BRAZING OF TITANIUM AT TEMPERATURES BELOW 800°C: REVIEW AND PROSPECTIVE APPLICATIONS

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Abstract

Brazing temperature of conventional Ti-Cu-Ni and Ti-Zr-Cu-Ni filler metals is usually above the β-transus temperature of titanium base metals that hurts mechanical properties of the base metal. Brazing titanium below the β-transus temperature using the Ag-based and Al-based filler metals of various compositions has been evaluated in the review. Some new Al-based filler metals were tested experimentally for joining thin-wall titanium structures. The effect of alloying elements on the aluminum braze alloys, especially for the intermetallic formation in the brazed titanium joints, was examined. Prospective applications of low-temperature brazing of titanium in Aerospace, Aviation, and Electronics are discussed, as well as potential technical solutions to improve mechanical properties of brazed joints.

0. Introduction

The development of titanium brazing began in early 1950s in an effort to reduce the weight of the launch vehicles and aircraft structures [1, 2]. To date, over 100 brazing filler metals (BFM) have been developed and tested in response to the industrial needs. The main emphasis of this activity was to improve strength and corrosion resistance of titanium-to-titanium and titanium-to-dissimilar metals brazed joints, particularly titanium-to-stainless steel.

Despite the fact that numerous BFM compositions have already been tested, we still do not have the filler metals for "low-temperature" (below 800˚C) brazing of titanium that are produced for commercial markets [3]. Only the simplest binary and ternary compositions of low-temperature brazing alloys based on aluminum, aluminum-silver, and aluminum-silicon systems have been tested and produced mixed results as low-temperature BFM. Consequently, neither one of them was selected for industrial applications.

The present review is focused on problems and prospects of low-temperature BFM capable of brazing titanium below the beta-transus temperature, and even below the temperature of aging of dispersion-strengthened alloys.

The intention to use low-temperature BFM is not only to achieve strong brazed joints, but also to save the energy on heating and reduce brazing time, which is very important, for brazing in Space. The focus of this work is on possibility of using low-temperature aluminum-based filler metals for brazing titanium in Space.

1. Temperature Classifications of Filler Metals Used for Brazing Titanium

All known titanium brazing filler metals can be roughly separated into five major families according to the base component in their chemical compositions (Table 1):

(1) silver-based (especially, Ag-Cu-based) alloys,
(2) titanium-based alloys,
(3) aluminum-based alloys,
(4) palladium-based alloys, and
(5) zirconium-based alloys.

The nature of titanium alloys (base metals) determines important temperature/time limits of brazing thermal cycles. These limits are caused by undesirable changes in the microstructure and properties of both the base metal and the joint:

- due to beta-transus, i.e., the critical temperature of the $\alpha \leftrightarrow \beta$ phase transformation, and
- due to the formation of brittle intermetallics at the interface between the base metal and brazed joint.

Table 1

MAJOR FAMILIES OF BRAZING FILLER METALS FOR JOINING TITANIUM ALLOYS

Brazing filler metals	Brazing temperature range °C	°F	Availability on the US market in 2006
Silver-based	720-950	1328-1742	Yes
Titanium-based	850-1020	1562-1868	Yes
Aluminum-based	600-750	1112-1382	Yes
Palladium-based	1050-1150	1922-2102	N/A
Zirconium-based	790-950	1454-1742	N/A

In order to avoid heating above the $\alpha \leftrightarrow \beta$ phase transformation:

- the brazing temperature of the α-titanium alloys should be below 900°C,
- the brazing temperature of the α+β titanium alloys should be below 935°C,
- the brazing temperature of most of the near-β titanium alloys should be below 870°C, and
- the brazing temperature of the β-titanium alloys should be below 800°C, preferably below 760°C.

The limitation of brazing temperatures by the beta-transus temperature is especially important for thin-wall structures usually used in the Aerospace applications. Undesirable structural changes in the thin-wall base metal may cause a drastic decrease of mechanical properties and reliability of the entire titanium article.

The effect of the brazing temperature on microstructure of brazed joints is not so unambiguous. On the one hand, the higher the brazing temperature is, the more intensive reaction occurs between the filler metal and base metal, and consequently, the thicker intermetallic layer may be formed at the interface. This brittle intermetallic layer is considered as a source of microcracks, which may appear during the mechanical or thermal cycling of the brazed joint.

On the other hand, it is well known that the higher brazing temperature range of 950-1050°C results in the increase of static strength of the brazed joints at room temperature [4]. This effect was explained by R. Wells [5], and Bostain O. and A. Rabinkin [6] as a result of forming specific microstructure of brazed joint at the optimal brazing temperature and cooling rate. The key parameter here is a cooling rate that should be as high as possible.

The amount of liquid filler metal also affects the joint microstructure and especially the thickness of the intermetallic layer at the interface. Generally speaking, small brazing gap ≤50 μm and small amount of liquid metal result in the discontinuous thin intermetallic layer or only "island" intermetallics which cannot generate cracks in the joint. The relatively thick joints (the joint clearance ≥100 μm) usually have continuous intermetallic layer which generates cracks at any thermal stresses.

The last metallurgical factor, that should be considered, is a susceptibility to erosion of titanium base metal in contact with the liquid filler metal at high brazing temperatures. A significant erosion of titanium alloys during brazing is well known, and it adversely affects the reliability of brazed structures, especially thin-wall structures. In order to prevent the erosion of the base metal, the brazing temperature should be as low as possible, and the time of contact between the liquid filler and the base metal should be limited, as well.

2. Criteria for Selection of Brazing Filler Metals for Joining Titanium in Open Space

Summarizing the above mentioned data, we can formulate the criteria to brazing filler metals suitable for manufacturing reliable thin-wall titanium brazed structures in Open Space:

- brazing temperature below 800°C, or even below 760°C,
- an ability to fill small brazing gaps ≤50 μm in vacuum,
- an ability to form intermetallic-free (or low-intermetallics) micro-structure of the joint at the high cooling rate,
- low erosion or non-erosion interaction of liquid filler metal with titanium base metals during the brazing, and
- satisfactory static and impact strengths of brazed joints at cryogenic temperatures.

According to Table 1, only aluminum-based BFM and some of silver- and zirconium-based brazing alloys may satisfy these criteria. These selected groups of low-melting BFM will be discussed below.

Further, we will call the filler metals that can be used at the brazing temperatures below 800°C as "Low-melting".

3. Silver-based Low-melting Brazing Filler Metals

3.1 Characterization of silver-based filler metals used for titanium brazing

The silver-based alloys dominated the titanium brazing industry in

1950-1960s due to their accessibility and well known technological behavior for that period of time. Titanium joints brazed at 1100°C by pure silver as a filler metal showed a pretty high strength of 22 ksi (150 MPa) and good ductility due to the relatively "ductile" nature of TiAg intermetallics at the interface [7].

Compositions and brazing temperatures of low-melting silver-based BFM are presented in Table 2. Strength data for titanium joints brazed in vacuum or argon furnaces (slow cooling) using Ag-based low-melting BFM is presented in Table 3.1 and brazed by induction or infra-red heating (fast cooling) is presented in Table 3.2.

Aluminum did not effectively depress the liquidus temperature of Ag-based BFM metals because of small amount of such depressant. Although, the liquidus of Ag-5Al alloy is as low as 810°C, the effective wetting of titanium alloy Ti-6Al-4V in vacuum by the filler metal Ag-5Al occurs only at 900°C [8] or at 830-850°C after holding for 30-50 seconds [9]. The filler metal Ag-5Al has demonstrated satisfactory strength of 172 MPa for Ti-6Al-4V brazed joints made at 950°C [10].

A complex study of the Ag-Al system for brazing fin-plate heat exchangers showed that an addition of titanium did not make serious changes in flow characteristics or mechanical properties of the brazed joints. Both Ag-5Al and Ag-5Al-5Ti brazing alloys demonstrated good flow at the brazing temperature 915°C and <u>low erosion</u> of titanium base metal, but unacceptable bend ductility due to the formation of a thick intermetallic layer in the joint [11].

Any increase of the content of aluminum deteriorated behavior of molten filler metals because the compositions became susceptible to early formation of intermetallics of the Al-Ag system, which affected the liquid metal flow.

The attempt to improve high-aluminum silver brazing alloys [12] by additions of Mn, Si, or Sn showed that the formation of stable defect-free joints is possible only at a brazing temperature in the range of 850-950°C despite an increase of the aluminum content in Ag-8Al-6Sn or Ag-15Al-1Mn-0.5Si brazing alloys.

Further increase of aluminum content in the silver BFM adversely affects the mechanical properties of the brazing joints. The shear strength of Ti-6Al-4V joints brazed at 600°C by the Ag-36Al-14Cu filler metal is only 2.5 ksi which is over 10 times lower than that of low-aluminum BFM [13] (Table 3.1).

This meant that non-standard BFM based on the Ag-Al system did not demonstrate neither temperature nor strength advantages against standard and widely-used Ag-Cu, Ag-Cu-Ti, or Ag-Pd-Ga filler metals which survived in this competition and which are used even today for brazing titanium. For example, the following BFM are readily available:

- BAg-8 (Ag-28Cu) having eutectic melting temperature of 780°C,
- Cusin-1-ABA® (Ag-34.2Cu-1Sn-1.75Ti) having melting range of 775-806°C,
- Ticusil® (Ag-26.7Cu-4.5Ti) having melting range of 780-900°C,
- Cusil-ABA® (Ag-35.2Cu-1.75Ti) having melting range of 780-815°C,
- Gapasil®-9 (Ag-9Pd-9Ga) having melting range of 845-880°C [14].

But attempts to find a balanced composition of the Ag-Al-Cu system were being continued despite of above-mentioned contradictory results, because theoretically this alloy system is attractive by low eutectic temperature and by the limited formation of intermetallics. X. Heberard and co-authors [15] tested another high-aluminum brazing alloy Ag-30Al-5Cu modified by 5 wt.% of copper. They found that this alloy forms contact angles 10-15° on titanium at 700°C, but only in 5 min of holding time. An important feature of this filler metal is its ability to fill relatively wide joint clearances up to 0.5 mm, although, the optimal clearance is only 0.05 mm.

Similar near-eutectic alloy Ag-28Al-5Cu-0.5Ti with small addition of titanium as the structure refiner, was also tested by A. E. Shapiro and I. P. Klyutchnikov in 1988 for brazing fin-plate titanium heat exchangers developed for life-support systems. The filler metal Ag-28Al-5Cu-0.5Ti exhibited perfect flow on titanium both during brazing in vacuum and in air (with a chloride flux) at 650-660°C. The corrosion resistance of the alloy was slightly improved by addition of Ti, but still was not sufficient. However, a relatively easy rolling ability is the technological advantage of this alloy that makes it possible to manufacture wire or foil performs. Since 2004, this alloy has been studied by Titanium Brazing, Inc. as a prospective filler metal suitable to repair titanium heat exchangers brazed with the TiBraze375 (Ti-37.5Zr-15Cu-10Ni). It is expected to test first wire samples of the Ag-28Al-5Cu filler metal in Spring 2008.

The standard eutectic brazing alloy BAg-8 provides satisfactory strength of titanium brazed joints in the range of 165-224 MPa but only at the brazing temperature above 800°C and holding ≤10 min (Table 3.1). Experiments with high-energy IR heating source showed that fast heating-cooling brazing cycle provides significant gain in the strength of titanium brazed joints [10]. The average shear strength of Ti-6Al-4V joints infra-red brazed with silver filler metals was 173 MPa while the furnace-brazed joints was only 117.5 MPa. Electron beam brazing of thin-wall titanium tubing with Gapasil®-9 also demonstrated an advantage of the fast brazing cycle which resulted in much thinner intermetallic layer at the interface, than that was after the furnace brazing [16].

A serious effort was mounted to test and implement an Ag-5Al-0.5Mn brazing alloy in the middle of 1970s. Evaluation of this filler metal was made as a part of Advanced Honeycomb Air Vehicle Structure Program sponsored by the Air Force Flight Dynamics and Materials Laboratories [17].

Another attempt to decrease the brazing temperature was made in 1975 in the USSR by introducing the silver filler metal VPr-68 (Ag-23Cu-5Sn) [18] which had a brazing temperature range of 820-850°C. This filler metal had a brazing temperature lower than that of Ag-5Al-0.5Mn alloy, but the same as the brazing temperature of BAg-8 and most of Ag-Cu-Ti filler metals. Therefore, this filler metal also did not find a wide application and was not re-produced in the USA at all.

The system of Ag-Cu-Sn offers many compositions which may be used as low-melting filler metals for joining titanium. Two of such alloys are presented on the market in the form of standard brazing filler metals BAg-18 and BAg-21 (Table 2), and presumably can be tried for brazing titanium below 800°C.

A promising filler metal BrazeTec VH720 (Ag-27Cu-13In) was developed by Degussa (Germany) in 1990s and successfully tested for brazing titanium [19] in 2002. This filler metal has solidus 605°C and liquidus 710°C, and has a brazing temperature range of 720-780°C which is significantly lower than that of traditional silver based alloys. This BFM showed tensile strength of brazing joints of Ti-6Al-4V alloy [21] as high as 370 MPa. Unfortunately, the BrazeTec VH720 filler metal was recently excluded from the BrazeTec production list [20], supposedly because of the high cost of indium which has grown up more than 10 times since 2003.

Indium is a very effective temperature depressant, and it is fair to notice that the BrazeTec VH720 is not the first indium-containing brazing alloy used for brazing titanium. The similar system of Ag-25Cu-25In was tested 25 years ago at the sensationally low brazing temperature of

680°C [15]. Brazed joints of Ti-6Al-4V made by this filler metal showed sufficient strength at room temperature, but had a low corrosion resistance in a marine environment. Based on this study, we can also expect insufficient corrosion resistance from the BrazeTec VH720, which contains a significant amount of indium. Also, strength at cryogenic temperatures of joints brazed with the above mentioned indium-containing alloys is presently unknown.

A filler metal Incusil-ABA® (Ag-27.2Cu-12.5In-1.25Ti) of this system activated and corrosion-protected by small amount of titanium has a melting range of 605-717°C. This alloy is the product of WESGO Metals [14] which has never been tested for brazing thin-wall titanium structures. This alloy can be definitely considered as a potential candidate for brazing in Space providing that testing its erosion activity and mechanical properties at cryogenic temperatures will produce positive results.

Comparison of strength data presented in Tables 3.1 and 3.2 shows that there is no difference in strengths between joints made by furnace heating (slow heating and cooling) – Table 3.1 and joints made by intensive local heating and fast cooling – Table 3.2. The most important factors in the strength consideration are (a) composition and strength of the base metal, (b) composition of the BFM, and (c) holding time at the brazing temperature.

Generally, the effect of holding time can be formulated as: titanium brazed joints made for short (1-5 min) holding time have significantly higher strength than that of joints brazed for 10-20 min. This strange effect of the brazing time on corrosion resistance was not studied completely and needs to be checked.

Data on corrosion resistance available in published technical literature confirm average level of resistance of titanium brazing joints or low corrosion effect of silver-based BFM. Only joints brazed with the Ag-Al-Cu filler metals showed insufficient corrosion resistance, however, the resistance could be significantly improved by decreasing brazing temperature.

3.2 Potential candidates of low-temperature silver-based filler metals

The following silver-based BFM can be selected as potential candidates for brazing at the temperature ≤800°C (≤1470°F) and for testing mechanical properties of joints at negative temperatures:

- **BAg18** (Ag-30Cu-10Sn) with the melting range of 602-718°C and **BAg21** (Ag-28.5Cu-2.5Ni-6Sn) with the melting range of 691-802°C,
- **Incusil-ABA®** (Ag-27.2Cu-12.5In-1.25Ti) with the melting range of 605-717°C, and
- **Ag-28Al-5Cu** or Ag-28Al-5Cu-0.5Ti alloy with the melting range of 558-580°C.

Table 2

COMPOSITIONS AND BRAZING TEMPERATURES OF COMMERCIAL Ag-BASED LOW-MELTING FILLER METALS FOR BRAZING TITANIUM

Brazing filler metal		Manufacturer	Solidus, °C	Liquidus, °C	Brazing temperature range, °C	Ref.
Tradename	Composition					
Silverbraz60Sn10	Ag-30Cu-10Sn (BAg-18)	Prince & Izant	600	720	720-800	22
Silverbraz63	Ag-28.5Cu-6Sn-2.5Ni (BAg-21)	Prince & Izant	691	800	800-820	22
Silverbraz72	Ag-28Cu (BAg-8)	Prince & Izant	779	779	790-850	22
Silverbraz71	Ag-28Cu-0.5Ni	Prince & Izant	779	796	800-850	22
Incusil-ABA	Ag-27.2Cu-12.5In-1.25Ti	WESGO Metals	605	715	720-800	14
	Ag-24Cu-15In	Indium Corp.	603	705	720-800	46
	Ag-28Cu-0.5Ni	Indium Corp.	775	785	800-850	46
BAg-1	Ag-15Cu-16Zn-24Cd		607	618	643	
BAg-1a	Ag-15Cu-16Zn-18Cd		627	635	682	
BrazeTec6488	Ag-26Cu-2Mn-2Ni-6In	Degussa Corp.			770-800	20
BrazeTec VH720	Ag-24Cu-14.5In	Degussa Corp.	605	710	720-780	19

Table 3.1

STRENGTH OF TITANIUM JOINTS BRAZED IN VACUUM OR ARGON FURNACE (SLOW COOLING) USING Ag-BASED LOW-MELTING FILLER METALS

Brazing filler metal							
Tradename	**Composition**	**Titanium base metal**	**Brazing temperature °C**	**Holding time, min**	**Shear strength, MPa**	**Tensile strength, MPa**	**Ref.**
Silver	Fine Ag	CP Titanium	970	30	104		1,2
		TI-2Al-3Mn	980	5	166		
BAg-8	Ag-28Cu	Ti-6Al-4V	850	1	224		10
			850	10	130		
			850	20	108		
			800	10	165		
			800	20	142		
BAg-8	Ag-28Cu	CP Titanium			47		1,2
BAg-1	Ag-15Cu-16Zn-24Cd	CP Titanium	650	30	105		1,2
BAg-1	Ag-15Cu-16Zn-24Cd	CP Titanium	650		57		1,2
BAg-1a	Ag-15Cu-16Zn-18Cd	CP Titanium	682		58		1,2
BrazeTec VH720	Ag-24Cu-14.5In	Ti-6Al-4V	720	10		370-480	19
	Ag-5Al-0.5Mn	Ti-6Al-4V	860	7	141-176		23
	Ag-5Al-0.5Mn	Ti-6Al-4V	850	N/A	137-167		24
	Ag-10Al-1Mn-0.5Si	Ti-4.5Al-2V	880	10	154	242	25
	Ag-12Al-0.2Mn	Ti-6Al-4V	>730	N/A	137-206		24
	Ag-30Al-5Cu	Ti-6Al-4V	680	N/A	431		24
	Ag-36Al-14Cu	Ti-6Al-4V	600	5	17	1.2	13
	Ag-3Li	CP Titanium	800	N/A	160		24
Gapasil-9 *	Ag-9Pd-9Ga	Ti-6Al-4V	890	1	166-193		26
Ticuni *	Ti-15Cu-15Ni	Ti-6Al-4V	950	5		960	26
Ticuni *	Ti-15Cu-15Ni	Ti-6Al-2Sn -4Zr-2Mo	970	2-5	304-317		27
Ticuni *	Ti-15Cu-15Ni	Ti-6Al-2Sn -4Zr-2Mo	970	2-5	200-207		27

* for comparison of low-melting filler metals with traditional Ag-based and Ti-based filler metals

Table 3.2

STRENGTH OF TITANIUM JOINTS MADE BY INDUCTION OR INFRARED BRAZING (FAST COOLING) IN ARGON USING Ag-BASED LOW-MELTING FILLER METALS

Brazing filler metal		Titanium base metal	Brazing temperature °C	Holding time, min	Shear strength, MPa	Ref.
Trade-name	Composition					
Silver	Fine Ag	CP Titanium	970	0.25	214-248	2
			980	1	152	
BAg-8	Ag-28Cu	CP Titanium	850	1	145	2
BAg-1	Ag-15Cu-16Zn-24Cd	CP Titanium	650	0.25	207-248	15
	Ag-5Al	Titanium/Copper	830	1	163.5	28
			830	5	190.5	
			850	1	198.5	
			850	5	160	

4. Aluminum-based Brazing Filler Metals

4.1 General consideration

Theoretically, aluminum-based BFM have considerable advantages over silver-based alloys. Aluminum-based filler metals have:

- lower melting points,
- lower densities, and
- good metallurgical compatibility with titanium alloys to be brazed, particularly, good wetting and flow in capillary gaps.

Aluminum alloy melts have perfect wetting on titanium both in vacuum and under the flux. Therefore, aluminum BFM attracted a particular attention of brazing engineers since a challenge of joining titanium became a subject of interest in the aerospace industry in 1950s.

Despite some successful applications, main efforts were made to overcome serious drawbacks of aluminum filler metals such as:

- low strength in comparison with silver-based and titanium-based BFM,
- low strength at elevated temperatures,
- sometimes not sufficient corrosion resistance, and
- reactivity to titanium which resulted in the fast formation of brittle intermetallic layers in the joints.

Many efforts were made to evaluate compatibility of aluminum BFM with titanium base alloys and to use them in the aerospace industry. After fifty years of trials, we could say that those efforts have failed because there is no single aluminum-based BFM being used routinely now for joining titanium.

The reason for the a lack of use of aluminum-based BFM is lower strength of brazed joints. P. Knepper and D. Lohwasser compared tensile strength of different brazing alloys during selection of materials for joining titanium structures in the Airbus project [21]. The strength of Ti-6Al-4V joints brazed with Al-12Si or Al-1Mn filler metals was below 200 MPa, while that of joints brazed with Gapasil-9, VH720, or Ag-26.5Cu-5Pd filler metals was in the range of 380-500 MPa. A comparison of the lap shear strength was also not in favor of aluminum filler metals. However, shear strength of the brazed joints can be tailored by increasing the overlap area to achieve a load-carrying capability approaching that of the base metal.

Brazing of titanium structures in Open Space gives another opportunity for considering the aluminum-based BFM because such applications do not require a high static or dynamic strength of joints, there is no corrosion conditions in Space, and the reactivity of the aluminum can be suppressed by the very short brazing thermal cycle. In this case, we can expect that the advantages of aluminum BFM (especially low melting point and good wetting and flow) may prevail over their drawbacks.

4.2 Compositions of aluminum-based filler metals and mechanical properties of titanium brazed joints

Compositions of tested aluminum-based BFM are shown in Table 4 and tensile, shear, and fatigue strengths are shown in Table 5.

Pure aluminum reacts with titanium very actively, and thin-wall brazed joints are characterized by unacceptable level of the base metal erosion. Even short exposure of Al melt to titanium during torch brazing may result in deep erosion of the base metal. Therefore, aluminum BFM are usually alloyed by such metals as Cu, Si, Mg, Fe, and Sn, which diminish the reactivity of pure aluminum. Magnesium is the most effective alloying element for this purpose because it does not react with titanium at all.

R. Wells found experimentally that additions of Mg or Li to the filler metal compositions improve the flow characteristics and may significantly decrease the brazing temperature [13]. Also, a small addition of Li improves corrosion resistance of the brazed joints, while alloying with Mg acts adversely on corrosion resistance, especially in Ag-Cu-Al filler metals.

Wetting and flow characteristics of any aluminum brazing alloys can be improved by raising the brazing temperature. It is useful to remember that a problem of flow of Al-based alloys into a small brazing gaps may be resolved by a simple raise of the brazing temperature by 50-100°C.

It is appropriate to note here, that effective flow temperatures of aluminum BFM on titanium are 90°C higher in vacuum than in 500 torr ($6.6x10^4$ Pa) of argon. This effect was not fully explored. However, R. Wells [13] concluded that it was not caused by evaporation of the braze components. We suggest that oxidation of titanium and liquid aluminum in dry argon is less than that in vacuum. This idea is based on the experience with brazing of Ni-based superalloys by Ni-Cr-Si-B filler metals, where the same effect was also observed.

The "retardation effect" of wetting is clearly revealed when brazing titanium aluminide using pure aluminum and AWS BAlSi-4. Dense and good quality brazed joints of TiAl plates were obtained at the respective brazing temperatures of 800˚C and 900˚C [9]. This is despite the fact that liquidus temperatures of these filler metals are 660˚C and 582˚C, respectively.

A detailed investigation of low-temperature joining of titanium thin-wall honeycomb structures was made by AVCO Corp. in 1971[29]. The alloy AVCO No. 48 (Al-4.8Si-3.8Cu-0.2Fe-0.2Ni) was recognized as the most suitable BFM for joining thin sandwich articles. Smooth fillets have already been formed at 510°C and 5 min holding time. Faster formation of the fillets and improvement of the joint strength was reached at the brazing temperature of 680°C. No brittle intermetallics at the interface were found. The last observation is somewhat in doubt since the considerable overheating above the liquidus of this filler metal should enhance a reaction between aluminum melt and titanium base metal.

An original experiment with brazing titanium in air using a low-melting aluminum brazing alloy was made in the University of Hannover (Germany). A thin Al foil was coated by copper to get an eutectic composition (33 wt.% Cu) which was placed between Ti-6Al-4V plates and used as the filler metal for the torch, induction, or electric resistance brazing at 550°C. Dense joints of good quality were obtained at the brazing clearance of 6-20 μm. But, the shear strength of brazed joints reached only 25 MPa which is sufficient only for large area joints [30]. This experiment showed that Al-Cu eutectic is sufficiently active to interact with titanium even in air.

Also, activity of the aluminum-copper eutectic and wetting of titanium are being improved by alloying with small amount of lithium [31]. The spreading area of Al-33Cu-0.5Li is at least two times larger than that of Al-33Cu eutectic filler metal in vacuum at 630˚C, 3 min. In this connection, we can suggest that standard aluminum-lithium alloys such as AA2090, AA8090, and especially Weldalite 049 which is manufactured in the form of welding wire may be used as low-melting filler metals for joining titanium. Compositions of Al-Li alloys are presented in Table 6. Melting range of these alloys is 500-650˚C [32].

Table 6

Compositions and melting temperatures of aluminum-lithium alloys

Alloy designation	Composition, wt.%	Melting temperatures, ˚C	
		Solidus	Liquidus
AA2090	Al-(2.4-3)Cu-(1.9-2.6)Li-0.1Si-0.2Mg-0.1Fe-0.1Ti	560	650
AA8090	Al-(1-1.6)Cu-(2.2-2.7)Li-0.2Si-0.1Mg-0.3Fe-0.2Zn-0.1Ti	600	655
Weldalite 049	Al-5.4Cu-1.3Li-0.4Mg-0.1Zr-0.4Ag	560	630

An improvement of wetting titanium by Al-10Si near-eutectic alloy was reached by alloying with 1 wt.% of Mg [31]. The Al-10Si-1Mg filler metal exhibited spreading 2.5 times better than that of binary Al-10Si alloy for 3 min at 630˚C in vacuum.

T. Takemoto with co-authors [33] tested a number of low-melting filler metals as potential materials for brazing titanium to aluminum, hence, the brazing temperature was limited by 630˚C.

First of all, a comparison of spreading areas of 15 filler alloys at the same temperature of 630˚C for 3 min in vacuum clearly showed that Ag-Al and Al-Ag-Cu systems have obvious advantage in wetting titanium against Al-Si, Al-Ge, and Al-Cu-Si alloys. Frankly, this knowledge doesn't help us much because all filler metals tested here are not commercial. But, we know at least that Al-Si or Al-Cu-Si alloys (which are represented among commercial filler metals) should be alloyed by such wetting promoters as Mg, Sn, or Li.

For example, we can expect that some standard aluminum alloys containing combinations of Al, Si, Cu, and Mg possess good wetting on titanium and can be selected as brazing filler metals. These alloys are AA2218 (Al-4Cu-1.5Mg-2Ni-0.9Si) and AA5556 (Al-5Mg-0.8Mn-0.2Si). Alloying with tin cannot be recommended due to the low solidus temperature and low strength of Al-Sn alloys. Some of these alloys TiBraze®Al-642 (Al-5Si-0.8Fe-0.2Ti), TiBraze®Al-645 (Al-5Mg-0.2Si-0.2Ti), and TiBraze®Al-655 (Al-6Cu-0.2Si-0.3Mn-0.2Ti) were already selected and tested for electron beam and furnace brazing of titanium tubing [16].

The microstructure of these brazed joints also revealed intermetallic layers formed at the titanium interface: Ti-Al-Si compounds for TiBraze®Al-642, and Ti-Al compounds for TiBraze®Al-645 (Fig. 1,2).

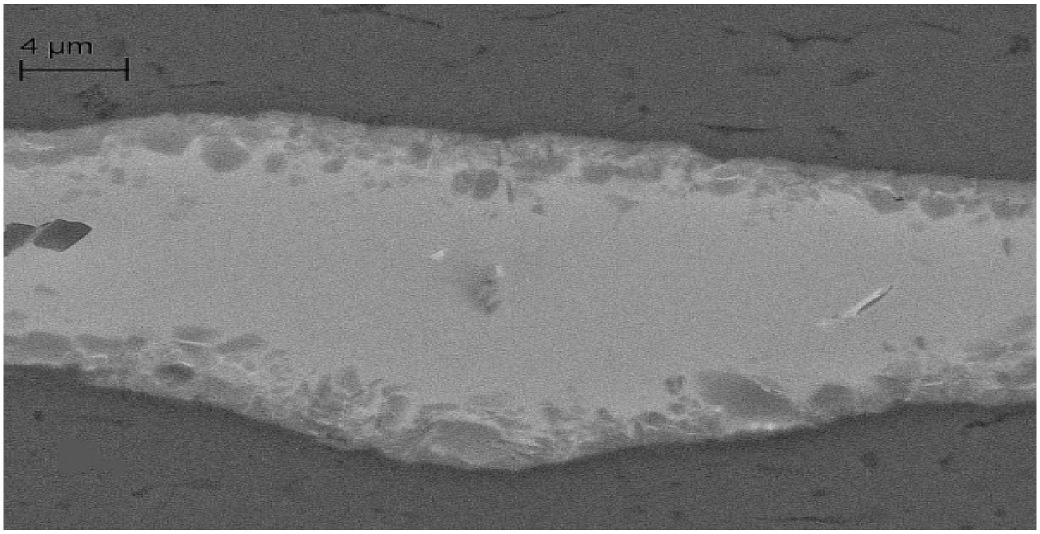

Fig. 1 Titanium joint EB brazed using TiBraze®Al-642 (Al-5Si-0.8Fe-0.2Ti). An Al-Ti intermetallic compound formed at the interface also has some Si [16].

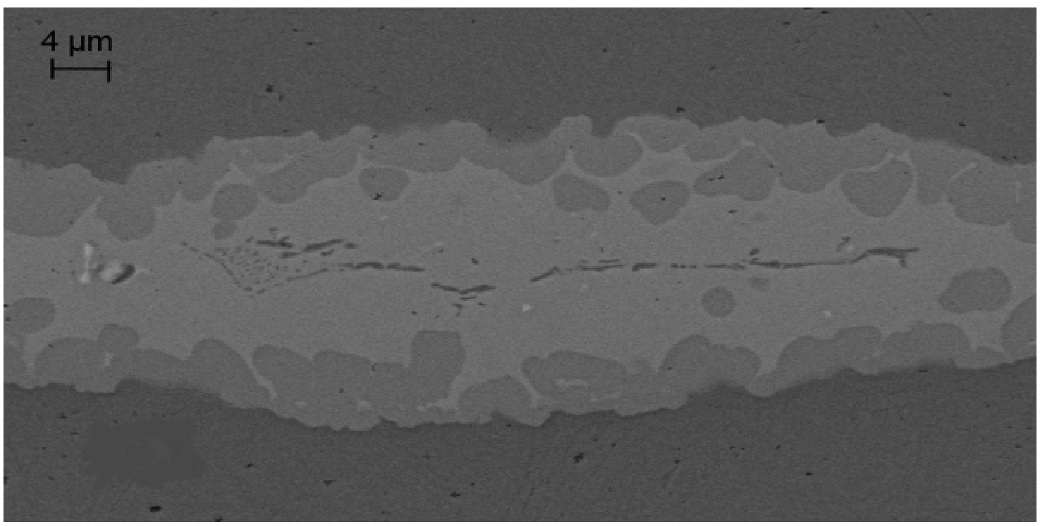

Fig. 2 Titanium joint EB brazed using TiBraze®Al-645 (Al-5Mg-0.2Si-0.2Ti). Note the absence of Mg in the interface layer, consisting of Al-Ti intermetallics. Magnesium is still in the solid solution of the Al brazing alloy [16].

A unique experiment was made by Takemoto T., Nakamura H., and Okamoto I. in measuring the effect of intermetallics formation on an ability of different filler metals to fill brazing clearances of ≤0.1 mm at one temperature 680˚C for 3 min in vacuum [33]. Results of this study clearly show that intermetallics formed on titanium during short time do not affect filling of the joint clearance. Moreover, the filled clearance length of each filler metal was 25-28 mm, indicating no dependence of the filler metal composition on filling titanium joints.

The following intermetallic phases were identified: (a) $TiAl_3$ and Ti_8CuAl_{23} in joints made with Al-10Cu-8Sn filler metal, (b) Al_3Ti, $CuAl_2$ and Ag_2Al in joints made with the Al-20Ag-10Cu filler metal, (c) $Ti_7Al_5Si_{12}$ and Ti_8Al_{23} in joints made with the Al-10Si-0.5Mg filler metal. The intermetallic layers at the interface were pretty thin, nevertheless, authors concluded that intermetallic compounds would act as the crack initiation sites.

The thicknesses of intermetallic layers were quite different. Pure aluminum filler metal had the largest thickness of the $TiAl_3$ layer, while any additional elements in aluminum alloys suppressed the growth of intermetallics. Particularly, a small addition of silicon remarkably decreased the layer thickness.

Higher brazing temperature promotes the growth of intermetallic phases, therefore the shear strength of titanium lap joints brazed at 710-720°C was by 10-20% lower than that of the joints brazed at 670-680°C.

In addition to temperature, the brazing time also has a great effect on strength of the brazed joint. Increase in holding time from 3 min to 20 min resulted in drastic, almost six fold drop of the strength of titanium lap joints brazed with pure aluminum filler metal, and a 30% drop for Al-0.8Si filler metal [33]. It is important to note, that the time increase from 3 min to 10 min had almost no affect on the strength of titanium joints brazed with Al-0.8Si filler metal, while the same time difference decreased the strength by 3 times in joints brazed with pure aluminum. This is a quite strong argument in favor of using alloyed aluminum alloys rather than pure aluminum for brazing titanium.

Controversial results about the negative effect of holding time on the joint strength were obtained by W.H. Sohn with co-authors [34] in their recent study of diffusion interaction between titanium and the liquid Al-10Si-1Mg filler metal. The maximum joint shear strength of 84 MPa was reached after brazing for 25 min, while the lowest strength ~30 MPa was measured after the brazing for <1 min, and the strength of ~50 MPa was obtained after holding for 120 min (Table 5). In order to explain these unusual results, authors proposed a “three-stage interaction” model. The diffusion bonding behavior was divided into three stages based on the change of joint strength with increasing holding time at the brazing temperature.

Initially, after 1 min or first stage, the strength of joints rapidly increases from 30 to 70 MPa with the increase of hold time. This happens due to complete wetting and removal of oxides from the base metal surface (second stage). A significant drop of the strength (from 84 to ~50 MPa) in the third stage (from 25 min to 120 min) caused by formation of shrinkage cavities and intermetallic layers $Al_5Si_{12}Ti_7$ and $Al_{12}Si_3Ti_5$ due to diffusion of silicon in titanium.

SEM study of the intermetallic’s morphology at the interface between titanium base metal and several aluminum BFM showed that discontinuous $TiAl_3$ phase distributed in aluminum solid solution or even as a thin intermetallic layer may improve shear strength of the joint [35]. The authors of this work also found that Al-Ni filler metal forms a layer of $TiAl_2$ intermetallic phase which is thinner than the layer of $TiAl_3$ usually formed at the interface. The authors explained this by a higher diffusion coefficient of Ni in titanium than that of aluminum. As such, nickel competes with aluminum in the reaction with titanium. A specific role of nickel in slowing down the growth of intermetallic layer at the interface requires additional investigation.

In the late 1970s, Boeing Co., Seattle, had carried out a big project of brazing titanium tailpipes using aluminum-based filler metals. Results of this efforts were reviewed by C.E. Kimball [36] in 1980. The Ti-3.5Al-2.5V alloy tailpipes and cowl(?) assemblies were brazed in vacuum using 3003 aluminum alloy (Al-1Mn-0.6Si-0.7Fe) as the filler metal to fabricate the noise reduction structure for jet engines. The assembly was heated to the braze melting point 660°C, and held at this temperature until thermal uniformity had been reached, and then, heated to 680°C and held for 3 min only. The short holding time was used in order to minimize the growth of intermetallic layers. The brazed structures went through long service evaluation with a jet engine, and no failures were reported except corrosion damage.

The same filler metal alloy 3003 was also used by NASA [37] for joining Ti-6Al-4V by a process which combines resistance spot welding and brazing. The spot welding was used to position and align the parts, and to establish suitable joint clearances. Test results showed that brazed joints were superior in tensile strength, stress rupture, fatigue, and buckling. The brazed joints were also hermetically sealed.

Standard aluminum alloys containing significant amount of Si, Mg, Cu, and Li should be also considered as filler metals suitable for brazing titanium at low temperatures. These brazing filler metals as well as the appropriate fluxes, have being studied by Titanium Brazing, Inc. for several years. [38] to develop joining process of titanium-to-titanium, titanium-to-aluminum, or titanium-to-copper in air. This work is yet completed, mostly because of the complexity of flux systems which are different for Al-Si, Al-Cu, and Al-

Mg brazing filler metals. But some metal-flux combinations proved an ability of standard aluminum alloys to work as brazing filler metals. Examples of successful brazing of thin-wall titanium specimens and tubes are shown in Figs. 3,4.

Metallurgical compatibility of titanium with some standard aluminum alloys used as filler metals for vacuum brazing was investigated by Nesterov A.F. and Dolgov Y.S. with co-authors [39]. They found that increase of temperature significantly improves wetting of such aluminum alloys as AD1 (Al-0.4Si-0.3Fe), AMTs (Al-1.2Mn-0.6Si-0.7Fe), and AMg6 (Al-6Mg-0.6Mn-0.4Si-0.4Fe-0.1Ti) on titanium alloys. The contact angles decreased from 70° at 670°C to 20-30° at 740°C. Calculation of wetting kinetics resulted in an original theory of the difference between interaction of titanium with molten aluminum at low and high temperatures.

The average activation energy of wetting at 670-700°C was 119 kJ/mol, while in the temperature range of 700-740°C it was only 45 kJ/mol. The first value is close to the activation energy of oxidation of titanium or the activation energy of oxygen diffusion in titanium, while the second value is close to the activation energy of aluminum diffusion in titanium. Authors concluded that an oxide film on molten aluminum is the main factor controlling wetting just after melting the aluminum filler metal at the temperature range of 670-700°C. After that, the wetting is driven by diffusion and formation of intermetallics at 700-740°C. This theory would be completed if the authors had explained what exactly happened at the "edge temperature" around 700°C, or for example, what happened with aluminum oxide which neither can be reduced by titanium nor dissolved in liquid aluminum at such low temperatures.

However, despite any questions, we can make the following conclusion, which is very important for brazing technology: the temperature of 700°C is critical in brazing titanium with aluminum-based filler metals. The brazing should be perform at the temperatures above 700°C to provide sufficient wetting of titanium and minimize formation of voids in the joint.

Fig. 3 CP Titanium plates (1 mm thick) torched brazed in air with TiBrazeAl-655 (Al-6.3Cu-0.3Mn-0.2Si-0.2Ti) filler metal using flux TBF-42. Gray and black phase in the joint is the Al-Cu eutectic [42]

On the negative side, brazing at higher temperatures results in active formation of intermetallics and the loss of the joint strength, as we have seen above. This means, that the range 680-700°C can be recommended for brazing titanium with low-alloyed aluminum filler metals.

This conclusion was confirmed by A.A. Suslov reporting successful vacuum brazing of ultra-thin (0.08 mm and 0.6 mm) titanium honeycomb structures at 690-710°C [40]. Honeycomb panels made of VT1-0 titanium alloy (ANSI Grade 2 Titanium) were brazed using 0.2 mm thick foil of AD1 (Al-0.4Si-0.3Fe) filler metal. The strength of brazed titanium panels was similar to the strength of welded honeycomb panels fabricated from steel.

A two-step brazing cycle was proposed by Y.S. Dolgov with co-authors to decrease the growth of intermetallics at the interface between thin-wall titanium and liquid aluminum filler metal [41]. The process was carried out by heating to 710-720°C for 3 min followed by holding for 40 min at 680°C. Authors reported retardation of the intermetallic growth and a notable strength increase in brazed thin-wall titanium honeycomb structures.

4.3 Corrosion resistance of titanium joints brazed by aluminum filler metals

Data on corrosion resistance of titanium joints brazed with aluminum-based BFM are somewhat more ambiguous than the strength data. Some researchers reported a low corrosion resistance in standard 3% NaCl vapors environment [21], while other researchers reported about the same resistance (and even better) than that of silver-based filler metals in the same environment [13].

Fig. 4 CP Titanium plates (1 mm thick) torch brazed in air with TiBrazeAl-642 (Al-5.3Si-0.8Fe-0.3Cu-0.2Ti) using flux TBF-60 [42]

4.4 What can be done to improve properties of titanium joints brazed with aluminum filler metals

As we have seen from the above mentioned review, there are two main reasons responsible for strength reduction in titanium joints brazed with aluminum BFM: (a) reactivity of liquid aluminum resulting in the fast growth of intermetallics, and (b) occasional problem of complete wetting and spreading.

The wetting of titanium and filling the joint gap can be improved both by raising the brazing temperature up to at least 690-700°C and by alloying aluminum with small amounts of lithium and/or magnesium.

Some standard aluminum alloys already contain not only wetting promoters but also such effective melting point depressants as silicon and copper. These alloys should be tested for brazing titanium.

Holding time at the brazing temperature is a very important parameter affecting the strength. Increase in holding time results in a drastic strength drop in titanium lap joints brazed with low-alloyed aluminum filler metals. Therefore, the time of reaction of the aluminum melt with titanium should be limited.

Alloying with silicon, copper, and magnesium significantly decreases reactivity of aluminum and hinders the growth of intermetallics. This is another reason to test standard aluminum alloys containing 2-5% of Si, Cu, and/or Mg as brazing filler metals.

Intermetallics formed around the joint center line also cause the reduction in strength. Therefore, we recommend joint clearances less than 0.1 mm in order to prevent the formation of such destructive intermetallics.

The ultrasonic C-scan technique provides an excellent inspection method for determining discontinuities in titanium brazed joints made with aluminum filler metals, - and this is another useful result we can pick up from a project by Northrop Corp. (Aircraft Division) made by R.R. Wells [13] in 1975.

4.5 Potential candidates of aluminum-based brazing filler metals for further investigation

The following aluminum-based filler metals can be selected as potential candidates for brazing at the temperature ≤700°C and for testing mechanical properties of joints at cryogenic temperatures:

- some Al-Ag alloys exhibited excellent wetting and spreading ability on titanium. For example, the alloy Ag-30Al-5Cu can be recommended for testing if it will be made available;
- the alloy AVCO No. 48 (Al-4.8Si-3.8Cu-0.2Fe-0.2Ni) looks also promising due low intermetallic formation at 680°C. It should be prepared and tested;
- standard aluminum-lithium alloys such as AA2090 (m.p. 650°C), AA8090 (m.p. 655°C), or Weldalite 049 (m.p. 630°C) should be tested because they contain 1-2 wt.% of lithium – the strong wetting promoter;
- such standard aluminum alloys as TiBrazeAl-642 (Al-5.3Si-0.8Fe-0.3Cu-0.2Ti), TiBrazeAl-655 (Al-6.3Cu-0.3Mn-0.2Si-0.2Ti), and TiBrazeAl-645 (Al-5Mg-0.2Si-0.2Ti) containing both wetting promoters and melting point depressant can also be recommended for brazing at temperatures <700°C because they already demonstrated they ability to braze titanium.

Table 4

COMPOSITIONS AND BRAZING TEMPERATURES OF ALUMINUM-BASED LOW-MELTING FILLER METALS FOR BRAZING TITANIUM

Brazing filler metal		Solidus, °C	Liquidus, °C	Brazing temperature range, °C	Ref.
Tradename	Composition				
	Aluminum		660	670-700	
AA3003	Al-1.2Mn-0.6Si-0.7Fe-0.2Cu	643	654	663	13
BAISi-4 (Alloy 718)	Al-12Si-0.8Fe-0.3Cu	577	582	582-604	22
AA4043	Al-5.5Si-0.8Fe-0.3Cu		649	649	13
AA2024	Al-4.3Cu-q.5Mg-0.6Mn-0.5Si-0.5Fe	502	627	638	13
	Al-32Cu-5Ag	538	560	604	13
	Al-32Cu-5Ag-0.01Li	538	554	566	13
	Al-25Ag-25Cu	530	543	588	13
	Al-33Cu	548	548	550-570	30
	Al-0.8Si			670-680	33

Table 5

STRENGTH AND BRAZING PARAMETERS OF TITANIUM JOINTS MADE USING ALUMINUM-BASED LOW-MELTING FILLER METALS

Brazing filler metal		Titanium base metal	Brazing temperature °C	Testing tempera ture °C	Shear strength, MP	Tensile strength, MPa	Ref.
Trade-name	Composition						
	Aluminum	Ti-6Al-4V	670	RT		160	21
	Aluminum	CP Titanium	680 (3 min)	RT	93		33
	Aluminum	CP Titanium	700 (10 min)	RT	26		33
AA1100	Al-0.3Si-0.8Fe-0.2Mg	Ti-6Al-4V	>660	RT	72		24
	Al-1Mn	Ti-6Al-4V	670	RT		170	21
AA3003	Al-1.2Mn-0.6Si-0.7Fe-0.2Cu	Ti-6Al-4V	663	RT	65		27
AA3003	Al-1.2Mn-0.6Si-0.7Fe-0.2Cu	Ti-6Al-4V	663	204	47**		27
AA3003	Al-1.2Mn-0.6Si-0.7Fe-0.2Cu	Ti-6Al-4V	663	370	32***		27
AA3003	Al-1.2Mn-0.6Si-0.7Fe-0.2Cu	Ti-6Al-4V	>660	RT	89		24
AA3003 + AA4004	(Al-1.2Mn-0.6Si-0.7Fe-0.2Cu) + (Al-10Si-1.5Mg-0.8Fe-0.2Cu)	Ti-6Al-4V	610	RT		206	24
BAlSi-4	Al-12Si-0.8Fe-2Cu	Ti-6Al-4V	600	RT		150	21
	Al-Si	CP Titanium	690 (10 min)	RT	67		35
BAlSi-4	Al-12Si-0.8Fe-2Cu	TiAl	800	RT	43-64		9
BAlSi-4	Al-12Si-0.8Fe-2Cu	TiAl	900	RT	65-86		9
	Al-10Si-1Mg	CP Titanium	620 (1 min)	RT	72		34
	Al-10Si-1Mg	CP Titanium	620 (25 min)	RT	84		34
	Al-10Si-1Mg	CP Titanium	620 (60 min)	RT	70		34
	Al-10Si-1Mg	CP Titanium	620 (120 min)	RT	50		34
	Al-25Ag-25Cu-0.01Li	Ti-6Al-4V	588	RT	3.4-40		13
	Al-32Cu-5Ag-0.01Li	Ti-6Al-4V	566	RT	4.8-69		13
	Al-Cu-Mn-Cr	CP Titanium	690 (10 min)	RT	37		12
AA6061	Al-1Mg-0.5Si-0.7Fe-0.3Cu	CP Titanium	677	RT	76		2
AA6061	Al-1Mg-0.5Si-0.7Fe-0.3Cu	CP Titanium	677	RT	193****		2
	Al-33Cu	Ti-6Al-4V	550	RT	25		30
	Al-0.8Si	CP Titanium	680 (3 min)	RT	93		33
	Al-0.8Si	CP Titanium	680 (10 min)	RT	86		33
TiBraze Al-642	Al-5.3Si-0.8Fe-0.2Ti	Grades 2 and 12	>632	RT	72-73*****		16
TiBraze Al-645	Al-5Mg-0.2Si-0.2Ti	Grades 2 and 12	>635	RT	75-81*****		16
TiBraze Al-655	Al-6Cu-0.2Si-0.3Mn-0.2Ti	Grades 2 and 12	>643	RT	97*****		16
Gapasil-	Ag-9Pd-9Ga	Ti-6Al-4V	890	RT	166-193		26

9 *							
Ticuni *	Ti-15Cu-15Ni	Ti-6Al-4V	950	RT		960	21
Ticuni *	Ti-15Cu-15Ni	Ti-6Al-2Sn-4Zr-2Mo	970	RT	304-317		27
Ticuni *	Ti-15Cu-15Ni	Ti-6Al-2Sn-4Zr-2Mo	970	590	200-207		27

* for comparison of low-melting filler metals with traditional Ag-based and Ti-based filler metals
** Fatigue strength of brazed joints was 50 ksi at 10^6 cycles
*** Fatigue strength of brazed joints was 42 ksi at 10^6 cycles
**** Induction brazing
*****Electron beam brazing

Table 7

COMPOSITIONS AND BRAZING TEMPERATURES OF TITANIUM-BASED AND ZIRCONIUM-BASED LOW-MELTING FILLER METALS FOR BRAZING TITANIUM

Brazing filler metal		Solidus	Liquidus	Brazing	
Tradename	**Composition**	**°C**	**°C**	**temperature range°C**	**Ref.**
Stemet® 1202	Ti-12Zr-22Cu-12Ni-1.5Be-0.8V	750	815	850 (15 min)	44
Stemet® 1406	Zr-11Ti-14Ni-13Cu	770	833	900 (15 min)	44
Stemet® 1409	Zr-11Ti-14Ni-12Cu-2Nb-1.5Be	685	767	800 (8 min)	44
BTi43ZrNiBe	Zr-43Ti-12Ni-2Be	795	816	900	45
	Zr-48Ti-4Be			927	11

Table 8

STRENGTH AND BRAZING PARAMETERS OF TITANIUM JOINTS MADE USING Ti-BASED AND Zr-BASED LOW-MELTING FILLER METALS

Brazing filler metal				Shear	Tensile	
Tradename	**Composition**	**Titanium base metal**	**Brazing temperature °C**	**strength, MPa**	**strength, MPa**	**Ref.**
Stemet® 1202	Ti-12Zr-22Cu-12Ni-1.5Be-0.8V	CP Ti	850 (15 min)		338	44
Stemet® 1406	Zr-11Ti-14Ni-13Cu	CP Ti	900 (15 min)	167	334	44
Stemet® 1409	Zr-11Ti-14Ni-12Cu-2Nb-1.5Be	CP Ti	800 (8 min), 650(1 h)	236	471	44
BTi43ZrNiBe	Zr-43Ti-12Ni-2Be	Ti-6Al-4V	900	152**		55
Gapasil-9 *	Ag-9Pd-9Ga	Ti-6Al-4V	900	135**		45
Ticuni *	Ti-15Cu-15Ni	Ti-6Al-4V	950	547**		45

* for comparison of low-melting filler metals with traditional Ag-based and Ti-based filler metals
** joint clearance was 0.05 mm (0.002 in.)

5. Zirconium-based Brazing Filler Metals

In the last decade, some zirconium-based alloys were successfully fabricated in the form of amorphous foil [43, 44] and demonstrated their ability to decrease the brazing temperature of Ti-based filler metals by 20-30°C. However, the recent jump of zirconium prices on both domestic and overseas markets may render this slight decrease in the brazing temperature economically unfeasible. Besides, the brazing temperature of some zirconium-based filler metals is higher than that of Ti-Zr-based filler metals.

Nevertheless, this class of BFM is also described in our review in order to present the full picture of comparable operational parameters and mechanical properties.

Compositions and melting temperatures of conventional Zr-based filler metals used for brazing titanium are presented in Table 7. Strengths of the brazed joints are shown in Table 8.

Brazing process and microstructure of titanium joints brazed with Zr-based filler metals are almost the same as of joints made with Ti-Zr-Cu-Ni filler metals due to close compositions of both classes of the filler metals.

On one hand, the Zr-based BFM provide a significantly higher strength of titanium brazed joints than that of silver- or aluminum-based filler metals. On the other hand, the brazing process with Zr-based BFM is carried out at a higher temperature despite their low melting range which sometimes can be even lower than that of silver filler metals, for example, the filler metal STEMET®1409 (Table 7).

G. Lesgourgaes compared Zr-based filler metal BTi43ZrNiBe (Zr-43Ti-12Ni-2Be) having liquidus at 816°C with Gapasil-9 and Ticuni®70 in one experimental work using almost “pure shear” type test specimen [45]. The zirconium filler metal resulted in shear strength of 20% higher than that of the joints brazed with Gapasil-9, but significantly lower than that of Ticuni®70 at the same joint clearance of 0.05 mm in all tests (Table 11). Author explained this effect by higher plasticity of the joints made with Ticuni®70, and by an appearance of the “Widmanstätten”-type microstructure in the diffusion zone, which is typical for Ticuni®70 but not common in the joints brazed with the BTi43ZrNiBe alloy. It is possible that the absence of copper in the filler metal composition prevented the formation of the “Widmanstätten” microstructure. Copper decreases the temperature of the $\alpha \leftrightarrow \beta$ transformation in the titanium base metal. Thus, a martensitic transformation was not completed in the case of brazing with the zirconium filler metal BTi43ZrNiBe.

D.G. Howden and R.W. Monroe obtained similar results when they compared Ticuni®70, Zr-48Ti-4Be, and Ag-5Al filler metals for brazing thin-wall titanium heat exchangers [11]. Microstructures of brazed joints clearly showed the formation of the “Widmanstätten” diffusion zone in joints made with Ticuni®70 and an absence of this in joints made with the Zr-48Ti-4Be filler metal. As a result, the joints of Ticuni®70 had better ductility in bending than the specimens brazed with zirconium-based filler metal.

At the same time, the authors compared flow and fillet formation of all three BFM. The silver-based Ag-5Al alloy exhibited excellent flow and fillet formation on titanium foil, the Zr-48Ti-4Be alloy had good flow, and Ticuni®70 had mediocre flow characteristics.

6. Conclusions:

6.1 Titanium joints brazed with low-melting silver-based and aluminum-based brazing filler metal have lower strength than those brazed with titanium-based filler metals. However, the manufacture of titanium brazed structures in Open Space gives another opportunity to low-melting aluminum and silver filler metals because such applications do not require a high static or dynamic strength of joints, there is no corrosion conditions in Space, and the reactivity of the aluminum can be suppressed by the very short brazing thermal cycle. In this case, we can expect that the benefits of using low melting point filler metals (especially low melting point and good wetting and flow) outweigh their shortcomings.

6.2 The fast heating-cooling brazing cycle provides a significant gain in the strength of titanium joints brazed with low-melting silver filler metals. The average shear strength of Ti-6Al-4V joints infra-red brazed with silver filler metals was 173 MPa, while the furnace-brazed joints – only 117.5 MPa.

The influence of brazing time-temperature is not so straight-forward for titanium brazed with aluminum-based filler metals. A holding time of at least 3 min can be recommended for brazing temperatures below 600°C in order to achieve a complete wetting of titanium and reduce void formation in the joint. The difficulty of Al-based filler metals to penetrate into small brazing clearances may be resolved by a simple raise of the brazing temperature by 50-100°C. Wetting may also be improved by using aluminum filler metals alloyed with lithium or magnesium.

6.3 A temperature range of 680-700°C can be recommended for brazing titanium with low-alloyed aluminum filler metals. Heating above 700°C always results in a fast growth of $TiAl_3$ intermetallics which affects the strength of brazed joints.

Alloying of aluminum-based filler metals with silicon, copper, and/or magnesium significantly slows down the growth of intermetallics at the titanium-aluminum interface.

Formation of intermetallics in the central area of the joint is the main reason of low strength of aluminum-brazed joints. The joint gaps less than 0.1 mm are strongly recommended in order to prevent the formation of such destructive intermetallics.

6.4 There are several promising low-melting filler metals both silver- and aluminum-based that can be further studied as candidates for both electron-beam brazing or furnace brazing of titanium. These brazing filler metals are listed in chapters 3.2 and 4.5 of the present review.

Also, a well known eutectic solder Au-20Sn having melting point of 278°C can be tested, despite the fact that no information about using this alloy for joining titanium has been found.

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