Metallophysics and Advanced Technologies
Металофіз. новітні технол.
Metallofiz. Noveishie Tekhnol.
2021, vol. 43, No. 2, pp. 209–217
https://doi.org/10.15407/mfint.43.02.0209
Reprints available directly from the publisher

© 2021 G. V. Kurdyumov Institute for Metal Physics,
National Academy of Sciences of Ukraine
Published by license under
the G. V. Kurdyumov Institute for Metal Physics–
N.A.S. of Ukraine Publishers imprint.
Printed in Ukraine.

CRYSTAL-LATTICE DEFECTS

PACS numbers: 68.35.Fx, 68.37.Xy, 81.05.Bx, 81.15.Jj, 81.20.Vj, 85.30.Hi

Investigation of Mass-Transfer Features at Using of Ion-Modified Blocking Layer in Commuting Plate of Thermoelements

V. F. Mazanko, Iu. V. Falchenko[*], O. O. Novomlynets[**],
I. V. Nahorna[**], and S. M. Yushchenko[**]

G. V. Kurdyumov Institute for Metal Physics, N.A.S. of Ukraine,
36 Academician Vernadsky Blvd.,
UA-03142 Kyiv, Ukraine
[*]*E. O. Paton Electric Welding Institute, N.A.S. of Ukraine,*
11 Kazymyr Malevych Str.,
UA-03150 Kyiv, Ukraine
[**]*Chernihiv Polytechnic National University,*
95 Shevchenko Str.,
UA-14035 Chernihiv, Ukraine

The problem of operation reliability of thermoelectric modules remains topical. Owing to pronounced anisotropy of properties and growth of the rate of semiconductor atoms' mobility, the diffusion of conductor atoms into semiconductor can occur in thermoelements. For prevention of diffusion of conductor atoms into semiconductor and for increasing of thermoelement useful life, diffusive barrier layers are applied for separating commuting plate and semiconductor material in their contact. Deposition of such barrier layers can be realized by different methods, but in all cases the layer is deposited on the semiconductor surface, thus the effectiveness of thermoelectric modules reduces. At present work, mass-transfer processes at diffusion welding in vacuum of copper and nickel through ion-modified layers are investigated. The expediency of prior modification of copper surface (commuting plate) by chromium for creation the barrier antidiffusive layer is determined. Using radioactive isotope method, it is defined the features of diffusive interaction of contact materials through surface layers of copper modified by chromium

Corresponding author: Volodymyr Fedorovych Mazanko
E-mail: vmazanko@imp.kiev.ua

Citation: V. F. Mazanko, Iu. V. Falchenko, O. O. Novomlynets, I. V. Nahorna, and S. M. Yushchenko, Investigation of Mass-Transfer Features at Using of Ion-Modified Blocking Layer in Commuting Plate of Thermoelements, *Metallofiz. Noveishie Tekhnol.*, **43**, No. 2: 209–217 (2021), DOI: 10.15407/mfint.43.02.0209.

due to ion treatment. As shown, the presence of such layers results in retardation of diffusive processes twice comparatively with contact interaction without modified layer. Blocking effect of such modified layer is confirmed by Auger electron spectroscopy on the example of heterogeneous joints of pair copper–nickel. As shown, a diffusion zone width after modification copper by chrome became 20 times lesser than one in non-modified sample.

Key words: antidiffusive barrier layer, diffusion welding, ion treatment, mass-transfer processes, radioactive isotope method, Auger electron spectroscopy.

Проблема підвищення надійності роботи термоелектричних модулів залишається актуальною. Внаслідок наявності різко вираженої анізотропії властивостей та швидкості росту рухливості атомів напівпровідника у термоелементах може відбуватися дифузія атомів шару провідника у напівпровідник. Все це призводить до зниження надійності та тривалості експлуатації термоелектричних елементів. Для запобігання дифузії атомів провідника у напівпровідник та підвищення терміну служби термоелементів застосовують дифузійні бар'єрні шари, які розділяють комутувальну пластину та напівпровідниковий матеріал у місці їх контакту. Нанесення таких бар'єрних прошарків може здійснюватися різними способами, однак у всіх випадках прошарок наноситься на поверхню напівпровідника, що знижує ефективність термоелектричних модулів. У даній роботі досліджено процеси масоперенесення у разі дифузійного зварювання у вакуумі міді та нікелю через модифіковані йонною обробкою прошарки. Встановлено доцільність попередньої модифікації поверхні міді (комутувальної пластини) Хромом для створення бар'єрного антидифузійного прошарку. З використанням методу радіоактивних ізотопів визначено особливості дифузійної взаємодії контактувальних матеріалів через поверхневі шари міді, модифіковані Хромом за допомогою йонної обробки. Показано, що наявність таких шарів сповільнює швидкість дифузійних процесів удвічі порівняно з контактною взаємодією без модифікованого шару. Блокувальний ефект такого модифікованого шару підтверджено також за допомогою електронної Оже-спектроскопії у з'єднаннях із різнорідних матеріалів на прикладі пари мідь–нікель. Показано, що ширина зони дифузійної взаємодії у разі модифікації міді Хромом у 20 разів менша, ніж у немодифікованого зразка.

Ключові слова: антидифузійний бар'єрний прошарок, дифузійне зварювання, йонна обробка, масоперенесення, метод радіоактивних ізотопів, електронна Оже-спектроскопія.

(Received September 17, 2020)

1. INTRODUCTION

The creation of qualitative barrier layers is one of the important tasks during designing and fabrication of semiconductive thermoelements. Antidiffusive layer (diffusive barrier) prevents passing of mutual diffusion of conductor material into semiconductor. These layers must ensure low-level specific resistance of ohmic contact and adhesion strength [1]. Nowadays, antidiffusive layers have deposited on the semiconductor surface by different methods. However, existent technologies of antidiffusive layer making, in most cases, have a negative influence on operation of thermoelements under high temperatures. It causes by increase of transition layer consisted of solid solutions as affected of temperatures. Whereas solid solutions have low mechanical strength, it causes reduction of contact strength [2–4].

It is possible to solve this problem by creation of antidiffusive layer on the surface of conductor using the effect of penetration of metal atoms from the surface deep into macroscopic distances of substrate under low temperature (up to 473 K) in conditions of ion bombardment in glow discharge [5]. At work [6] it has been determined, that the most optimal material for barrier layer can be chrome whereas copper with chrome has significantly limited solubility, and chemical-resistant chrome oxide in the transition zone additionally intensify blocking effect.

In this connection, it is necessary to investigate blocking effect of such layers. Radioactive isotope method and Auger electron spectroscopy are widely used as effective methods of studying of diffusive processes. Their high sensitivity, accuracy and informativity allow to investigate mass-transfer processes and to analyse character of element distribution in welded joints at diffusive welding in vacuum [7–9]. The effectiveness of these methods confirmed at works [10, 11].

2. EXPERIMENTAL METHODOLOGY

The results of investigation of atom redistribution and diffusion rate at diffusion welding of copper and copper with nickel through ion-modified layers have presented at this work.

Copper details with dimensions $10\times8\times4$ mm^3 and copper and nickel samples with dimensions $12\times7\times3$ mm^3 have been used for investigations. On the copper surface, the chromium layer by 3 mm thickness had been deposited by ion-plasmic method using technique defined at [5]. Then all copper details with chromium layer, except basic, had been subjected to treatment by argon ions for making antidiffusive barrier layer. Deposition of chromium layer had been realized on the vacuum plant for resistive spraying URN-3. After that, the diffusion welding had been carried out on the modernized plant VU-1A. Conditions of surface preparation and welding conditions have been presented at Table 1.

The effect of blocking of copper diffusion by chromium layer, first of all, had been studied on the welded joints of pair Cu–Cu (sample 1 and 2).

For the purpose of confirmation of presence the blocking effect in heterogeneous thermoelectric materials, the investigation by the example of pair Cu–Ni had been carried out (sample 3 and 4), as far as materials which are sufficiently widely used on practice for fabrication of thermoelements [2–4]. It is necessary to point, that values of the annealing temperature correspond to operating and application conditions of thermoelement.

3. RESULTS AND DISCUSSIONS

The sample 1 (conditions I) is basic. Other conditions differ from basic and from each other by argon ion treatment of Cr barrier layer and carrying out of annealing of ion-modified layer during temperature-time conditions.

Conditions I and II (Table 1) correspond the investigations of welded joints Cu–Cu. Diffusion processes in the contact zone had been studied by autoradiography method. Radioactive isotope of cobalt ^{60}Co with beta emission energy 1.48 MeV had been used. It had been deposited by electrolytic method on one of the surfaces of Cu. The isotope layer had the thickness ~0.3–0.5 μm and the activity $5\cdot10^3$ impulse per minute.

Assembly of copper details before welding had been carried out by the scheme: Cu (^{60}Co)–Cu (sample 1) and Cu (^{60}Co)–(Cr) Cu (sample 2). Detail with radioactive isotope ^{60}Co had been put from below. After welding samples had been placed on photosensitive film for autoradiography with following exposure on it during 14 days. Then the film had been developed and photometered. After that, the concentration distribution of radioactive isotope into pure copper and ion-modified copper is determined. Assessment of mass-transfer coefficient values had been realized by technique described at [7].

The estimate of mass-transfer coefficients had carried out by Einstein's formula [12]:

$$D = X^2/2\tau, \quad (1)$$

TABLE 1. Preparation and welding conditions of samples.

Number of		T_{weld},	τ_{weld},	τ_{treat} Ar,	U_{accel},	P,	Cr layer thickness,	T_{anneal},	τ_{temp},
sample	cond.	°C	min		V	MPa	μm	°C	hours
1	I	850	30	0	0	5	0	0	0
2	II	850	30	60	500–600	5	3	0	0
3	III	900	30	0	0	5	0	350	2
4	IV	900	30	60	500–600	5	2	350	2

where X—isotope penetration depth, cm; τ—welding process duration, s.

The analysis of autoradiograph impresses shown that number of relational nigrescence units (S) is directly proportional to concentration of radioactive isotope in samples. At Figure 1, the concentration curves of isotope ^{60}Co distribution in Cu, as a result of diffusion welding in conditions I and II, are presented (detail with radioactive isotope—at the left).

The study of concentration curves shows that in both cases of welding the results vary by form of curves and by isotope penetration depth. The results of analysis of concentration curves are presented in Table 2.

Sample 1. In this case isotope penetration depth into the detail with isotope is equal to 165 μm, and into opposite one it is 115 μm. Values of mass-transfer coefficients, found by Einstein's formula, are: $7.6 \cdot 10^{-8}$ cm^2/s in the left detail and $3.7 \cdot 10^{-8}$ cm^2/s in the right one, that is the ratio of coefficients is equal 2.1. Thus, motility of isotope into the detail with isotope is in 2.1 times higher than in the detail without it.

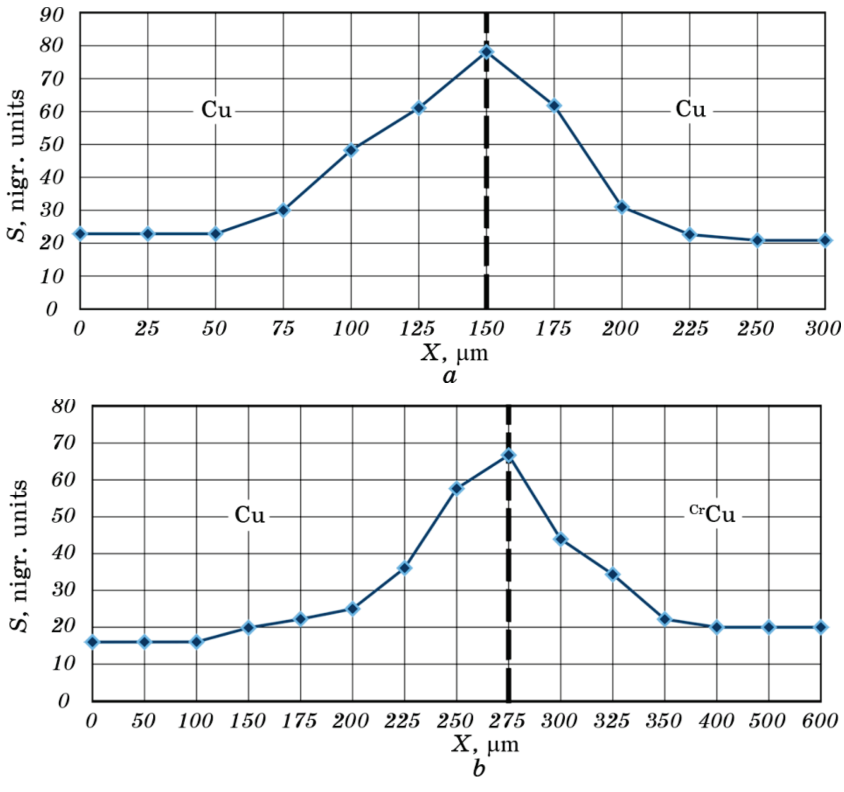

Fig. 1. Concentration curve distribution of ^{60}Co in Cu as the result of diffusion welding Cu + Cu: under conditions I (a), under conditions II (b).

TABLE 2. Results of analysis of concentration curves.

No. of sample	X, μm		τ_{treat} Ar, min		τ_{weld}, min		U_{accel}, V	
	Cu (^{60}Co)	Cu	Cu (^{60}Co)	Cu	Cu (^{60}Co)	Cu	Cu (^{60}Co)	Cu
1	115	85	–	0	30	30	0	0
2	165	115	–	60	30	30	500–600	500–600

Sample 2. Isotope penetration depth in this case is less than in the sample 1. It is equal about 115 μm into the detail with isotope and 85 μm into opposite one. The estimate of mass-transfer coefficients gave such results: $3.7 \cdot 10^{-8}$ cm^2/s in the left detail, $2.0 \cdot 10^{-8}$ cm^2/s in the right one. The ratio is equal 2.

It is worth mentioning that in both cases the asymmetry of concentration curves regarding contact surface occurs. The asymmetry can be concerned with the presence of stress gradient at the contact zone.

Findings of investigation of mass-transfer in copper samples are given at Table 3. The data obtained allow to assert that the diffusion rate in modified sample is twice lesser than in non-modified one. Lowering of diffusion rate in modified sample is probably connected with decrease of diffusive penetrability of grain boundaries [13, 14].

The next stage of investigation has been carried out by the example of pair copper-nickel using Auger electron spectroscopy. This stage has been realized to confirmation of blocking effect due to chromium layer at the operational regime of thermoelectric elements. The conditions III and IV correspond to study of such samples. The assembly of details before welding has been realized by scheme: Cu–Ni (sample 3) та Cu (Cr)–Ni (sample 4).

At the heart of Auger electron spectroscopy method underlies the measurement of energy and quantity Auger electrons, which are arised at bombardment of solid surface by electron beam with the energy of a few keV that characterizes element composition of the first monolayers. This method allows studying element distribution on the surface with high spatial distribution and locality (under 0.1 μm) [15].

The investigation has been carried out at the base of E. O. Paton Electric Welding Institute of the National Academy of Sciences of

TABLE 3. Characteristics of diffusive processes as the result of mass-transfer in of Cu + Cu.

No. of sample	D_m, cm^2/s		$D_m^{Cu(^{60}Co)} / D_m^{Cu}$	lg(D_m)	
	Cu (^{60}Co)	Cu		Cu (^{60}Co)	Cu
1	$7.6 \cdot 10^{-8}$	$3.7 \cdot 10^{-8}$	2.1	−7.1	−7.4
2	$3.7 \cdot 10^{-8}$	$2.0 \cdot 10^{-8}$	2.0	−7.4	−7.7

Ukraine. It has been used Auger microprobe JAMP-9510F, which possesses the highest spatial distribution in the world. It also allows getting picture of sample surface, assessing homogeneity of material, carrying out the element mapping [15].

The results obtained and distribution curves of elements lengthways of welded samples along spectrum 1 have been presented at Figs. 2 and 3, correspondingly.

It is followed from the analysis of concentration distribution that the diffusive layer width in the sample 4 (conditions IV) is equal about 1 μm, whereas it is nearly 20 μm in the sample 3 (conditions III).

Consequently, the results of diffusive processes investigation due to Auger electron spectroscopy also confirm the effectiveness of blocking action of ion-modified surface layer of copper by chromium. The diffusive zone width in the welded sample with intermediate antidiffusive layer is 20 times lesser than one in samples welded directly.

Using element analysis by Auger spectrometer it had been deter-

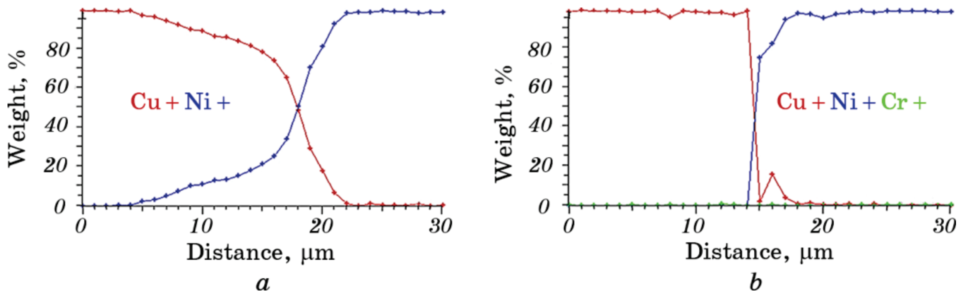

Fig. 2. Concentration of elements along welded specimen as the result of diffusion welding of Cu + Ni (spectrum 1, Fig. 3): under conditions III (*a*), under conditions IV (*b*).

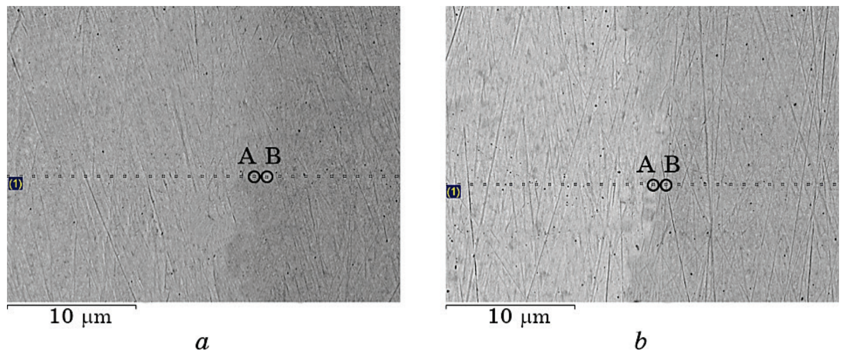

Fig. 3. Photographs of welded zone as the result of diffusion welding of Cu + Ni: under conditions III (*a*), under conditions IV (*b*).

TABLE 4. Transition zone element composition as the result of diffusion welding of Cu + Ni (% by weight).

No. of sample	C	O	Ni	Cu	Cr
3 (point A)	0.8	0.2	69.88	29.12	–
3 (point B)	1.37	0.6	80.62	17.41	–
4 (point A)	1.66	0.18	0	98.17	0
4 (point B)	1.38	0.28	96.64	1.7	0

mined the percentage composition of elements in the transition zone of welded joint. The results of analysis along spectrum 1 in the points A and B (Fig. 3) are presented at Table 4.

The results shows that at the transition zone of modified sample 4 the sharp change of percentage composition of Ni and Cu (74.64% and 96.47% at point A and point B, respectively) is observed, while in the non-modified sample 3 this change insignificant (10.74% and 11.71%, respectively). This fact is evidence of considerable decrease of penetration depth of copper into nickel owing to blocking action of modified layer.

The general results of investigation show the availability of blocking effect due to ion-modified chromium layer on the surface of commuting copper plate that hereafter will permit to improve present technology of fabrication the thermoelements, ensure the stability of their operating characteristics and increase the lifetime of thermoelectric modules.

4. CONCLUSIONS

It has been determined the effectiveness of making ion-modified antidiffusive layer of chromium on the surface of copper purposely prevention of copper diffusion into the semiconductor when production and operation of thermoelements. Using the autoradiography method it has been defined that diffusion rate of isotope ^{60}Co in ion-modified copper twice lesser than in copper without modification. By means of Auger electron spectroscopy, using copper-nickel welded joints it has been ascertained, that the diffusion zone width in the presence of antidiffusive layer is 20 times lesser than in welded samples obtained directly.

REFERENCES

1. Ya. Ya. Kudrik, *Tekhnologiya i Konstruirovanie v Elektronnoy Apparature*, No. 6: 3 (2013) (in Russian).
2. R. Hara, I. Aoyama, K. Tomita, and K. Ishida, *Thermoelectric Module*, Patent

6700053B2 US (Published March 2, 2004).
3. V. M. Bashkov, A. O. Belyaeva, T. A. Gorbatovskaya, S. A. Meshkov, O. S. Naraykin, A. S. Osipkov, D. G. Ryabinin, K. N. Talakin, I. A. Fedorenko, and V. D. Shashurin, *Sposoby Izgotovleniya Termoelektricheskogo Modulya s Uvelichennym Srokom Sluzhby* [Method of Production of Thermoelectric Module with Enlarged Useful Life], Patent 2425434 RU (Published April 27, 2011) (in Russian).
4. C. Uher, *Skutterudite-Based Thermoelectrics. Handbook of Thermoelectrics* (Ed. D. M. Rowe) (CRC Press: 2006).
5. G. P. Bolotov, M. G. Bolotov, and M. M. Rudenko, *2016 IEEE 36th Int. Conf. on Electronics and Nanotechnology (Apr. 19–21, 2016)* (Kyiv, Ukraine: 2016).
6. G. K. Kharchenko, O. O. Novomlynets, I. O. Prybytko, and I. V. Nagorna, *2016 II Int. Young Sci. Forum on Applied Physics and Engineering (Oct. 10–14, 2016)* (Kharkiv, Ukraine: 2016).
7. B. S. Bokshtien, S. S. Ginsburg, S. T. Kishkin, and L. M. Moroz, *Elektronno-Mikroskopicheskaya Avtoradiografiya v Metallovedenii* [Electron-Microscopy Autoradiography in Material Science] (Moscow: Metallurgiya: 1978) (in Russian).
8. V. F. Popov and Yu. N. Gorin, *Protsesy i Ustanovki Elektronno-Ionnoy Tekhnologii* [Processes and Plants of Electron-Ion Technology] (Moscow: Vysshaya Shkola: 1988) (in Russian).
9. V. F. Mazanko, A. V. Pokoev, V. M. Mironov, D. S. Gertsriken, D. V. Mironov, D. I. Stepanov, and G. V. Lutsenko, *Diffusionnye Protsesy v Metalakh pod Deystviem Magnitnykh Poley i Impulsnykh Deformatsiy* [Diffusive Processes in Metals under Magnetic Field and Impulse Deformations] (Moscow: Mashinostroenie: 2006), vol. 1 (in Russian).
10. V. F. Mazanko, G. K. Kharchenko , T. R. Hanieiev, O. O. Novomlynets, and I. V. Zavalna, *Metallofiz. Noveishie Tekhnol.*, **37**, No. 2: 233 (2015).
11. O. O. Novomlynets, S. V. Oleksiienko, S. M. Yushchenko, M. G. Bolotov, and I. V. Nahorna, *2019 IEEE 2nd Ukraine Conf. on Electrical and Computer Engineering (July 2–6, 2019)* (Lviv, Ukraine: 2019).
12. J. Manning, *Kinetika Diffuzii Atomov v Kristalakh* [Kinetics of Atom Diffusion in Crystals] (Moscow: Mir: 1971) (Russian translation).
13. P. Shjumon, *Diffuzia v Tverdykh Telakh* [Diffusion in Solids] (Moscow: Metallurgia: 1966) (Russian translation).
14. S. Z. Bokshtein, L. B. Vasilenok, Ye. N. Kablov, I. V. Radin, and G. G. Ryabova, *Mikrolegirovanie Borom i Strukturnaya Stabilnost Nikelevykh Splavov* [Microalloying by Boron and Structural Stability of Nickel Alloys] (1986) (in Russian).
15. *Sistemy Microanalyza* [Systems of Microanalysis] (Internet resource: http://surfanalysis.ru/products/auger/jamp-9510f.html).