Exploring Solid-State Synthesis of Powder Filler Metals for Vacuum Brazing of Titanium Alloys

Titanium brazing filler metals of Ti-Zr-Cu-Ni and Ti-Cu-Ni systems can be successfully manufactured by mechano-chemical synthesis in the solid state

BY E. Y. IVANOV, A. E. SHAPIRO, AND M. G. HORNE

ABSTRACT. The technology of producing small-size batches of mechanically alloyed filler metals from elemental metal powders or hydrides by the solid-state synthesis in a high-energy ball mill was developed to cut the production costs (associated with the manufacturing of small batches) by 40–50%. Some of these alloys such as TiBraze®375 (Ti-37.5Zr-15Cu-10Ni), TiBraze®260 (Ti-26Zr-14Cu-14Ni-0.5Mo), and TiBraze®15-25 (Ti-15Cu-25Ni-0.5Mo) have been successfully tested and used by the aerospace industry.

These mechanically alloyed filler metals are characterized by a low erosion of the base materials, a tensile strength of Ti-6Al-4V brazed joints in the range of 91–107 ksi (626–740 MPa) depending upon the brazing joint clearance and temperature, a shear strength of joints between 75–84 ksi (520–580 MPa), and by a relatively low brazing temperature in the range of 1562°–1634°F (850°–890°C). The combined properties of these filler metals allow for effective brazing below the β-transus temperature of most titanium-base alloys.

Solid-state synthesis of Ti-Zr-Cu-Ni alloys was investigated by varying the time of high-energy ball milling. The products were studied via differential thermal analysis (DTA), energy-dispersive spectroscopy (EDS) analysis, and scanning electron microscopy. Clear evidence of solid-state reactions obtained in this study confirm that the resulting products are partially prealloyed and comprise Cu and Ni, which are dispersed throughout the Ti and Zr phases. Differential thermal analysis results displayed a decrease in the liquidus temperature as a result of this milling. The notable effect of milling is the induced exothermic effect prior to melting of mechanically alloyed brazing alloys.

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Introduction

Titanium alloys play an important role in many modern industries, particularly in aerospace, due to their high performance characteristics, namely high strength, low density, exceptional fatigue and corrosion resistance, and good strength-to-density ratio.

Today, as cost control continues to become more prevalent within the aerospace industry, a major goal is to achieve economic efficiency of commercial and military airplanes. That can be accomplished through weight reduction using titanium alloys that have attractive strength-to-weight ratios. Therefore, we expect that the amount of titanium used in the next generation of aircraft components will continue to grow in both the turbine engine and airframe components. For example, titanium alloys currently comprise about one-third of the total weight of the new F-119 engine. However, many of the prospective titanium alloys have limited weldability, therefore brazing is either preferred or is the only applicable method of joining such materials as titanium aluminides and titanium matrix composites reinforced by ceramic particles or fibers (Ref. 1).

Vacuum brazing of titanium is widely utilized in aerospace manufacturing. The composition of titanium alloys determines important temperature and time limits of the brazing cycle. These limits are a consequence of changes that occur in the microstructure and properties above the so-called "beta-transus," or the critical temperature of α–β phase transformation. In general, filler metals with a brazing temperature below the beta-transus are preferable because they provide high mechanical properties of titanium brazed parts and do not induce phase transformations within the base materials.

KEYWORDS

Ti-Zr-Cu-Ni
Titanium
Brazing
Differential Thermal Analysis (DTA)
Energy Dispersive Spectroscopy (EDS)

Compositions of Mechanically Alloyed Brazing Filler Metals

Titanium alloys are typically brazed in the U.S.A., Japan, and Russia with two powder (or clad foil) filler metals of the Ticuni® family having compositions of 70Ti-15Cu-15Ni and 60Ti-15Cu-25Ni, prealloyed filler metals of the Ti-Zr-Cu-Ni system such as Ti15-10™, VPr16™, and VPr28™ powders, and amorphous foils of the Stemet® family. All of these brazing materials are characterized by their high cost, which may be attributed to both the high cost of the component powders and the high manufacturing costs associated with the atomization process of Ti- and Zr-based alloys, and the production of amorphous tapes.

Therefore, a method utilizing a high-energy attritor to produce mechanically alloyed filler metals from elemental metal powders or hydrides was developed to cut manufacturing expenses by 40–50%. Some of these alloys such as TiBraze®375 (Ti-37.5Zr-15Cu-10Ni), TiBraze®375A (Ti-37.5Zr-15Cu-10Ni-1Mo), TiBraze®260 (Ti-26Zr-14Cu-14Ni-0.5Mo), and TiBraze®15-15 (Ti-15Cu-15Ni-0.5Mo) were successfully tested and have been used in the industry since 1998.

Lower cost is not the only advantage of a mechanical alloying approach. Another important advantage is the flexibility of such a process, in which one can easily change the alloy composition to design customized filler metals with improved properties. Addition of such components as Mo, Nb, and Cr in amounts up to 4.5%

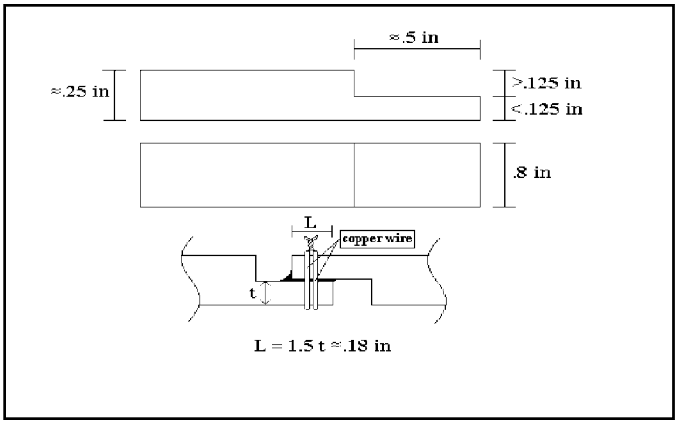

Fig. 1 — Design specifications for mechanical testing of brazed samples.

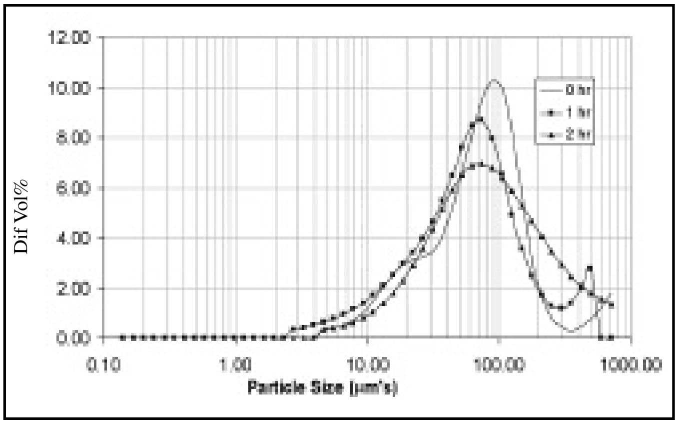

Fig. 2 — Particle size of the synthesized Ti-37.5Zr-15Cu-10Ni alloy for different time periods of solid-state synthesis.

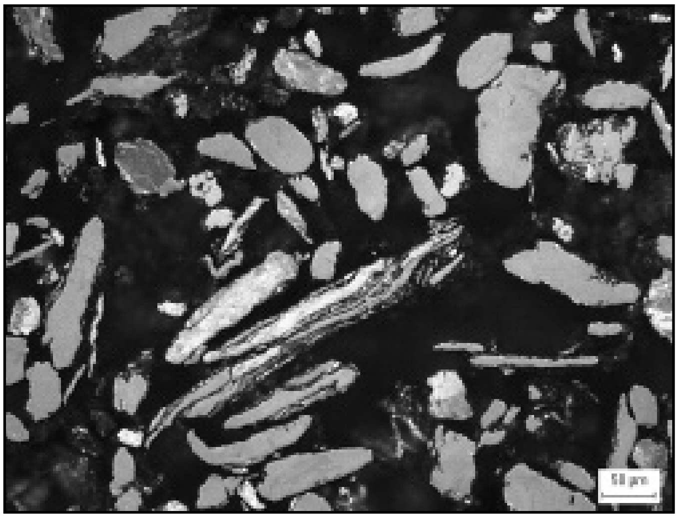

Fig. 3 — Flake-shaped particles of mechanically alloyed powder Ti-37.5Zr-15Cu-10Ni.

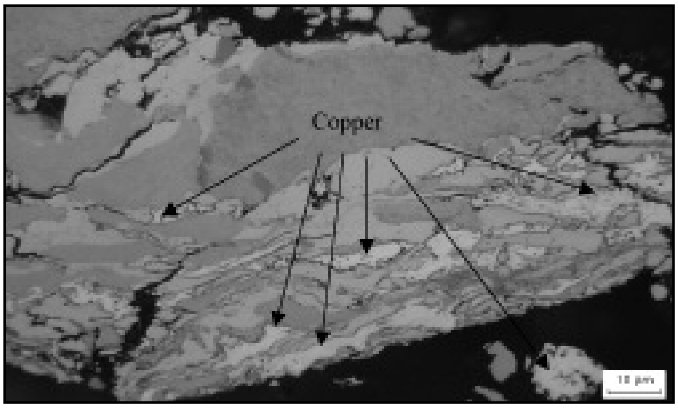

Fig. 4 — Metallography of the mechanically alloyed Ti-37.5Zr-15Cu-10Ni particle showing copper distribution.

allows for an improved strength or corrosion resistance of brazed joints without significantly changing the brazing temperature. Also, mechanically alloyed filler metals are characterized by less erosion of the base materials than prealloyed filler metals. The inhomogenity of particle composition within mechanical-alloyed powder mixtures allows for particles of a higher melting point to be dissolved in the lower melting point phase of the brazing filler metals. This process results in fast alloying and solidification of the brazing filler metal; thus, its erosion activity at the interface of the base metal is suppressed.

Experimental

The experimental work was aimed to evaluate the following: 1) the effect of mechanical alloying parameters on the formation of alloy and intermetallic phases; 2) the effect of mechanical alloying parameters on melting range of the filler metals and brazing temperature; and 3) the shear strength of brazed joints.

The base metals utilized were commercial purity (CP) Grade 2 titanium and the alloy Ti-6Al-4V (Grade 5). Brazing filler metals Ti-37.5Zr-15Cu-10Ni and Ti-26Zr-14Cu-14Ni-0.5Mo were prepared from elemental powders of titanium, zirconium, copper, nickel, and molybdenum by milling in a Fritsch P-5 high-energy ball mill with a consistent ball-to-powder ratio for 1 or 2 hours at the rate of 200 rpm. The particle size of all initial powders was –325 mesh (–44 µm). Differential thermal analysis was performed on each of the milled alloys to determine the liquidus and solidus temperatures. Metallography was also performed to observe the effect of milling on the microstructure, and elemental mapping by EDS was utilized to

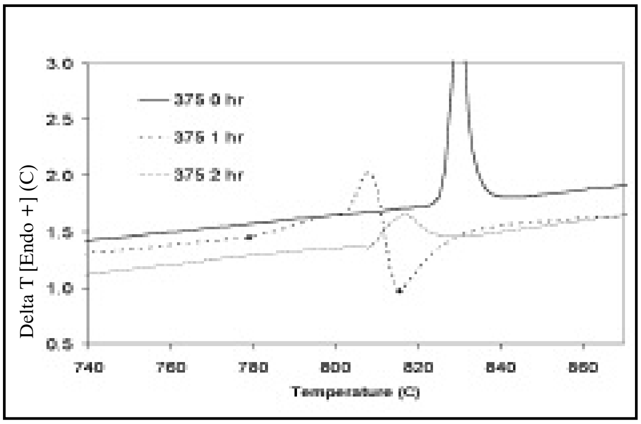

Fig. 5 — Differential thermal analysis of mechanical-alloyed TiBraze375 powder after different lengths of milling.

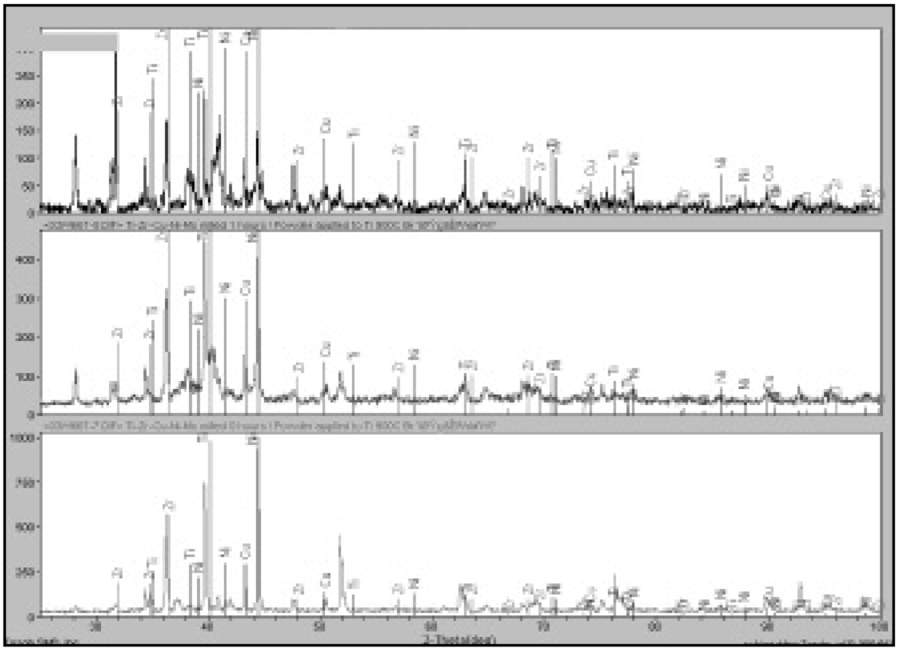

Fig. 6 — XRD analysis of mechanically alloyed Ti-37.5-15Cu-10Ni powder. The lower graph is of the initial mixture (elemental powders, no milling), the middle graph is after synthesis of 1 hour, and the top graph is after synthesis of 2 hours.

verify the compositional distribution of products. X-ray difractometry was used for identification of intermetallic phases. All brazed joint samples were made in a vacuum furnace at 10^{-4} Torr.

Brazed samples were analyzed utilizing scanning electron microscopy (SEM), and subjected to shear and tensile tests at room temperature. The design specification of shear test samples is shown in Fig. 1. Standard specimens 0.2 in. thick were used for tensile tests of brazed joints according to AWS B2.2-91, *Standard for Brazing Procedure and Performance Qualification,* Appendix A. Thus, the effectiveness of the filler metal in terms of microstructure and overall strength for potential brazing applications could be assessed.

Results and Discussion

Particle analysis of produced powder alloys shown in Fig. 2 indicates that milling first causes a decrease in particle size, but milling longer than 1 hour has no further pronounced effect on the particle size. The process of milling leads to flake-like particles — Fig. 3. However, these flake particles can be interpreted as larger, round, thin particles when viewed normal to the surface to create an inaccurate particle size analysis. Although the average composition responses to the specification, individual particles of the powdered alloy may differ by the content of Cu and Ni, thus the subsequent sieve's classification of the mechanically alloyed powder is not recommended, in order to avoid a loss of the average composition balance.

The true objective of milling is to obtain a homogeneous composition and microstructure that will provide uniform wetting of base metal and isotropic properties of the filler metal. Separation of Cu powder was observed macroscopically in the initial powder mixture blend, and the hope was to reduce this occurrence with milling. Figure 4 shows the cross section of a particle with copper dispersed within a layered composite structure, seen to increase with attrition time. The average particle size of the resulting powder alloys was in the range of 40–100 microns.

The mechanical alloying resulted in the formation of a range of metallurgically bonded alloy particles with clear evidence of not only intimate contact of elemental powders but also diffusion interaction that occurs during the milling process.

Energy-dispersive spectroscopy mapping showed intermetallic compound formation, indicating partial alloying. The reaction between elemental powders was sufficient enough that the melting point of mechanically alloyed brazing powders was similar to that of cast alloys of the same compositions. The melting point of the synthesized Ti-37.5Zr-15Cu-10Ni alloy was 1515°F (825°C), and the synthesized Ti-26Zr-14Cu-14Ni-0.5Mo alloy exhibited a melting point of 1558°F (848°C).

Differential thermal analysis results display a decrease in the liquidus temperature, due to attrition — Fig. 5. However, the notable effect of milling is the induced exothermic reaction noticeable on the 1-hour mechanically alloyed DTA curve. The resulting curves are therefore the net effect of both an exothermic reaction and the expected endothermic melting reaction.

The exothermic effect is a result of the formation of the solid phase, and we suggest that in our case, this is due to the thermal formation of intermetallics within the product. For this to hold true, some intermetallics must have formed during the first hour of milling, due to the intermixing of the elemental powders. As expected, the Cu and Ni are dispersed throughout the Ti and Zr powders. Energy-dispersive spectroscopy confirms that milling increases the surface area contact of elemental powders and leads to partial formation of intermetallics. As seen in Fig. 6, the elemental peaks decrease in intensity and new peaks form and increase in intensity with increased time of the mechanochemical synthesis (possibly due to this formation of intermetallic compounds). However, due to the infinite number of alloy combinations and the relative low intensity and of XRD reflections, it was impossible to precisely identify the intermetallic compounds.

We speculate that the intermetallics most likely forming are NiTi, $NiTi_2$, $TiCu_2$, $TiCu_3$, and $NiZr_2$. As is the case for most binary systems, intermetallics of certain compositions have lower liquidus temperatures than pure component elements. Thus, as these intermetallics melt at lower temperatures, the release of energy associated with this process, then, initiates an endothermic melting reaction in neighboring phases, causing the entire system to melt at a lower temperature. In other words, once melting is initiated at one intermetallic source, the entire alloy particle follows. In this case, the rate at which the surrounding regions begin melting is inherent to both the initial system and compositions (Ref. 2). Such a process of melting is similar to the melting of particles during high-temperature combustion synthesis (Refs. 3–5).

These mechanically alloyed filler metals are characterized by a low erosion of the base materials and a relatively low brazing temperature in the range of 850°–890°C that allows one to perform the brazing process below β-transus temperature of most titanium-base alloys — Fig. 7. The two-step thermal cycle is recommended for brazing with mechanically alloyed filler metals: a) heating to 1400°–1470°F (760°–800°C), holding 15–20 min, and b) heating to the brazing temperature and holding 10–15 min. The first step enhances the diffusion interaction in multilayer particles and promotes a

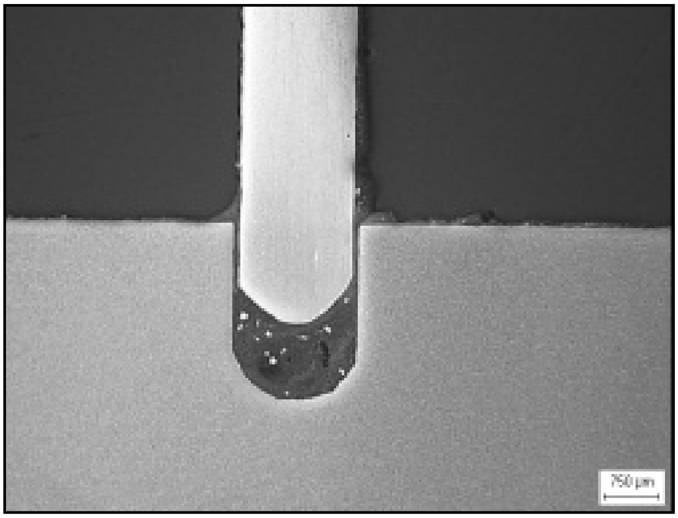

Fig. 7 — *Macrostructure of brazed joint of Ti-6Al-4V (Grade 5) impeller made with the mechanically alloyed Ti-37.5Zr-15Cu-10Ni filler metal. No erosion of the base metal witnessed.*

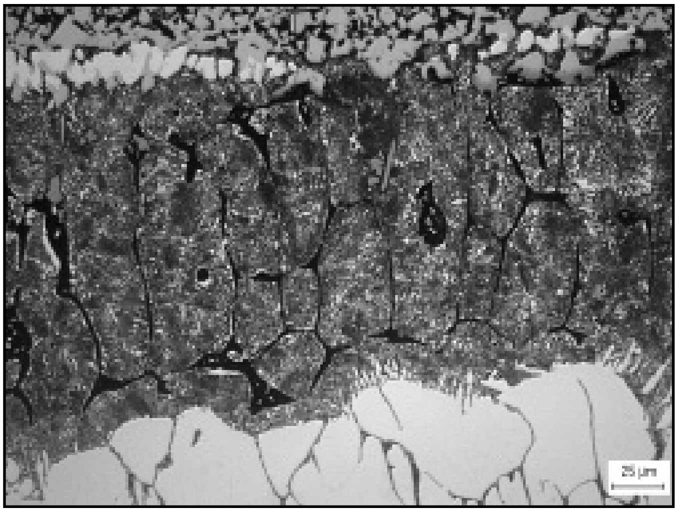

Fig. 8 — *Microstructure of brazed joint of CP Grade 2 titanium made by mechanically alloyed Ti-37.5Zr-15Cu-10Ni filler metal. Dark phase displays an eutectic microstructure.*

solid-phase dissolution of the components, as the contact between particles is improved. Such processing provides uniform melting of the filler metal despite the different chemical compositions of particles.

Brazing utilizing filler metal Ti-37.5Zr-15Cu-10Ni was carried out at 1562°–1580°F (850°–860°C) and that with filler metal Ti-26Zr-14Cu-14Ni-0.5Mo was at 1616°–1634°F (880°–890°C). Microstructure of brazed joints demonstrates an active diffusion interaction between the filler metal and base metal — Fig. 8.

Tensile strength of Ti-6Al-4V brazed joints was in the range of 91–107 ksi (626–740 MPa), depending upon the brazing joint clearance and temperature, and the shear strength of the joints is between 75 and 84 ksi (520 and 580 MPa). The shear strength of the Grade 2 titanium joints was 45–61 ksi (308–420 MPa). The relatively big deviation of the testing results can be explained by the fact that the size of brazing joint clearance was not consistent at assembling and brazing of the specimens. Nevertheless, the obtained values of mechanical strength are quite sufficient to reach the strength of the base metal at the overlap length in the range of 2–3 thicknesses of the base metal part.

Conclusions

1. Titanium brazing filler metals of Ti-Zr-Cu-Ni and Ti-Cu-Ni systems can be successfully manufactured by mechano-chemical synthesis in the solid state using the technology of mechanical alloying of elemental powder blend in a high-energy ball mill.

2. The mechano-chemical synthesis results in the formation of metallurgically bonded alloy particles, diffusion interaction during the high-speed milling process, and possible formation of intermetallic compounds, indicating partial alloying. The solid-state reaction between elemental powders is sufficient enough to provide a melting point of mechanically alloyed brazing powders similar to that of cast alloys of the same compositions.

3. The strength of brazed joints made with mechanically-alloyed filler metals is sufficient to manufacture reliable titanium brazed structures such as low-weight heat exchangers, honeycomb plates, compressor vanes, and others. High-temperature strength and fatigue resistance of joints need to be investigated in further work.

4. The solid-state synthesis of powdered brazing filler metals based on the Ti-Zr-Cu-Ni system is a cost-effective method for the fabrication of small-scale parties of the filler metals, as well as for the preparation and testing of new alloys due to the process flexibility of alloying various compositions.

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