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INFLUENCE OF DIRECT ELECTRIC CURRENT ON THE PROCESSES OF CONTACT FUSION IN THE BISMUTH–TELLURIUM SYSTEM

A. M. Nazhmudinov, L. S. Patskhverova,
and M. R. Khairulaev

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We have investigated contact fusion (CF) in the Bi–Te binary system with a complex state diagram under different programs of heating the contact of specimens in the current and currentless regimes. CF at temperatures below the fusion temperature of the lowest eutectics has been revealed. It has been established that the known state diagram of the Bi–Te system is metastable and, depending on the contact heating rate, the CF processes proceed differently. It has been shown that the values and directions of the direct current passed through the contacts of Bi and Te specimens can control the phase-formation processes and the CF kinetics.

Up to now, the kinetic parameters of CF in systems with intermediate phases and the influence of direct electric current (DEC) on the process kinetics and the phase composition of contact interlayers practically have not been investigated. Therefore, the aim of the present work is to investigate the influence of DEC on the character of the advacing of the phase-formation and CF processes and their features and the possibility of controlling these processes.

The interest in investigating the Bi–Te system is due to the great difference of opinions about the construction of the state diagram of this system, which has existed for a long time [1–6]. Moreover, in the experiments performed by many researchers [7–11] there are wide discrepancies between the values of the contact fusion temperature and in the explanation of its mechanism in the system under consideration. The inconsistency of the results of these works became a stimulus for investigating the CF in the Bi–Te system under different heating conditions and in a wide temperature range.

Preparatorily to performing experiments, we considered the possible reasons for the above discrepancies between the results of the previous researchers, one of which may be purity of the materials used to obtain specimens. We used high-purity bismuth and tellurium: the maximum content of impurities in bismuth was 0.0003% and in tellurium 0.0018%. The specimens were polycrystalline cylinders of diameter 2–3 mm and height 10 mm. The contacting surfaces of the specimens were given a mirror-like polish.

Contact fusion was carried out in a special improved facility in a medium of purified hydrogen (Fig. 1). The specimens prepared for the experiment were placed in holders 1 and 3 so that they did not touch each other. The specimens were brought into contact at a steady-state temperature by drive 5. The time of appearance of the liquid state was evaluated visually and by the jump of the displacement meter, whose sensor was capacitor 4. The upper plate of this capacitor is connected with the upper specimen, and as the liquid flows out of the contact zone (steady-state regime of CF) the capacitor capacity changes. The electronic displacement meter was connected as the vibration and displacement meter of [12]. The rate of the CF process in the steady-state regime was recorded by a KSP-4 self-balancing potentiometer.

Under unstable conditions of CF, to prevent liquid outflow from the contact zone, we put glass jackets on the specimens, fitting them. The CF rate was calculated by the liquid phase measured by a V-630 cathetometer. The temperature was measured by means of chromel-alumel thermocouples 2 with an accuracy of $\pm 0.05^{\circ}$C, which was increased by calibrating the thermocouple in the temperature range from 200 to 460°C, using for measurements high-precision instruments: an F116/1 microvoltmicroampere meter and an R37 dc potentiometer. Owing to the loca-

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Dagestan State Pedagogical University, 57, Yaragskii Str., Makhachkala, Dagestan, 367013, Russia; email: khairulayev47@mail.ru. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 78, No. 6, pp. 34–41, November–December, 2005. Original article submitted February 18, 2004; revision submitted May 30, 2005.

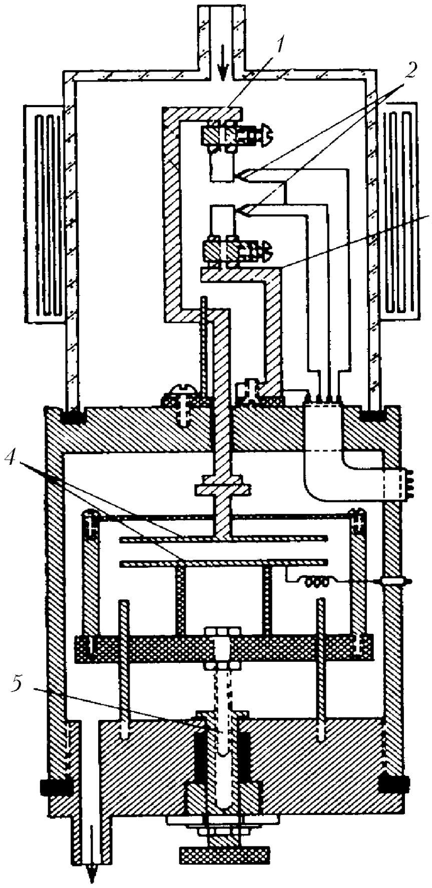

Fig. 1. Scheme of the contact fusion chamber.

tion of the regulating thermocouple junction between the furnace heating-element coils, a high stabilization of the working chamber temperature was attained. The temperature was held constant by a VRT-2 high-frequency regulator.

In systems with chemical interaction of components, an increase in the contact temperature is possible owing to the occurrence of the exothermal reaction of intermetallic formation. This additional heating was measured by a differential thermocouple, one of whose junctions was inserted into the specimen contact and the other of which was placed in the furnace near the controlled specimens.

To investigate the influence of DEC on the processes in CF, we connected a current stabilizer as the one described in [13]. Investigations were performed under both stationary and nonstationary conditions with the passing of DEC of strength from 0.5 mA to 5 A in either direction at various temperatures and holding times. To create equal conditions at different potential polarities on tellurium, experiments were performed on a system of joint Te–Bi–Te specimens.

Contact fusion was carried out in the following two regimes of heating Bi and Te specimens:

1. The specimens were brought into contact in the hydrogen medium at room temperature; then they were heated at rates of 5–70°C/min to a certain temperature at which they were held for 0.1–3.0 h ("slow" heating conditions).

2. The specimens secured in the holder were heated in the hydrogen medium to a certain temperature and only then were brought into contact. Obviously, the conditions for CF in this case were the same as under exceedingly fast heating. For the sake of brevity, this heating regime is called the "pulsed regime."

Upon fast cooling by liquid nitrogen vapors, the solidified contact interlayers were investigated by the methods of radiographic, microstructure, and local x-ray spectroscopic analysis and by microhardness measurements.

Microstructure analysis was carried out with MBI-6 and MII-4 microscopes with preliminary grinding, electrochemical polishing, and ion etching of metallographic sections on a VUP-4. Electrochemical etching was performed at an anode current density of 20 A/dm^2 for 2 sec in the medium of a saturated solution of sodium chloride (980 ml)

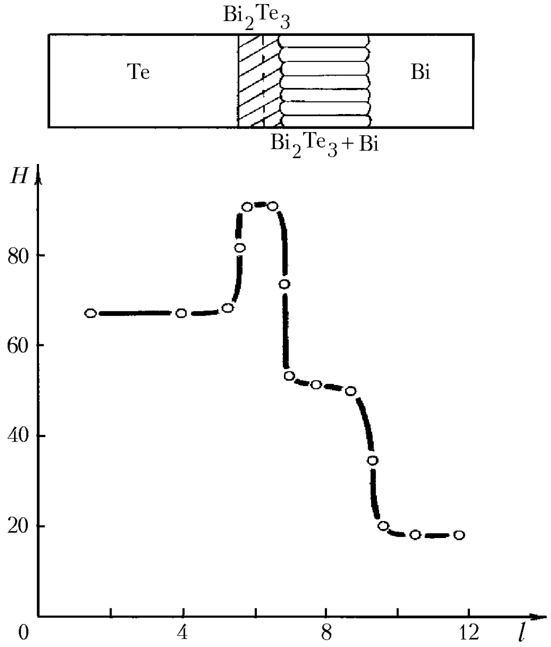

Fig. 2. Change in microhardness along the specimens of the system Te–contact-interlayer–Bi. *H*, kg/mm^2; *l*, mm.

with sulfuric acid (20 ml). Radiographic studies were made on a URS-50I facility. X-ray spectroscopic analysis was performed on an MV-1 microprobe ("Cameca," France), and microhardness measurements were made on a PMT-3.

Currentless Regime of CF. Heating of joint specimens at rates of 5, 10, 20, and 50^{o}C/min in the contact of Bi and Te at temperatures between 125 and 160^{o}C and a holding time of 5–10 min leads to the formation of a thin layer of the chemical compound Bi_2Te_3. The thickness of this layer increases with further increase in the temperature and approaches some constant value, i.e., a kind of "saturation" takes place. At t = 266^{o}C, the primary liquid phase appears. According to the state diagram of the Bi–Te system, this temperature corresponds to the fusion temperature of the $Bi + Bi_2Te_3$ eutectics. The x-ray photographs of the fast frozen interlayers show lines of pure bismuth and the Bi_2Te_3 compound. The appearance of liquid in the contact of Bi and Te specimens at the eutectic temperature can be explained by the appearance on the defects and local inhomogeneities of the structure of microregions of the eutectic $Bi + Bi_2Te_3$ composition as a result of the diffusion of Bi atoms in Bi_2Te_3. CF usually begins at the cites of good atomic contact of components and forms a discontinuous fusion front.

Under pulsed heating of the contact of specimens, CF is observed at a temperature of 263^{o}C, which is 3^{o}C lower than the fusion temperature of the lowest equilibrium eutectics. The intensity of the appearance of liquid in the contact of the specimens is insignificant and the liquid interlayer is not seen. However, when the specimens are moved apart, liquid straps are observed. It has been established that the crystallized liquid interlayer is the $Bi + Bi_2Te_3$ eutectics.

Thus, in the Bi–Te system, in both regimes of heating the contact of the Bi and Te specimens the $Bi + Bi_2Te_3$ eutectics is registered, i.e., the process of intermetallic Bi_2Te_3 formation proceeds, avoiding other intermetallic compounds, in particular, $Bi_{14}Te_6$, and Bi_2Te, and BiTe. These results are also confirmed by the measurements of microhardness (Fig. 2) along fused specimens in both regimes of CF.

All this suggests that the slow heating of the contact of Bi–Te specimens for the given system is also fast enough and the process proceeds with the formation of metastable $Bi + Bi_2Te_3$ eutectics, i.e., the state diagram of this system, which is given in [2] as an equilibrium one, in fact is metastable. This suggestion is also supported by the secondary fusion of the interlayers obtained in the Bi and Te contact in both regimes of contact heating.

The observed decrease in the CF temperature by 3^{o}C under pulsed heating of joint specimens can be attributed to the local increase in the temperature in the contact zone as a result of the proceeding of the exothermal reac-

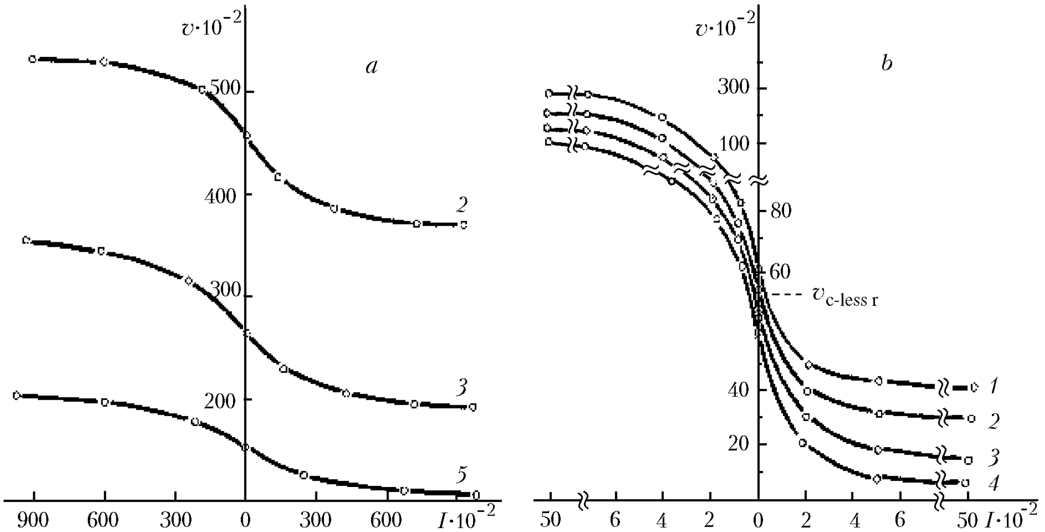

Fig. 3. Dependence of the mean CF rate on the Bi–Te system DEC at currents from −50 to +50 mA (potential sign with respect to Te): a) stationary slow heating regime; b) nonstationary regime [1) t = 269; 2) 268; 3) 267; 4) 266.5; 5) 266°C]. v, mm/min; I, A.

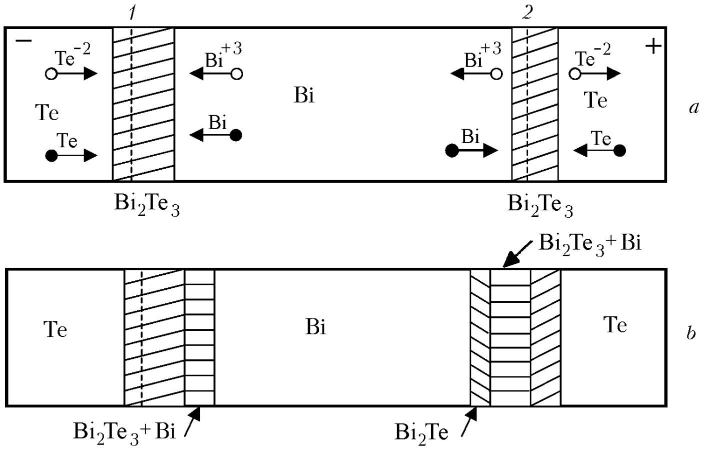

Fig. 4. Model representation of the phase formation at DEC of 50 mA in the Bi–Te system: a) $t < t_{eut} = 266^oC$; b) $t \geq t_{eut}$.

tion of formation of the Bi_2Te_3 intermetallic. Such an increase, as was noted in [7], was observed experimentally in powder pills of a mixture of bismuth with tellurium.

From comparison of the temperature dependences of the mean CF rates under different conditions, it is seen that under stationary conditions the CF rate increases faster with increasing temperature (Fig. 3a) than under nonstationary conditions (Fig. 3b), since in the latter case the rapidly growing thickness of the liquid interlayer weakens the diffusion mass transfer of the components through it.

Current Regime of CF. At the contact points of joint Te–Bi–Te specimens at low currents (up to 50 mA) before the appearance of liquid contact interlayers (at temperatures below $t_{eut} = 266^oC$) the Bi_2Te_3 intermetallic layers grow (Fig. 4a). At boundary 1, the process of Bi_2Te_3 formation is more intensive than at boundary 2. We attribute this to the fact that under the action of DEC part of the Bi and Te atoms goes to the Te^{-2} and Bi^{+3} states. As a result, at boundary 1 to the diffusion counter flows of Te and Bi atoms the counter flows of Te^{-2} and Bi^{+3} ions are added due to the influence of the electric field. At boundary 2, there are only diffusion counter flows of Te and Bi atoms, since Te^{-2} and Bi^{+3} ions are thrown off from the boundary by the electric field.

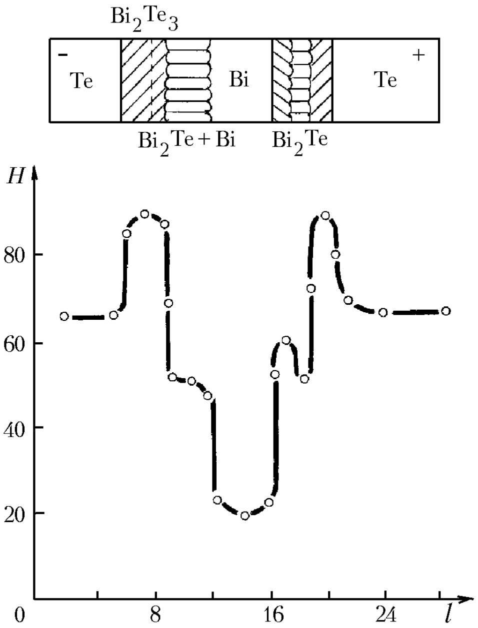

Fig. 5. Change in microhardness along the contact interlayers obtained at t = 268°C and I = 50 mA. H, kg/mm^2; l, mm.

Now, instead of a chain of original Te–Bi–Te specimens, we have a complex system: Te–Bi_2Te_3–Bi–Bi_2Te_3–Te, in which at 266°C in the regions where Bi_2Te_3 layers have been formed a liquid appears. This fact is explained, as in the case of CF in the currentless regime, by the formation of microregions of a composition corresponding to the Bi–Bi_2Te_3 eutectics.

As a result of the ongoing diffusion of atoms and the electrotransfer of bismuth and tellurium ions, concurrently with the liquid formation there is a growth of the Bi_2Te_3 intermetallic. The formation of a Bi_2Te compound on the Bi specimen surface facing boundary 2 has also been registered (Fig. 4b). The picture of phase formation described is confirmed by the measurement data for the contact interlayer hardness (Fig. 5).

An increase in the direct electric current intensifies all processes at both boundaries: at the first boundary to a greater extent and at the second boundary to a lesser extent. But if in the course of the experiment the potential polarity on the Te specimens is changed, then the picture will be reversed: at the first boundary the phase-formation processes will be retarded and the CF rate will decrease, whereas at the second boundary a rapid growth of intermetallics and an increase in the CF rate will be observed. Under the influence of DEC, the CF kinetics changes appreciably (see Fig. 3).

Thus, small currents and the change in their direction make it possible to control the processes in the contact of the Bi and Te specimens but do not affect the CF temperature.

Let us see what processes occur in the contact of the Bi and Te specimens at boundaries 1 and 2 when currents from 1 to 5 A are passed through the Te–Bi–Te system. At a 1 A current at boundary 1 (Fig. 6a), CF is already observed at a temperature of 235°C, which is 31°C lower than the equilibrium eutectic temperature. Our investigations have revealed that in this case CF proceeds between pure Bi and Te components with the formation of metastable Bi + Te eutectics. At the second boundary, where Te has a positive potential, the contact interaction between pure Te and Bi does not take place at all, so the preliminary polish of the surfaces is preserved. We think that the absence of traces of interaction between the Bi and Te specimens in the contact at boundary 2 can be explained on the basis of the electronic structure of Bi (...$6s^2\,6p^3$) and Te (...$5s^2\,5p^4$). Probably, at 1 A currents a considerable number of tellurium atoms go to the state ...$5s^2\,5p^6$, i.e., to the ionized state Te^{-2}. The bismuth atoms are in the state Bi^{+3} (or Bi^{+5}). Then the electric field at boundary 2 prevents the bismuth and tellurium atoms from crossing the boundary; this is why no interaction between the specimens brought into contact is observed. At boundary 1 a different picture is observed: the intensive counter flow of Te^{-2} and Bi^{+3} ions creates a high degree of nonequilibrium of the state of the near-boundary surfaces, which leads to low-melting metastable Bi + Te eutectics.

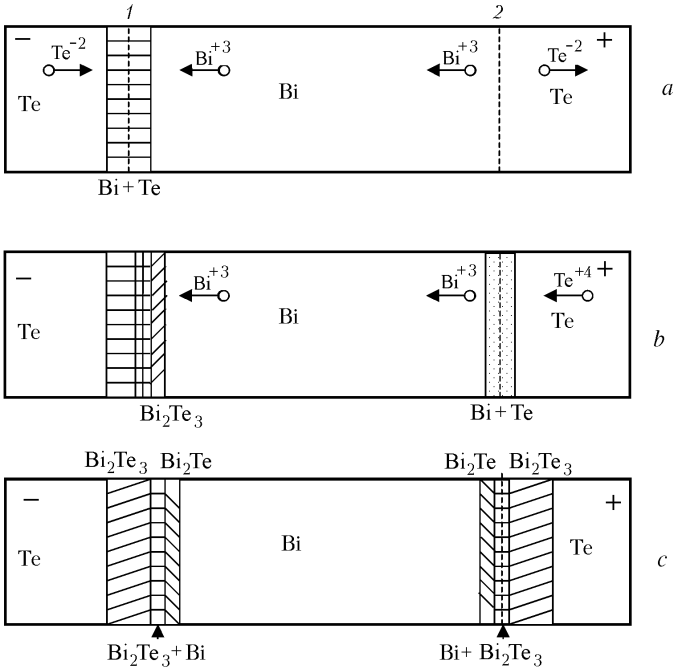

Fig. 6. Model representation of the phase formation in the contact interlayers in the Bi–Te system obtained at a temperature of 235°C under DEC: a) I = 1; b) 2; c) above 2 A.

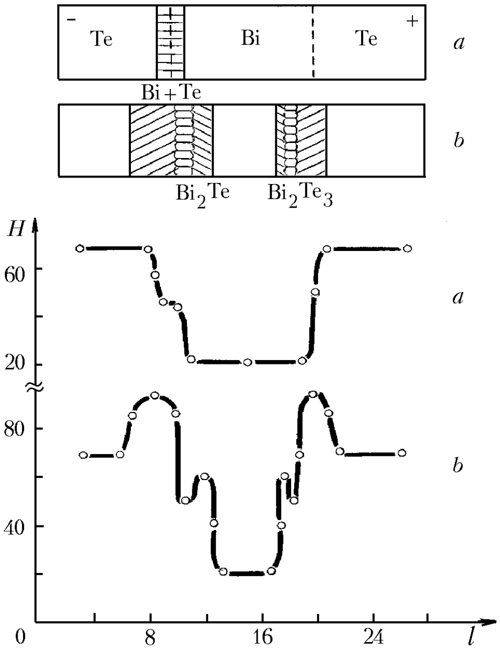

Fig. 7. Model of the phase formation under CF and change in the microhardness of the BiTe-Te system at a temperature of 235°C: a) 1; b) 5H, kg/mm^2; l, mm.

As the current is increased to 2 A, at boundary 2 (Fig. 6b) at 235°C CF begins, which points to the fact that in the contact in this case nonequilibrium conditions are also created and metastable Bi + Te eutectics is formed. We associate this nonequilibrium with the transition of tellurium to the Te^{+4} (or Te^{+6}) state. Then there occurs a diffusion of bismuth ions through the Bi + Te liquid towards the tellurium specimen at boundary 1 and diffusion through the same liquid of tellurium ions towards the bismuth specimen at boundary 2. These diffusion flows and the enrichment of the liquid interlayers with bismuth (boundary 1) and tellurium (Fig. 6b, boundary 2) with increasing current lead to a solidification of liquids and a growth of intermetallics based on the crystallized liquid interlayers. The process of formation of a metastable Bi + Te liquid at boundary 2 lags behind the same process at boundary 1 because of the late onset of CF; therefore, the thickness of the left interlayer is larger. As a result, as tellurium ions diffuse through the thinner interlayer (Fig. 6c, boundary 2), in the latter, closer to the Te specimen surface, a Bi_2Te_3 layer begins forming, and as the tellurium ions reach the Bi specimen surface, Bi_2Te intermetallic grows on it. Inside the Bi_2Te_3 layer, microregions corresponding to the $Bi_2Te_3 +$ Bi composite are also formed. At boundary 1 analogous processes proceed, but closer to the Bi surfaces a Bi_2Te layer grows, and near the Te specimen surface a Bi_2Te_3 layer is formed and, accordingly, microregions of the $Bi_2Te_3 +$Bi composite arise. This has been tested experimentally: an increase in the temperature of the furnace containing the system Te–interlayer–Bi–interlayer–Te to 266°C leads to the liquid formation at both boundary 1 and boundary 2. The phase composition of the interlayers is also confirmed by the graphs of change in microhardness along the CF region and by the change in the electrical resistance of the contact interlayer in the CF process.

CONCLUSIONS

1. In the Bi–Te system, in the currentless regime under slow and pulsed heating of joint Bi and Te specimens in the contact Bi_2Te_3 intermetallic is formed, avoiding other intermetallic compounds ($Bi_{14}Te_6$, Bi_2Te, BiTe). Contact fusion in both heating regimes occurs at 266°C, which corresponds to the fusion temperature of $Bi_2Te_3 +$ Bi eutectics [1, 2]. This suggests that also the so-called "slow" heating of the contact (3–10° C/min) for the given system is fast enough, and the processes proceed according to the metastable state diagram; the Bi–Te state diagram [2] is, in fact, metastable.

2. It has been established that by changing the value and direction of the DEC passed through the Bi and Te specimens brought into contact, one can control the phase-formation processes in the region of contact of the specimens and the CF kinetics. Thus, one can influence by 0.5–0.50 mA current the growth of particular phases and the CF kinetics. Currents of the order of 1 A make it possible, depending on their direction, to carry out contact fusion in the Bi–Te system at a temperature of 235°C, which is 31°C lower than the lowest eutectic temperature, or prevent interaction of Bi and Te in the contact. At currents of 2–5 A, CF also occurs at 235°C for any direction of the current, a change in which can influence the process of phase formation and the CF kinetics.

3. Control of the processes occurring in the contact of Bi and Te specimens by means of DEC becomes possible due to the transition of Te atoms under the influence of electric current to the ionized Te^{-2} and Te^{+4} (or Te^{+6}) states.

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