A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
Volume 52 2007 Issue 4

A. WINIOWSKI*

IMPACT OF CONDITIONS AND PARAMETERS OF BRAZING OF STAINLESS STEEL AND TITANIUM ON MECHANICAL AND STRUCTURAL PROPERTIES OF JOINTS

WPŁYW WARUNKÓW I PARAMETRÓW LUTOWANIA TWARDEGO STALI NIERDZEWNEJ Z TYTANEM NA WŁASNOŚCI MECHANICZNE I STRUKTURALNE POŁĄCZEŃ

Joining of materials having diversified physical and chemical properties by means of welding methods and obtaining joints characterised by good operation properties constitutes today a significant problem in relation to research and technology. The issue concerns also the joining of stainless steels with titanium as well as with titanium-based alloys and composites. Apart from specialised welding technologies, brazing is one of the basic methods applied for joining such material combinations in the production of systems and heat exchangers for chemical industry as well as subassemblies of nuclear reactors and aircraft engines and accessories. Similarly as in case of welded joints of stainless steel and titanium, the mechanical properties of brazed joints of the aforesaid materials are connected with the occurrence of hard and brittle intermetallic phases appearing in the form of continuous layers on braze boundaries.

This work reports testing of strength properties and investigation of structures of vacuum-brazed joints of stainless chromium-nickel steel (X6CrNiTi18-10) and titanium (Grade 2) at 820÷900°C for 5÷40 min by means of silver brazing filler metal (B-Ag72Cu-780). The structural tests were conducted taking advantage of optical microscopy; by means of a scanning electron microscope (SEM), transmission electron microscope (TEM) and and energy-dispersion spectrometer (EDS). The test results enabled the identification of phases in brazes and their diffusion zones and proved that strength properties of joints depend on brittle and very hard layers of intermetallic phases such as $Cr_{13}Fe_{35}Ni_3Ti_7$, $CuTi_2$, $CuFeTi_2$ and CuTi types (with significant content of Fe) formed on the steel side. The determination of the kinetics of qualitative and geometrical changes in joint structures depending on temperature and brazing times allowed to specify the most convenient brazing parameters of the tested material system from the mechanical properties point of view.

Keywords: brazing, vacuum brazing, stainless steel, titanium, intermetalics phases, mechanical properties of brazed joints, brazing parameters

Łączenie metodami spawalniczymi materiałów o zróżnicowanych własnościach fizycznych i chemicznych oraz uzyskiwanie połączeń o wymaganych dobrych własnościach eksploatacyjnych stanowi ważny i aktualny problem badawczy oraz technologiczny. Dotyczy to między innymi połączeń stali nierdzewnych z tytanem a także stopami i materiałami kompozytowymi na osnowie tego metalu. Lutowanie twarde obok specjalistycznych metod spawania i zgrzewania jest jedną z podstawowych metod łączenia takich układów materiałowych w produkcji instalacji oraz wymienników ciepła dla przemysłu chemicznego, a także podzespołów reaktorów nuklearnych oraz osprzętu i silników lotniczych. Własności mechaniczne połączeń lutowanych stal nierdzewna-tytan, podobnie jak połączeń spawanych i zgrzewanych tych materiałów, są związane z występowaniem twardych i kruchych faz międzymetalicznych, wydzielających się w postaci ciągłych warstw na granicach lutowin.

W niniejszej pracy przeprowadzono badania własności wytrzymałościowych oraz badania struktur połączeń stali nierdzewnej chromowo-niklowej X6CrNiTi18-10 z tytanem Grade 2 lutowanych próżniowo w temperaturach 820÷900°C i czasach 5÷40 min lutem srebrnym B-Ag72Cu-780. Badania strukturalne prowadzono z wykorzystaniem mikroskopii świetlnej , mikroskopów elektronowych: skaningowego (SEM) i transmisyjnego (TEM) oraz spektrometru dyspersji energii (EDS). Wyniki badań pozwoliły na identyfikację faz w lutowinach i ich strefach dyfuzyjnych a także wykazały, że za własności wytrzymałościowe połączeń odpowiedzialne są powstające od strony stali kruche i bardzo twarde warstwy faz międzymetalicznych typu $Cr_{13}Fe_{35}Ni_3Ti_7$. $CuTi_2$, $CuFeTi_2$, i CuTi (z dużą zawartością Fe). Określenie kinetyki zmian jakościowych i geometrycznych w strukturach połączeń w zależności od temperatur i czasów lutowania pozwoliło na ustalenie najkorzystniejszych ze względu na własności mechaniczne parametrów lutowania badanego układu materiałowego.

* INSTITUTE OF WELDING, 44-100 GLIWICE, BŁ. CZESŁAWA 16/18 STR., POLAND

1. Introduction

Joining of materials having diversified physical and chemical properties and obtaining joints characterised by good operation properties constitutes today a significant problem with reference to research and technology. The issue is related to constructions and subassemblies used in modern sectors of industry and economy as they take advantage of joints of stainless steels with light metals such as aluminium and titanium (being a reactive metal at the same time) as well as alloys and composites based on the aforesaid metals. Apart from specialised welding technologies, brazing is one of the basic methods applied for the joining of such material combinations [1÷8], particularly, due to low joining temperatures, convenient metallurgical conditions of the process and the possibility of combining subassemblies of structures composed of many elements of various shapes and dimensions.

Brazing is especially recommendable for joining stainless steels and titanium in the production of systems and heat exchangers for chemical industry as well as subassemblies of nuclear reactors and aircraft engines and accessories. Furthermore, quite often in case of titanium constructions, technical specifications allow for the replacement of some titanium elements with those made of considerably cheaper stainless steel. This, however, is conditioned by good operation properties (especially mechanical) of joints. Brazing is applicable also in the aforesaid area.

Similarly as in case of welded joints of stainless steel and titanium, the mechanical properties of brazed joints of the aforesaid materials are connected with the occurrence of hard and brittle intermetallic phases [9,11÷14]. Titanium, being a reactive metal, forms intermetallic phases with the basic components of most brazing filler metals. Particularly negative on the mechanical properties of brazed joints is the impact of intermetallic phases formed in a peritectic reaction as continuous brittle and hard layers on braze boundaries. Such layers, poorly connected to a parent metal and braze, being significantly different from them in relation to thermal expansion coefficient, facilitate cracking as early as at the stage of braze solidification. In the event of the occurrence of tensile or shearing stress, the layers are also responsible for significant weakening of the joint.

Available information concerning mechanical properties of such joints, usually formed with silver brazing filler metals, is quite diversified and so are recommendable temperature- and time-related brazing parameters [1÷9, 18÷22]. It has also been impossible to trace scientific and technical publications containing detailed information about the structural investigation of the aforesaid joints.

This article presents the results of tests related to time and temperature conditions of vacuum brazing of stainless chromium-nickel steel with titanium by means of Ag72Cu28 brazing alloy (B-Ag72Cu-780) and their impact on the quality and mechanical properties as well as the structure of joints.

The purpose of the above investigation was to determine the optimum technological brazing conditions ensuring the best possible quality and mechanical properties of joints.

2. Course and results of tests

2.1. Parent and brazing filler metals

The following parent metals were used during the investigation:

- stainless steel – a rod of a diameter of 28 mm, grade X6CrNiTi18-10 pursuant to PN-EN 10088-1, with the chemical composition according to the analysis (% m/m): 0.017%C; 18.09%Cr; 9.64%Ni; 0.78%Si; 1.37%Mn; 0.20%Ti;
- titanium – a 25-mm thick sheet, Grade 2, pursuant to ASTM B 26579 (maximum impurity content: 0.1%C; 0.25%O; 0.03%N; 0.0125%H; 0.03%Fe).

The brazing filler metal used in the tests was silver brazing alloy, grade B-Ag72Cu-780 (AG 403) pursuant to PN-EN 1044:2004, with the chemical composition according to the analysis (% m/m): 72.45% Ag, the remaining part being Cu in the form of a band being 0.08 and 0.25 mm thick.

3. Preparation of joint samples for strength and structural tests

Shear strength tests and structural investigation of brazed joints of stainless steel (X6CrNiTi18-10) with titanium (Grade 2) involved the application of butt-brazed samples of cylindrical elements having slightly diversified diameters i.e. the stainless steel - ∅ 25×15 mm, the titanium – ∅ 20×15 mm.

Silver brazing filler metal (B-Ag72Cu-780) in the form of profiles having the dimensions of ∅ 20×0.25 mm and ∅ 20×0.08 mm was inserted between elements to be joined distancing in this way brazing gaps between these elements.

As it has been proved during tests conducted with limited wettability materials creating brittle phases in joints when used with brazing alloy, this type of a sample (cylindrical sample used for the testing of diffusion-brazed joints) ensures a free course of diffusion processes in a braze and features quite a strong reaction in case of the occurrence of brittle phases impairing the quality of joints [25, 26].

The brazing of steel-titanium samples etched in solutions of appropriate acids was performed in TORVAC-manufactured S-16 furnace in vacuum conditions within the range of $1.33{\cdot}10^{-1} \div 1.33{\cdot}10^{-2}$ Pa, applying brazing temperatures of 820, 860 and 900°C measured directly on the samples subject to brazing.

It should be here mentioned that the melting temperature of the B-Ag72Cu-780 brazing alloy amounts to 780 (779)°C and the model temperature of vacuum brazing of relatively easy wettable materials e.g. copper with the said solder does not exceed 810÷830°C.

The selection of brazing temperatures in case of steel-titanium joints was conditioned by the brazing properties of the metals to be joined. On the one hand, due to the occurrence of allotropic change ($\alpha \rightarrow \beta$) and excessive growth of titanium grains resulting in the reduction of titanium mechanical properties and creation of brittle intermetallic phases in a braze, the brazing temperature should not exceed 900°C. On the other hand, however, owing to the poor wettability of stainless chromium-nickel steel by silver brazing alloy in vacuum conditions, the brazing temperature should be over 850°C and even exceed 900°C [1÷9,15].

The hold time of the samples at the brazing temperature was selected within quite a vast range of 5÷40 min (accordingly: 5, 10, 15, 20 and 40 min) in order to learn the impact of this parameter on the course of structural changes in the joints. It needs to be emphasized that in case of titanium, the commonly recommended hold time should be possibly short in order to limit the formation of brittle intermetallic phases with brazing alloy components, especially with copper. However, in order to ensure complete wetting of stainless steel, a slightly longer time than that for brazing is required. Preliminary technological tests have proved that the time should not be shorter than 5 min.

4. Strength tests of brazed joints

The brazed joints were first subject to quality-related visual inspection. The inspection demonstrated the absence of complete fusion and propagation of the brazing filler metal in the gaps of joints performed at 820°C with hold time of 5 min. The joints formed at the temperatures and hold times of accordingly: 820°C/15÷40 min, 860°C/5÷40 min and 900°C/5÷40 min demonstrated a comparatively good quality and filled the brazing gaps completely. They also showed the side surface of the titanium element coated by the silver brazing alloy; titanium being better wettable with brazing silver in vacuum conditions than stainless steel. The joints performed at 860 and 900°C with the longest i.e. 40-minute hold time showed, in turn, slight erosion of the edges of the titanium element resulting from intense dissolution of the titanium in the brazing alloy.

Shear tests of the obtained cylindrical samples were performed with special jaw chucks eliminating the effect of transverse bending of the sample upon shearing. The tests were conducted by means of Instrom-made testing machine. The results are presented in Figure 1.

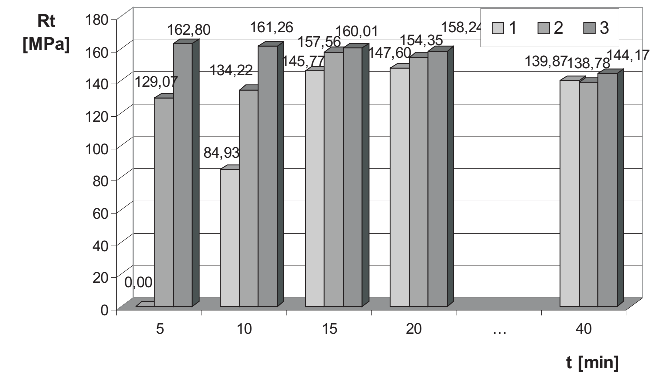

Fig. 1. Shear strength (Rt) for stainless steel – titanium joints brazed with B-Ag72Cu-780 silver brazing alloy at temperatures of 820°C (1), 860°C (2), 900°C (3) and time 5÷40 min

The test showed higher results for the joints performed with the 0.25 mm-thick brazing filler metal. All the samples became separated on the steel side. The highest values of shear strength were obtained at 900°C with the hold time of 5÷10 min (160÷162 MPa) and at 860°C with the hold time of 15 min (158 MPa). Quite a high strength was also characteristic of the joints performed at the above temperatures with the hold time of 20 min (154÷158 MPa) but the results obtained thus showed a relatively significant scatter of values. The remaining joints obtained at 820°C as well as 860 and 900°C, but with shorter or longer hold times, demonstrated lower strength properties (135÷147 MPa). The reasons for the weakening of such joints may be attributed to lower wettability of stainless steel at lower temperatures and shorter hold times and, which was demonstrated during the structural investigation, to the growth of brittle intermetallic phases at higher temperatures and longer hold times. However, the reason for slightly lower strength of the joints brazed with the brazing filler metal of lower thickness (0.08 mm) may be attributed to a proportionally higher fraction of brittle and hard phases in the braze of relatively lower thickness (containing less deposited metal formed from the brazing filler metal). Such a braze constitutes a sharper material and structural notch.

For comparison, the strength of the joints connecting elements of chromium-nickel (austenitic) stainless steel brazed with B-Ag72Cu-780 filler metal is 210÷250 MPa, whereas for joints connecting titanium elements it amounts to 130÷180 MPa [6÷10].

5. Metallographic and structural investigation of brazed joints

The joints of the X6CrNiTi18-10 stainless steel with titanium (Grade 2) brazed with the B-Ag72Cu-780 silver brazing alloy in specific and changeable technological conditions were subject to structural investigation including:

– observation of joint structures performed with Leica-manufactured MEF4M optical microscope;
– morphological investigation of sample surfaces carried out with JEOL-made JSM-6480 scanning electron microscope (SEM) featuring a pure tungsten cathode;
– qualitative and quantitative chemical analysis of phases in structures performed with IXRF-manufactured energy-dispersion spectrometer (EDS);
– diffraction analysis of phases conducted by means of JEOL-made JEM 3010 transmission electron microscope (TEM) equipped with an energy-dispersion spectrometer (EDS) and a "slow-scan" type of camera;
– measurements of microhardness of the phases in joint structures conducted with Wilson Wolpert-manufactured 401MVD microhardness tester.

The morphological investigation of sample surfaces by means of scanning electron microscope (SEM) with a pure tungsten cathode was performed using images obtained in secondary (SEI) and backscattered electrons (BEI).

The chemical analyses of phases by means of the spectrometer (EDS) were conducted using the standard calibration method. The chemical composition of the materials subject to tests was determined by means of IXRF-developed EDS2004 1.3 rev. M software. All the measurements were performed with accelerating voltage U_p = 20 kV and a working distance of 10 mm.

The diffraction tests of braze structures with transmission electron microscope (TEM) were performed using thin foils obtained by means of the cross-section method. Digitally recorded diffraction patters (electronograms) were initially analysed by means of the DigitalMicrograph programme. The further analysis of the aforesaid patterns was conducted with the ELFDyf programme used for a phase analysis on the basis of obtained point electronograms.

The tests conducted by means of the scanning electron microscope (SEM), transmission electron microscope (TEM) and energy-dispersion spectrometer (EDS) were performed at the Department for Structural Investigation of the Institute of Materials Science at Silesian University.

The results of the metallographic and structural investigation of the brazed joints of titanium and stainless steel demonstrated significant (related to titanium reactivity) diffusion changes in the brazes made with brazing alloy of eutectic structure and relatively big diffusion zones of the brazes on the boundaries with joined metals. The structures of the aforementioned brazes varied quite significantly depending on brazing temperatures (820, 860, 900°C) (Fig. 2÷7). As was demonstrated by the electron diffraction, the phases present in the structures were mostly solid solutions, often based on intermetallic phases. The compositions of the solutions were diversified and in some cases diverged from stoichiometric compositions attributable strictly to such phases [23, 24]; the decisive factor being the location in the braze structure.

On the titanium side the samples demonstrated the formation of an eutectoid structure of lamellar constitution composed of solid solutions of titanium and copper (AB-Fig.3÷5, Tables 1, 2). In the samples brazed at 900°C the arrangement of the solutions had three layers and was provided with characteristic acicular Widmanstätten structure (ABC-Fig. 6, 7, Table 3).

Under the two-phase lamellar layers, in the structures of the tested samples brazed at 820°C and 860°C, the layer of the phases of titanium and copper was detected; the said layer was composed of sublayers with Cu and Ag content growing towards the braze centre (CDE-Fig. 3, CDEF-Fig. 4, CDE- Fig. 5, Tables 1, 2). The diffraction electron analysis of the aforementioned area of joints revealed the existence of a complex structure. The sublayers, ending with a corrugated and pillared surface were composed of solid solutions based on the $CuTi_2$, CuTi and Cu_4Ti_3 (nearer the titanium) phases and on the Cu_3Ti_2 phase with particles of solutions based on the Cu_4Ti and Cu_2Ti intermetallic phases separated on the grain boundaries as well as of titanium and silver grains.

The solid solution based on the Cu_3Ti_2 phase was also present in the form of inclusions in the Cu-Ag eutectic structure, in the central part of the brazes prepared at 820°C (Y-Fig. 3, Table 1).

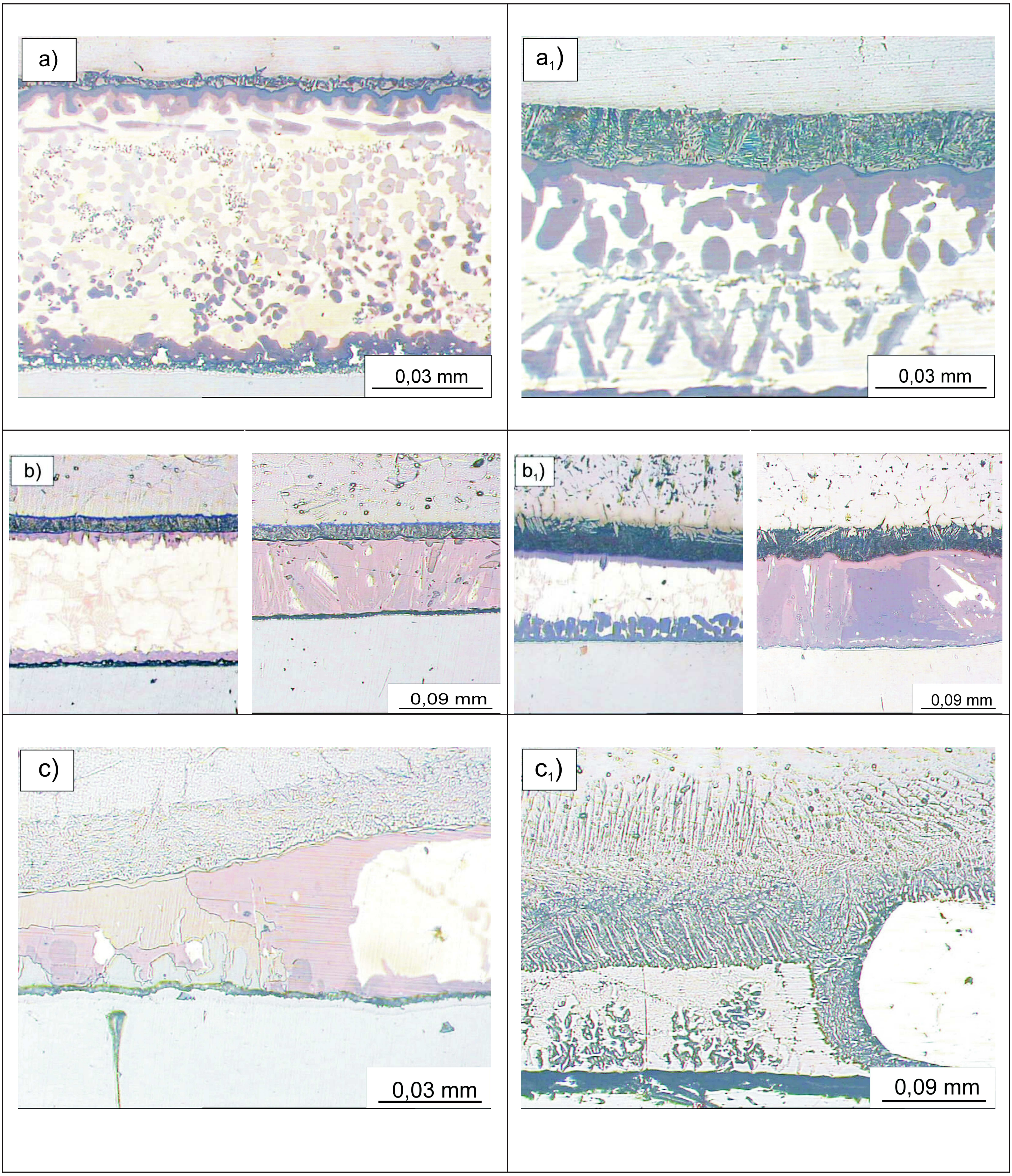

Fig. 2. Microstructure of stainless steel (down) – titanium (up) joints brazed with silver B-Ag72Cu-780 brazing alloy at temperatures of 820°C (a,a_1), 860°C (b, b_1), 900°C (c, c_1) and time 15 min (a, b, c) and 40 min (a_1, b_1, c_1)

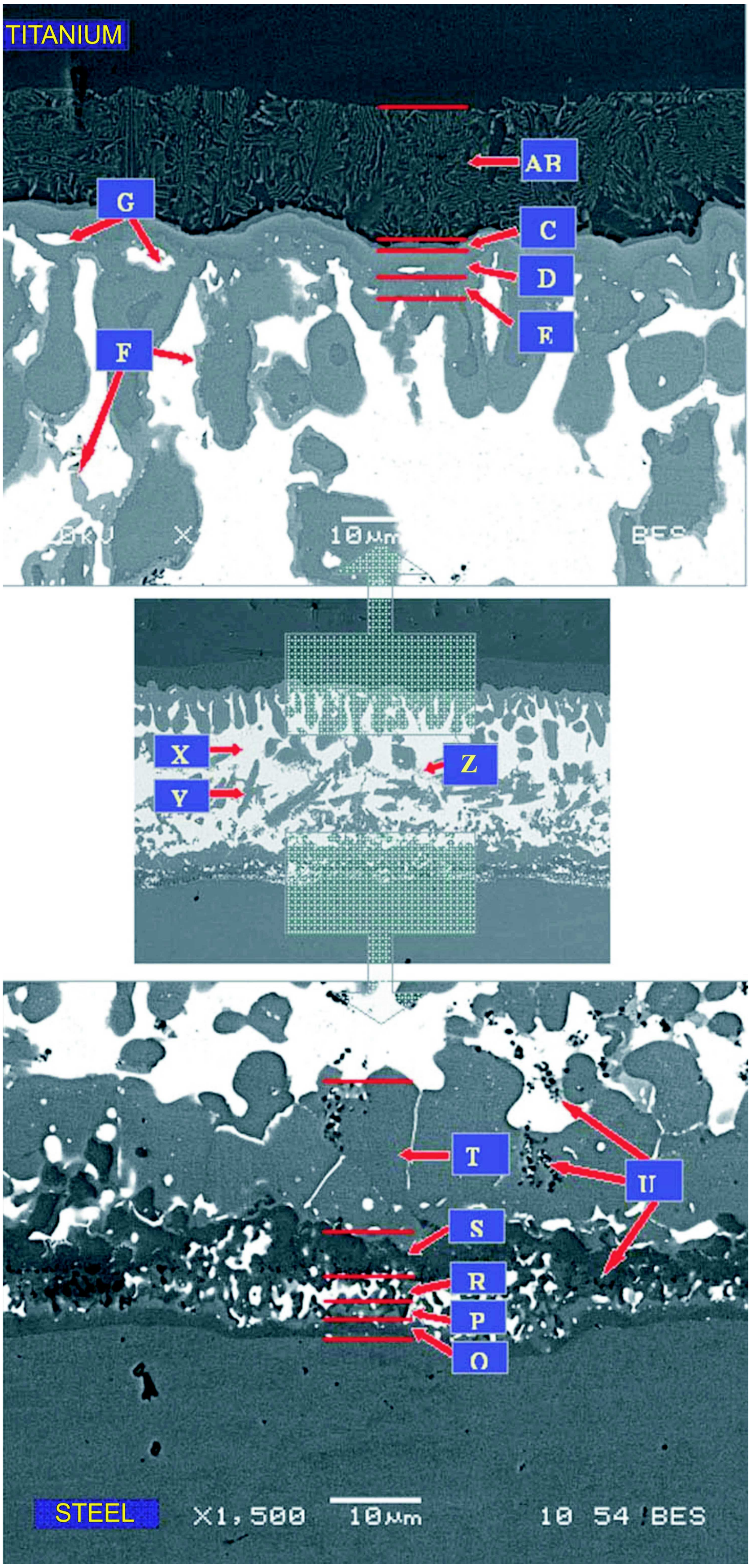

Fig. 3. Microstructure of stainless steel – titanium joint brazed with B – Ag72Cu-780 silver brazing alloy at temperature 820°C (phase composition – tabl. 1), SEM

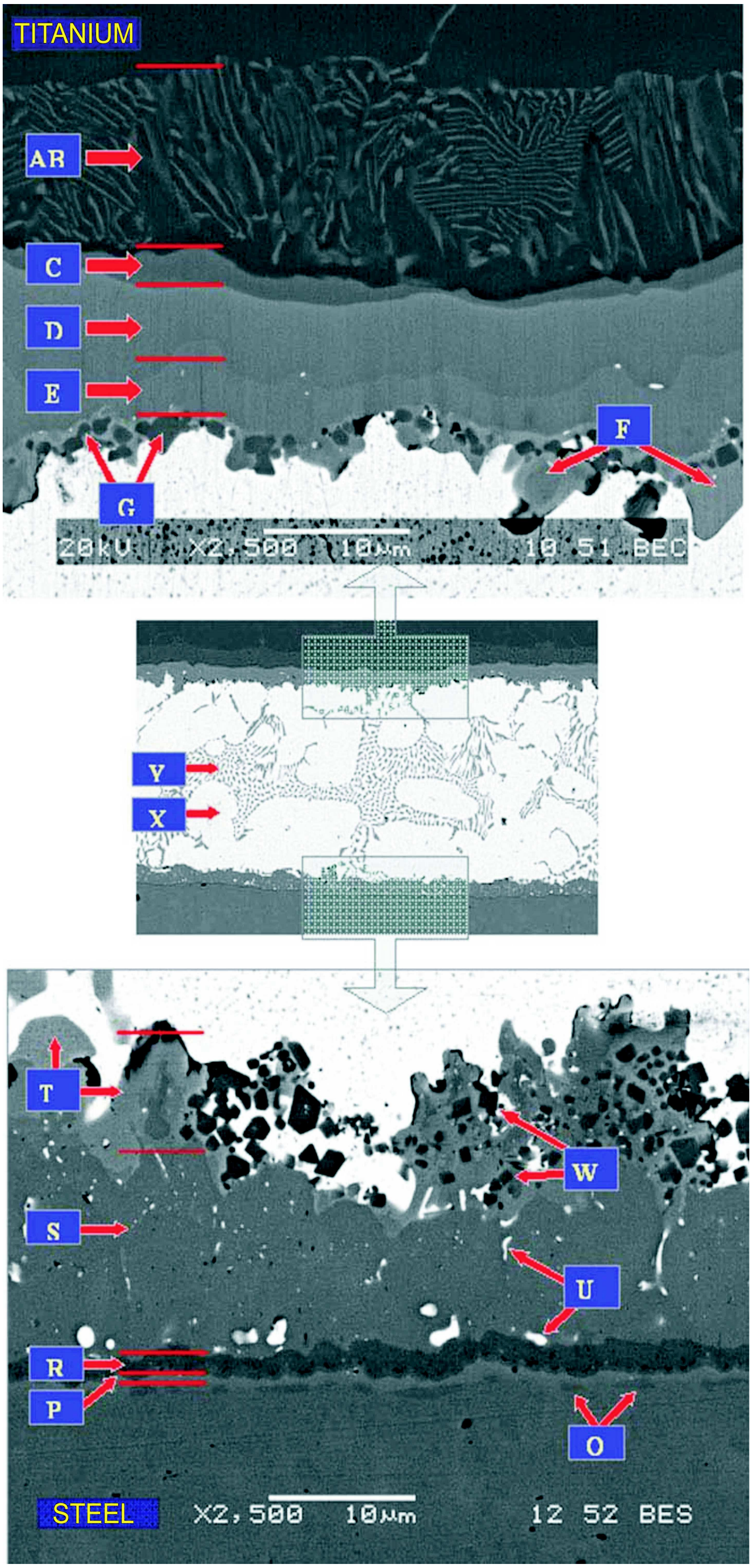

Fig. 4. Microstructure "enriched in silver" of stainless steel – titanium brazed with B – Ag72Cu-780 silver brazing alloy at temperature 860°C (phase composition – tabl. 2), SEM

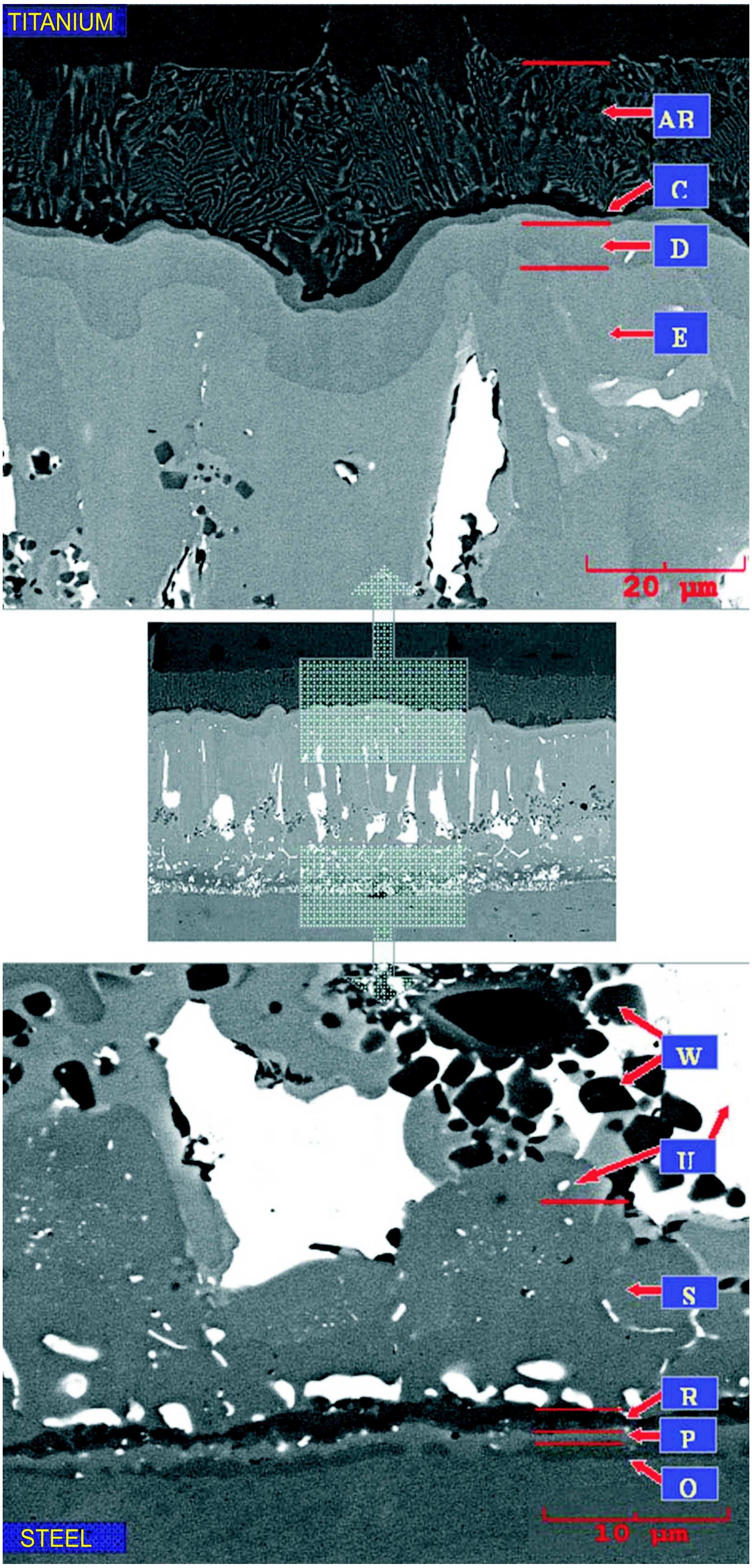

Fig. 5. Microstructure "enriched in copper and titanium" of stainless steel – titanium joint brazed with B – Ag72Cu-780 silver brazing alloy at temperature 860°C (phase composition – tabl. 2), SEM

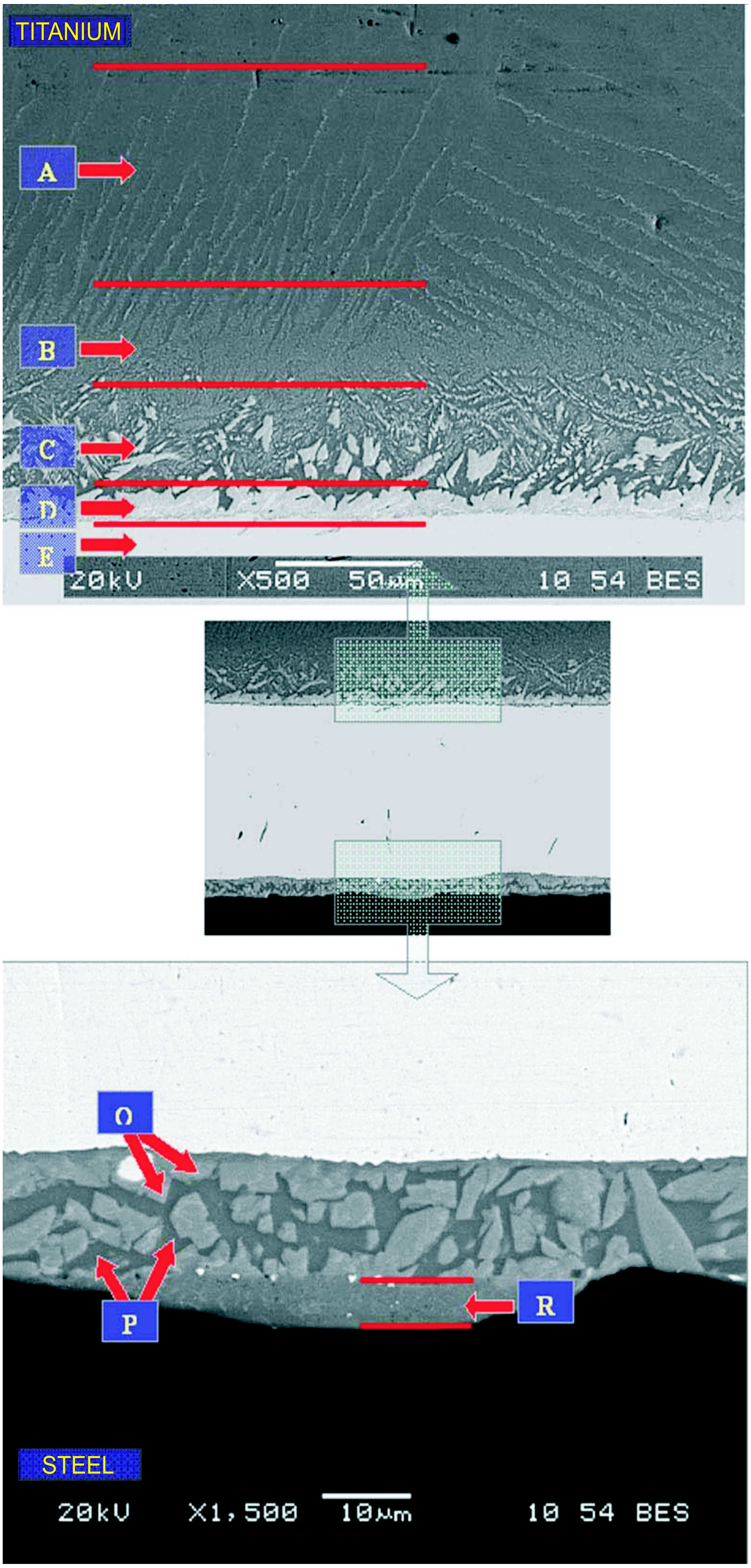

Fig. 6. Microstructure “enriched in silver” of stainless steel – titanium joint brazed with B – Ag72Cu-780 silver brazing alloy at temperature 900°C (crack in braze metal, phase composition – tabl. 3), SEM

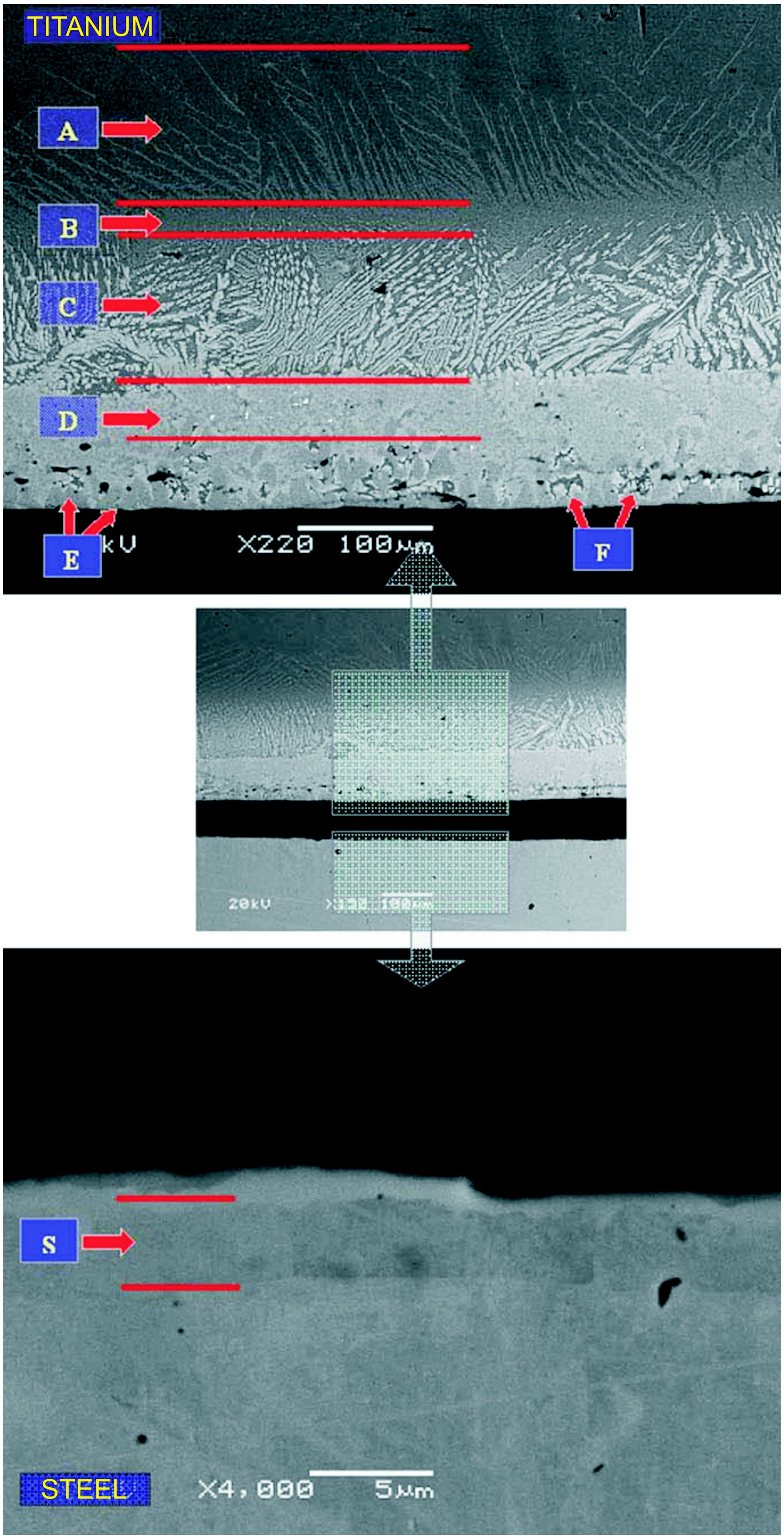

Fig. 7. Microstructure "enriched in copper and titanium" of stainless steel – titanium joint brazed with B – Ag72Cu-780 silver brazing alloy at temperature 900°C (crack in braze metal, phase composition – tabl. 4) SEM

TABLE 1

EDS results of microstructures of stainless steel – titanium joint brazed with silver braze alloy B – Ag72Cu-780 at temperature 820°C (Fig. 3)

Type of structure	Field of analysis	Phase designation	Chemical composition, %at.							
			Ti	Ag	Cu	Fe	Cr	Si	Mn	Ni
Fig. 3	Titanium interface	A(dark)	96.01	0.37	3.62	–	–	–	–	–
		B(bright)	89.90	0.55	9.54	–	–	–	–	–
		C	71.10	1.65	27.25	–	–	–	–	–
		D	54.14	2.45	43.41	–	–	–	–	–
		E	45.69	1.78	52.53	–	–	–	–	–
		F	35.98	3.99	60.03	–	–	–	–	–
		G	1.68	90.51	7.81	–	–	–	–	–
	Middle of braze metal	Y	41.10	1.23	47.79	6.09	1.81	–	–	1.97
		X	–	90.6	9.3	–	–	–	–	–
		Z	4.97	3.21	89.40	1.73				
	Steel interface	O	1.13	0.28	0.57	65.22	28.18	0.95	0.56	3.11
		P	8.45	0.99	0.64	59.12	26.23	1.68	0.43	2.47
		R_{sr}	7.04	76.66	4.43	8.90	2.40	–	–	0.57
		S_{sr}	50.87	–	11.04	30.92	2.19	–	–	4.97
		T	42.55	0.80	40.08	12.22	1.73	–	–	2.62
		U_{Ti}	57.21	2.00	28.87	5.97	1.60	–	–	4.35
		U_{Ag}	42.91	6.99	43.89	2.88	0.00	0.64	–	2.69

In case of the joints brazed at the higher temperatures i.e. 860 and 900°C (Fig. 2, 4÷7) it was possible to observe two types of structures in the brazes i.e. the one "enriched in copper and titanium" (darker) and the one "enriched in silver" (brighter). This fact would confirm the observation of the disintegration of the eutectic structure of Ag-Cu alloy after dissolution of Ti therein; the observation being published in works [16, 17]. It was also ascertained that with the increase in temperature and time of brazing, the areas of the structure "enriched in silver", originally in the form of intermittent sections present in the intersection of the joint, became concentrated in its central part to form the shape of a "flattened drop" (Fig. 2). The base of the structure in the joints performed at 860°C is a silver-based solid solution with a relatively high content of this chemical element (X-Fig. 4, Table 2), whereas the base of the structure "enriched in copper and titanium" is a solid solution based on the Cu_3Ti_2 intermetallic phase (E-Fig. 5, Table 2).

In the structure of the joints performed at 900°C, in the area "enriched in silver", on the titanium side, behind the complex layer of lamellar and acicular structure it was possible to observe a homogeneous layer composed of a solid solution based on the $Ag_{17}Cu_{17}Ti_{66}$ phase (D-Fig. 6, Table 3), while the centre of the braze was a silver solution with separated copper grains and a solid solution based on the $CuTi_2$ phase (E-Fig. 6, Table 3). A solid solution based on this phase ($CuTi_2$) constituted also the central part of the braze in the structure "enriched in copper and titanium" (D-Fig. 7, Table 3).

On the steel side, in the structures of the joints performed at 820°C it was possible to observe layers of mixtures of solid solutions based on the Cu_3Ti_2, Cu_4Ti_3 phases (T-Fig. 3, Table 1) and CuTi (S-Fig. 3, Table 1) with inclusions of the $Ag_{17}Cu_{17}Ti_{66}$, AgTi, Cu_3Ti and Cu_4Ti types of phases and solid solutions based on silver and copper.

In the structures of the joints performed at 860°C the layers (S-Fig. 4, 5 Table 2) were composed of a solid solution based on the CuTi phase with inclusions of grains of solutions based on the Cu_3Ti_2 and $CuFeTi_2$ phases as well as of solid solutions of the Cu_4Ti_3 and $CuTi_2$ (nearer the steel) phases with inclusions of grains of solid solutions based on silver and copper.

In the samples made at 900°C it was possible to observe a separated solid solution based on the $CuFeTi_2$ phase (PR-Fig. 6, E-Fig. 7, Table 3) and in the structure "enriched in silver" – additionally with inclusions of a solution based on the $Ag_{17}Cu_{17}Ti_{66}$ phase.

In all of the above brazed joints, the steel was separated from the braze by a relatively thin layer of a solid solution based on the $Cr_{13}Fe_{35}Ni_3Ti_7$ phase (OP-Fig. 3÷5, S-Fig. 6, 7, Tables 1÷3).

The strength tests of the said brazed joints and microhardness measurements of the structural phases

TABLE 2

EDS results of microstructure of stainless steel – titanium brazed with silver braze alloy B – Ag72Cu-780 at temperature 860°C (Fig. 4 i 5)

Type of structure	Field of analysis	Phase designation	Chemical composition, %at.							
			Ti	Ag	Cu	Fe	Cr	Si	Mn	Ni
Fig. 4	Titanium interface	A(bright)	88.25	0.56	11.19	–	–	–	–	–
		B(dark)	97.46	0.38	2.17	–	–	–	–	–
		C	69.92	1.68	28.40	–	–	–	–	–
		D	54.21	2.56	43.23	–	–	–	–	–
		E	46.49	1.76	51.76	–	–	–	–	–
		F	41.28	2.54	56.18	–	–	–	–	–
		G	61.52	7.13	29.18	1.12	–	–	–	1.06
	Middle of braze metal	X	0.00	90.06	9.94	–	–	–	–	–
		Y	2.79	5.82	91.38	–	–	–	–	–
	Steel interface	O	1.33	–	0.91	69.98	19.57	0.80	0.91	6.49
		P	2.39	–	4.28	60.70	27.52	0.80	1.31	2.99
		R	29.41	0.70	4.24	36.56	10.17	3.00	0.67	3.25
		S	35.00	0.53	51.10	10.35	1.35	–	–	1.67
		T	17.35	1.55	80.02	0.52	0.00	–	–	0.55
		U	10.02	70.40	14.99	4.59	0.00	–	–	0.00
		W	57.34	4.55	31.68	2.46	0.00	–	–	3.96
Fig. 5	Titanium interface	A(dark)	89.13	0.47	10.14					
		B(bright)	97.61	0.30	2.08	–	–	–	–	–
		C	71.84	1.28	26.88	–	–	–	–	–
		D	54.78	2.03	42.52	–	–	–	–	–
		E	47.24	1.86	49.76	–	–	–	–	1.14
	Steel interface	O	1.69	0.15	0.63	66.29	26.72	0.91	0.86	2.74
		P	6.10	0.35	0.94	58.74	28.57	1.49	1.07	2.74
		R	41.42	0.51	6.02	38.22	7.38	3.29	0.37	2.78
		S	41.68	2.71	43.94	8.41	1.25	–	–	2.00
		U	3.29	86.54	8.12	2.04	–	–	–	–
		W	67.06	0.66	24.82	2.85	–	–	–	4.61

demonstrated that the hard (microhardness of 407÷420 HV 0.01) and brittle layers located nearest to the boundary between the braze and the steel had the strongest impact on the strength of the joints The layers were composed of solid solutions based on the $Cr_{13}Fe_{25}Ni_3Ti_7$ (Fig. 8) and $CuFeTi_2$ (Fig. 9) intermetallic phases as well as on the CuTi phase with a significant content of Fe (Fig. 10). The aforesaid area was also subject to cracking and separation of samples caused by the load exerted during the shear tests. In addition, in the corresponding phase layers of the samples it was possible to observe a slight and gradual increase in hardness accompanying the increase in a brazing temperature. Such a phenomenon was due to the growing content of chemical elements contained in the steel (Fe, Cr, Ni and, in some cases, also Ti) and responsible for hardening of the phases.

Additional investigation by means of the energy-dispersion spectrometer (EDS) covering the changes of the chemical composition of the basic phases in the structures of the joints brazed at 860 and 900°C with short (5 min) and longer (15, 40 min) hold times showed only some small changes. In the phases creating the structures of the joints performed with the hold time of 40 min it was possible to observe an increasing content of the basic steel ingredients, particularly chromium and nickel. The microscopic examination of these structures showed the increase of layer and pillar phase separations in the diffusion zones on the braze boundaries both on the titanium and steel sides. The geometrical relationships between increasing widths (h(t)) responsible for the strength of brittle phase layers in joints and the hold time (t) at the brazing temperature are presented as straight lines defined by the following regression equations:

- at the brazing temperature of 820°C
  layer S Fig. 3 – h(t) = 0.128 t + 3.99 (R = 0.98)
  layer OP Fig. 3 – h(t) = 0.0208 t + 2.038 (R = 0.98)
- at the brazing temperature of 860°C
  for the part of the structure "enriched in silver"

layer S Fig. 4 – h(t) = 0.7704 t + 4.425 (R = 0.98)
layer OP Fig. 4 – h(t) = 0.075 t + 1.775 (R = 0.96)
for the part of the structure “enriched in copper and titanium”
layer S Fig. 5 – h(t) = 0.8267 t + 5.696 (R = 0.99)
layer OPR Fig. 5 - h(t) = 0.125 t + 1.225 (R = 0.98)

– at the brazing temperature of 900°C

for the part of the structure “enriched in silver”
layer S Fig. 6 – h(t) = 0.2496 t + 15.93 (R=0.91)
layer RP Fig. 6 – h(t) = 0.1385 t + 2.231 (R = 0.98)
for the part of the structure “enriched in copper and titanium”
layer E Fig. 7 – h(t) = 0.5177 t + 37.363 (R=0.97)
layer S Fig. 7 – h(t) = 0.1265 t + 2.419 (R = 0.94)

TABLE 3

EDS results of microstructure of stainless steel – titanium brazed with silver braze alloy B – Ag72Cu-780 at temperature 900°C (Fig. 6, 7)

Type of structure	Field of analysis	Phase designation	Chemical composition, %at.							
			Ti	Ag	Cu	Fe	Cr	Si	Mn	Ni
Fig. 6	Titanium interface	A(bright)	93.25	–	6.29	–	–	–	–	–
		A(dark)	98.88	–	0.93	–	–	–	–	–
		B	92.97	1.37	5.32	0.33	–	–	–	–
		C(bright)	77.62	8.49	13.45	–	–	–	–	–
		C(dark)	93.76	2.96	2.49	–	–	–	–	–
		D	64.19	22.75	12.84	0.11	0.11	–	–	–
		E	0.72	97.42	1.87	0.00	–	–	–	–
	Steel interface	O	66.41	12.17	17.35	2.32	0.23	0.63	0.10	0.80
		P	50.41	1.86	20.36	21.37	2.32	0.55	0.15	3.10
		R	53.15	1.27	17.38	22.02	1.72	0.94	0.17	3.34
		S	1.64	–	0.39	67.53	25.12	1.03	0.98	3.31
Fig. 7	Titanium interface	A(dark)	92.59	–	2.91	2.83	–	–	–	0.83
		A(bright)	99.15	–	0.39	–	–	–	–	–
		B	87.14	0.72	5.18	5.64	0.72	–	–	0.27
		C(bright)	71.21	6.24	20.71	0.81	0.31	–	–	0.49
		C(dark)	83.59	1.58	4.41	6.73	2.75	0.26	–	0.50
		D	64.20	4.46	23.19	5.43	0.89	0.35	–	1.37
		E	54.48	1.38	25.96	14.05	1.72	0.37	–	1.88
		F	53.63	1.47	16.30	24.17	4.10	0.60	0.20	2.74
	Steel interface	S	1.44	–	0.73	65.91	26.73	0.78	1.14	3.24

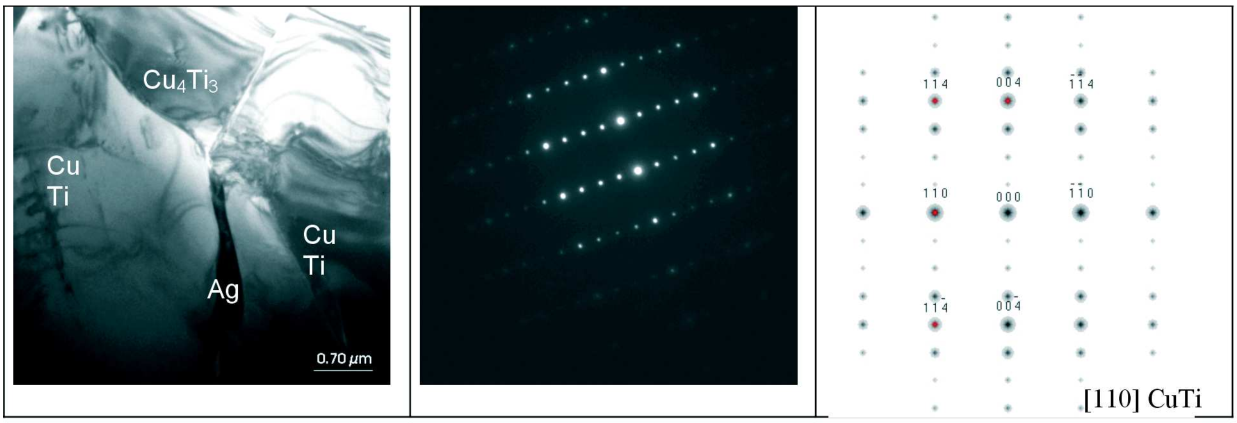

Fig. 8. TEM image of structure containing CuTi phase, selected area diffraction pattern of this phase and solution of diffraction pattern

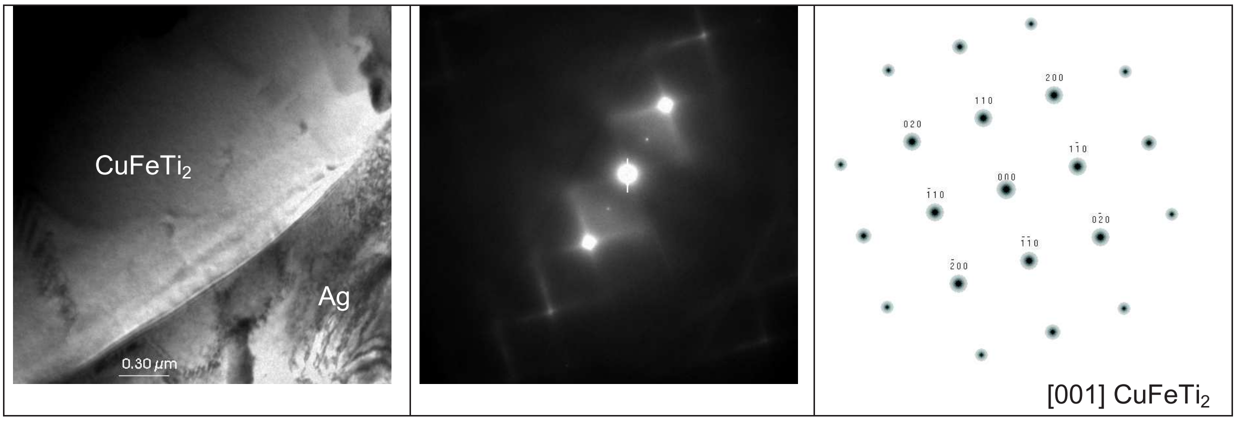

Fig. 9. TEM image of structure containing $CuFeTi_2$ phase, selected area diffraction pattern of this phase and solution of diffraction pattern

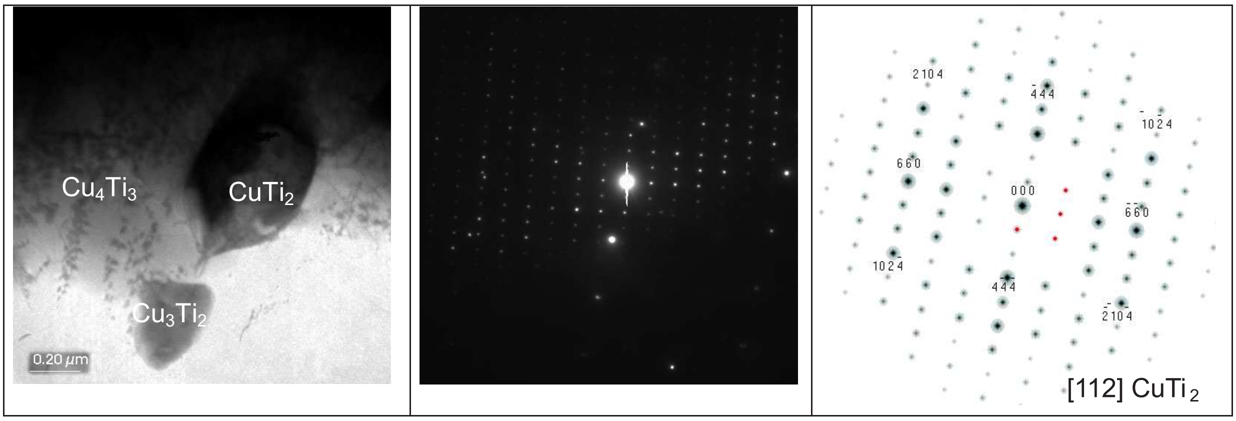

Fig. 10. TEM image of structure containing $CuTi_2$ phase, selected area diffraction pattern of this phase and solution of diffraction pattern

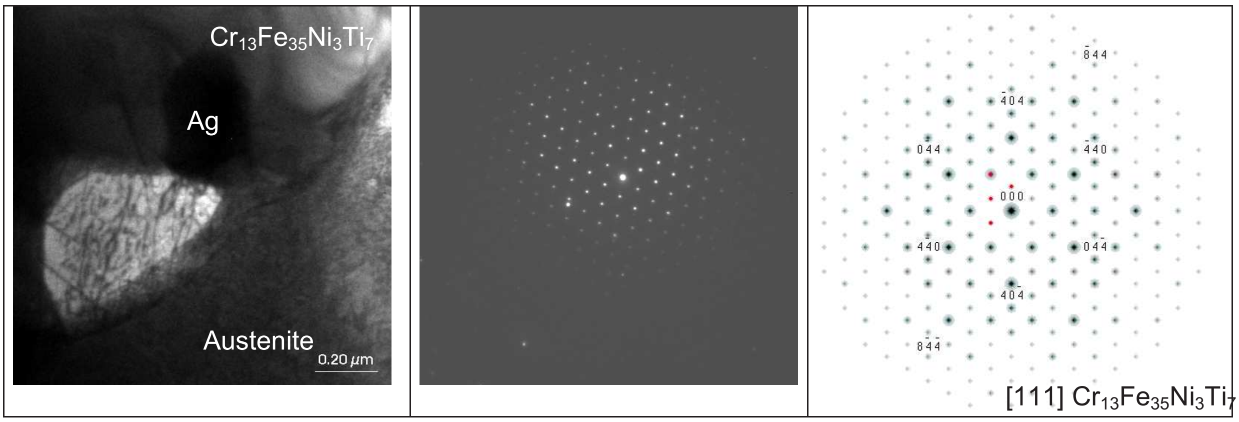

Fig. 11. TEM image of structure containing $Cr_{13}Fe_{35}Ni_3Ti_7$ phase, selected area diffraction pattern of this phase and solution of diffraction pattern

On the basis of the presented test results and technological observations made during the investigation it was possible to meet the assumed objective of this work and develop technological guidelines for brazing stainless steel with titanium.

It was established that the best properties of joints of titanium and stainless steel brazed with the B-Ag72Cu-780 silver brazing filler metal can be obtained at 900°C with the hold time of 5÷10 min well as at 860°C with the hold time of 15 min.

6. Conclusions

1. A good quality and high shear strength (160 MPa) are typical of joints connecting stainless steel (type 18-10) with titanium brazed by means of the B-Ag72Cu-780 silver brazing filler metal in a furnace in vacuum conditions exceeding 1.33×10^{-1} Pa, at 900±10°C and the hold time of 5÷10 min (at the brazing temperature) as well as at 860±10°C and the hold time of 15 min.
2. The structural metallographic analysis complemented by the electron-diffraction analysis and the phase microhardness tests demonstrated the existence of complex layers of eutectoid mixtures and solid solutions containing two- and multi-component intermetallic phases of titanium with copper, silver, iron, chromium and nickel located in the joints of stainless steel with titanium brazed by means of the B-Ag72Cu-780 silver brazing filler metal at 820÷900°C and the hold times of 5÷40 min; the complex layers could be found both on the titanium and stainless steel sides.
3. In the tested joints brazed at 860 and 900°C it was possible to observe the division of the structure into the area "enriched in copper and titanium" (darker) and the one "enriched in silver" (brighter) formed as intermittent sections along the braze. It was also established that with an increasing temperature and a longer hold time, the phase "enriched in silver" concentrated in the central part of the joint to form a "flattened drop".
4. The strength tests and structural investigation of the brazed joints of stainless steel and titanium, characterised by a complex phase structure, explicitly demonstrated that the formation and growth of brittle layers of the solid joints based on the $Cr_{13}Fe_{35}Ni_3Ti_7$, $CuFeTi_2$ and the CuTi intermetallic phases (the last one with a significant content of Fe) located on the boundary of the steel with the braze resulted in the decreasing strength of the brazed joints at the hold times exceeding 20 min.
5. The reason for the lower strength of the said joints brazed at the lower temperatures (820, 860°C) and shorter hold times (5÷10 min) can be attributed to low wettability of steel in vacuum and the aforesaid temperature as well as time conditions.
6. On the basis of the presented test results and technological observations made during the investigation it was possible to meet the assumed objective of this work and develop technological guidelines for brazing stainless steel with titanium by means of silver brazing filler metal.

Acknowledgements

The investigation was performed within Research Project No. 3 T08C 037 027 financed by the Ministry of Science and Higher Education.

REFERENCES

[1] Joint publication, Poradnik Inżyniera. Spawalnictwo. T. 1 i 2. WNT, Warszawa 2004/2005 (in Polish).
[2] M. Schwartz, Brazing. Ed. 2, ASM International, Materials Park, Ohio, 107-117 (2003).
[3] Joint publication, Brazing Handbook. AWS, Miami, 359-379 (1991).
[4] W. Müller, J. U. Müller, Löttechnik. DVS, Düseldorf, 1995 (in German).
[5] N. F. Łaško, S. V. Łaško, Pajka metałłov. Mašinostrojenie, Moskva 338-353, 1984 (in Russian).
[6] Praca Zbiorowa: Spravočnik po pajkie. Mašinostrojenie, Moskva 281-284, 2003 (in Russian).
[7] V. Ruża, Pajeni. SMTL-Alfa, Praha, 355-359, 1988 (in Czech).
[8] R. Messler, Joining of advanced materials. Butterworth-Heinemann, Boston **397-400**, 417-419 (1993).
[9] I. E. Pietrunin i inni, Metałłoviedienie pajki. Metałłurgia, Moskva, 19-20, 1976 (in Russian).
[10] V. I. Dybkov, Reaction diffusion and solid state chemical kinetics. IPMS Publications, Kijev 2002.
[11] L. S. Kireev, V. V. Peškov, Joining titanium to steel. **11/2**. Harwood Academic Publishers 1998.
[12] L. S. Kireev, V. N. Zamkov, Fusion welding of titanium to steel (reviev). Titanium. E.O. Paton Electric Welding Institute, NASU, 156-160, (2006).
[13] L. S. Kireev, V. N. Zamkov, Solid-state joining of titanium to steel (review). Titanium. E.O. Paton Electric Welding Institute, NASU, 151-157 (2006).
[14] N. Kahraman, B. Gulenc, F. Findik, Joining of titanium/stainless steel by explosive welding and effect on interface. Journal of Material Processing Technology **169**, 127-133 (2005).

[15] A. Shapiro, A. Rabinkin, State of art of titanium based brazing filler metals. Welding Journal 10, 36-43 (2003).

[16] W. N. Jeremienko, J. Bujanov, N. M. Paščenko, Obłast rasstojenia w żidkom sostojanii w sistemie Cu-Ag-Ti. Izd. A.N. USSR, nr 5, 1969 (in Russian).

[17] J. W. Najdič, W. S. Żuravlev, N. J. Frumina, Razrabotka i ispytanie robočich parametrov spajev okonnogo tipa iz sapfira. Adgezja Raspławov i Pajka Materiałov 56-58, nr 7/1981 (in Russian).

[18] T. Noola, T. Shimizu, M. Okabe, T. Iikubo, Joining of TiAl and steel by induction brazing. Materials Science and Engineering **A 239-240**, 607-618 (1997).

[19] R. K. Shiue, S. K. Wu, S. Y. Chen, Infrared brazing of TiAl intermetallic using BAg-8 braze alloy. Acta Materialia **51**, 1191-2004 (2003).

[20] K. Matsu, Y. Miyazawa, Y. Totsuka, T. Ariga, Brazing of CP-Ti to stainless steel. Lectures of International Conference "Brazing, high temperature brazing and diffusion welding", Aachen, 57-60 (2004).

[21] W. Qu. Zuang, A. Khan, Y. Yang, Brazing titanium alloy and stainless steel with copper-based filler metal. Lectures of International Conference "Brazing, high temperature brazing and diffusion welding", Aachen, 317-321 (2004).

[22] F. W. Bach i inni, Flussmittelfreies Lötten von Lichtmetall – Stahl Verbindungen. Lectures of International Conference "Brazing, high temperature brazing and diffusion welding", Aachen, 206-210, 1998 (in German).

[23] T. B. Massalski, Binary alloy phase diagrams. ASM International, Materials Park, Ohio 1991.

[24] P. Villars, A. Prince, H. Okamoto, Handbook of tenary alloy phase diagrams. T. 7 i 8. ASM International, Materials Park, Ohio 1995.

[25] A. Winiowski, J. Niagaj, Badania technologiczne lutowania materiałów trudno lutowalnych i opracowanie nowych materiałów spawalniczych (Investigation of brazing technology of materials hard to braze and development of new welding consumables). Praca badawcza Instytutu Spawalnictwa w Gliwicach (Research output of Institute of Welding-Gliwice) nr Gn-12/ST-195/2002 (no published).

[26] A. Winiowski, B. Rams, Określenie wpływu technologii lutowania na właściwości połączeń aluminium z innymi metalami oraz badanie szkodliwości materiałów lutowniczych (Description of influence brazing technology on characteristics aluminum joints with another metals and investigation of brazing consumables harmful). Praca badawcza Instytutu Spawalnictwa w Gliwicach (Research output of Institute of Welding-Gliwice) nr Cc-49/ST-180/2001 (no published).

Received: 20 May 2007.