in the alloys the topography was studied using the methods of AFM and scanning electron microscopy (SEM) (Fig. 5). It is seen that the structure of the surface of the end-product represents a mixture of large faceted tetragonal crystals up to 8 μm in size (see Fig. 5, *a*) and local areas consisting of fine-dispersed $CuGa_2$ intermetallide with particle size of 150–250 nm (see Fig. 5, *b*).

Bismuth is located on crystal faces and $CuGa_2$ grain boundaries, as well as local areas are formed up to 10 μm in size.

In the course of interaction of mechanosynthesized solid solutions, for example Cu(In), whose second component (In) is dissolved in metal melt (for example, gallium), the formation of the main intermetallic compound occurs. The crystallization of the second component exhibits an incubation period occurring under corresponding concentration supersaturation inherent in the present system of components.

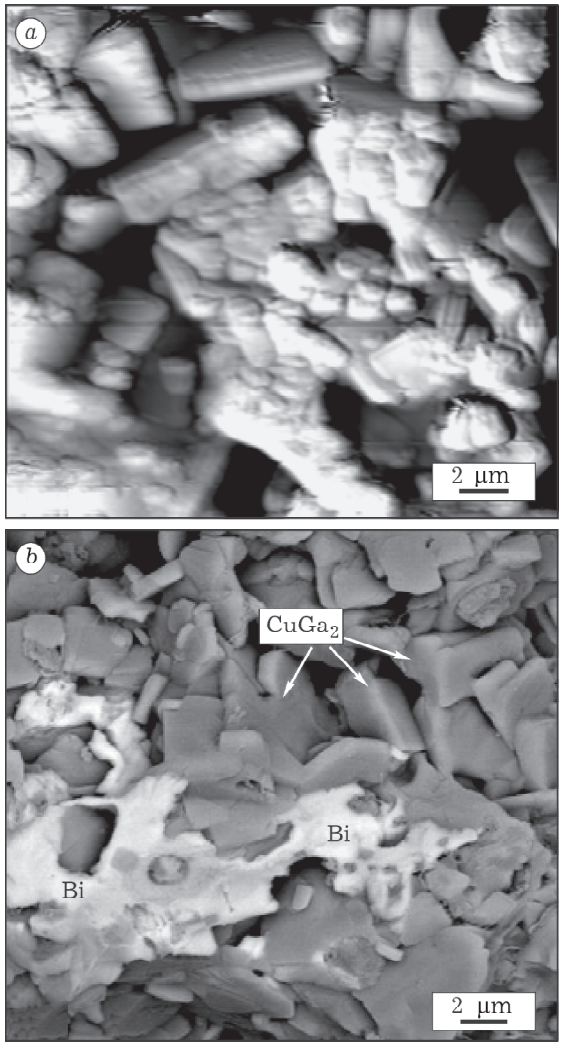

Fig. 5. Topography of Cu/10 % Bi + Ga alloy: AFM (*a*) and SEM (*b*) images, backscattered electrons. White areas correspond to bismuth segregation.

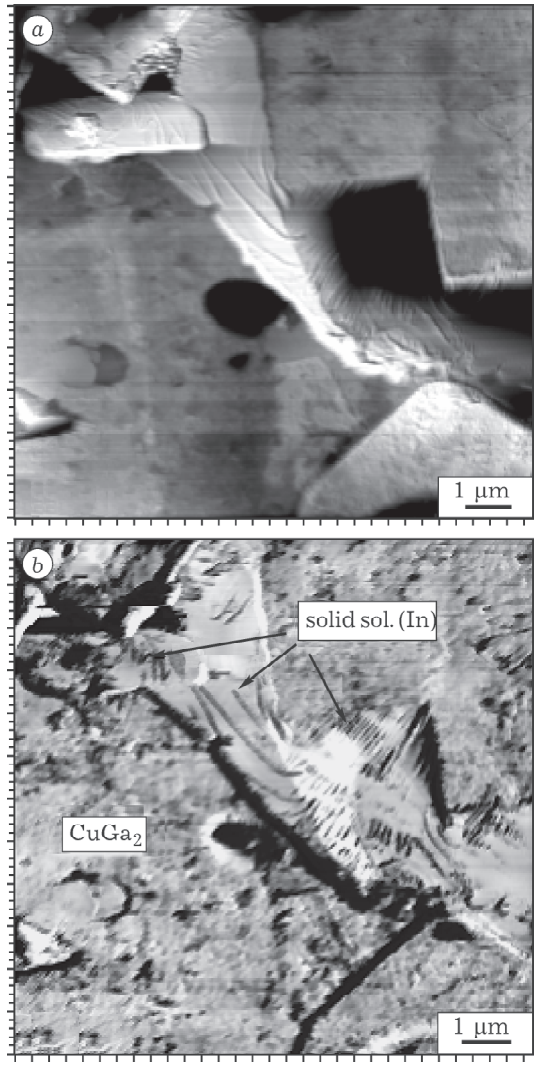

Fig. 6. AFM topography of Cu/12 % In + Ga sample (*a*), the image of this site in the torsion mode (*b*).

The investigation of Cu(In) + Ga alloys employing the AFM method with the reduction of the scanning pitch and with simultaneously obtaining the images of lateral forces has allowed us to reveal the features of the phase structure of gallium-in-indium solid solution (Fig. 6). The distinctive feature of such alloys consists in the presence of deformation distortions (strands, cords) on the crystal interfaces those are well seen on the torsion image (see Fig. 6, *b*). The size of separate crystals of the indium solid solution amounts to more than 10 μm.

Another feature of the surface of samples obtained under the interaction between Cu/In and liquid gallium consists in the presence of dendritic structures on the surface of $CuGa_2$ crystals and grains those are more distinctly visible on AFM images (Fig. 7, *a*). Similar formations are also observed on SEM images (see Fig. 7, *b*). The formation of structures on intermetallide surface could be connected with indium adsorption phenomena on the surface of growing crystals characterized by an increase in the surface concentration of dissolved substances at the interface.

Studying the alloys obtained *via* the interaction between Cu/Bi mechanocomposite with gallium–indium eutectic, is complicated with

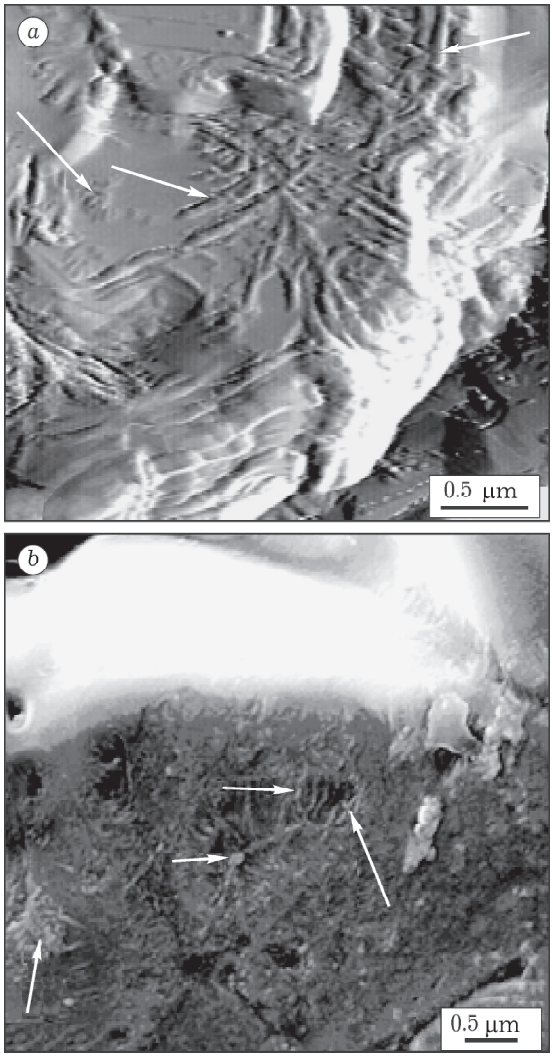

Fig. 7. AFM (*a*) and SEM (*b*) images of the face of intermetallide obtained in the interaction between Cu/20 % In with gallium melt.

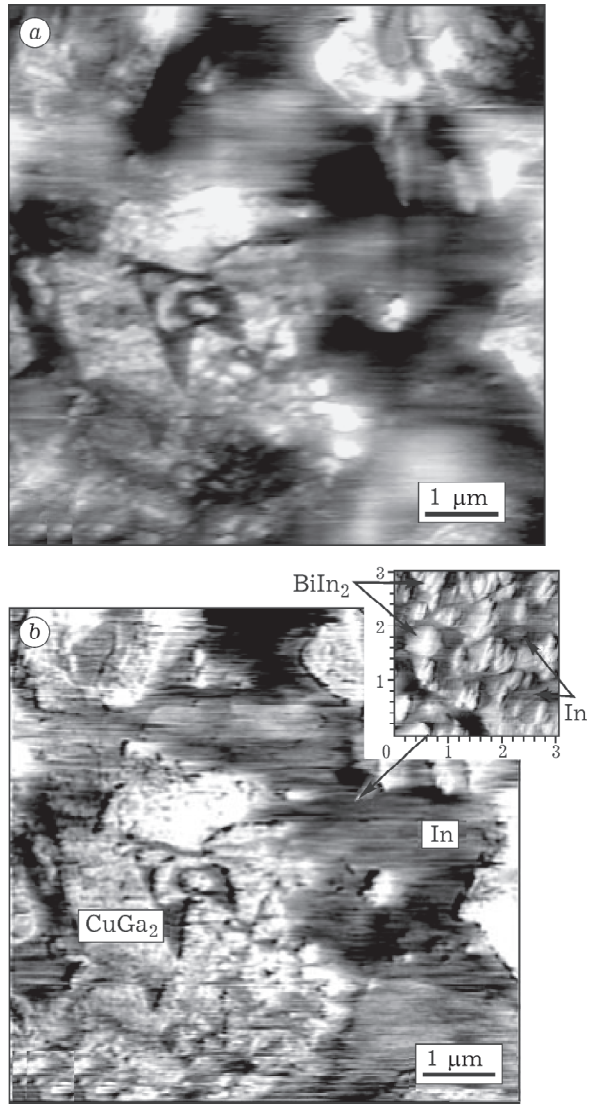

Fig. 8. Thopography of the surface of Cu/10 % Bi + Ga/25 % In alloy: *a* – AFM image of the topography of fine-dispersed $CuGa_2$; *b* – the distribution picture for lateral (torsion) forces within $BiIn_2$ area in indium.

the fact that the components Bi and In segregating in forming $CuGa_2$ enter into chemical reaction with the formation of intermetallic compound $BiIn_2$ [7]. The particles of this compound are formed simultaneously with $CuGa_2$ and could serve as additional crystallization centres. The studies of such alloys using the AFM method has demonstrated that the size of particles of the main intermetallic compound $CuGa_2$ decreases down to 0.1–0.5 μm.

The data of the AFM image of the topography of fine-dispersed $CuGa_2$ (120–150 nm) (Fig. 8, *a*) indicate that the relief of the surface is poorly pronounced, *i.e.* structural components formed are of small size. The picture of distribution obtained simultaneously with the topography of lateral forces allows one to distinguish different phases (see Fig. 8, *b*). For example, the phase with a lower friction coefficient corresponds to dark colour (In). As it is seen from Fig. 8, intermetallic compound $BiIn_2$ exhibits no pronounced contrast on the topographical image being visualized in the picture of lateral force distribution obtained within a smaller scanning range, owing to derable distinctions in tribological properties of indium and $BiIn_2$. The particles of intermetallic compound $BiIn_2$ exhibit needle shape, their size amounting to 150–300 nm. According to scanning data obtained for different areas of the sample surface, the particles of the second phase could locate between of the crystals $CuGa_2$ in the matrix of indium as well as could form local clusters up to 10 μm in size.

CONCLUSION

The studies performed have demonstrated that the data obtained employing the AFM method concerning the topography and morphology of the structural components of metal cements based on gallium are in a good agreement with SEM data. Moreover, the use of the AFM method allows one to visualize the features of structure those cannot be revealed employing the SEM method. It allows researchers to measure the sizes of elements in plane and to monitor spatial defects with the size less than 500 nm, with a lateral resolution ranging from 5 to 30 nm, and a vertical resolution amounting to 0.2 nm. In addition, the use of the AFM method allows one to form a three-dimensional configuration of microrelief (as opposite to the SEM method that results in a pseudo-three-dimensional image of sample surface).

It should be noted that the use of the AFM method allows one to study samples with the specified resolution in air. As opposite to SEM and TEM, the investigation employing the AFM method does not demand any complicated sample preparation, whereas the technique itself belongs to non-destructive methods.

With help of AFM one could investigate both powder mechanocomposites, their dispersity level and morphology, and adsorption phenomena, long-duration crystallization processes, as well as the topography of interaction products obtained, the morphology of structural components, phase distribution and defect formation.

REFERENCES

1 T. F. Grigorieva, A. P. Barinova, N. Z. Lyakhov, Mekhanokhimicheskiy Sintez v Metallicheskikh Sistemakh, Novosibirsk, 2008.
2 E. Ivanov, V/ Patton V., T. F. Grigorieva, *Mater. Sci. Eng.,* A217/218 (1996) 277.
3 T. F. Grigorieva, A. P. Barinova, N. Z. Lyakhov, *J. Nanoparticle Res.*, 5, 5–6 (2003) 439.
4 V. L. Mironov, Osnovy Skaniruyushchey Zondovoy Mikroskopii, Nizhny Novgorod, 2004.
5 N. Z. Lyakhov, A. I. Ancharov, Yu. D. Kaminsky, T. F. Grigoryeva, A. P. Barinova, V. Sepelak, K. D. Becker, S. A. Petrova, A. Yu. Fishman, VII Ros.-Izrail. Konf. "Optimizatsiya Sostava, Struktury i Svoystv Metallicheskikh, Oksidnykh, Kompozitsionnykh, Nano- i Amorfnykh Materialov (Treatises), Perm, 2008, pp. 91–107.
6 A. A. Chernov, in: Sovremennaya Kristallografiya, Moscow, 1980, vol. 3, pp. 5–232.
7 N. P. Bochvar, in: Diagrammy Sostoyaniya Dvoynykh Metallicheskikh Sistem, in N. P. Lyakishev, Mashinostroyeniye, Moscow, 1996, vol. 1, pp. 649–651.