Diffusion vacuum brazing of TiAl47 casting alloy based on TiAl (γ) intermetallic compound using Ag-Cu-Ti braze alloy

M. Różański*, A. Winiowski

Welding Technologies Department, Instytut Spawalnictwa w Gliwice, Bł. Czesława 16-18, Gliwice 44 100, Poland

Received 14 November 2013, received in revised form 27 February 2014, accepted 6 March 2014

Abstract

The basic physical and chemical properties of titanium aluminide alloy based on intermetallic phase TiAl (γ) as well as its brazeability have been discussed. The principles of the diffusion brazing process and application conditions have been presented. The shear strength and structures of the joints of TiAl47 alloy based on the TiAl (γ) phase diffusion brazed with the use of 63Ag-35.3Cu-1.75Ti alloy interlayers as well as brazing conditions have been given. The structural tests were conducted using light microscopy, scanning electron microscopy (SEM) and energy – dispersion spectrometer (EDS). The results of shear strength tests and microhardness tests were also presented.

Key words: TiAl (γ) alloy, silver filler metal, diffusion brazing, structure, mechanical properties

1. Introduction

Alloys based on ordered inter-crystalline phases containing aluminium (Ti-Al, Ni-Al and Fe-Al) belong to a new generation of high-temperature creep resisting metal materials characterised by advantageous physical and mechanical properties enabling applications at high temperature and in strongly corrosive environments.

Since mid-1990’s it has been possible to observe an increase in the popularity of titanium alloys based on inter-metallic phases from the Ti-Al equilibrium system, in particular Ti₃Al (α₂) and TiAl (γ) [1]. The aforesaid alloys, combining the features of metals and ceramics, i.e., corrosion resistance, heat resistance, high-temperature creep resistance, high hardness and behaviour at a low density, are very attractive and prospective structural materials. The most popular of Ti-Al phases is the phase γ (TiAl), characterised by a high melting point (1460°C), relatively low density (3.8 × 10³ kg m⁻³), high relative resistance, good creep resistance, good oxidation resistance and no spontaneous combustion propensity – a disadvantage characteristic of technical titanium (Fig. 1). The phase is also characterised by high hardness and low plasticity – its elongation at the room temperature amounts to mere 1–3 % and significantly decreases in the presence of even small amounts of impurities. In addition, the phase TiAl (γ) undergoes a strong grain growth during plastic working, which makes further...
working difficult or practically impossible. For this reason, in most cases alloys which find technical applications are those in the form of castings. In order to improve the properties of such castings they are usually provided with three groups of alloying agents, i.e., those improving plasticity (chromium, manganese, vanadium), those increasing high-temperature creep resistance and oxidation resistance (niobium, tantalum, tungsten and molybdenum), and those causing grain refinement (boron, carbon, silicon, oxygen and rare-earth elements).

The industrial application of modern structural materials is connected with the necessity of subjecting them to various technological processes, e.g., combining into one functional whole. As it is practically not possible to weld casting alloys based on the intermetallic phases of titanium [1, 2], brazing seems to be a promising, and in some cases the only possible welding method which enables obtaining good quality joints. However, it should be emphasized that these alloys, similarly as technical titanium and its conventional alloys, belong to hard-to-braze materials [3–5] and can be successfully joined by means of diffusion brazing. This method, combining the features of diffusion welding and brazing, is usually defined as a brazing process, in which the brazing process is decisive for the chemical composition and the physical properties of a brazed joint being joined [5, 6].

Depending on the formation mechanism and the structure of a brazed joint obtained, diffusion brazing can be divided into low- and high-temperature brazing. In the first type, the diffusion of the components of a brazing metal and those of a material being joined leads to the formation of intermetallic phases having melting points higher than the temperature at which the process of brazing takes place. In the other case the process is carried out in such a manner that the joint does not contain intermetallic phases and the joint area is a solid solution [7]

The analysis of the available scientific and technical reference publications reveals that the problems of the diffusion brazing of titanium, and particularly the brazing of titanium casting alloys based on intermetallic phases, has not been the subject of thorough research and is presented fragmentarily and only generally [1–6, 8].

The works [6, 7, 11] present the results of tests on the possibility of the diffusion brazing of an alloy based on the intermetallic phase TiAl (γ) using pure copper, eutectic silver brazing metal B-Ag72Cu-780 and an Ag96Cu alloy as a filler metal. The tests conducted revealed the possibility of obtaining high-quality joints, the shear strength of which, however, was not higher than 150 MPa. Taking into consideration the intended use of the said alloy based on the intermetallic phase TiAl (γ), such shear strength values of brazed joints may turn out to low.

Specialist publications on brazing [2–5, 10] increasingly often contain information about the possibility of using active silver brazing metal with a titanium addition, intended for joining hard-to-braze materials, e.g., joining ceramic materials (with each other) or joining ceramic materials with metals. Such brazing metals are characterised by significantly more advantageous brazing properties, i.e., high wettability and spreadability on these materials (not wettable by classical brazing metals) and the possibility of obtaining high-strength joints.

This publication presents the results of tests on the diffusion brazing of the TiAl47 casting alloy based on the phase TiAl (γ) using the active brazing metal type of Ag-Cu-Ti (63Ag-35.3Cu-1.75Ti). The tests aimed to determine the effect of the material-technological conditions of diffusion brazing on the structure and the mechanical properties of brazed joints.

2. Course and results of test

2.1. Base metals and brazing filler metals used in tests

The research-related tests involved the use of an alloy based on the phase TiAl (γ) having the nominal chemical composition TiAl47 (max content of impurities C, S and Si 0.6 %), prepared in the form of cast roller (ø 10 × 120 mm2) at the Department of Materials Science of the Silesian University of Technology in Katowice.

The filler metal used in diffusion brazing of the aforementioned material was the alloy 63Ag-35.3Cu-1.75Ti having a melting point 780–810°C and prepared in the form of 0.1 mm thick band.

2.2. Test joints

The structural tests and shear strength tests of the brazed joints of the alloy TiAl47 involved the use of cylindrical specimens composed of elements having the size of ø 10 × 12 mm2. These elements were subjected to butt brazing. Before the process they were placed freely, coaxially, win the vertical position. This type of a sample (cylindrical) as well as the use of proper fixtures enable obtaining the pure shear of a brazed joint during strength tests and make it possible to prevent the brittle brazed material from cracking during shearing.

In order to increase the area of adhesion and the passage for the diffusion of the components of the ma-
terial being joined and those of the brazing metal, prior to brazing the surfaces of elements were subjected to grinding with abrasive paper. Directly before brazing the elements underwent etching in the solutions of hydrofluoric and nitrous acids, respectively, and next in the solution of NaOH. The profiles made of the 63Ag-35.3Cu-1.75Ti brazing filler metal band, shape-matched to the joint were degreased in acetone and placed between the elements to be joined.

The samples were brazed in a TORVAC-manufactured S 16 vacuum furnace at a vacuum of $10^{-4}$–$10^{-5}$ mbar.

The brazing temperature and time were determined on the basis of available reference publications and the analysis of the phase interaction of titanium with copper and silver on the basis of their phase equilibrium systems as well as on the basis of the author's own experience [3–7, 9, 11]. The joints were made at 850, 900 and 950°C. The brazing times at each temperature were 1 and 5 min. On the basis of the author’s own experience [6, 7], longer brazing times were not used as it would lead to the total reaction of the brazing metal interlayer with the base of the material being joined and the formation of a hard and very brittle braze having a shear strength of only a few MPa. In each case heating to the brazing temperature was carried out with isothermal holding at 700°C for 20 min in order to conduct the desorption of gases from the surfaces of the elements being brazed and for the compensation of temperature in the whole volume of the samples.

During visual inspection it was possible to observe that all the joints represented a good quality. In each case the brazing gap between the cylindrical elements joined was filled with the brazing metal. It was also possible to notice that the side surfaces of the samples were whitened with the liquid brazing metal, which indicates that the latter was well wetted.

### 2.3. Structures of the brazed joints

The samples for metallographic tests with the use of light microscopy were subjected to grinding with abrasive paper and polished by means of polishing cloth with an addition of diamond and corundum slurry, respectively, as well as by etching in the aqueous solution of FeCl$_3$.

The metallographic examination was carried out in the bright field using a Leica-manufactured metallographic light microscope MeF4A. The tests revealed the significant differentiation of joint structures corresponding to an increase in brazing temperature and time (Table 1). The differentiation was manifested by an increase in the width of precipitates forming diffusion layers on the braze boundaries. They can be ascribed to the diffusive effect of the brazing metal components with the components of the material being joined. On the basis of previous research [6] it is possible to assume that such precipitates were caused by the copper from the brazing metal reacting with the titanium from the alloy TiAl ($\gamma$).

In the structure the joints made at the lowest temperature, i.e., 850°C (brazing times of 1 and 5 min) these layers were of an insignificant width. In addition, in the central part of the joint it was possible to observe dispersive phase precipitates of similarly dark colouring (Table 1). Increasing the brazing temperature to 900°C and to 950°C caused further increasing of the width of the diffusion layers. In the case of the joints made at 950°C (brazing times of 1 and 5 min) practically the whole volume of the braze was filled with the dark-coloured phase.

In order to more precisely investigate the structure of the joints as well as to more accurately identify the phases present in them it was necessary to carry out additional structural tests using a scanning electron microscope LEO GEMINI 1525 provided with a ROENTE-type energy dispersion microanalyzer (EDS). The investigation also involved the measurement of the microhardness of the individual phases present in selected brazed joints. The microhardness tests were carried out by means of a KB50BVZ-FA microhardness tester (KB Prüftechnik GmbH) applying a load of 10 g (HV0.001). The structural tests with the use of electron microscopy included the joints brazed for 5 min at the lowest and intermediate temperatures, i.e., 850 and 900°C. The joint selected for the measurement of the microhardness of individual phases present in the welded joint was that brazed at 900°C for 5 min. The structural test results are presented in Figs. 2 and 3, whereas the results of the hard-
Table 1. Microstructures of TiAl47 alloy joints brazed using interlayer of 63Ag-35.3Cu-1.75Ti filler metal, etch. FeCl₃

| Temp. (°C) | Brazing time |
|-----------|--------------|
|           | 1 min | 5 min |
| 850       | ![Image](image1) | ![Image](image2) |
| 900       | ![Image](image3) | ![Image](image4) |
| 950       | ![Image](image5) | ![Image](image6) |

ness measurements related to the individual phases in the brazed joint are presented in Fig. 4.

The metallographic tests conducted using electron microscopy and energy dispersion spectrometry (EDS) revealed a very diversified layer structure of the joints tested (Figs. 2, 3). Following the assumptions of the work [11, 12] it was possible to notice the dominant fraction of phases rich in titanium and copper (points 3–5 in Fig. 2 and points 2, 3 and 5 in Fig. 3) in the joints tested. Titanium and copper have a significant chemical affinity and form a complex phase equilibrium system with numerous intermetallic phases. Reacting with each other in the brazing conditions titanium and copper caused the decomposition of the Ag-Cu filler metal structure into a phase rich in copper and titanium and a phase rich in silver (point 6 in Fig. 2 and point 4 in Fig. 3). In the case analysed it was possible to observe that the precipitates of the phase rich in copper and titanium stoichiometrically correspond to the phase AlCu₂Ti (points 3–5 in Fig. 2 and points 2 and 3 in Fig. 3), in accordance with the triple phase equilibrium system Al-Cu-Ti [14]. Similar
results were encountered in the works [13, 15] related to brazing of Ti-Al alloy types with Ag-Cu type silver brazing metals. These works state that these phases are responsible for deteriorating the mechanical properties of the joints.

Silver very poorly reacts with the TiAl alloys forming only solid solutions with copper and small amounts of aluminium and titanium (point 6 in Fig. 2 and point 4 in Fig. 3).

Some part of the volume of the joint brazed at the higher brazing temperature (point 4 in Fig. 3) is a solution, the chemical composition of which is similar to the composition of the filler metal with a small amount of dissolved aluminium coming from the material being brazed.

Extending the time and increasing the temperature of brazing lead to almost complete alloying of the brazing metal and the presence of phases rich in copper (Table 1).

The microhardness measurements (HV0.001) of the individual phases present in the joint revealed that the phases of the darker colouring, stoichiometrically corresponding to the phase AlCu2Ti were characterised by the greatest hardness amounting to 410–460 HV0.001 with the hardness of the base metal being 430 HV0.001 and that they might be the reason for the brittleness and weakening of the joint. The hardness of the phases rich in silver and of the phase the chemical composition of which corresponds to the brazing filler metal used did not exceed 100 HV0.001 (Fig. 4).

2.4. Shear strength of the brazed joints

The mechanical properties of the brazed cylindrical samples were determined with a testing machine manufactured by the Instron company (model 4210) by subjecting them to shearing in special holders designed in such a manner that the samples were subjected to shear forces only, without bending (Fig. 5).

The results of the shear tests of the TiAl47 alloy joints diffusion-welded using the 63Ag-35.3Cu-1.75Ti brazing filler metal are presented in Fig. 6.

The strength for the joints made at 850 °C for 1 and 5 min was 200 and 190 MPa, respectively. The same joints made at 900 °C revealed slightly lower strength, i.e., of 199 and 172 MPa, respectively. In turn, us-
ing the brazing temperature of 950 °C significantly decreased the shear strength of the joints, which for the samples brazed for 1 min and 5 min amounted to 172 and 136 MPa, respectively. The reasons for the reduction of the mechanical properties of the joints brazed at higher temperatures and for a longer time were those of greater volume of hard and brittle intermetallic phases in braze.

3. Conclusions

1. The material-technological tests conducted enabled obtaining proper diffusion-brazed joints of the TiAl47 alloy using the active silver brazing metal 63Ag-35.3Cu-1.75Ti as well as applying the brazing temperature of 850–950 °C and a holding time between 1–5 min.

2. The highest shear strength (200 MPa) characterised the joints of the TiAl47 alloy diffusion-brazed with the 63Ag-35.3Cu-1.75Ti brazing filler metal at 850 °C, with a hold time of 1 min. Increasing the temperature and time of brazing led to a decrease in the strength of these joints.

3. The structural tests utilising light microscopy, scanning electron microscopy and energy dispersion spectrometry (EDS) of the joints of the TiAl47 alloy diffusion-brazed with the 63Ag-35.3Cu-1.75Ti brazing filler metal revealed that a decrease in the joint strength along with an increase in the brazing temperature and time was primarily affected by the presence of the layer composed of the hard and brittle AlCu2Ti phase building up (in such conditions) on the braze peripheries.

References

[1] Szklinarz, W.: Intermetallic Phase Based Alloy From Ti-Al System. Silesian University of Technology, Gliwice 2007.
[2] Lütjering, G., Williams, J.: Titanium. Heidelberg, Springer 2003. doi:10.1007/978-3-540-71398-2
[3] Wallis, I. C., Ubki, H. S., Bacos, M.-P.: Intermetallics, 3, 2004, p. 303. doi:10.1016/j.intermet.2003.11.002
[4] Shine, R. K., Wu, S. K., Chen, S. Y.: Acta Materialia, 51, 2003, p. 1991. doi:10.1016/S1359-6454(02)00606-7
[5] Jacobson, D. M., Humpston, G.: Principles of Brazing. Materials Park, Ohio, ASM International 2005.
[6] Mirski, Z., Róźański, M.: Materials Engineering, 2, 2010, p. 161.
[7] Mirski, Z., Róźański, M.: Archives of Foundry Engineering, 1, 2012, p. 371.
[8] Wojewoda, J., Zięba, P.: Materials Engineering, 1, 2004, p. 11.
[9] Róźański, M., Adamsiec, J.: Solid State Phenomena, 191, 2012, p. 249.
[10] Shapiro, A., Rabinkin, A.: Welding Journal, 10, 2003, p. 36.
[11] Mirski, Z., Róźański, M.: Archives of Civil And Mechanical Engineering, 13, 2013, p. 415. doi:10.1016/j.acme.2013.04.007
[12] Shine, R. K., Wu, S. K., Chen, S. Y.: Acta Materialia, 51, 2003, p. 2991. doi:10.1016/S1359-6454(02)00606-7
[13] Tetsui, T.: Intermetallics, 9, 2011, p. 253. doi:10.1016/S0966-9795(00)00129-1
[14] Massalski, T. B.: Binary Alloy Phase Diagrams. Materials Park, Ohio, ASM International 1990.
[15] Wallis, I. C., Ubki, H. S., Bacos, M.-P.: Intermetallics, 3, 2004, p. 303. doi:10.1016/j.intermet.2003.11.002