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PRODUCING NITINOL BRAZED JOINTS (REVIEW)

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ABSTRACT

Shape-memory alloys are becoming ever wider accepted in different industries, in particular in aerospace, medical, automotive sectors and in consumer electronics manufacturing. Application of these materials as hybrid structure elements is a promising direction when creating products with a unique set of properties: high mechanical values, superelasticity, damping ability, higher wear resistance and thermomechanical memory. Production of nitinol permanent joints by welding leads to formation of brittle phases of Ti_2Ni type, which degrade the product quality. This review discusses the possibility of producing high-strength permanent joints of nitinol with nitinol and with other alloys by brazing. The main advantage, compared to other methods, is the fact that the base metals do not melt, and some structural transformations can be avoided. At nitinol brazing in the atmosphere, brazing filler metals of Ag–Cu–Zn–Sn–Ni system have proven themselves well, when using 25AgCl–25KF–50LiCI flux. We should specially mention application of silver brazing filler metals and interlayers from pure metals, for instance, niobium, providing a strong metallurgical bond with the base metal. At brazing temperature of 1180 °C an alloy based on quasibinary NiTi–Nb eutectic system is formed, ensuring the reliability of brazed elements when creating prototypes of superelastic honeycomb shapes from titanium nickelide.

KEYWORDS: titanium nickelide (nitinol), shape-memory alloys (SMA), brazing filler metals, brazing, welding, wetting, intermetallic brittle compounds, strength, structure

INTRODUCTION

Nowadays alloys with a reverse martensite transformation, characterized by varying degrees of shape-memory properties, are of considerable interest. These are Ni–Ti; Ni–Ti–Cu, Ni–Ti–Pd; Ni–Ti–Fe; Ni–Ti–Nb, Ni–Fe–Ga, Ni–Ti–Co, Ni–Al, Ni–Co, Ti–Nb; Fe–Ni, Cu–Al, Cu–Al–Ni, Pt–Ti, Ag–Cd, Au–Cd, etc. [1, 2], and they are widely accepted in different engineering sectors. After plastic deformation, these alloys restore their original geometry as a result of heating (shape-memory effect) or directly after load removal (superelasticity). The mechanism determining the shape memory properties is the reverse crystallographic thermoelastic martensite transformation — Kurdyumov effect. This is a kind of polymorphous phase transition with a change of crystalline lattice that depends of temperature or loading level. Martensite transformation is accompanied by volume change, ensuring the shape memory [3]. The high-temperature phase is austenite, which transforms into martensite (low-temperature phase) at stress application. After stress relieving, martensite transforms into austenite and restores its original shape. Such processes can run several times at thermal cycling [4, 5].

A typical representative of shape-memory materials is nitinol (Figure 1), in which a transition from the cubic (B2 austenitic phase) into a monoclinal phase (B19 martensite) takes place at cooling or under the impact of applied stresses [6, 7]. Special corrosion resistance of titanium nickelide is due to its ability to form TiO_2 oxide on its surface, which acts as a protective barrier owing to its pronounced hydrophobic properties that prevents nickel dissolution in an aggressive environment of the human body and ensures its complete biocompabitility on the level of corrosion-resistant steels (316LVM (03Kh18N14M2) and Ti–6V–4Al alloy [8]. It belongs to the best studied shape-memory materials, is applied in different industries and is the most promising material for manufacturing superelastic medical implants (in biomedicine, owing to its biological compatibility and corrosion resistance in the human body), tool (Figure 2, *a*–*c*), as well as in automotive and microelectronic sectors and in manufacture of thermomechanical elements for aerospace and aviation engineering (aircraft, rockets, space structures with improved flight characteristics

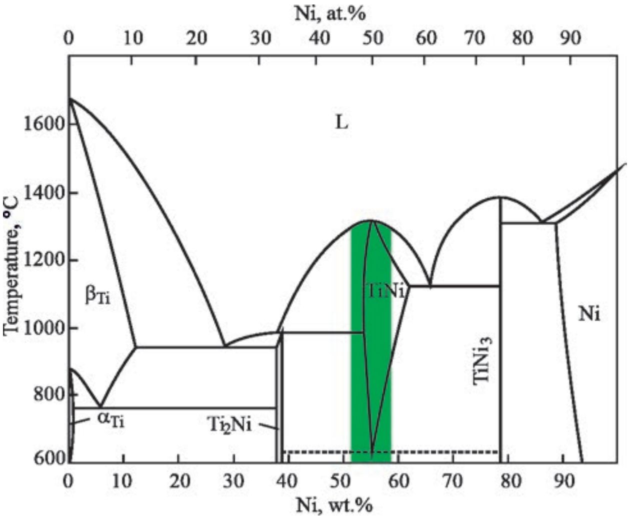

Figure 1. State diagram of Ni–Ti system [7]

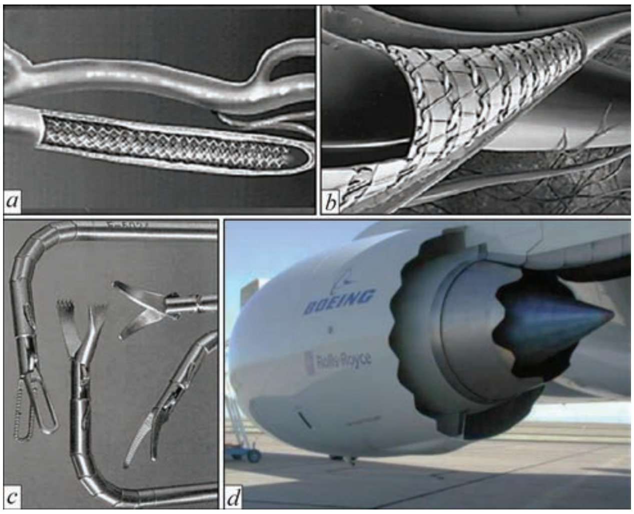

Figure 2. Medical stents (*a*, *b*), tool (*c*), serrated nozzle of aircraft (*d*) [9]

and lower level of noise and vibrations) (Figure 2, *d*) [9]. Application of this material when creating structures with certain service characteristics requires investigation and development of different joining processes that may lead to its wider application. Nowadays, the process of joining nitinol in similar and dissimilar combinations is insufficiently studied.

This review considers the possibilities of producing permanent joints of an intermetallic alloy — nitinol with application of different methods of high-temperature brazing and using pure metal interlayers, ensuring contact melting at the temperature that is much lower than their autonomous melting temperature.

PRODUCING PERMANENT JOINTS OF NITINOL (NiTi)

Nitinol is an alloy based on an equiatomic intermetallic compound, which contains titanium and nickel. The concentration of the latter is from 48 to 52 at.%.

Unique functional properties of nitinol are due to the temperature and rate of deformation, chemical composition, heat treatment parameters, etc. Even a slight change of nickel concentration within 2 % (from 50 to 52 at.%) leads to lowering of phase transition temperature by almost 27–127 °C that enables controlling the physico-mechanical properties in a certain temperature range [4].

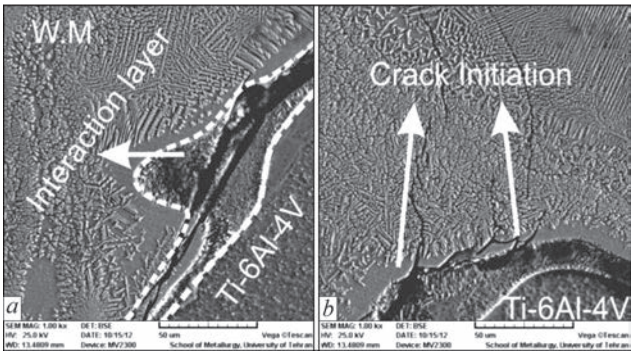

Figure 3. Reaction layer near the interface with Ti–6Al–4V titanium alloy (*a*) and cracks (*b*) at laser welding of dissimilar materials of nitinol with titanium alloy [11]

Various welding methods are widely used for the processes of material joining: arc, laser, beam, contact, explosion, friction, diffusion welding etc. [1, 4, 9]. Joining shape-memory alloys (SMA) by welding is possible, but it has a tendency to formation of intermetallic phases (Ti_2Ni), which are characterized by considerable brittleness [9, 10]. Moreover, deterioration of shape-memory effect is possible, which is the result of high-temperature, partial melting of base metal and presence of a cast dendritic structure in the seam zone. It is obvious that welding changes the phase transformation temperature that may reduce the area of its application. When welding the shape-memory alloys, it may be necessary to apply alloying elements preventing formation of intermetallic phases, but such data are very scarce at present [5].

Application of the method of shock capacitor-discharge welding [1] did not provide joints of sufficient strength. It should be noted that low strength values are found in the case of absence of intersolubility of dissimilar materials being welded [10]. At application of fusion welding, a transition cast HAZ always forms, which may have increased brittleness, compared to the base metal. It significantly lowers the welded joint strength, particularly in the case, when one of the materials being joined is an intermetallic alloy which already has low ductility.

Laser welding usually results in formation of narrow welds, and it can be better than the arc process, due to the possibility to produce finely dispersed microstructure and lower thermal stresses and strains, remaining after the welding cycle. The laser welding method allows producing joints of nitinol with titanium with tensile strength of 109 MPa and its joints with Ti–6Al–4V alloy with the strength of 28.4 MPa. In welded joints produced by electron beam and argon-arc welding (TIG), this value was 70, 85 and 108 MPa, respectively [10]. The cause for low mechanical properties is formation of Ti_2Ni brittle phase in the weld zone, in which microcracks initiate (Figure 3) [11].

Application of a copper interlayer during laser welding of nitinol with Ti–6Al–4V titanium alloy leads to lowering of weld microhardness that is due to lower microhardness of Ti_2Cu intermetallic phase rich in titanium, compared to a similar characteristic of Ti_2Ni phase. It allows reducing the amount of brittle Ti_2Ni intermetallic phase, avoid formation of transverse cracks in the weld and increasing the joint strength to 300 MPa [11].

Table 1. Chemical composition of brazing filler metals [12]

System	Chemical elements, wt.%					Melting range, °C
	Ag	Cu	Zn	Sn	Ti	
AgCu (eutectic)	71.9	28.1	–	–	–	779
AgCuZnSn I	52	22	18	8	–	590–635
AgCuZnSn II	50–68	10–30	12–20	0–10	–	640–730
AgCuTi I	70.5	26.5	–	–	3	780–805
AgCuTi II[1]	63	35.25	–	–	1.75	780–815
AgCuTi III[2]	68.8	26.7	–	–	4.5	830–850
AgTi	96	–	–	–	4	970

[1]Cusil ABA. [2]Ticusil®.

PRODUCING NITINOL JOINTS WITH APPLICATION OF BRAZING FILLER METALS

As regards brazing, there exists a multitude of processes, usually named by the heating methods: flame, induction, ultrasonic, dip brazing, etc.

During brazing, the base metals do not melt that may promote avoiding some high-temperature processes, which include high-temperature oxidation, element segregation, grain coarsening, that may impair the original properties of base metal — SMA. Brazing [10] provides wide possibilities of variation of the phase and chemical composition of the joint zone. At brazing, however, the base metal interacts with the brazing filler metal and diffusion processes take place. Shape-memory alloys on the whole and NiTi in particular are rather active to oxygen, carbon, nitrogen and hydrogen, making certain requirements to brazing atmosphere. Vacuum brazing conditions can be more attractive, compared to other methods. It is recommended to perform vacuum brazing using ductile brazing filler metals (Table 1), which contain active elements [12].

In the presented brazing filler metals (Table 1) the base is Ag–Cu system alloy, which is alloyed by an adhesion-active element — titanium. Other studies reported application of Au and Au- [13] and Nb-based alloys [14], as alloying elements.

Vacuum brazing (rarefaction of 10^{-3} Pa) with eutectic Ag–Cu brazing filler metal (72 wt.% Ag, melting temperature of 779 °C) can provide quite good strength and ductility, but it depends on the overlap length [12]. A significant increase of strength is achieved at increase of overlap length from 1 to 4 mm. The brazed specimen with overlap size within 1 and 2 mm fails at the load of 360 and 600 N, respectively, while a specimen with 4 mm overlap fails at 980 N (close to 820 MPa).

The produced microstructure (Figure 4) was used as an example to show formation of a typical classic eutectic structure of a brazed seam at application of brazing filler metals of Ag–Cu system, which is created by two solid solutions based on silver (white matrix) and on copper (dark rods).

Shear strength of the brazed joint is higher than 100 MPa, and rupture occurs in the reaction layer adjacent to the base metal and brazing filler metal. The brazed specimen demonstrates a good shape memory [15].

The reaction layer on the interface between the base metal and brazed seam metal [15] is identified as a phase of XTi_2 type, where X = Ni + Ag + Cu. According to a binary state diagram, Ni and Cu have complete mutual solubility at brazing temperature, while at low temperature (354 °C) the spinodal disintegration causes separation into α_1 and α_2 phases. As there is no thermodynamic barrier for the reaction in the spinodal region, disintegration is determined solely by diffusion. No intermetallics form in binary state diagrams of Ag–Cu and Ag–Ni metal systems. More over, limited solubility of nickel in silver is observed, however, all the elements (Ag, Cu, Ni) form numerous intermetallic compounds with titanium (Table 2). It may lead to formation of intermetallics on the interface of brazing filler metal — base metal [13].

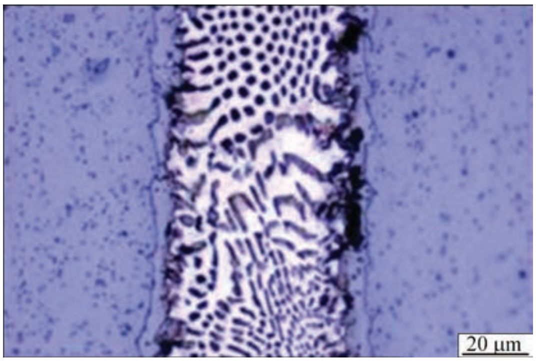

Figure 4. Microstructure of NiTi/NiTi brazed joint [15]

Table 2. Intermetallics in Ti_xX_y system (X = Ag, Cu, Ni) [16]

Element	Compounds					
Ag	AgTi	$AgTi_2$	–	–	–	–
Cu	Cu_4Ti	Cu_2Ti	Cu_3Ti_2	Cu_4Ti_3	CuTi	$CuTi_2$
Ni	Ni_3Ti	NiTi	$NiTi_2$	–	–	–

At application of commercially available brazing filler metals, mainly based on Ag–Cu system alloy [12], special attention is given to studying the nitinol brazing processes with application of infrared, laser and microwave heating. At brazing, similar to welding, a certain deterioration of the original base metal properties is to be anticipated due to formation of intermetallic phases. On the one hand, running of the diffusion processes on the joint boundary promotes achieving strong bonds between the component elements of the base metal and brazing filler metal with formation of common phases, but on the other hand, it can also adversely affect the joint strength, because of their brittle nature, for instance XTi_2 phases (where X = Cu, Ni, Ag).

Copper is known to have a high solubility in nitinol and up to 30 wt.% of nickel in NiTi can be replaced by copper atoms without lowering the SME [17]. Therefore, pure copper and copper-alloyed brazing filler metals (Ti70Cu15Ni15; Cusil: 63 at.% Ag, 35.25 at.% Cu and 1.75 at.% Ti; Ticusil® 68.8 Ag, 26.7 at.% Cu and 4.5 at.% Ti) [9] were used. Microstructural studies showed that three copper-containing phases were present in brazed seams, produced with application of pure copper foil, namely a copper-rich phase containing more than 90 at.% Cu, and CuNiTi (Δ) and Ti(Ni, Cu) phases. It is reported [9] that absence of CuNiTi phases impairs the SME of the alloy, while Ti(Ni, Cu) presence does not have any effect at all on the alloy shape-memory effect. It is noted that the quantity of CuNiTi phase decreases with increase of brazing time that has a positive impact on the shape-memory effect of brazed joints. In brazed joints produced with application of TiCuNi system alloy as brazing filler metal, Ti_2(Ni,Cu) brittle intermetallics forms on the interface of brazing filler metal — base metal, which makes determination of the shape-memory effect difficult. Titanium presence in Cusil-ABA brazing filler metal promotes improvement of base material wetting, but formation of CuNiTi phase impair the shape-memory effect of the produced brazed joint. At brazing by Ticusil® brazing filler metal (with a higher titanium content), $TiCu_2$ intermetallic phase forms in the brazed seam, which has a weaker influence on the shape-memory effect, but at the same time the brazed seams are characterized by a much weaker shape-memory effect, compared to base metal (nitinol) in the initial state [9]. However, brazing remains the most promising method of joining shape-memory materials.

The problem of passive oxide formation may arise both in welding, and in brazing of Ni–Ti alloys. Its formation can be avoided by application of active fluxes and low-temperature brazing filler metals of Sn–Ag or Au–Sn system (from 200 to 300 °C). As an alternative, a barrier coating from nickel or gold can be used before brazing, which may improve the brazed joint quality [12].

A high concentration of titanium, which readily forms resistant oxide films on the surface of the studied NiTi alloy under atmospheric conditions, requires application of flux, where the effective components are fluorides and AgCl, LiCl compounds. Proceeding from the obtained results, the authors [18] decided using a flux consisting of 25 AgCl–25KF–50LiCl (wt.%), which improves wetting by silver brazing filler metal BAg-7 (Table 3) of NiTi surface at high-temperature brazing in air atmosphere.

When making brazed joints, the authors [18] used nitinol “metallization”, which consists in application of flux and brazing filler metal (10 mg) on the surface, heating in an electric furnace up to the temperature of 1000 °C and subsequent cooling. Slag was removed from the specimen surface by a wire brush. After such a preparation, the flux was applied on the “metal-

Table 3. Brazing filler metals and melting temperature [18]

Brazing filler metal (grade)	Chemical elements, wt.%					Solidus, °C	Liquidus, °C
	Ag	Cu	Zn	Sn	Ni		
BAg-7	56.5	20.3	16.3	6.9	–	623	655
A-1	59	23	15	1	2	668	710
A-2	60	30	–	10	–	738	761
A-3	60	28	–	10	2	739	766
A-4	60	30	10	–	–	650	745
A-5	60	28	10	–	2	715	755
A-6	61	24	15	–	–	685	717
A-7	59.5	23.5	15	–	2	688	724
A-8	60.2	23.5	15.3	1	–	655	718

lized" specimens, they were mounted with an overlap of 2.5 mm, 100 g load was applied for fixing the specimens, and in such a position they were placed into an electric furnace. Brazing temperature is in the range of 700 to 900 °C.

In brazed nitinol specimens produced with application of BAg-7 brazing filler metal at the temperature of 900 °C and of A-1 at 930 °C, formation of a reaction layer was observed on brazing filler metal — base metal interface (Figure 5, shown by arrow 1).

Ti and Ni weight ratio (in at.%) in it is equal to 1:3, so that it is identified as $TiNi_3$ intermetallic. The authors [18] regard the following as the specific features of formation of nitinol brazed joints. First of all, a significant liquation of tin is found at application of BAg-7 brazing filler metal, leading to reaction layer enrichment in a large quantity of this element (from 25 to 35 wt.%) that is much higher than its concentration, compared to brazed specimens at application of A-1 brazing filler metal. Secondly, titanium and oxygen peaks are observed on the reaction layer-base metal interface. In other words, titanium oxide is present in these areas, that corresponds to inclusions, observed in the interphase zone (shown by arrow 2). Application of A-1 brazing filler metal, alloyed by tin up to 1 % and by nickel up to 2 % ensures maximum strength of brazed joints on the level of 300 MPa, while other brazing filler metals demonstrated maximum strength, which is lower than 200 MPa [18]. It is noted that Sn and Zn lower the melting temperature of brazing filler metals and improve base metal wetting. At Ni introduction into the brazing filler metal an increase of the amount of the melt and improvement of base metal wetting at brazing are observed. Therefore, it may be assumed that increase of liquid metal amount results in removal of titanium oxide from the interface and increase of brazed joint strength.

NITINOL BRAZING TO OTHER METALS

Earlier study of the potential of SMA application in engineering structures, such as adaptive serrated nozzle (ASN) shows that joining nitinol to titanium-based alloys is an extremely complicated process, which requires systemic studies and development of effective joining methods [9]. Vacuum brazing advantages are known and they consist in ensuring absence of oxygen in furnace atmosphere, and producing clean sound defectfree seams. However, application of vacuum furnaces is not rational for adaptive serrated nozzle manufacturing, so that local heating is to be used. Brazed joints, produced in this study, do not quite meet the requirements made, that is why optimization of the brazing process is required in order to improve the joint properties. It is shown that application of interlayers at vacuum brazing improves the brazed joint properties. However, mechanical properties of brazed joints are much lower than those required for an adaptive serrated nozzle. Further optimization of the process and studying the influence of alloying elements and brazing systems will allow improvement of brazed joints [9]. A noticeable improvement of brazed joint quality is achieved at application of brazing filler metals, containing not more than 25 at.% nickel, and alloyed by titanium. Further research is required to study and more precisely determine the titanium impact in the brazing filler metals [9].

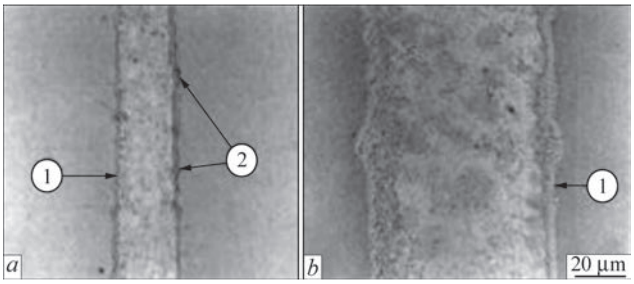

Figure 5. Brazed joint microstructure: *a* — with BAg-7 brazing filler metal; *b* – with A-1 brazing filler metal. Arrow (1) points to $TiNi_3$ intermetallic, arrow (2) — to titanium oxide [18]

Examples of the produced joints of nitinol with Ti–6Al–4V alloy and corrosion-resistant steel are presented in works [9, 19, 20]. Application of silver brazing filler metal BAg-8 allowed producing a permanent joint of maximum shear strength that is equal to 219 MPa [19]. Vacuum brazing of nitinol to Ti–6Al–4V alloy was studied at application of brazing filler metals of Ti–Cu–Ni, Ti–Cu–Ni60 systems and Ti–Ni67 alloy. Maximum shear strength of brazed joints was achieved at application of TiCuNi60 brazing filler metal, and it was equal to approximately 30 MPa [9]. Thus, correct selection of the brazing filler metal chemical composition largely depends on the quality of a permanent joint of nitinol with titanium and its alloys. Note that intermetallic phase formation occurs irrespective of the joint type and joining method.

Studies of wetting, microstructure and strength of brazed dissimilar joints of Ti50Ni50 nitinol with Ti-15-3 alloy (β-Ti alloy type, which is readily deformed and contains in wt.%: 3Al, 3Cr, 3Sn, 15V, Ti) at application of BAg-8 (72Ag–28Cu) (wt.%) and Ticusil® (68.8Ag–26.7Cu–4.5Ti) (wt.%) brazing filler metals showed [21] that wetting of Ti50Ni50 base metal by 72Ag–28Cu eutectic brazing filler metal is greatly improved at addition of 4.5 wt.% Ti to the alloy. Only active Ticusil® brazing filler metal readily wets the substrates of both the base metals at infrared brazing. The structure of Ti-15-3/Bag-8/Ti50Ni50 brazed joint produced at *T* = 800 °C with soaking for 300 s, consists of Cu_2Ti intermetallics, which crystallize against the background of silver-based solid solution. Now at increase of brazing temperature up to 850 °C (τ = 300 s), just a matrix forms which is enriched in Ag. Formation of Cu(Ti,V) reaction layer on the contact boundary with Ti-15-3 titanium alloy and of $(CuxNi_1{-}x)_2Ti$ phase is attributed by the authors to active wetting of both the substrates and diffusion processes [21]. The best results of brazed joint strength at application of BAg-8 and Ticusil® brazing filler metals are 197 and 230 MPa, respectively. The shortcomings of these joints include crack formation on the interphase of brazing filler metal–Cu(Ti, V) reaction layer and along the central zone of Ti_2Ni intermetallic compound.

Formation of $(Cu, Ni)_2Ti$ phase is also observed, when brazing dissimilar joints of nitinol with nickel-based superalloy of Hastelloy C-276 grade (containing in wt.%: 55 Ni, 14.5–16.5 Cr; 15–17 Mo; 4–7 Fe; 3–4.5 W). At nitinol brazing to austenitic corrosion-resistant steel a phase with a high content of Fe and Cr forms on the interphase of brazing filler metal-base metal [12]. As formation of the reaction layer is a process controlled by diffusion that is due to a gradient of concentrations, by temperature and time, these parameters in combination with the selected brazing filler metal are highly important at brazing.

During laser brazing of NiTi to corrosion-resistant steel using AgCuZnSn II brazing filler metal shown in Table 1, the low heat input promoted low values of ultimate strength of 190–210 MPa [22]. At application of greater heat input, strength was increased to 320–360 MPa. Considering that the ultimate strength of Ni–Ti base metal in the initial condition was higher than 1100 MPa, the considerable loss of the joint strength was caused by the brazing process. Similar results were obtained at application of AgCuZnSn I brazing filler metal (see Table 1) [12]. As stated by the authors, mutual diffusion of Ag, Cu, Zn and Sn chemical elements occurs. These elements diffuse from the filler metal both into the base metal — NiTi, and into stainless steel, while Ti and Ni from nitinol base metal, and Fe, Cr and Ni from the steel diffuse into the filler metal.

At infrared brazing of joints of nitinol with Ti–6Al–4V titanium alloy containing wt.%: 5.76 Al, 4.03 V, 0.28 Fe, 0.06 C, using copper-silver brazing filler metal BAg-8 (in the form of 50 μm thick foil), good wetting of Ti–6Al–4V titanium alloy and somewhat poorer wetting of nitinol is observed [19]. In keeping with AWS specifications, BAg-8 brazing filler metal contains 71–73 % silver, the balance being copper, and it is characterized by a eutectic structure (T_m = 780 °C) [23, 24]. Investigations showed that after infrared brazing at the temperature below 850 °C, a hypoeutectic structure forms in the seam, which is based on two solid solutions: silver-based and copper-based one. Silver does not react with either of the base metals, and forms no intermetallic compounds, but copper reacts with titanium with formation of $TiCu_4$, Ti_3Cu_4, TiCu and Ti_2Cu intermetallic phases on the interphase of brazing filler metal–titanium alloy (Ti–6Al–4V) and of CuNiTi phase on brazing filler metal – nitinol interface. Titanium partially dissolves in Ti–6Al–4V titanium alloy that improves wetting of both the metals. At increase of brazing temperature to 900 °C (for more than 60 s) and abrupt change of the microstructure occurs, which is due to formation of a large quantity of Ti_2Ni phase. The average strength of the specimens, brazed by infrared radiation at the temperature of 800 °C, is equal to approximately 200 MPa. Although the presence of CuNiTi intermetallic phase has a positive effect on wetting Ti50Ni50 base metal substrate by molten brazing filler metal, it has a negative influence on the strength of Ti50Ni50/BAg-8/Ti–6Al–4V brazed joint [19]. Maximum shear strength values on the level of 343 MPa were obtained at infrared brazing at the temperature of 950 °C (soaking for 60 s) [24].

PRODUCING JOINTS WITH INTERLAYER APPLICATION AND WITHOUT BRAZING FILLER METAL

Investigations in the field of nitinol brazing and welding have been performed for many years. These studies are still relevant and require development of an affordable and inexpensive joining method, which will ensure joint formation without brittle phases at development of specific functional elements of various structures.

The problem of producing strong and reliable structures can be solved by application of interlayers from pure metals on the material to be brazed. Selection of optimal interlayer compositions, which allow avoiding formation of brittle intermetallic phases between titanium and nitinol is an important task of today [10]. Application of the respective ductile interlayer can be a good choice for prevention of excess diffusion and compensation of thermal deformations which are due to mismatch of the coefficients of thermal expansion. Performed research showed that mutual diffusion takes place at niobium contact with the ordinary forged nitinol, leading for formation of the liquid phase, which actively wets both pure niobium and NiTi [5, 25–31].

Performed research was the base for development of a new reactive process of brazing titanium nickelide by application of pure niobium, which provides a strong metallurgical bond with the base metal (quasibinary Ni38Ti36Nb24 eutectic) and opens up possibil-

Table 4. Chemical heterogeneity of brazed joint of NiTi with pure niobium [5]

Studied zone	Element (wt.%)		
	Ni	Ti	Nb
1 (hypoeutectic dendrites)	45.1	47.9	7
2 (NiTi)	49.5	50.5	–
3 (eutectic)	37.3	39.4	23.3

ities for creation of prototypes of superelastic cellular honeycomb shapes from ordinary titanium nickelide. This method allows implementation of complex 3D truss structures, honeycomb panels, and built-in thermally activated multifunctional structures based on Ni–Ti alloy [14].

Pseudoelasticity of shape-memory NiTi alloys is a unique property of the material, which may be characterized by complete recovery of the preformed shape of the component by changing the conditions of thermal or mechanical loading after deformation. Unlike elastic deformation of such ordinary materials as steel, nitinol capabilities are 20 times higher than the elastic deformation rate which is due to increased temperature, or stress, and it promotes diffusion-free transformation of austenite crystalline lattice into martensite and vice versa. Such alloys are often used as components of implants or stents, so that extremely high requirements are made to their reliability and biocompatibility with the human body [5]. From the view point of producing the joints, vacuum brazing is a particularly acceptable method for making joints from components, which preserve maximum pseudoelasticity. In such a study [5], it was shown that the process of vacuum brazing at the temperature of 1180 °C ($\tau = 6$ min) using pure niobium, is readily combined with heat treatment, and it is performed in one cycle of heating in the furnace. NiTiNb eutectic forms in the central zone of the brazed seam, which contains up to 23 % niobium (Figure 6, Table 4, zone 3).

Eutectic composition correlates with other studies, where it was determined that niobium concentration is within 20–26 % [5, 25]. Titanium-based hypoeutectic dendrites containing 7 % niobium are observed between the base material and eutectic (Figure 4, Table 4, zone 1), which corresponds to niobium solubility in NiTi at brazing temperature of 1180 °C [5]. Moreover, it was proved that the fraction of ductile hypoeutectic NiTiNb-phase increased significantly with longer soaking time (Figure 7), and the brazed seam is much wider (100–150 µm), compared to the width of the niobium foil in the initial condition (50 µm).

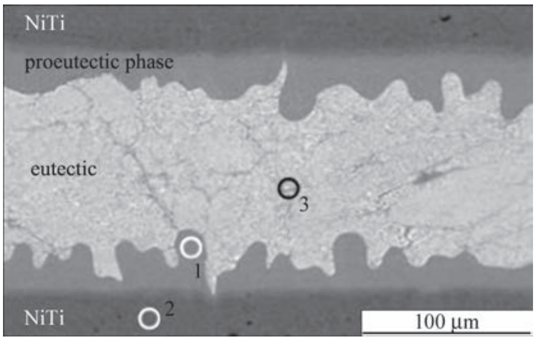

Figure 6. Seam structure with regions where local elemental composition was determined in NiTi brazed joint produced using pure niobium (50 µm) as brazing filler metal ($T_m = 1180$ °C, $\tau = 6$ min) [5]

Maximum tensile strength (1022 MPa) of nitinol specimen was achieved at brazing temperature of 1180 °C with 6 min soaking. Fracture occurred through the eutectic phase and in the hypoeutectic dendrite zone (Figure 7, *d*, *e*). Of considerable interest is investigation of the influence of soaking time and heat treatment on NiTi structure and pseudoelasticity of brazed joints. The authors note that Nb, NbZr1, Cu and AuCu65 are promising for application as brazing filler metals. They provide partially pseudoelastic behaviour in NiTi/NiTi brazed joints [5].

Nititnol wires (300 µm diameter) can be brazed with application of NiTi and Nb powders as brazing filler metals [29], which are mixed with polyvinyl alcohol and water in a certain proportion (to obtain a suspension) and are applied on the contact surfaces of two parallel wires. A liquid phase forms between NiTi and Nb at the temperature of 1170 °C due to a eutectic reaction (in keeping with NiTi–Nb17 quasibinary diagram), which wets the base metal wires, filling the gaps between. Overheating by 10° (up to 1180 °C) and soaking for 4 min promote good wetting and formation of a tight brazed seam, containing a eutectic component (Figure 8).

The seam structure contains round grains of a phase enriched in Nb (N′), rod (R) and platelike (L) eutectic (Figure 8, *b*). Moreover, faceted phase parti-

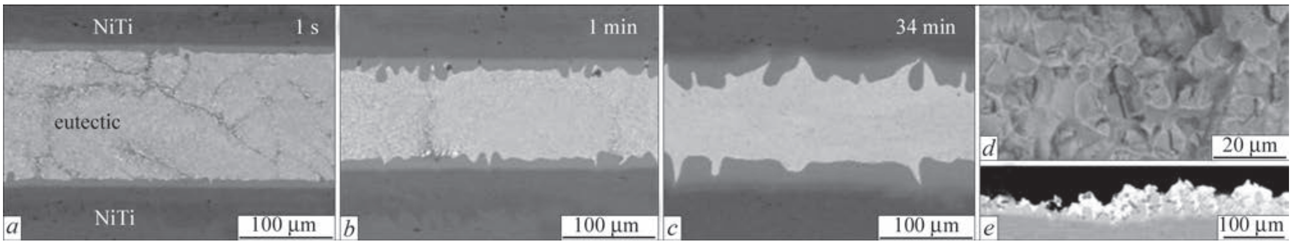

Figure 7. Microstructure of NiTi brazed joint produced under vacuum at brazing temperature of 1180 °C and at different soaking (*a*–*c*) and fracture surface (*d*) and cross-section of the specimen in the fracture zone (*e*) [5]

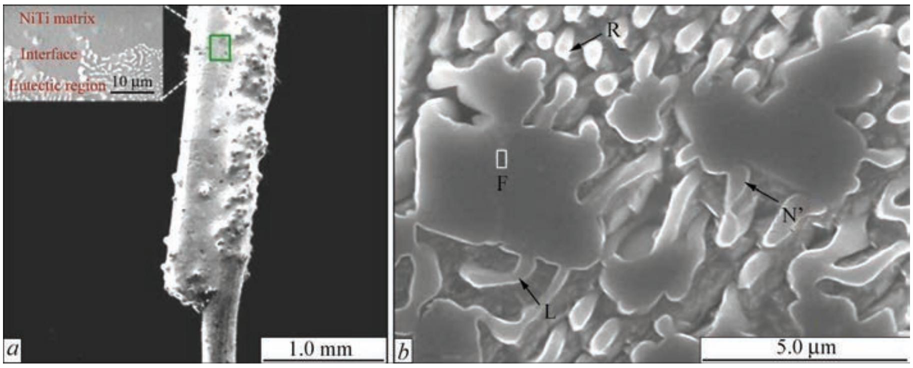

Figure 8. SEM micrographs: *a* — joined parallel NiTi wires; *b* — eutectic region in a polished brazed region. R and L — eutectic microstructure of the rod and platelike, respectively; N′ — Nb-rich rounded phase, F — Ti-rich faceted particle [29]

cles are present, which are enriched in titanium (F). It is reported that the rod-type eutectic forms, when the volume fraction of Nb phase in NiTi–Nb eutectic is below the critical volume (close to 30 %) for platelike eutectic [29]. The authors of [29] found that phase transformation of B2 into B19′ slows down after heat treatment at 520 °C for 30 min, both for NiTi wire, and for the eutectic region of the brazed seam. It confirms the presence of a greater transformation barrier for B19′ phase transformation. R phase transformation takes place predominantly on the interface of NiTi and eutectic region (brazed seam metal) during crystallization. A separate Nb-based phase largely promotes formation of an elastic deformation field. Thus, a high fraction of R-phase transformation is induced in this region.

The authors of [30] lay a metallurgical basis for a reliable method of joining NiTi shape-memory alloys and superelastic alloys. It is based on application of pure niobium as a depressant, which causes contact melting with NiTi at acceptable temperatures. Butt specimens were brazed by pure niobium at 1180 °C for 6 min, cooled in the furnace and annealed at 350 °C for 90 min before testing. Brazed specimens failed at a pressure of a little less than 800 MPa, created by the impact of loading. The stress-strain curve for the joined butt specimens of superelastic NiTi plates (3 mm) shows that the brazing filler metal strength is equal to approximately 800 MPa [30]. This fact can have far-reaching consequences for NiTi application in complex aerospace structures, and it will allow expansion of NiTi application with various materials, including ceramics. It is shown that the quasibinary eutectic nature of equilibrium of NiTi–Nb system is the base for a reliable brazing technique, when joining NiTi sections with pure niobium application.

Alloys based on NiTiNb system are well-known as those with a wide hysteresis and with shape memory. They have important applications as joining materials. Proceeding from the existence of a quasibinary NiTi–Nb eutectic region in this ternary system, a new brazing method was developed to form metallurgical bonds between functional regions of nitinol [31]. When NiTi and pure Nb come into contact at a temperature above 1170 °C, spontaneous melting occurs, which leads to formation of a liquid phase which is extremely active. It not only wets the NiTi surface, but, obviously, dissolves the oxide precipitates, eliminating the need for fluxes, while ensuring an effective capillary flow into the joint gaps. The melting process is regulated by diffusion, and it is limited by Nb diffusion coefficient in the liquid phase. The brazing filler metal in the liquid state crystallizes at cooling with formation of a microstructure which contains predominantly ordered NiTi and disordered solid solution of niobium (BCC lattice). Mechanical testing showed that the brazed joints are strong, ductile and biocompatible with the human body. At appropriate aging after brazing, the functional characteristics of NiTi base alloy can be recovered. Microalloying of niobium filler metal by zirconium or tungsten showed a high potential for brazed seam strengthening. For applications, where biocompatibility is not a problem, niobium can be replaced by pure vanadium as the brazing filler, which has sufficient rupture strength and can potentially be superior to the analogs with niobium [31].

Of particular importance are dissimilar joints designed for medical applications [32]. Successful joining of dissimilar metal tubes will allow selective application of unique biocompatible materials, such as stainless steel and shape-memory materials (NiTi) for locally providing certain properties of medical devices — implants. Application of a new process of autogenous laser brazing, which uses the heat accumulation mechanism to produce joints of dissimilar tubular specimens (without brazing filler metal) from nitinol and stainless steel (1 mm diameter) ensures the appropriate strength, composition and microstructure. The influence of laser parameters on the thermal profile and joining mechanism is studied experimentally and by numerical modeling. The joint strength obtained using this process reaches 500 MPa [32] that is close to the stresses of phase transformation of NiTi base material, as well as to rupture strength of tempered stainless steel. It is shown that this process is promising for application, but it requires additional studies as regards the particular tubular parts.

CONCLUSIONS

Analysis of published sources shows the relevance and importance of studies, related to producing permanent joints of nitinol — a promising shape-memory material, which needs to be joined in structure fabrication in different industries, including aerospace, medical sectors, etc.

Features of different methods of joining this material were high-lighted, and temperature-time parameters of the process of brazing NiTi intermetallic alloy in a similar combination and in combination with other materials were revealed. It is shown that at brazing nitinol in the ambient atmosphere brazing filler metals based on Ag–Cu–Zn–Sn–Ni system and AgCl–KF–LiCl flux have proven themselves well, ensuring the maximum joint strength of ~ 300 MPa.

At vacuum brazing (10^{-3} Pa) by brazing filler metal of Ag–Cu system the strength is in the range of 360–600 MPa that is due to the overlap value. At the same time, note that the eutectic brazing filler metal based on Ag–Cu system is alloyed by titanium in order to improve base metal wetting.

When producing permanent dissimilar joints of nitinol with titanium alloys, the following brittle phases form in the brazed seam: Ti_2Ni, $(Cu_xNi_{1-x})_2Ti$, Cu_2Ti, Cu(Ti, V), which promote cracking on the interphase of brazing filler metal-reaction layer and along the central zone of Ti_2Ni intermetallic compound, impairing the joint quality. Their formation in the joint zone can be avoided using brazing filler metal of a certain composition or interlayers, which improve the nitinol brazed joint properties at vacuum brazing. It should be specially noted that vacuum brazing of NiTi using pure niobium leads to a high quality and strength of the joints (close to 800 MPa). More over, at brazing nitinol using brazing filler metals, the following materials are promising: Nb, NbZr1, Cu and AuCu65, which promote partially pseudoelastic behaviour of NiTi/NiTi brazed joint.

At the same time, it should be noted that the process of producing permanent joints by brazing requires performance of further systemic studies with application of up-to-date computational and experimental methods, which will allow preserving the main properties of shape-memory alloys and will ensure the appropriate service properties of brazed products.

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CONFLICT OF INTEREST

The Authors declare no conflict of interest

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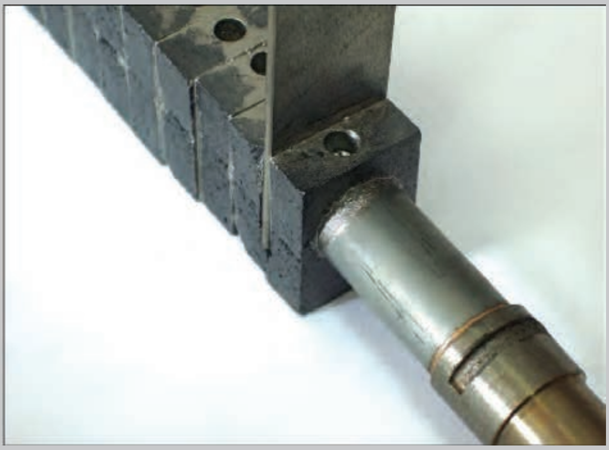

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