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THERMAL EFFECTS IN THE CONTACT FUSION OF THE ANTIMONY-TELLURIUM SYSTEM

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We have investigated the contact fusion in a binary system with a complex state diagram for different techniques of heating the contact of massive antimony and tellurium specimens with the use of the autothermal e.m.f. method. A decrease in the contact fusion temperature compared to the fusion temperature of the metastable eutectic due to the action of metastable processes has been revealed by experiment. We have established the formation of a metastable Sb + Te eutectic by X-ray structural, X-ray microspectrum, and microstructural analyses and by microhardness measurements of contact interlayers as well as by secondary fusion. Theoretical calculations of the heat released as a result of the exothermal reaction of intermediate Sb_2Te_3 *phase formation have been performed.*

Keywords: *contact fusion, eutectic, metastability, microhardness.*

Introduction. The interest in the investigation of the phenomenon of contact fusion (CF) in the antimony-tellurium system is multi-faceted. First, the investigation of the CF between a metal and a semiconductor is important from the point of view of their practical application and for the CF theory. Second, in investigating the CF in systems with chemical interaction of components a decrease in the CF temperature compared to the lowest-possible eutectic has been revealed. In this connection, note that the state diagram of the Sb–Te system has one homogeneous compound Sb_2Te_3 (61.12 weight %) with a fusion temperature of 621.5^{o}C, which forms an eutectic with tellurium ($Te + Sb_2Te_3$) at a temperature of 424^{o}C, and two intermediate phases: the β-phase (18–38 at. % of Te) and the γ-phase (42–55 at. % of Te) formed by peritectic reactions at 550 and 558^{o}C [1]. Telluride Sb_2Te_3 has a hexagonal C33-type lattice. Third, there exist several views concerning the mechanism of decrease in the CF temperature in systems whose state diagrams contain intermediate compounds [2]:

1. The CF temperature turns out to be lower than the eutectic temperature as a consequence of the formation in the contact of a metastable low-fusible eutectic (ΔT-effect of CF: $\Delta T = T_{\text{eut}} - T_{\text{c.f}}$). The necessary condition for the ΔT-effect of CF to manifest itself is very fast heating of the contact of specimens or their contacting at a stable temperature.

2. Another possible reason for hypoeutectic CF is a local increase in the temperature in the contact of specimens due to the exothermal reaction of formation of intermetallides [3]. In this case, however, a decrease in the temperature of appearance of the liquid in the contact is not observed in practice and the ΔT-effect is actually absent although it seems to be present. Therefore, the appearance of a liquid in the contact of specimens at a furnace temperature below the eutectic temperature upon local heating of the contact due to the exothermal reaction of formation of intermetallides is called the "spurious" ΔT-effect of CF [4].

Methods. To realize CF, we obtained specimens from "high-purity" materials (the maximum content of impurities did not exceed 0.001–0.008 weight %) in the form of polycrystalline cylinders of diameter 3–4 mm and height 10 mm. The contacting surfaces of the specimens were mirror-polished. Before experiments, the specimens were annealed for 5–6 h in a hydrogen medium to remove the internal stresses and working strains.

After experiments the contact zones of the specimens were investigated with the use of microstructural, radiographic, and local X-ray spectroscopic analyses; their microhardness was also measured. CF was carried out in a hydrogen medium with the aim of creating a reducing atmosphere. Hydrogen was obtained by means of electrolysis of

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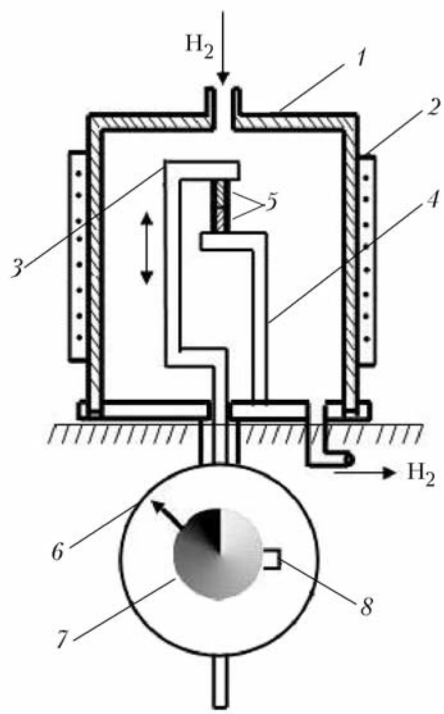

Fig. 1. Chamber for contact fusion: 1) quartz envelope; 2) electric furnace; 3, 4) upper and lower specimen holders; 5) specimens; 6) micrometer; 7) photographic film with gradient filling; 8) optocouple.

an aqueous alkali solution. Purified hydrogen was fed into the chamber in which CF was carried out (Fig. 1). The holders of specimens 3, 4 are screw clamps that permit mounting strictly centered specimens 5 independent of their geometric sizes. For galvanic isolation, the specimen holder 4 is connected to the chamber base through a porcelain spacer. The upper holder 3 moves freely vertically and its lower end rests on the pickup of the displacement meter (micrometer of the type of KI 0.01 mm).

At the level of the specimens in the chamber there is a window (not shown in Fig. 1) through which specimens are visually observed and photographed in the CF process, and the contact interlayer growth is measured by a V-630 cathetometer. The role of the thermostating furnace 2 is played by a nichrome coil wound along a quartz tube 1 and connected to a high-frequency temperature regulator (VRT-2). High stabilization of the temperature in the chamber is provided by placing the junction of the regulating thermocouple between the turns of the heating element of the furnace.

The principle of measuring the displacement of the upper specimen holder is based on the dependence of photodiode voltage on the translucence of the film with a gradient "polar" filling placed between a light-emitting diode and a photodiode glued to the micrometer pointer. The device reading information from the photofilm is an optocouple 8 (light-emitting diode and photodiode) operating in the infrared frequency range.

The specimen temperature was determined by means of chromel-alumel thermocouples with an accuracy of up to $\pm 0.01^{\circ}$C. The temperature measurement accuracy was increased due to the thermocouple calibration in small temperature ranges and the application for measurements of high-frequency devices — an F116/1 microvoltammeter and a P37 dc potentiometer.

To investigate the temperature increase in the contact zone due to the chemical exothermal reactions of intermetallide formation, we used the autothermal e.m.f. method [5]. Specimens 5 are connected by electric conductors to a sensitive microvoltmeter and placed, in separated positions, in the chamber for CF. As soon as the required temperature ($T_{\mathrm{c.f}}$) is set, they are brought into contact. The contact zone of specimens plays the part of the measuring junction of the differential thermocouple. The contacts of specimens with wires having the thermostat temperature act as a control junction of the differential thermocouple. The thermal effects are registered by measuring the temperature differ-

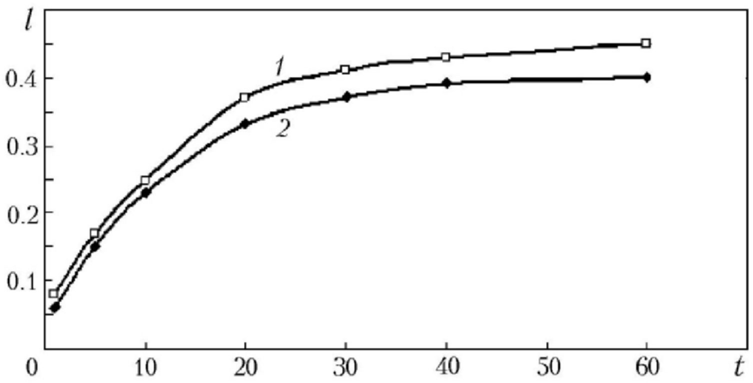

Fig. 2. Growth-time curves of the Sb_2Te_3 compound: 1) 415°C; 2) 410°. *l*, mm; *t*, min.

ence between the thermostat and the reaction zone, and the value, duration, and sign of the thermal effect are determined by the thermoelectric current value, duration, and direction.

To optimize the process of collection and processing of data (contact temperature of specimens, CF rate in the steady-state regime, autothermal e.m.f. of specimens, voltage drop on specimens in the current regime, visual observation, etc.), we used an NI cRIO-9211 analog-to-digital converter complete with an NI USB-9161 Carrier adapter. It was connected to the USB assembly of a personal computer and we also used adequate programs for processing results.

The contact fusion was investigated in two regimes of heating specimens:

1) specimens were brought into contact in a hydrogen medium at room temperature, then the furnace was turned out and the specimens were heated at various rates to a certain temperature at which they were held for 0.1–3.0 h (slow heating of the contact of specimens);

2) specimens fastened in the holders were heated separately in a hydrogen medium to a certain temperature upon attaining which they were brought into contact (flash heating of the contact).

We have made systematic studies of the CF in the Sb–Te system under slow and flash heating of the contact of specimens in a wide temperature range.

Results. *Slow heating.* In our investigations, in the contact of pure component Sb and Te at a temperature of 250°C and above under slow heating a layer of intermetallide Sb_2Te_3 is formed. As the temperature and the holding time increase, the thickness of this intermediate phase grows (Fig. 2). The presence of the β- and γ-phases in the interlayer is not revealed by the X-ray structural analysis. The change in the parameters of the Sb crystal lattice due to the possible formation of solid solutions is not registered.

An increase in the intermediate phase under low heating of the contact leads to a change in the autothermal e.m.f. of specimens, which is seen from Fig. 3 (curve 2, section a). When a temperature of 420°C is attained, a stepwise increase in the thermal e.m.f. is observed (Fig. 3, curve 2, section b), which points to a sharp increase in the temperature in the contact zone. As follows from the figure (section b), the process of synthesis of a chemical compound proceeds with a gradual decrease in the autothermal e.m.f. during 5 min. This is due to the decrease in the diffusion flow through the intermediate compound layer formed, and the downward jump in section c is due to the appearance of an ample primary liquid phase. But this change is not detected by the external thermocouples (Fig. 3, curve 1).

The further increase in the autothermal e.m.f. (Fig. 3, curve 2, section d) is explained by the liberation of an intermediate compound from the liquid eutectic phase at a temperature somewhat lower than the eutectic temperature. In X-ray photographs of interlayers, lines of the compound Sb_2Te_3 and pure Te are observed. This points to the fact that the interlayer is a $Sb_2Te_3 + Te$ eutectic.

In the specimens prepared for metallographic investigations, we measured the microhardness. To identify the interlayer layers, we obtained alloys corresponding to the stoichiometric compositions of all intermediate phases and the $Sb_2Te_3 + Te$ eutectic and measured the microhardness. As a result of the investigations, it has been found that the

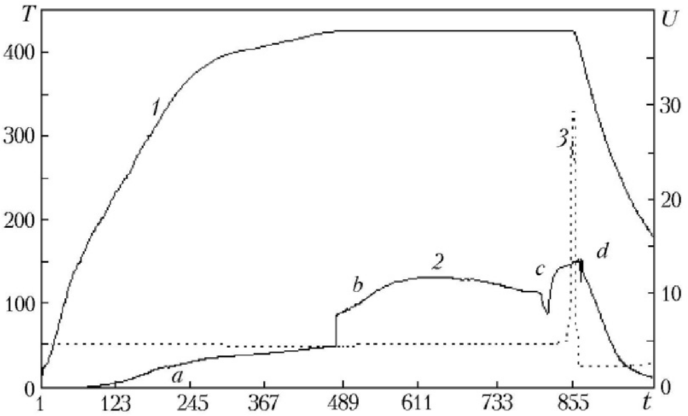

Fig. 3. Curves of the time dependences of: 1) the specimen temperature; 2) the autothermal e.m.f. of specimens; 3) the relative displacement of specimens in the Sb–Te system under slow heating. T, ^{o}C; t, sec; U, mV.

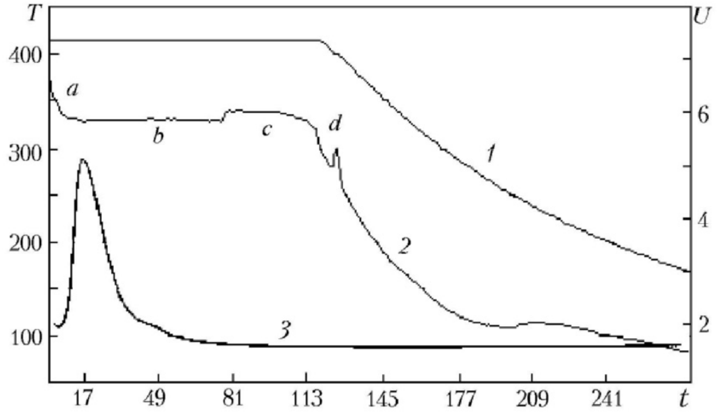

Fig. 4. Curves of the time dependences of: 1) the specimen temperature; 2) the autothermal e.m.f. in the Sb–Te system under flash heating; 3) the displacement of specimens. T, ^{o}C; t, sec; U, mV.

microhardness of the interlayer obtained under slow heating corresponds to the intermediate phase Sb_2Te_3 and its eutectic with tellurium.

Thus, the CF in the Sb–Te system under slow heating occurs with a slight deviation from the stable state diagram. First, the formation of the β- and γ-phases, for which many hours of holding at temperatures above 500^{o}C are needed, is not registered. Second, the appearance of the primary liquid phase is observed at a furnace temperature 4^{o}C lower that the fusion temperature of the $Sb_2Te_3 + Te$ eutectic. This is attributed to the temperature increase in the contact zone due to the exothermal reaction of synthesis of the compound Sb_2Te_{3e} and is also confirmed by the increase in the autothermal e.m.f.

Flash Heating. Under flash heating of Sb and Te the liquid phase in the contact is formed at 410^{o}C, which is 14^{o}C lower than the lowest eutectic temperature according to the equilibrium state diagram. The appearance of the liquid phase is registered by the displacement pickup and visual observation with an MBS-2 microscope.

Measurements of the autothermal e.m.f. have shown that immediately after contacting at a temperature of 410^{o}C the thermal e.m.f. of the contact decreases (Fig. 4. section a), which we attribute to the formation of the metastable liquid phase Sb + Te. The metastable liquid phase Sb + Te formed exists in the liquid form for 4–5 min (Fig. 4, curve 2, section b), after which in the contact the intermediate phase Sb_2Te_3 begins to form, which is seen from section a of curve 2. In so doing, in the contact two phases coexist: the metastable phase Sb + Te and the interlayer of intermetallide Sb_2Te_3. But if the liquid interlayer is sharply cooled by liquid nitrogen vapors, then the

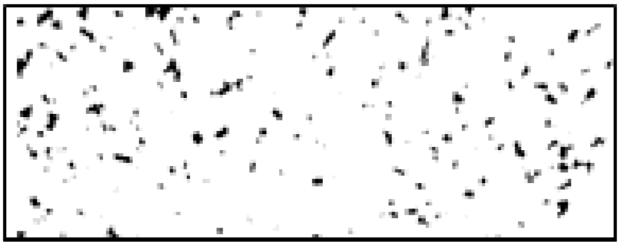

Fig. 5. Microstructure of the nitrogen-vapor-frozen CF zone under "flash" heating of the Sb–Te system (temperature of 410°C, holding time of 4 sec). × 2000.

TABLE 1. Calculation of the X-ray Pattern of the Contact Interlayer of the Sb–Te System under Flash Heating (radiation wavelength of $\mathrm{Cu}_{K\alpha}$ $\lambda = 1.5418$ Å)

N	*I*	Θ	*d*	*hkl*	Composition
1	v.w	13.81	3.23	101	Te
2	v.w	14.36	3.109	102	Sb
3	w	14.75	3.05	015	Sb_2Te_3
4	m	19.14	2.351	102	Te
5	m	20.05	2.248	014	Sb
6	s	21.3	2.16	110	Sb_2Te_3
7	w	24.84	1.835	201	Te
8	m	26.2	1.79	119	Sb_2Te_3
9	w	28.49	1.616	202	Te
10	s	31.7	1.53	2.0.11	Sb_2Te_3
11	v.w	32.95	1.48	1.1.15	Sb_2Te_3
12	m	36.95	1.36	125	Sb_2Te_3
13	v.w	38.45	1.32	1.1.18	Sb_2Te_3
14	w	41.04	1.174	213	Te
15	w	47.30	1.15	2.0.25	Sb_2Te_3
16	w	52.2	1.08	2.0.23	Sb_2Te_3
17	v.w	47.84	1.039	222	Te
18	v.w	55.6	0.934	226	Sb
19	w	59.13	0.898	0.2.11	Sb
20	v.w	62.70	0.867	305	Te

Note. v.w = very weak, w = weak, m = medium, s, strong radiation.

metastable phase can also be observed with a microscope (Fig. 5). In such a form it is able to stay at room temperature for 2–3 days.

The increase in the autothermal e.m.f. of the contact (Fig. 4, curve 2, section c) is due to the exothermal reaction of Sb_2Te_3 compound formation. However, the released heat does not suffice to increase the contact temperature to the formation temperature of a stable eutectic. In many events, the appearance of the secondary liquid phase is not registered by the displacement pickup (Fig. 4, curve 3).

In the course of time there occurs a smooth descent of the autothermal e.m.f. curve in section c (Fig. 4, curve 2). This is due to the difficulty of further formation of intermetallide Sb_2Te_3. When the furnace is turned off, a decrease in the chamber temperature and, accordingly, a decrease in the autothermal e.m.f. in the contact zone begin. The jump on the autothermal e.m.f. curve (Fig. 4, curve 2, section d) after the furnace is turned off is explained by the additional formation of the intermediate phase Sb_2Te_3 due to the crystallization of the contact interlayer.

Microscopic and radiographic studies of contact interlayers frozen in liquid nitrogen revealed no intermediate phase Sb_2Te_3 and no eutectic of tellurium with this compound. The results of the calculation of X-ray patterns of specimens from the material of the nitrogen-vapor-frozen interlayer zone give only lines of pure components Sb and Te (see the Table 1). The studies of the concentration distribution of the components in the contact interlayer made on a "*Camera*" X-ray microanalyzer (France) point to the absence of the Sb_2Te_3 compound from the interlayer.

Figure 6 gives the average rates of CF in the stationary and nonstationary regimes under slow and flash heating of specimens. From a comparison of the temperature dependence of curves 1 and 2 it is seen that in the first case

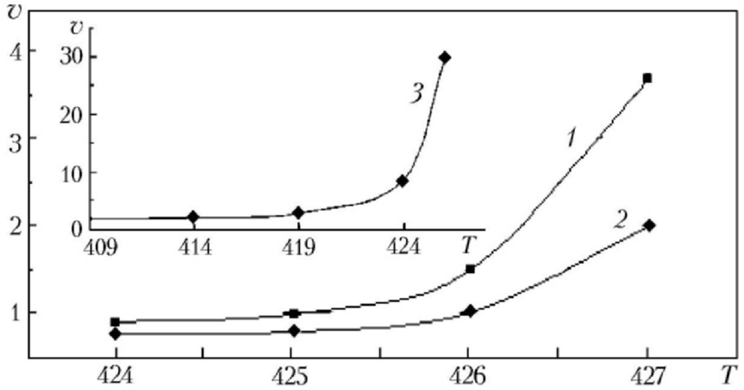

Fig. 6. Curves of the time dependences of the average CF rate in the Sb–Te system: 1, 2) under slow heating in the stationary and nonstationary regimes, respectively; 3) under flash heating in the stationary regime. v, mm/min; T, ^{o}C.

the CF rate increases faster than in the second one. This is due to the fact that in the second case at the start of the process the rapidly growing liquid interlayer attenuates the diffusion flow of atoms of the components through it. The CF rate under flash heating of the contact at 410–413^{o}C does not exceed 2 mm/min; however, as the temperature is increased to 426^{o}C, it sharply increases to 30 mm/min (Fig. 6, curve 3).

All these results, as well as the investigations of the microhardness of the contact interlayer (Fig. 7) obtained at 410^{o}C, have shown that in the Sb and Te contact under flash heating first the metastable liquid interlayer Sb + Te representing an eutectic of pure components is formed. The microhardness of this phase has an intermediate value as compared to the microhardness of the pure components.

Under secondary slow heating of specimens with a solidified metastable Sb + Te interlayer fusion occurs at 424^{o}C, and in so doing, on the side of tellurium an Sb_2Te_3 intermetallide layer is formed, and then an $Sb_2Te_3 + Te$ interlayer follows. But if specimens with an Sb + Te interlayer are placed in the furnace preheated to 410^{o}C, then this interlayer fuses and its crystallization occurs with the formation of the Sb_2Te_3 compound.

To verify the experimental data, we constructed by the method of [6] a metastable state diagram possible for the Sb–Te system. The CF temperature of the calculated metastable eutectic Sb + Te (410^{o}C) with a concentration $x_{\text{eut}} = 0.585$ coincides with the CF temperature under flash heating.

To exclude the thermal hypothesis of hypoeutectic contact fusion (HCF), we also made a theoretical quantitative estimate of the temperature increase in the contact zone to the stable eutectic temperature (424^{o}C) by the thermodynamic data of [7–9] due to the exothermal reaction ($2Sb + 3Te \rightarrow Sb_2Te_3$) of compound Sb_2Te_3 formation at a temperature of 410^{o}C. Calculations were made with the provision that at 410^{o}C upon flash heating the thickness of the Sb_2Te_3 interlayer does not exceed 0.45 mm after holding for up to 5 min. These assumptions were made in favor of the thermal hypothesis.

The calculations have shown that for the Sb–Te system the quantity of heat released due to the exothermal reaction of compound Sb_2Te_3 formation is insufficient for increasing the temperature of the contact zone of specimens from 410^{o}C (furnace temperature) to 424^{o}C (fusion temperature of the $Sb_2Te_3 + Te$ eutectic).

The results of experiments under flash heating of the contact of specimens in the Sb–Te system can be interpreted in accordance with the Ostwald step rule [10]. In so doing, the transition of the system from the initial nonequilibrium state to the equilibrium state occurs definitively through a sequence of intermediate states each of which has a lower thermodynamic potential compared to the previous one. In the contact, the metastable liquid phase should be the first to appear, which is explained by the smaller surface energy of the liquid–crystal system compared to the surface energy between the initial crystals and the growing intermediate compound [11]. Then this liquid crystallizes to form a chemical compound.

In accordance with the above hypothesis it may be assumed that the CF process occurs in the following sequence: 1) formation of a nonequilibrium system upon bringing the specimens into contact; 2) CF with the formation of a metastable liquid; 3) crystallization of the metastable liquid with the formation of the intermediate Sb_2Te_3 phase.

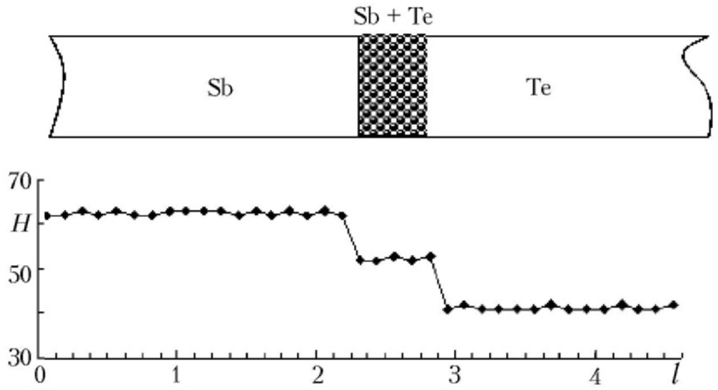

Fig. 7. Change in the microhardness along the contact interlayer of the Sb–Te system obtained at 410°C (flash heating) and frozen by nitrogen vapors. *H*, kg/mm^2; *l*, mm.

The initiation of a new phase in a nonequilibrium system has a probabilistic character. As applied to the phenomenon under consideration, this means that the formation of a metastable liquid phase in the contact of specimens inevitably leads with time to the initiation and development of a stable intermediate phase. The process of interlayer formation ends with the suppression of the growth of the metastable liquid phase Sb + Te and its adsorption by the growing compound Sb_2Te_3. And the crystallization front velocity in a supercooled melt is usually assumed to be constant. Therefore, at the first stage upon contacting, the metastable liquid phase grows faster than the solid intermediate phase, but in the course of time the growth rate of the liquid phase decreases at a constant growth rate of the solid phase. Therefore, in due course, the metastable liquid phase completely crystallizes. However, a decrease in the rate of motion of the liquid phase boundaries does take place because of the gradual mutual withdrawal of the liquid-feeding boundaries and the interfering influence of the growing intermediate solid phase [12].

Conclusions. The formation of the metastable Sb + Te eutectic has been established by us experimentally, proved by X-ray structural, micro-X-ray spectroscopic, and microstructure analyses of the contact interlayers, and by theoretical calculations, as well as by secondary fusion. We explain the formation of hypoeutectic CF in the given system by the formation of the metastable Sb + Te eutectic. Experiments confirm the stepwise character of the relaxation processes in the contact fusion of massive specimens, and the hypothesis about the proceeding of metastable processes is verified.

NOTATION

$Cu_{K\alpha}$, X-rays obtained by irradiating a copper cathode by helium atoms; *d*, interplanar spacing in the crystal, Å; *H*, microhardness, kg/mm^2; *hkl*, Miller indices — unique notation for a plane in the crystal; *I*, intensity of X-rays reflected from atomic planes, is determined visually (or interferometrically) by the blackness of lines in the X-ray photograph; *l*, intermetallide thickness, mm; *N*, line numbers in the X-ray photographs; *t*, time, sec, min; *T*, temperature, °C, K; *U*, voltage at the ends of specimens resulting from the contact heating due to the Seebeck effect, mV; *v*, rate of relative motion of specimens due to the formation of the liquid phase in the contact, mm/min; x_{eut}, concentration, %; Θ, angle of reflection of X-rays from atomic planes, deg; λ, wavelength, Å. Subscripts: c.f, contact fusion; eut, eutectic.

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