Vacuum Brazing of Zirconium-Based Alloy and 321 Stainless Steel Using Titanium Based Filler Metal

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ABSTRACT

Both Zirconium-based alloys and 321stainless steel are widely used as engineering alloys due to their good mechanical properties. Conventional fusion welding techniques for Zr alloys and stainless steel are not feasible due to the formation of brittle intermetallic compounds such as (Zr_3Fe, $ZrFe_2$ and Zr_2Fe) and corrosion cracking. Brazing is one of the most widely used techniques for joining dissimilar alloys.Using titanium base filler metal decreases the diffusion and the formation of brittle intermetallic compounds. In this study, wetting experiments were done at 820, 850, 865ºC and 3, 5, 7 and 10 min. Also, joining of these two alloys was carried out at 850 and 865ºC for 10 and 15 minutes. Optical microscope, scanning electron microscope (SEM), XRD, shear test and micro-hardness test were used for metallurgical and mechanical investigations. The results show that 20 ºC/min heating and cooling rates at 850ºC and 10 min brazing condition lead to a proper joint without any brittle intermetallic compounds.

1. Introduction

Zirconium base alloys such as Zr-Nb containing 1-2.5 % Niobium, (ZY-4)4-Zircaloy, and (ZY-2)2-Zircaloy are the basic materials used in nuclear reactors. Aqueous and high-temperature corrosion resistance, creep resistance, and low neutron absorption cross-section are the main reasons for their mentioned utilization [1].

Due to their high corrosion resistance, Zirconium and its alloys are also used in manufacturing heat exchangers, surgical instruments, chemical equipments, electrical components, and jewelry. Zirconium production and processing is difficult and costly, so it is mostly used in components inside the reactor core such as fuel rods and spacers. Stainless steels, which are more economical, are used outside the reactor core [2].Joining these two materials is inevitable in manufacturing components of certain reactors such as heavy water reactors and *CANDU*. Given that these two materials are dissimilar and their crystal structure and thermal expansion coefficient are completely different, achieving a proper joining method requires a careful study of the conditions.

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If such physical properties as melting point, thermal expansion and conductivity coefficient of the two materials be very different, joining by fusion welding will be difficult. Even if this problem is solved, when the two materials are incompatible from a metallurgical point of view, the joint may not be proper. Metallurgical incompatibility can lead to the formation of brittle microstructure, both in weld zone and heat affected zone, without sufficient strength [3].The joints created by electric arc welding are brittle, containing crack and having a weak mechanical strength [4]. Spark and resistance welding also failed to create a good joint [5]. Another way to join these two materials is diffusion welding. Phase equilibrium diagrams show that stainless steel main elements form intermetallic and eutectic product compounds with zirconium. Intermetallic compounds are formed as a result of the reaction between iron, chrome and nickel diffused out of stainless steel with zirconium. These intermetallic compounds are naturally brittle, reducing the joint strength [6]. Some researchers have tried to decrease the diffusion of elements using intermediate layer of iron [7], titanium[3], tantalum[6], niobium, nickel, copper[8], and multiple layers [9,10]. They have limited the formation of brittle intermetallic compounds, but diffusion welding cannot still create an intact joint without any crack or brittle in compounds. Brazing by amorphous filler metals is one of the best techniques for joining these two alloys. In this method, components spend less time in the process temperature. This reduces the diffusion within the interface width, and limits the brittle intermetallic compounds formation.The rate of this method makes brazing a normal industrial phenomenon [11]. In this research, Stemet 1228 amorphous titanium based filler metal has been used for brazing Zirconium based alloy and stainless steel.

2. Experimental procedure

Base metals compositions applied in this study are shown in Table 1. Sheet form samples have been sectioned from 321 stainless steel and Zr-Nb2.5 in 4mm× 10mm ×10mm dimensions. They were polished using 1000 grit paper. After cleaning, samples were degreased and acid dipped using a chemical solution. Then 100 μm thickness filler metal were used between the two samples. Base metals and filler metal have been fit with each other by (H13) hot working steel clamp. Composition of the Stemet (1228) filler metal is shown in Table 2. Immediately after acid dipping and horizontally putting it in the keeper, samples were put in a 40mm diameter quartz tube; then its cap was closed and the tube was sealed for ensuring no leakage. The quartz tube was joined to a vacuum system containing rotary and turbo molecular pumps, and its inner pressure reached $<5\times10^{-4}$ Pa. To maintain the provided vacuum atmosphere, vacuum pumps were turned on during brazing. They were continuously discharging the Quartz chamber atmosphere until the samples became cold. After the process fulfillment, argon injection was used for breaking the chamber vacuum atmosphere. *AdamelL'Homargy*, programmable tunnel electric furnace which was able to provide maximum 1200 °C ±5 °C, was used for providing the required thermal energy of joining experiments. According to the wetting experiment results, joining these two base metals was carried out at 850, 865ºC and 10, 15 min.0.1±%1 gram of filler metal's foil was shaped in a quasi-spherical form and placed on the base metal. After cooling in the furnace, samples were sectioned for determining wetting angle, and optical microscope image of each sample's cross section was prepared. *AutoCAD*® software was used to determine the angle value.OLYMPUS-BX51M optical microscope and Tescan SEM (Vega), which was equipped with EDS chemical analysis device, and XRD (STADIMP, Germany), were used for metallurgical examinations. For mechanical examination, shear test and Vickers indenter micro-hardness were done using Struers, Duramin device under the weight of 200gr.
Etching solution used for joint metallographic test is shown in Table 3.

Table 1.Base metals chemical composition.

(wt%)	Ti	Zr	Nb	Fe	C	Mn	Cr	Si	S	P	Ni
Zr-2.5Nb	-	Bal.	2.5	0.01	0.021	-	0.01	0.025	0.45	-	-
321 SS	0.8	-	-	Bal.	0.08	2.0	18.0	1.0	0.3	0.04	9

Table 2. Stemet 1228 braze alloy composition.

(wt%)	Zr	Ti	Ni	Cu	Nb	Be	Melting Range	Brazing Temperature
Stemet 1228	26	46.8	13	14	0.7	0.2	790°C	>830°C

Fig.1. Fixture used for this study.

Table 3. Chemical composition of etchants

Used metals	70% HNO_3	48%HF	H_2O	HCl	$CuCl_2$
321Stainless steel	10 mL	-	-	5 mL	0.1 gr
Zr-2.5Nb	40mL	10mL	45mL	-	-

3. Results and discussion

The wetting diagram of base metals with titanium based filler metal is shown in figure 2. According to this diagram, with increasing temperature or brazing time, wetting angle of both two base metals is reduced, and wetting is expected to be modified. If wetting temperature and time be less than 850ºC and 10min respectively, none of the base metals are to be proper. But, at the time and temperature above 10min and 850ºC, Zr-2.5Nb base metal wetting will be better than 321 stainless steel base metal. In low temperatures, capillarity cannot overcome the surface tension of molten droplet, preventing the molten droplet to flow on the base metal surface. With increasing temperature to and above 850°C, physical and chemical wettings are modified. This leads to the reduction of wetting angle. In those cases where reactivity of the brazing components is relatively high (like the alloys in this research), the dominant wetting mechanism is the chemical wetting. Wetting can be physical or chemical. Physical wetting is a kind of adhesion existing where creating an interface is possible according to the level of energy. So an interface is formed via reversible physical forces such as van der Waals forces, and electrostatic attraction forces. But, in chemical wetting, interface contains proper chemical bonds. Chemical bonds are formed when the electronic structure of the surface atoms is changed in both materials. The electronic structure changes may be caused in two ways. One can be during the transfer or movement of electric charge [12], and the other one is the dissolution of surfaces in each other. These two different mechanisms of chemical wetting are known as the charge transfer wetting and dissolution wetting. In chemical wetting systems, when drop makes an obtuse angle with solid surface, wetting will not be in the system. It is completely reasonable due to the

high contact angle. But when the drop makes an acute angle with the solid surface, because of the reaction between this molten drop and the solid surface, the reaction product is formed exactly in the metal/metal interface. Naturally, the reaction product creates a new interface. This new interface contains intermetallic compounds which are formed in the joint place, forming a layer on the solid surface. Since in this study chemical reaction between filler metals and base metals and also, filler metals diffusion into the base metals are visible in wetting experiments, it can be inferred that there is a chemical wetting in brazing of 321 stainless steel and Zr-2.5Nb via 1228 Stemet filler metal.

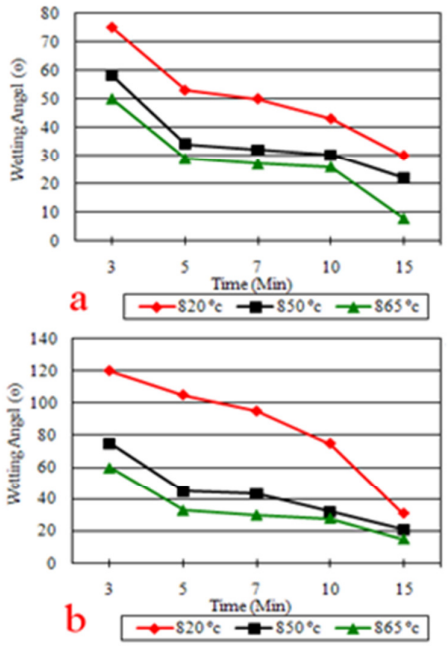
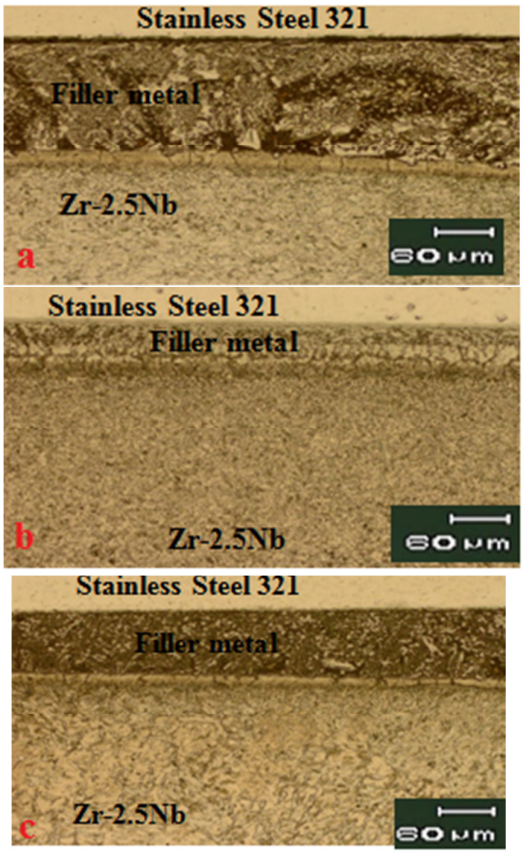


Fig.2. Wetting curve of base metals using Stemet 1228 braze alloy: (a) Zr-2.5Nb,(b) 321 stainless steel.

It should be considered that at a temperature and time less than 850°C and 10min, base metals wetting via 1228 Stemet filler metal isnot proper. Furthermore, regarding the fact that brazing time and temperature make brittle intermetallic compounds, temperatures 850ºC and 865ºC and time duration of 10min and 15min were chosen as the brazing time and temperature.

Optical microscope images of joint sections in different times and temperatures have been displayed in Fig. 3. As can be seen from the images, both base metals have been wetted by the filler metal, and no apparent defects including holes and cracks can be observed with the joint clearance being completely filled. With increasing brazing time and temperature, the joint width is reduced in all images. As the parts are under constant pressure, increasing fluidity of molten filler metal with increasing brazing time and temperature is one of the reasons for the reduction of the joint width. This increased fluidity makes the given pressure reduce the joint width.



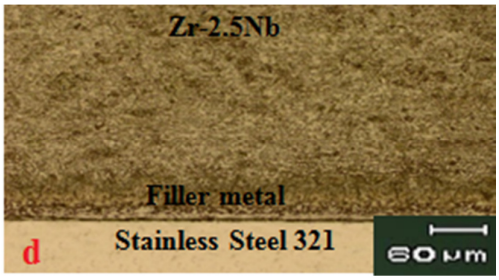


Fig. 3. Optical microscopy image of brazed joint: (a) 850ºC, 10min (b) 850ºC, 15 min (c) 865ºC, 10min,(d) 865ºC, 15min.

Electron microscope images were used for detailed analysis. A SEM image of the brazed sample at 850°C in 10 min is shown in Fig. 4.The main joint band, which is uniform and without any defect, has been shown in area No.1 of Fig. 4. It indicates that the filler metal has been solidified immediately after melting. Brazing time was short enough so that the elements had little opportunity to diffuse from base metals to filler metal and vice versa.

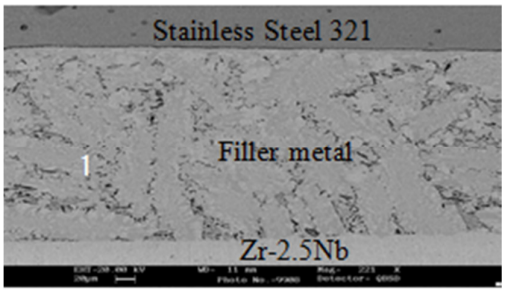


Fig. 4. SEM-BSE image of brazed joint for 850ºC and 10min.

Interface of the samples was analyzed separately (Fig. 5). The EDS analysis results of 1and 2 brazed points are shown in Table 4.

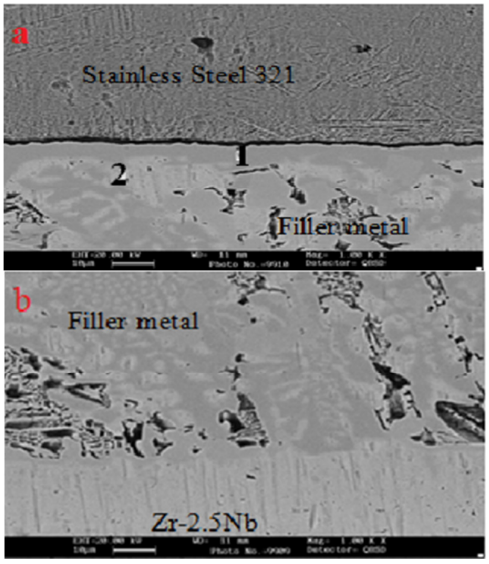


Fig. 5. SEM-BSE image of interface of brazed joint for 850ºC and 10min: (a) stainless steel 321-filler metal Interface (b) Zirconium-filler metal Interface.

Table 4. EDS chemical analysis results of brazed joint for 850ºC and 10min.

wt%	Fe	Ni	Cr	Ti	Cu	Zr
1	7.2	2.3	5.8	20.15	-	Bal.
2	-	-	-	12.51	-	Bal.

In area No.1, (Fig. 5), some iron and chrome were diffused from stainless steel to the joint area. But due to the low percentage of these elements in joint area and the low temperature and brazing time, the probability of brittle intermetallic phases formation is very low, and good properties can be expected from this joint.SEM image of brazed joint at 850ºC and 15 min has been shown in Fig. 6. According to the image, there is not any micro-crack or defect in the interface. EDS analysis has been done for different joint points (Table 5).

The SEM image of brazed joint at 865ºC and 10 min has been shown in Fig. 7. The interfaces of the samples have been separately analyzed (Fig. 8). EDS analysis results are also shown in Table 6. According to the chemical analysis results, the probability of formation of brittle intermetallic compounds such as Zr_3Fe in the point 1 (Fig. 8) is very high.

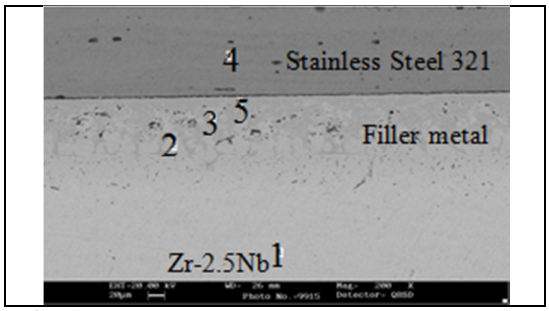


Fig. 6. SEM-BSE image of brazed joint for 850ºC and 15 min.

Table 5. EDS chemical analysis results of brazed joint for 850ºC and 15min.

wt%	Fe	Cr	Ni	Ti	Cu	Zr
1	-	-	-	-	-	100
2	-	-	-	19.12	-	80.88
3	5.85	1.27	10.10	18.75	8.79	55.24
4	72.13	18.30	9.57	-	-	-
5	15.07	3.20	10.17	22.57	6.86	42.13

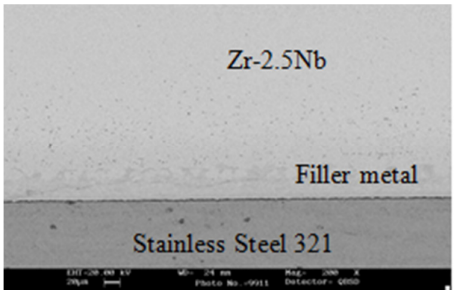


Fig. 7. SEM-BSE image of brazed joint for 865ºC and 10 min.

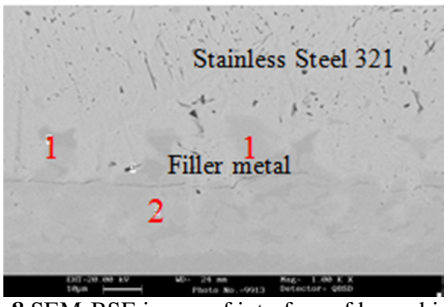


Fig. 8.SEM-BSE image of interface of brazed joint for 865 ºC and 10min.

Table 6. EDS chemical analysis results of brazed joint for 865ºC and 10min.

wt%	Fe	Cr	Ni	Ti	Cu	Zr
1	9.82	1.72	9.14	23.96	8.69	Bal.
2	-	-	-	18.55	-	Bal.

The SEM image of brazed joint at 865°C and 15 minutes has been shown in Fig. 9. As can be seen, there is not any defect in the interface. According to Table 7, due to the high percentage of iron and chrome in points 1, 3, possibility of the formation of brittle intermetallic phases such as $ZrFe_2$ and Zr_3Fe is very high in these points.

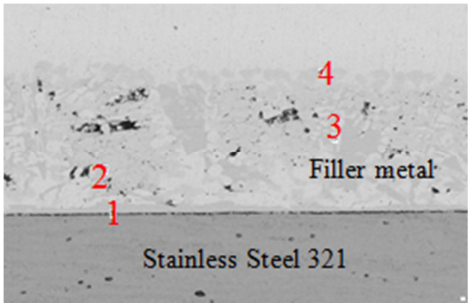


Fig. 9. SEM-BSE image of brazed joint for 865ºC and 15 min.

Table 7. EDS chemical analysis results of brazed joint for 865ºC and 15 min.

wt%	Fe	Cr	Ni	Ti	Cu	Zr
1	47.57	8.60	9.40	7	-	27.38
2	-	-	-	9.48	-	90.52
3	8.56	2.18	37.20	8.15	2.33	41.58
4	-	-	-	9.30	-	90.70

As can be seen from the SEM images, filler metal partly prevented the diffusion. Considering that the main element is the 1228 titanium filler metal, it can be used as a barrier against the diffusion of iron and chrome to zirconium. So the main factor for limiting the diffusion of iron and chrome to the brazed joint or 1228 filler metal is the high percentage of titanium (>45 wt%) in filler metal.

Since beam diameter of X-Ray is almost 1mm, and the width of brazed area is almost 100µm, for a more accurate analysis of the joint's phases, XRD patterns from fracture surface of the shear test samples were taken.

XRD results of joint cross section in different times and temperatures have been shown in Fig.10. Phases consistent with each peak are indicated above it.

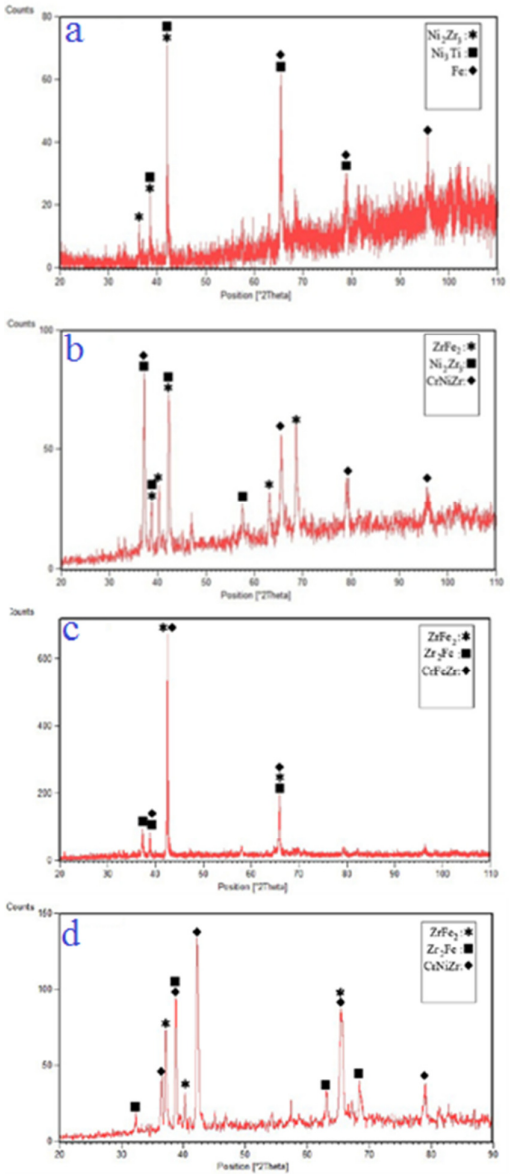


Fig. 10. XRD results. (a) 850ºC, 10min (b) 850ºC, 15 min (c) 865ºC, 10min (d) 865ºC, 15min.

In order to do shear strength test, the samples, as can be seen in Fig. 11, were aligned in the holder in such a way that basic component was tightened from one side to the holder via a bolt, and on the other side, interface and the other basic components were removed from the holder and held with the tensile jaw. In order to reduce the friction between components and to ensure the increased accuracy of the test, lubricant was used in contact areas.

The jaw movement rate which was applied in this test was 0.2 mm/min. The first sharp reduction in force shown by the device was considered to be a crack in interface, while the maximum recorded number was regarded as a required force for fracture. Equation 1 has been used for converting them to shear stress.

$$\delta_s = \frac{F}{A}$$

(Equation 1)

F= required force for disconnecting interface

A= Fracture surface

δ s= shear stress of fracture (MPa)

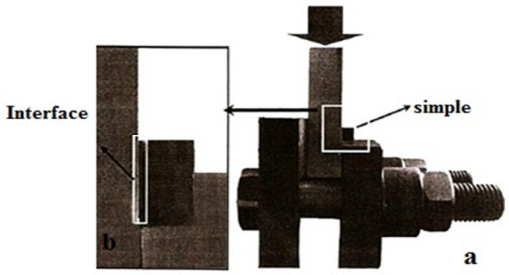


Fig. 11. A view of the alignment of joint holders for shear strength test. As the image "B'' isspecified, the interface and the basic components are removed from the holder.

Shear strength of joints has been shown in Fig. 12. According to the shear strength results, stress in all temperatures and times is higher than half of the joint design strength (50 MPa). Design strength is usually equal to half of the yield strength of the weaker base metal [5]. As can be seen from Fig. 12, with increasing brazing time and temperature, shear strength of joints decreases. This sharp reduction can be due to the fact that high

brazing time and temperature form many brittle intermetallic and reaction compounds which reduce the joints strength.

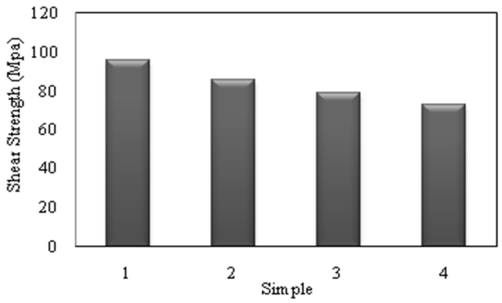
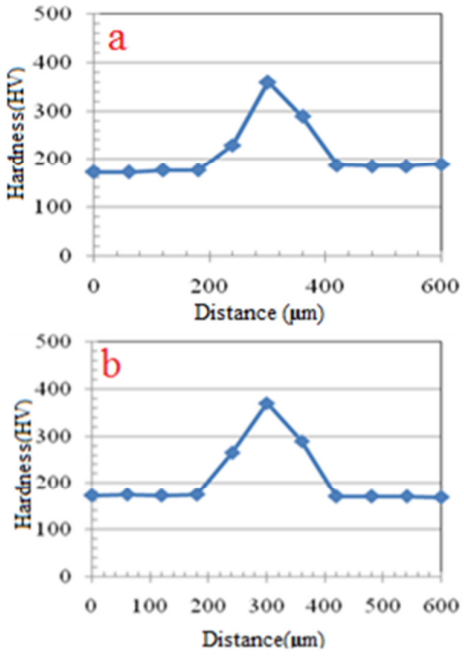


Fig. 12. Shear test results.

The micro-hardness-distance brazed joint diagram in different times and temperatures is shown in Fig. 13.Hardness of applied stainless steel and zirconium alloy in this study is 200 Vickers, respectively. In order to extract the final results, micro-hardness test was done in three different areas of the samples. Their average was reported as the hardness value. Also, the deviation of the obtained data was about ±4HV.



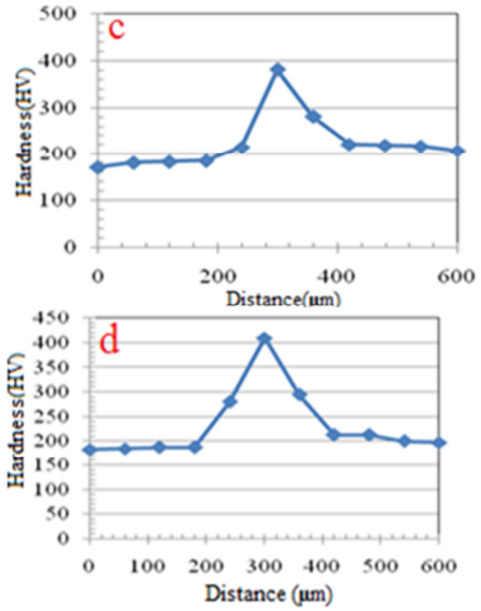


Fig. 13. Micro-hardness results of brazed joint: (a) 850ºC, 10min. (b) 850ºC, 15 min. (c) 865ºC, 10min. (d) 865ºC, 15min.

XRD results showed that some base metals' alloying elements diffuse to the brazed joint. Diffusion of these elements makes some compounds in joint area, increasing the hardness and decreasing the strength. The micro-hardness values shown in the figure confirm the above notes. It is clear that with increasing brazing time and temperature, brazed joint hardness is also increased.

4. Conclusions

A proper joint without any crack is possible for zirconium based dissimilar alloys such as Zr-2.5Nb and 321stainless steel at 850°C and 10 minutes, using titanium based filler metal. Brazing can be a good alternative method which does not have the welding problems in this particular dissimilar joining.

Iron and chrome form brittle intermetallic compounds and make the joint brittle. High temperature brazing makes the conditions similar to the fusion welding, and diffusion of elements forms the brittle intermetallic phases.Using Stemet 1228 titanium based amorphous metals with high flexibility and chrome form brittle intermetallic compounds

and make the joint brittle. High temperature brazing makes the conditions similar to the fusion welding, and diffusion of elements forms the brittle intermetallic phases. Using Stemet 1228 titanium based amorphous metals with high flexibility and 100µm thickness can be a good choice for brazing zirconium alloys and the stainless steel. With increasing brazing time and temperature, formation of intermetallic compounds in joint area is increased and shear strength of joint is decreased.

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