Brazing of Titanium with New Biocompatible Brazing Filler Alloys

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ANNOTATION
Brazing of titanium with new biocompatible brazing filler alloys, using resistance brazing techniques, was investigated for biomedical applications. Several titanium and zirconium based alloys, with iron or manganese as an alloying agent to reduce the liquidus temperature were used. Brazing was conducted at temperatures from 900 to 1300 °C and for 30, 60 and 90 seconds in an argon inert gas atmosphere with cp-Ti grade 2 samples. The brazing fillers were used as pastes, made by mixing the powdered alloys with an organic carrier. The influence of a vacuum annealing step below the α/β transition temperature (6 h) / 800 °C following the brazing procedures was also investigated in order to obtain a better distribution of the alloying elements. The microstructure of the joints was metallographically examined. The influence of the brazing time and brazing temperature could also be explained by the development of the microstructure. The solidus and liquidus temperatures and the wetting and erosion behaviour of the brazing filler alloys were also determined.

Keywords: brazing, filler metal, biocompatibility, cp-titanium grade 2, resistance brazing

1. INTRODUCTION

Since the beginning of the industrial use of titanium and titanium alloys a number of brazing filler metals have been tested for brazing without complete success concerning the properties obtained. The use of silver and aluminium or their alloys, which has been examined since the 1950's could not prevail [1,2,3]. In contrast to the good wetting properties and low brazing temperatures, joints showed a low corrosion resistance and poor mechanical properties such as low tensile strength or ductility [4,5,6,7].

In the past years interest has become focused on titanium and zirconium based alloys as brazing filler metals because of their corrosion resistance and ther good bonding due to a high solubility in the base material. To achieve brazing temperatures below the α/β or α+β/β transition temperatures of titanium (882 °C) or α+β-titanium alloys ternary eutectic systems of titanium and zirconium, as for example the systems Zr-Ti-Cu-Ni, Zr-Cu-Fe, Ti-Zr-Ni-Be, Zr-Ti-Cu or Ti-Cu-Ni were investigated. High tensile strengths up to the values of the base metal could be reached using these alloys [8,9,10,11,12].

The corrosion resistance of the titanium and zirconium based alloys was much better than that of the silver or aluminium alloys [13,14]. These alloys have been used in different processes like vacuum furnace brazing or HF induction brazing in argon or vacuum. Due to its biocompatibility, titanium has found a large number of biomedical applications, especially for different types of implants. The use of the above-mentioned filler alloys has to be seen critically because of their contents of nickel, copper or beryllium which are considered to be non-biocompatible or even toxic in the case of beryllium. Thus, in the case of brazed parts for biomedical devices or implants, biocompatibility could be improved if brazing filler alloys composed of biocompatible alloys agents were available.

2. EXPERIMENTAL

The cp-Ti grade 2 samples were joined in a resistance brazing process in a flowing argon inert gas atmosphere. The temperature was controlled and regulated with a pyrometer. For the tensile and bending tests butt joints of 6 mm diameter and 25 mm length were produced.

In the first step the influence of the brazing temperature and of the brazing time on the microstructure of the seam was investigated. Samples were brazed at 900, 1100 and 1300 °C for 30, 60 and 90 seconds with a commercially available amorphous Zr-Ni-Ti brazing foil (T_{liq} = 825 °C). The composition of the foils was...
Zr16.5Ni9Ti. Samples of each brazing temperature were annealed after brazing for 6 h at 800 °C in a furnace in a vacuum of <10⁻⁴ mbar. The mechanical properties were determined by tensile and 3-point bending tests. One sample of each combination of process parameters was prepared metallographically and investigated by optical and scanning electron microscopy. The phases present were determined by EDX spectroscopy.

In the second step different brazing filler alloys based on titanium or zirconium were developed from elements which are not considered to be toxic or allergenic. The alloys were melted in an arc furnace in a purified argon atmosphere. For different tests the alloys Ti35Zr24Fe, Ti36Zr23Fe5Al, Ti35Zr20Fe, Ti34Zr18.5Fe2.5Al, Ti35Fe15Mn, Zr15Fe5Al and Zr20Fe11.5Al were produced. The alloys were milled in a ball mill and the powder with a particle size of < 45 µm was used for the brazing experiments. The powders were mixed with an organic carrier and applied as a paste. Before brazing the organic carrier had to be evaporated at a temperature of <300 °C. The solidus and liquidus temperatures were measured by thermal analysis under vacuum. Because of the different working temperatures of the alloys brazing was conducted only at 1100 and 1300 °C.

3. RESULTS

The results of the tensile tests of samples brazed with the amorphous Zr-Ni-Ti foil are shown in Fig. 1. There is a continuous increase of the tensile strength with increasing temperature and a less marked increase with the brazing time. Thus, for example, brazing at 900 °C resulted in tensile strengths of almost 225 - 270 MPa and brazing at 1300 °C in tensile strengths between 355 and 415 MPa. The results of the bending tests are shown in Fig. 2. In the bending test all joints brazed at 900 and 1100 °C had low bending strength values of 600 - 700 MPa. Only the brazings which were conducted at 1300 °C had a significantly higher bending strength at 830 MPa. The bending angles of all 900 °C, 1100 °C and the 30 and 60 s brazements at 1300 °C could not produce values of more than 10°. Only the brazing at 1300 °C for 90 s resulted in values between 10 and 20°.
the system Zr-Ni-Ti was found [15]. At these brazing parameters the phase Ti25Zr2Ni forms only a very thin layer at the interface to the base metal.

Bending Strength
Amorphous ZrNiTi-foil

Fig. 2: Results of the bending tests of a specimen brazed with an amorphous foil of Zr16.6Ni9Ti at 900, 1100 and 1300 °C

Tensile Strength
Brazing fller alloy ZrNiTi-amorphous foil

Fig. 3: Influence of an annealing at 800 °C / 6 h on the tensile strength of samples brazed with an amorphous foil of Zr16.5Ni9 Ti
Fig. 4: Microstructure of a joint brazed at 900 °C for 30 s. 1: Titanium Base Metal, 2: Zr55Ti43Ni2, 3: Zr58Ti25Ni17, 4: Ti73Zr25Ni2

Fig. 5: Microstructure of a joint brazed at 1300 °C for 30 s
Fig. 6: Microstructure of a joint brazed at 900 °C for 30 s and annealed for 6 h at 800 °C

In the 1300 °C sample the phase with low nickel and zirconium contents, Ti25Zr2Ni, caused by diffusion of zirconium and nickel into the base material, has expanded over the whole joint area. An almost identical structure was found in a 900 °C joint which had been annealed for 6 h at 800 °C (Fig. 6).

The results of the thermal analysis are given in Table 1. Because of the different melting temperatures, the brazing experiments with these alloys were conducted only at 1100 or 1300 °C.

Table 1: Solidus and liquidus temperature of the various nickel-free alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Solidus Temperature</th>
<th>Liquidus Temperature</th>
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<tbody>
<tr>
<td>Ti35Zr15Fe15Mn</td>
<td>985 °C</td>
<td>T_lia &gt;1050 °C</td>
</tr>
<tr>
<td>Ti38Zr24Fe</td>
<td>940 °C</td>
<td>940 °C</td>
</tr>
<tr>
<td>Ti36Zr23Fe15Al</td>
<td>950 °C</td>
<td>995 °C</td>
</tr>
<tr>
<td>Ti35Zr20Fe</td>
<td>925 °C</td>
<td>925 °C</td>
</tr>
<tr>
<td>Ti34Zr18.5Fe2.5Al</td>
<td>955 °C</td>
<td>970 °C</td>
</tr>
<tr>
<td>Zr15Fe5Al</td>
<td>885 °C</td>
<td>960 °C</td>
</tr>
<tr>
<td>Zr20Fe1.5Al</td>
<td>870 °C</td>
<td>870 °C</td>
</tr>
</tbody>
</table>

Fig. 7 shows the tensile strengths as a result of some tensile tests which were conducted with samples brazed for 30 s at 1300 °C with the nickel-free alloys in comparison with those obtained with the ZrNiTi alloy. It can be seen that in the case of the alloys Ti38Zr24Fe and Ti35Zr15Fe15Mn lower values and in the case of the alloys Ti36Zr23Fe5Al and Ti15Fe5Al values similar to those of samples brazed with ZrNiTi foil could be obtained.

The aluminium containing brazing filler alloys had a higher tensile strength than the alloys without the addition of aluminum.

Just as in the case of the ZrNiTi alloy the tensile strength could be increased by vacuum annealing. A value of 495 MPa could be obtained in a joint which had been brazed with Zr15Fe15Al at 1300 °C for 30 s and annealed (6 h / 800 °C). In the bending test, samples brazed with Zr15Fe5Al at 1100 °C for 30 s and annealed at 800 °C (6 h) had a bending strength of 1275 MPa and an average bending angle of 17.5°.
Tensile Strength
1300°C / 30 s

Fig. 7: Results of the tensile tests of specimens brazed at 1300 °C for 30 s with different Ni-free alloys as compared to ZrNiTi foil

Fig. 8: Microstructure of a joint brazed with the alloy Ti38Zr24Fe at 1100 °C for 30 s
1: Titanium Base Metal, 2: Ti92Zr5.5Fe2.5, 3: Ti45Zr35Fe20, 4: Ti77Zr18Fe5

Fig. 8 shows that a brazing seam produced at 1100 °C / 30 s with the filler metal Ti38Zr24Fe is comparable to that of the ZrNiTi filler metal. The same structure consisting of a diffusion zone with a high titanium content, a phase with a higher zirconium content, a low iron content and an iron-rich phase in the center could be
observed. The composition of the different phases is given in the figure. In the brazing seam of the joints brazed with alloys containing aluminium, no precipitations containing aluminium were found.

4. DISCUSSION

The results of the mechanical tests conducted with the ZrNiTi brazing foil show that brazing temperatures of 900 and 1100 °C produce joints with relatively poor mechanical properties, especially with regard to the bending tests. These mechanical properties are due to the existence of the brittle, near-eutectic phase in the middle of the seam. The embrittlement is caused by the high nickel content which forms intermetallic phases with zirconium and titanium. With increasing brazing time and brazing temperature the nickel content is dissolved by interdiffusion of the brazing alloy and the base material. The continuous improvement of the mechanical properties in tensile and in bending tests is the consequence. The results of the bending tests show that an improvement of the values for bending strength and bending angle requires brazing at 1300 °C for 90 s. It can also be seen from the tensile tests that the increase of the brazing temperature has a much greater influence than the increase of the brazing time. This can be explained by the exponential correlation between temperature and diffusion constant.

In spite of the positive effects of increasing brazing time and temperature, brazing above the α/β transition temperature of titanium leads to a grain growth which results in poorer mechanical properties of the base metal. As a consequence, if brazing is not possible below the α/β transition temperature of titanium, brazing cycles should be conducted as near to the working temperature of the brazing filler alloys as possible. This problem can be avoided by the use of combined cycles of short brazing steps and subsequent annealing processes below the transition temperature. The brazing cycle should only enable the brazing filler alloy to wet the surface of the base metal and flow into the gap.

The experiments with a brazing temperature of 900 °C and a subsequent diffusion annealing illustrate this. By this method even better results than in the case of brazing at 1300 °C could be obtained in tensile (Fig. 3) and also in bending tests. With the exception of Zr20Fe11.5Al the thermal analysis of the other alloys (Table 1) shows that no liquidus temperatures below the α/β transition temperature of titanium could be found, but it should be noted that the liquidus temperatures of the alloys are below the transition temperatures of many α+β alloys like Ti6Al4V or Ti15Al2.5Fe. The absence of a detectable temperature difference between the liquidus and the solidus temperature shows that the alloys Ti38Zr24Fe, Ti35Zr20Fe and Zr20Fe11.5Al are eutectic or near eutectic.

The metallographic investigation of the nickel-free alloys showed a microstructure similar to that of the Zr-Ni-Ti brazing foil (Fig. 4 and Fig. 8). In the middle a phase with a high iron content was found, which is responsible for brittle behaviour of the joints, especially those brazed at low temperatures and with short brazing cycles. As a consequence of their relatively high iron or iron and manganese contents, the alloy Ti38Zr24Fe or Ti35Zr15Fe15Mn tend to produce broader brittle zones in the middle of the joint, which results in poorer mechanical properties. As in the case of the Zr-Ni-Ti brazing foil, the structure can be changed by heat treatment and subsequent interdiffusion: This could be proved by the joints brazed with the alloy Zr15Fe15Al which, after brazing and annealing, had a tensile strength of 495 MPa and a bending strength of 1275 MPa. These were the highest values in this investigation.

From these results of mechanical testing it can be seen that also brazing filler alloys which do not contain elements like nickel are suitable for brazing titanium, providing mechanical properties similar to those of the ZrNiTi alloys. The fact that the tensile strength of joints brazed with the alloys Ti38Zr24Fe and Ti35Zr15Fe15Mn at 1300 °C was lower (295 and 225 MPa) than that of the Zr-Ni-Ti foil can be attributed to the high content of elements like iron or manganese which can embrittle the joint by forming intermetallic phases in the brazing seam. This lower strength can also be detected after an annealing process (6 h / 800 °C). Therefore it is useful to compose brazing filler alloys with elements which are soluble in the base metal.

The results of the brazings with the alloys Zr15Fe15Al and Ti36Zr23Fe5Al show that, in comparison with results of aluminium-free brazing filler alloys, the addition of aluminium to the brazing filler alloys can increase the tensile strength of the joints. A precipitation hardening process of extremely fine aluminide precipitations (Ti₅Al) which cannot be detected in the SEM investigations, not even in samples which were submitted to a diffusion annealing process, could be possible.

5. SUMMARY

This investigation shows that it is possible to produce brazing filler alloys for brazing titanium or titanium alloys which do not contain the non-biocompatible or even toxic elements usually used, for example, nickel, copper or beryllium. With brazing fillers alloys based on titanium and/or zirconium with contents of iron, manganese and
aluminium together with optimized brazing and annealing cycles, mechanical properties equivalent to those of the alloys most commonly mentioned up until now in the literature could be obtained. In the case of the filler metal Zr20Fe11.5Al the liquidus temperature was below the \( \alpha/\beta \) transition temperature of titanium.

6. REFERENCES