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

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Abstract

Titanium alloys are typically brazed in the USA and Russia with two powder filler metals of Ticuni® family having compositions of 70Ti–15Cu–15Ni and 60Ti–15Cu–25Ni, several pre-alloyed filler metals of Ti–Zr–Cu–Ni system such as VPr16 and VPr28 powders, and amorphous foils of Stemet® family. All these brazing materials are characterized by high price that may be attributed to both the cost of the components and atomization process of Ti- and Zr-based alloys or with the production of amorphous tapes. The technology of producing 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®260 (Ti–26Zr–14Cu–14Ni–0.5Mo), and TiBraze®15-15 (Ti–15Cu–15Ni) were successfully tested and accepted by the USA industry. These mechanically-alloyed filler metals are characterized by low erosion of base materials, tensile strength of Ti–6Al–4V brazed joints in the range of 670–740 MPa depending on the brazing gap and temperature, shear strength of joints 520–580 MPa, and by relatively low brazing temperature in the range of 850–890 °C that allows to perform the brazing process below 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 by DTA, EDS analysis, and scanning electron microscopy. Clear evidences of solid-state reactions obtained in this study confirm that the resulting alloys are partially pre-alloyed and comprise Cu and Ni dispersed throughout the Ti and Zr phases. DTA results displayed a decrease in the liquidus temperature. The notable effect of milling is the induced exothermic effect prior to melting of mechanically-alloyed brazing alloys.

INTRODUCTION

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

Today, the major goal in aerospace development is to achieve high economical efficiency of commercial and military airplanes. Therefore, we may expect that the amount of titanium to be used in next generation of aircrafts will continue to grow in both the turbine engine and airframe components. For example, titanium alloys comprise about one third of the total engine weight of the new F-119 engine.

Brazing is widely applied in aerospace manufacturing [1]. The nature of titanium alloys determines important temperature/time limits of brazing cycle. These limits are a consequence of changes in the structure and properties occurring above the so-called “beta-transus”, that is 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.

COMPOSITIONS OF MECHANICALLY-ALLOYED BRAZING FILLER METALS

Titanium alloys are typically brazed in the USA and Russia with two powder filler metals of Ticuni® family having compositions of 70Ti–15Cu–15Ni and 60Ti–15Cu–25Ni, several pre-alloyed filler metals of Ti–Zr–Cu–Ni system such as VPr16 and VPr28 powders, and amorphous foils of Stemet® family. All these brazing materials are characterized by high cost that may be attributed to both the cost of the components and the manufacturing cost associated with the atomization process of Ti- and Zr-based alloys or with the production of amorphous tapes.

Therefore, a technology of producing 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®260 (Ti–26Zr–14Cu–14Ni–0.5Mo), and TiBraze®15–15 (Ti–15Cu–15Ni) were successfully tested and accepted by the USA industry.

Lower cost is not the only advantage of mechanically-alloying approach. Another important advantage is a possibility of easy changing of 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 % allows improving strength or corrosion resistance of brazed joints without a considerable change of the brazing temperature. Also, mechanically-alloyed filler metals are characterized by lower erosion of base materials than pre-alloyed filler metals.

EXPERIMENTAL

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

Base metal was commercial purity (CP) titanium Grade 2. Brazing filler metals TiBraze375 (Ti–37.5Zr–15Cu–10Ni) and TiBraze260 (Ti–26Zr–14Cu–14Ni–0.5Mo) were prepared from elemental powders by milling in Fritsch P-5 high energy ball mill with a consistent ball to powder ratio for 1 or 2 h at the rate of 200 rpm. Differential thermal analysis (DTA) was performed on each of the milled alloy to determine the liquidus and solidus temperatures. Metallography was also made to observe the effect of milling on the microstructure, and Elemental Mapping was completed to find out the composition distribution of products.

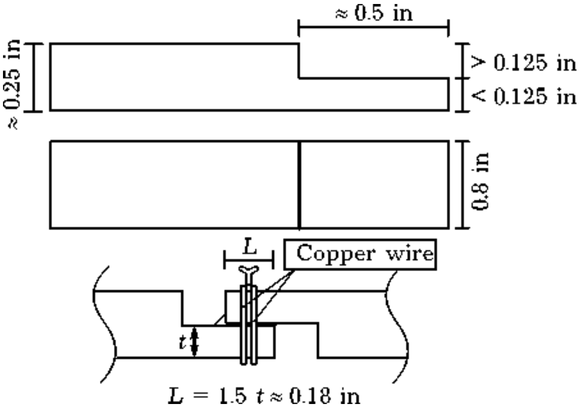

Fig. 1. Overlap joint machined before brazing for shear test.

Brazed samples were analyzed utilizing SEM, and subjected to shear test at room temperature. Design of mechanical test samples is shown in Fig. 1. Thus, the effectiveness of the filler metal in terms of microstructure and overall strength for potential brazing applications could be assessed. All brazing samples were made in vacuum furnace at 10^{-4} Torr.

RESULTS AND DISCUSSION

Particle analysis of produced powder alloys shown in Fig. 2 indicates that milling causes a decrease in particle size but the length of milling above 1 h has no pronounced effect on particle size. The process of milling leads to flake-like particles which can be interpreted as large, round but thin particles when viewed normal to the surface. The true objective of milling is to obtain a microstructure close to homogeneous, which 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 3 shows the cross section of a particle, with copper dispersed within typical layered composite structure with the increase of attrition time. The average particle size of the resulting powder alloys was in the range of 40–100 μm.

The mechanical alloying resulted in the formation of a range of metallurgically-bonded alloy particles with clear evidence that not only

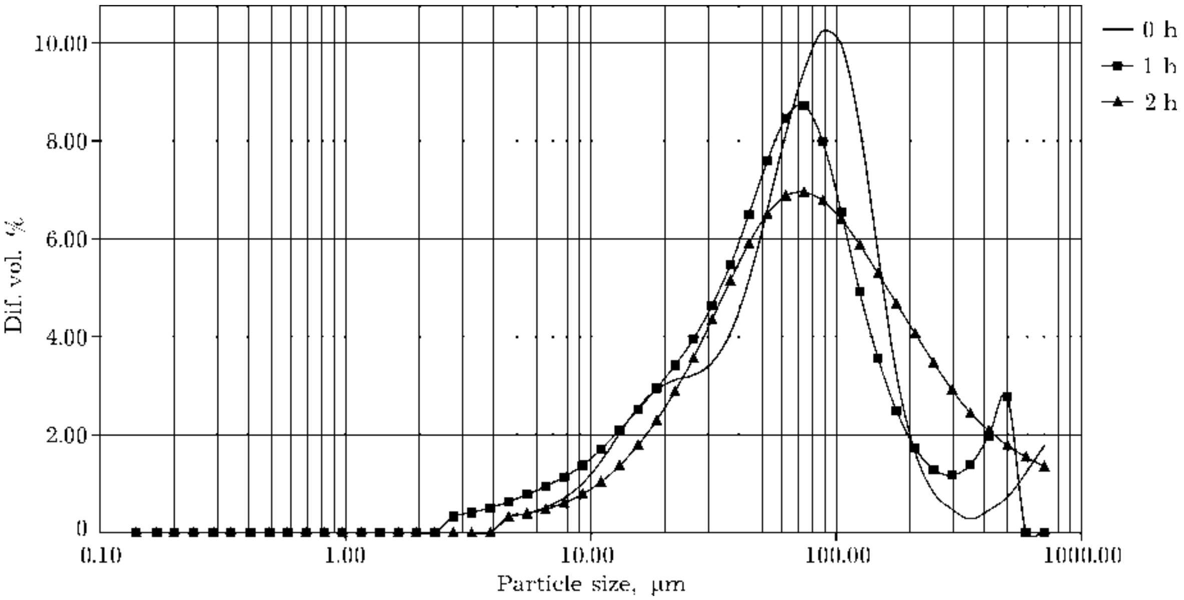

Fig. 2. Alloy 375 particle size analysis for different milling times.

intimate contact of elemental powders but also diffusion interaction occurs during the milling process. EDAX mapping showed intermetallic compound formation, indicating partial alloying. The reaction between elemental powders was sufficient enough so that melting point of mechanically-alloyed brazing powders was similar to that of cast alloys of the same compositions. The melting point of Ti−37.5Zr−15Cu−10Ni alloy was 825 °C and Ti−26Zr−14Cu−14Ni−0.5Mo was 848 °C.

DTA results (Fig. 4) display a decrease in the liquidus temperature, due to attrition. However, the notable effect of milling is the induced exothermic reaction noticeable on 1 h MA DTA curve. The exothermic reaction is coupled with the expected endothermic melting reaction to yield the curves that were recorded.

For this to hold true, some intermetallics must have formed during the milling due to the intermixing of the elemental powders in the first hour of milling. As expected, the Cu and Ni are dispersed throughout the Ti and Zr powders. XRD confirms that the increase of surface area contact of elemental powders leads to the formation of intermetallics. The elemental peaks decrease in intensity and new peaks form and increase in intensity (possibly due to formation of intermetallic compounds) with increased milling time. However, due to low intensity and number of new XRD reflections it was impossible to precisely identify the inter-

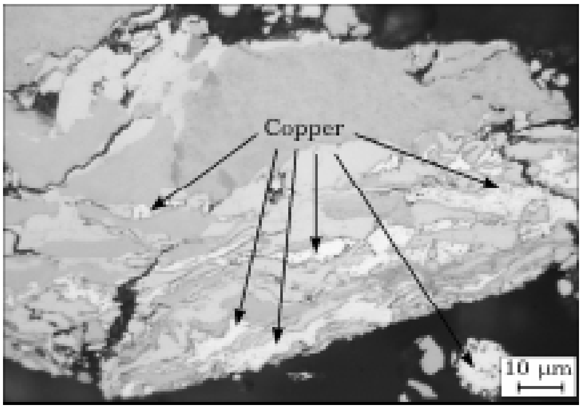

Fig. 3. Metallography of MA Alloy 375 particle showing copper distribution.

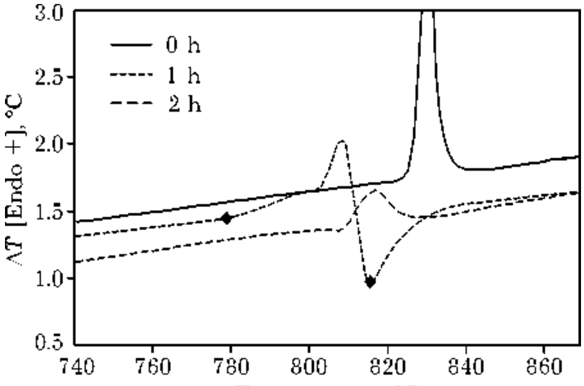

Fig. 4. DTA of Alloy 375 at different milling times.

metallic compounds. The intermetallics that are more likely forming are $NiTi_2$, $CuTi_3$, 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 decomposition, then, initiates an endothermic melting reaction in neighboring phases, causing the entire system to proceed at lower temperature. In other words, once melting is initiated at one intermetallic source, the entire alloy particle follows. The rate at which the surrounding regions begin melting is inherent to both the initial system and compositions [2, 3].

The mechanically-alloyed filler metals are characterized by low erosion of the base materials and by 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. Tensile strength of Ti–6Al–4V brazed joints was in the range of 670–740 MPa depending on the brazing gap and temperature, shear strength of Titanium Grade 2 joints – 308–420 MPa, shear strength of Ti–6Al–4V joints – 520–580 MPa.

CONCLUSIONS

1. Titanium brazing filler metals of Ti–Zr–Cu–Ni and Ti–Cu–Ni systems can be successfully manufactured by mechanical alloying of elemental powder blend in a high-energy ball mill.

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

3. 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.

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