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POLSKA AKADEMIA NAUK

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 60 2015 Issue 4

DOI: 10.1515/amm-2015-0419

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COMPARISON OF MICROSTRUCTURE AND MECHANICAL PROPERTIES OF INDUCTION AND VACUUME BRAZED JOINT OF TITANIUM VIA COPPER AND Ag-Cu EUTECTIC FILLER METAL

MIKROSTRUKTURA I WŁAŚCIWOŚCI MECHANICZNE POŁĄCZEŃ TYTANU LUTOWANYCH INDUKCYJNIE I PRÓŻNIOWO Z UŻYCIEM SPOIWA MIEDZIANEGO I EUTEKTYCZNEGO Ag-Cu

This study presents the basic physico-chemical properties and describes the brazeability of titanium. The work contains the results of macro and microscopic metallographic examination as well as the results of strength-related tests of vacuum and induction brazed joints made of Grade 2 technical titanium using the Cu 0.99 and Ag 272 filler metal interlayers and F60T flux intended for titanium brazing in the air atmosphere.

Keywords: induction brazing, vacuum brazing, titanium, mechanical properties of brazed joints, microstructure of brazed joint

W niniejszej pracy przedstawiono podstawowe właściwości fizyko – chemiczne i opisano lutowność tytanu. Przestawiono wyniki badań metalograficznych makro i mikroskopowych oraz wytrzymałościowych połączeń tytanu technicznego Grade 2 lutowanych próżniowo oraz indukcyjnie z użyciem warstwy przekładkowej ze spoiwa miedzianego w gat. Cu 0,99 i Ag 272 z zastosowaniem topnika F60T, przeznaczonego do twardego lutowania tytanu w atmosferze powietrza.

1. Introduction

Fast developing aviation, automotive, power and chemical industries cause an increasingly high demand for new engineering materials whose properties must withstand such extreme operating conditions as a high operating temperature, significant loads or operation in a flue gas environment. On the other hand, important and desirable material properties include high strength and corrosion resistance (also in an aggressive flue gas environment) but, first of all, low density [1, 5]. The use of engineering materials combining all the properties should ensure long service life and operational reliability of modern machinery components used in the most adverse conditions. Due to such properties as low density ($4.5 \cdot 10^3$ kg/m^3), high strength (tensile strength between 500 MPa and 700 MPa) and excellent corrosion resistance, titanium and its conventional alloys are both presently used and perceived as prospective structural materials in aviation, automotive, power, chemical, petrochemical and food industries [1].

The industrial applications of any structural materials entail the necessity of subjecting such materials to various technological processes, e.g. joining into one functional whole. Due to a number of difficulties connected with disadvantageous structural changes and changes of titanium and conventional titanium alloy properties during welding, brazing seems to be a promising joining method. Pure titanium as a reactive metal belongs to poorly brazeable materials [2, 3]. One of the technically most advantageous joining methods is diffusion vacuum brazing. This method, combining the features of diffusion welding and brazing is usually defined as "a brazing process in which the braze formation mechanism is based mainly on diffusion between materials being joined and a brazing metal" or as "a brazing process in which diffusion determines the chemical composition and physical properties of a braze obtained by melting a brazing metal added or a brazing metal formed at the interface of workpieces" [2, 4]. A significant limitation related to diffusion brazing is the necessity of performing the process in a vacuum.

In "classical" brazing the phenomenon of diffusion does not play such an important role and the process temperature is always higher than the melting point of a brazing metal used. In spite of a short time at which materials being joined are exposed to a high temperature, the high reactivity of titanium causes the formation of numerous intermetallic phases containing titanium and brazing metal components usually present on the boundary of dissolving and of mutual diffusion [2, 3]. Unfortunately, the very same high chemical activity of titanium with air atmosphere gases causes strong oxidation and nitriding of titanium surface. For this reason it is commonly understood that the obtainment of high-quality brazed joints requires vacuum conditions.

Reference publications contain test results indicating the possibility of brazing titanium in the air atmosphere [6, 7]. The major problems following such a process include removing the

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layer of very durable titanium oxides not wettable by liquid brazing metals and formed on brazed surfaces as well as protecting titanium against re-oxidation at an elevated brazing temperature. For this reason it is recommended that titanium brazing should involve the use of a highly active specialist brazing flux ensuring the proper course of brazing phenomena. Such a flux should reduce the surface tension of a brazing metal and provide the required wettability and spreadability of the brazing metal as well as ensure the filling of capillary brazing gaps. The flux activity also includes a chemical reduction and dissolving oxide layers on the surface of materials being joined and of the brazing metal as well as preventing their re-oxidation during brazing. In 2011 Instytut Spawalnictwa in Gliwice developed an innovative flux designated as F60T which found application in the flame and induction brazing of the Grade 2 titanium with silver filler metals in the air atmosphere [6, 7].

This publication presents the results of structural and mechanical tests of vacuum or induction brazed Grade 2 titanium joints made using a copper and a silver brazing metal.

2. Course and results of test

Parent and Filler Metals Used in Tests

The parent metal used in the tests was the Grade 2 titanium according to ASTM B 265-13 [14] (maximum amounts of impurities in % by weight: 0.1%C; 0.25%O; 0.03%N; 0.0125%H; 0.03%Fe) out of which cylindrical specimens were made (Ø 20 x 15 mm).

The interlayer used in vacuum brazing and induction brazing of titanium was the Cu 099 grade copper brazing metal and the Ag 272 grade silver brazing filler metal according to EN ISO 17672 [13] having a thickness of 0.1 mm.

Induction brazing involved the use of the F60T fluoride-chloride flux in the form of paste applied on both interfaces of workpieces before brazing.

3. Preparation of joint samples for tests

Butt-brazed specimens were positioned freely and coaxially in the vertical position. Prior to brazing in order to increase the faying surface area and the diffusion length of parent metal and brazing metal components the surfaces of workpieces underwent grinding with abrasive paper of a final granularity amounting to 800. Directly before brazing the workpieces were etched in the aqueous solution of hydrofluoric and nitric acid. Prior to brazing joint shape-matched brazing metal interlayers were degreased in acetone and placed between the workpieces. In induction brazing the surface of the brazing metal and that of the workpiece were provided with a flux layer.

The process of vacuum brazing was conducted using a TORVAC- manufactured S 16 vacuum furnace in a vacuum of 10^{-4}÷10^{-5} mbar.

The temperature and time of vacuum brazing were determined on the basis of information available in reference publications and by analysing the phase interaction of titanium and copper on the basis of their phase equilibrium system [2 ÷ 4,8]. Vacuum brazing using the Ag 272 eutectic silver brazing metal was performed at

960°C and vacuum brazing carried out using the Cu 099 copper brazing metal was conducted at 1030°C. In order to reduce diffusion phenomena the time of brazing amounted to 1 minute in each case. Heating up to the brazing temperature was performed with 20-min-long isothermal holding at 700°C in order to conduct the desorption of gases from the surface of workpieces.

The induction brazing process was conducted using a NG-15 device produced by Instytut Spawalnictwa, having a nominal power of 15 kW and operating frequency of 10 ÷ 40 kHz. The specimens were heated to the moment of brazing metal melting. Afterwards, the specimens were left for cooling in air.

While visually assessing the brazed joints it was possible to observe the complete filling of the brazing gap and coating of the side walls of the vacuum brazed specimens. The induction brazed joints contained brazing gap areas not filled with the brazing metal. In addition, during brazing the surface underwent strong oxidation and in the direct neighbourhood of the braze it was possible to observe hard-to- remove flux slag.

4. Structures of grade 2 titanium brazed joints

The specimens for microscopic metallographic examination were prepared by grinding with abrasive paper having a gradation of 80, 320, 1000 and 2500 respectively. Afterwards the specimens were polished using polishing cloth with diamond and corundum polishing slurries having a grain size of 3 and 0.05 μm respectively.

The microstructure of the brazed joints was revealed by etching the specimens in the Buehler's reagent. The metallographic examination was carried out in the bright field using a Leica-manufactured MeF4A metallographic light microscope. The cross-section of the brazed joints was used in microhardness measurements performed with a KB Prüftechnik GmbH-made KB50BVZ-FA microhardness tester under a load of 0.49N (HV0.05).

The metallographic examination of the joints brazed in a vacuum at a temperature of 960°C for 1 minute, made of the Grade 2 titanium and the Ag 272 brazing filler metal revealed the complex joint structure. The joint contained a clearly visible diffusion zone in the parent metal, a wide layer of dark-coloured intermetallic phases building up on the parent metal side and areas of lighter colour in the braze central part (Fig. 1a). This indicates the occurrence of the phenomenon consisting in eutectic brazing metal alloying in contact with titanium (described in reference publications) [4]. In the case of vacuum brazing performed using the Cu 099 brazing metal, similarly as in the case of the brazed joint made using the silver brazing metal, it was possible to observe a wide dark-coloured diffusion zone in the parent metal. In the braze it was possible to observe a clearly visible layered joint structure with individual layers being of different colours (Fig. 1b). The middle brighter-coloured layer was probably a phase rich in copper (e.g. $TiCu_2$). In turn, the dark layer of the phase building up from the side of the line of dissolving and of mutual diffusion was probably a phase rich in titanium (e.g. TiCu) [4]. It should be noted that in spite of the short brazing time (1 minute) the inertia of the vacuum furnace chamber where the brazing process took place was significant. Therefore, the time at which the specimen was exposed to a temperature above 915°C (temperature of $Ti_\alpha \rightarrow Ti_\beta$ transformation) [9] exceeded 15 minutes. It should be emphasized that the coefficients of metal diffusion in titanium β are by several orders of magnitude greater than in titanium α.

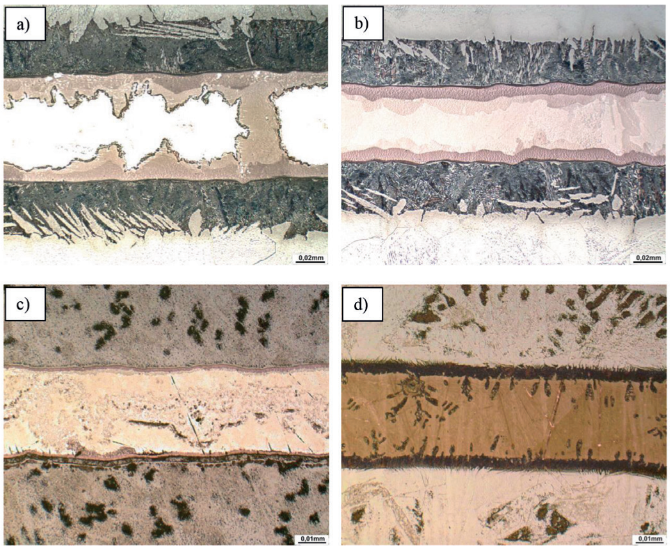

Fig. 1. Microstructures of titanium (Grade 2) joints diffusion brazed using interlayer of Ag 272(a), Cu 099 (b) and induction brazed using interlayer of Ag 272 (c) and Cu 099 (d), etching: Buehler reagent

In the induction brazed joint made using the Ag 272 brazing metal the very short time at which the metal was exposed to a temperature exceeding the brazing metal melting point and, probably, lower than the $Ti_\alpha \rightarrow Ti_\beta$ transformation temperature was responsible for the fact that diffusion phenomena were very limited, which was also mentioned in the reference publications [12]. This conclusion is supported by the lack of the darker-coloured diffusion zone in the parent metal, characteristic of vacuum brazing. In addition, the limited amount of titanium reacting with the liquid brazing metal did not lead to eutectic brazing metal alloying onto the areas rich in copper and in silver. The width of the layer of the intermetallic phase in the braze, building up on the line of dissolving and of mutual diffusion was significantly smaller than that observed in the vacuum brazed joints (Fig. 1c). The line of dissolving and of mutual diffusion revealed a material discontinuity which can significantly affect joint mechanical properties. In addition, many braze areas contained numerous gas pores significantly decreasing the joint active cross-section (Fig.2a).

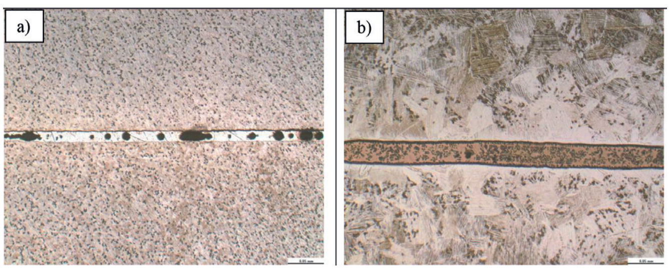

Fig.2. Macrostructure of induction brazed joint of titanium Grade 2 using Ag 272 (a) and Cu 099 filler metal and F60T flux.

The parent metal of the induction brazed joint made using the Cu 099 brazing metal and F60T flux revealed the presence of the darker-coloured diffusion zone characteristic of vacuum brazing, which was narrower than that observed in the vacuum brazed joints (Fig. 1d). The greater diffusion intensity than that of the joint brazed using the Ag 272 brazing metal can be ascribed to the high copper brazing metal melting point (above 1085°C) and the significant acceleration of diffusion phenomena in titanium β [12]. The joint did not reveal the banded structure but only slight phase precipitates building up inside the braze from the line of dissolving and of mutual diffusion. The joint did not contain many voids and gas pores characteristic of joints brazed using the Ag 272 brazing metal (Fig. 2b).

The microhardness measurement (HV0.05) performed on the joint cross- section revealed that in the induction brazed joint made using the Ag 272 brazing filler metal the hardness of the braze and that of the parent metal with the diffusion zones did not exceed 195 HV0.05. In the case of the joint made using the Cu 099 brazing metal the hardness of the parent metal amounted to approximately 250 HV0.05 and increased to 325 ÷ 346 HV0.05 in the braze. The greater parent metal hardness than that observed while brazing with the Ag 272 brazing metal can be ascribed to the greater copper content in the solid solution responsible for the hardness increase [10]. In addition, the process was conducted at a temperature above 1085°C, i.e. at the presence range of titanium β, which while cooling down might have transformed into phase α'. The martensitic transformation in titanium causes its hardness increase [10].

The hardness of the vacuum brazed joints using the copper brazing metal was restricted within the 215 ÷ 415 HV0.05 range. The parent metal hardness amounted to 214 ÷ 247 HV0.05 and that of the diffusion zone was approximately 200 HV0.05. The greatest hardness, i.e. 393 HV0.05, was observed in the central part of the joint. This was probably the TiCu4 phase known to be characterised by significant hardness [11]. In the joints brazed using the Ag 272 brazing metal the parent metal hardness amounted to 186 ÷ 247 HV0.05. The greatest hardness of 273 HV0.05 characterised the dark-coloured phase. The hardness of the bright-coloured phase did not exceed 100 HV0.05. The significant hardness differences concerning the joints made using various methods and the same brazing metals can be ascribed to the longer time at which the braze remained in the liquid state during vacuum brazing and to the greater intensity of diffusion phenomena leading to the formation of numerous intermetallic phases.

TABLE 1

Microhardness HV0,05 test results and arrangement of measuring points (location of measurement points)

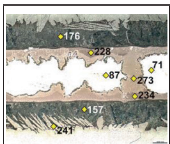	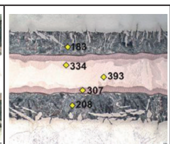	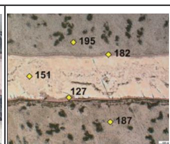	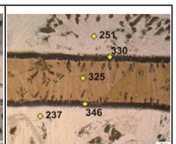
vacuum brazingbrazing filler metal: Ag 272	vacuum brazing brazing filler metal: Cu 099	induction brazing brazing filler metal: Ag 272	induction brazing brazing filler metal: Cu 099

TABLE 2
Static shear test results concerning Grade 2 titanium vacuum and induction brazed joints made using the 0.1 mm thick Ag 272 silver brazing metal and Cu 099 copper brazing metal for a time of 1 minute and at a temperature of 960°C

Brazing method	**Brazing filler metals**	**Shear strength, MPa**		
		Results from n = 5 tests	**x[2)]**	**Sx[2)]**
1	2	3	4	5
Vacuum	Ag 272	42,9; 38,9; 49,3; 53,5; 48,2	46,6	5,7
	Cu 099	131; 99,3; 136; 128; 115	122	14,7
Induction	Ag 272	29,96; 60,83; 106,3; 78,47; 52,91	65,7	28,6
	Cu 099	259,21; 209,56; 250,58; 198,71; 224,92	228	25,9

[1)] T_L – brazing temperature, t_w – brazing time

[2)] x – average value, S_x –standard deviation

5. Shear tests of titanium brazed joints

The mechanical properties of the brazed cylindrical specimens were determined using an Instron-made testing machine model 4210. The specimens were sheared in special clamps designed in a manner allowing the specimens to be exposed only to shear forces, without bending.

The results of the static shear test of the vacuum and induction brazed joints are presented in the Table 2 and Fig. 3.

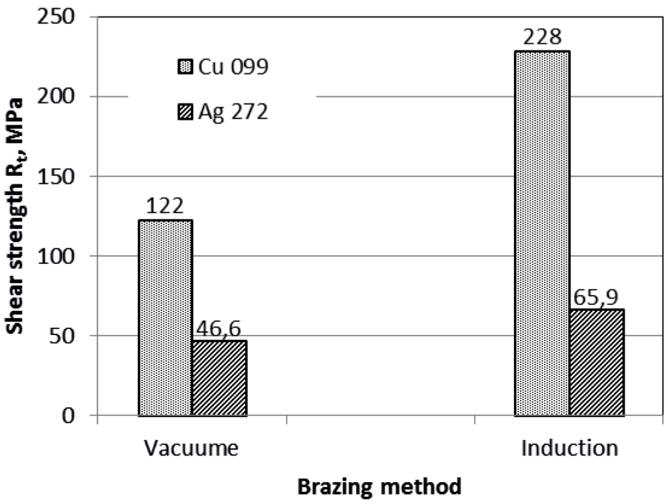

Fig.3. Effect of the brazing method on the shear strength of the Grade 2 titanium brazed joints made using the 0.1 mm thick of Cu 099 copper and Ag 272 silver brazing filler metals

The greatest shear strength was observed in the joints brazed using the Cu 099 brazing metal. The shear strength of the vacuum brazed joints amounted to 122 MPa and that of induction brazed joints was 228 MPa. The shear strength of the joints made using the Ag 272 brazing filler metal was significantly lower and amounted to 46.6 MPa for the vacuum brazed joint and 65.7 MPa for the induction brazed joint. The probable reason for the significantly lower mechanical properties of the vacuum brazed joints was the presence of numerous mutually incoherent intermetallic phases and a wide diffusion zone in the parent metal. In addition, the brazed joints contained numerous cracks formed on the interphase boundaries of the vacuum brazed joints, definitely reducing the shear strength of the joints.

6. Conclusions

1. The material–technological tests conducted enabled the obtainment of proper vacuum and induction brazed titanium joints (Grade 2) using the interlayers made of the Cu 099 Ag 272 brazing filler metals.
2. The greatest shear strength value for the titanium brazed joints (Grade 2) amounting to 228 MPa was obtained for the induction brazed joint made using the Cu 099 brazing filler metal.
3. The vacuum brazed joints were characterised by significantly lower shear strength, i.e. 122 MPa for the joint made using the Cu 099 brazing metal and 46.6 MPa for the joint made using the Ag 272 brazing metal than the induction brazed joints (228 MPa and 65.9 MPa respectively).
4. The probable reason for the reduction of the shear strength of the vacuum brazed joints is the significantly longer time at which the joints were exposed to the temperature close to the brazing temperature, which caused the intensive growth of intermetallic phases of low interphase coherence and with the parent metal.

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Received: 20 January 2015.