EUROfusion

WPMAT-CPR(18) 21231

M Sanchez et al.

Development of self passivating W/Eurofer brazed joints

Preprint of Paper to be submitted for publication in Proceeding of 30th Symposium on Fusion Technology (SOFT)

This work has been carried out within the framework of the EUROfusion Consortium and has received funding from the Euratom research and training programme 2014-2018 under grant agreement No 633053. The views and opinions expressed herein do not necessarily reflect those of the European Commission.

Development of self passivating W/Eurofer brazed joints

J. de Prado[a], M. Sánchez[a*], A. Calvo[b], C. García-Rosales[b], A. Ureña[a]

[a] *Materials Science and Engineering Area. ESCET. Rey Juan Carlos University, C/Tulipán s/n, 28933 Móstoles, Madrid, Spain*

[b] *Ceit-IK4 Technology Center, Paseo de Manuel Lardizabal 15, E-20018 San Sebastian, Spain*

The present work proposes a brazing procedure to join a self-passivating tungsten alloy (W-10Cr-0.5Y) with Eurofer. The results indicated the achievement of high quality W-Eurofer joints using 80Cu-20Ti filler material. The resulting microstructure of the braze changes considerably compared to the brazing attempts with pure tungsten, which is associated to the reactive character of chromium. A high interaction between molten filler and W base material close to the braze was detected, with preferential grain boundary penetration of Cu-Ti into W alloy. It gave rise to a loss of hardness at the W base material near the joint. Regarding to the strength of the joints, shear strength of ~ 90 MPa was obtained, which ensures not only the operative brazeability but also the metallurgical brazeability.

Keywords: Tungsten alloy, Self-passivating alloy, Plasma-facing materials, Brazing, Eurofer.

1. Introduction

The development of the future DEMO fusion reactor is highly associated to the improvement of the current materials, especially tungsten materials, to withstand the extreme conditions giving inside the reactor vessel during service life. This fact makes necessary a special effort in the fields or areas where the selected materials have weaker properties.

Tungsten is the main candidate material for the first wall for its high melting point, low erosion yield, and low tritium retention [1]. Also, in case of a loss-of-coolant accident in combination with air-ingress into the vacuum vessel would lead to temperatures of the in-vessel components exceeding 1000 ºC, resulting in the formation of volatile and radioactive tungsten oxides. A possible solution for the challenge of oxidation is alloying of W with elements like Cr, which, in presence of oxygen at high temperatures, promote the formation of a self-passivating layer protecting tungsten from further oxidation [2]. These new alloys have to be joined to other materials (i.e. Eurofer) in order to conform the plasma facing components. Therefore, joining technologies need to be implemented to fulfill the requirements of the reactor environment.

The development of W-Eurofer joints has been studied by different authors [3-5] using different techniques such as diffusion bonding, spark plasma sintering, brazing, etc. The use of filler material between both base materials is commonly used in this type of joints to prevent the propagation of cracks coming from the plasma face side of the joint, therefore it is a relevant variable to achieve a quality joint. The aim of this work is join a self passivating W material to Eurofer using a Cu–Ti alloy as filler. The microstructure, the microhardness and the shear strength of brazed joints were characterized.

2. Experimental procedure

2.1 Materials

Eurofer and tungsten alloy were the base materials used in brazing tests. Eurofer was supplied by Karlsruhe Institute of Technology with a standard composition and microstructure [6]. Self passivating tungsten was supplied by CEIT with the following nominal composition: W-10Cr-0.5Y (in wt.%). The alloys were produced by mechanical alloying and subsequent Hot Isostatic Pressing (HIP), starting from elemental powders of pure W (99.95%, 15-30 μm), Cr (99.95%, 74 μm) and Y (99.9%, 20-30 μm). These powders were mechanically alloyed under Ar atmosphere in a planetary ball mill using WC grinding jars and balls. The MA parameters were optimized such as to obtain a homogeneously alloyed powder at the minimum milling time to keep impurities from jars and balls as low as possible. The alloyed powder was introduced in metallic capsules, which were evacuated, degassed, sealed and HIPed at 1250 °C for 2 h at 150 MPa.

80Cu-20Ti fillers were fabricated using pure metallic Cu and Ti powders (*Stream Chemical* 99.9% purity, 100 mesh and *Alfa Aesar* 9.95% purity, −200 mesh, respectively). Both pure powders in the studied proportion were mixed by means of a rotator milling process. To manufacture the fillers, the powders were mixed with an organic binder (powder/binder mass ratio: 95/5) and laminated to obtain flexible tapes of 250 μm width. The binder used was polypropylene carbonate (PPC, QPAC 40) supplied by *Empower Materials* in pellets form.

2.2 Brazing tests

Both base materials were cut with the dimension of 8 × 8 x 4 mm for the brazing tests and their surfaces were ground to grit size P4000 with a silicon carbide paper in order to control the surface roughness. The laminated filler was placed between the two parent materials. Brazing tests were carried out in a high vacuum furnace

author's email: maria.sanchez@urjc.es

at the residual pressure of 10^{-6} mbar. Brazing temperature and dwell times were optimized in previous studies in which successful joints were obtained using brazing temperatures of 50 ºC over the liquidus temperature (960 ºC) holding the temperature for 10 min [7].

2.3 Characterization techniques

The microstructural analysis of the cross section of brazed samples was performed using Scanning Electron Microscopy (*SEM, S3400 Hitachi*) equipped with energy dispersive X-ray spectroscopy (EDS) and stereoscopic microscope (Leica/S6P). The samples were metallographically prepared following the standard polishing technique.

The mechanical properties of the joints were evaluated by means of microhardness and shear tests. The hardness study gives information about the effect of the brazing process on the mechanical properties of the base materials. Thus, microhardness profile was made across the joint with a *MHV-2SHIMADZU* equipment. A 100 g load was applied during 15 s and three measurements were obtained for each position. Distances between neighbour indentations were longer than three times the residual imprint sizes. Shear strength values were obtained using a shear fixture that was placed between compress platens in a Universal Testing Machine (*Zwick Z100)* at a speed of 1 mm/min. Three samples were tested in order to ensure accuracy.

3. Results

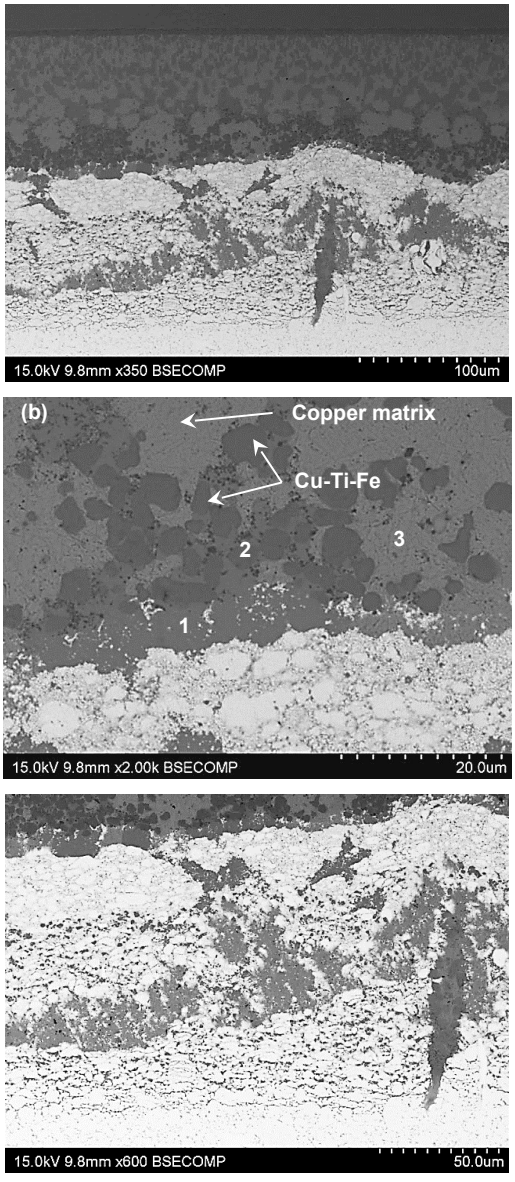
3.1 Microstructural characterization of the brazed joints

Self-passivating tungsten-Eurofer brazed joint showed high metallic continuity along both interfaces reaching 100 % of metallic contact (Fig. 1a). The exiting literature regarding pure tungsten-Eurofer joints bonded by means of brazing or diffusion bonding techniques have shown the low chemical interaction and diffusion phenomenon between pure tungsten and the braze [8,9]. This fact is associated to the high chemical stability of tungsten in vacuum atmosphere and the high melting point of tungsten that limits the diffusion phenomena below the temperature range of 1200-1400 ºC. However, the microstructure of the self passivating alloy after HIP consisted of two main phases identified as a W-rich phase with Cr in solution (αW,Cr) a Cr-rich phase with W in solution ((αCr,W), discontinuous phase), being the average grain size of the matrix in the order of 100 nm.

Besides, a dispersion of Y_2O_3 nanoparticles of about 15 nm size was formed mainly at the grain boundaries [2].

The Cr-rich phase (αCr,W) favoured a high interaction between tungsten and the molten filler during brazing cycle as it is described below.

The analysis of the microstructure from the top to the bottom showed two different zones of interaction (Fig. 1). The top half of the joint (Eurofer-braze interface) is characterized by a microstructure similar to that found when Eurofer is brazed to pure tungsten using 80Cu-20Ti as filler material [7]. TiC precipitated at the Eurofer grain boundary close to the braze up to a distance of 11 μm from the interface. A layer of alloying elements was observed at the interface due to diffusion phenomena from the steel to the filler during the brazing cycle.



author's email: maria.sanchez@urjc.es

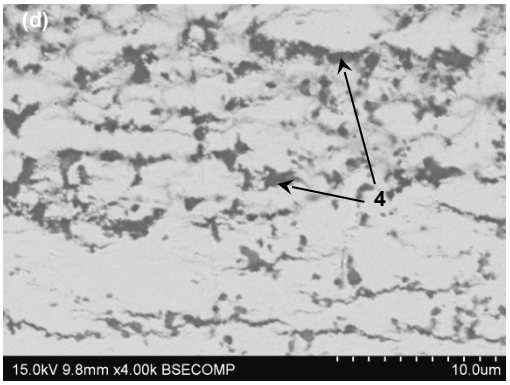


Fig 1: SEM micrographs of the W-10Cr0.5Y / Eurofer brazed joint. (a) General view of the joint and (b, c and d) Detail of braze/W alloy base material interaction zone at different magnifications.

Just below, a Fe-Ti rich phase with a massive precipitation of TiC is formed. Next, in the braze, it was observed that the presence of TiC and Cu, Ti and Fe phases with an increment in Cu content as getting into the joint.

Close to the joint, the microstructure of the braze was formed by a copper matrix with Cu_4Ti acicular compounds and Cu-Ti-Fe ternary compounds (51.7Cu, 36.7Ti, 11.6Fe in at. %) identified by EDS microanalysis, as it is indicated in Fig. 1b. As it approaches to the half of the joint, the microstructure changed drastically as a consequence of a dilution process between the molten filler and the self-passivating tungsten base material. Phase 1 (43Ti - 39Cu -10Fe - 5Cr - 3W in at. %) and phase 2 (53Ti - 22Fe - 14Cr - 8Cu - 3W in at. %), located at the interaction front, contained certain quantity of tungsten and chromium in their composition as it was it was seen by EDS microanalysis. A copper matrix and Cu_4Ti acicular compounds without interaction with the base material formed region 3.

Fig. 1c, showed that a considerably quantity of 80Cu-20Ti braze that penetrated into the tungsten alloy through the grain boundary of the base material. The EDS microanalysis of the dark phase 4 (39Cr-31Ti-20Fe-6W-4Cu in at.%) showed the presence of Cu, Ti and Fe in the Cr-rich phase of W alloy (Fig. 1d). It means that Cr promoted the interaction with the molten filler and this phenomenon could be associated to the reaction between Cr-rich phase of the base material and Ti coming from the filler forming a phase with a low melting point that favoured the penetration of the molten filler through the grain boundary of the base material.

3.2. Mechanical characterization of brazed joints

The microhardness profile showed in Fig. 2 gives information about possible recrystallization process, diffusion phenomenon or phase transformation along the self passivating W alloy/Eurofer joint during the brazing process. The mean microhardness value of the Eurofer is around 350 HV0.1 but close to the braze hardness dropped down to 120 HV0.1. This softening was associated to the loss of steel alloying elements, mainly C, at the interface proximity. Besides, the grain coarsening of the steel contributed to the softening of this region [9]. The microhardness of the braze was around 210 HV0.1 with a high error bar due to the variety of the phases formed.

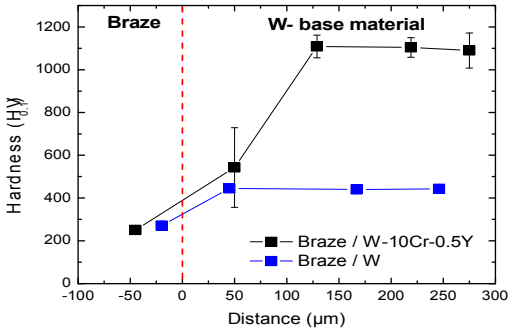


Fig 2: Microhardness profiles across the joint.

The microhardness of the self-passivating base material close to the joint was around 500 $HV_{0.1}$ and increased up to 1100 $HV_{0.1}$ from a distances of 100 μm from the braze/W interface. It indicated that the self-passivating base material far from the joint was not affected by the brazing process because the microhardness was similar to the as received value (1153 ± 83 HV0.1). However, the drop of HV close to the joint associated to the penetration of Cu-Ti filler through the grain boundary.

An increase of the microhardness of W alloy base material was observed in comparison to the microhardness of the pure W (~ 450 $HV_{0.1}$) in W/Eurofer joints. The considerable increase of the base material microhardness was associated to the refined microstructure of the self passivating alloy with a grain size around 100 nm [2].

The strength of the joint measured by shear mode was 89 ± 28 MPa, which is lower than that of the joints brazed using pure tungsten instead self-passivating one that reported 130 MPa. The difference was associated to the extensively reaction observed between the base material and the filler and the change in the fracture mechanism as it can be observed in Figure 3. However, the result indicated still high degree of adhesion properties achieve by the joint. Fracture followed a brittle mechanism giving rise to sharp surfaces as it can be seen in the fracture surface of Eurofer base material (Figure 3a).

author's email: maria.sanchez@urjc.es

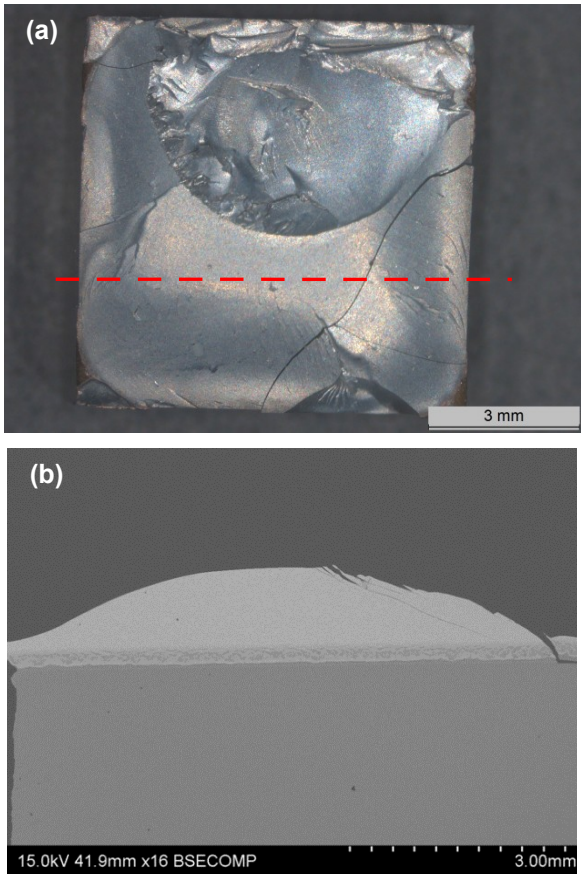


Fig 3: a) Stereoscopic image of the Eurofer fracture surface. b) Image of the fracture cross section following the dashed line.

The cross section analysis revealed that the propagation of the crack took place mainly inside the tungsten base material. The nucleation started at the braze itself and it progressed towards the interior of the tungsten base material to then return to approach the interface following a fracture mechanism typical of materials that present a high degree of residual stresses (Figure 3b).

4. Conclusions

Self passivating tungsten alloy and Eurofer were successfully joined using high vacuum brazing technique and 80Cu-20Ti filler material.

The microstructure of the braze was influenced by the chromium alloying element of the tungsten base material that favored the penetration of the molten filler through the grain boundary of base material.

The microhardness of the self passivating alloy far from the braze was not affected by the brazing process. The drop of microhardness measured close the braze was associated to the penetration of 80Cu-20Ti through the grain boundary.

Shear strength ~ 90 MPa ensured not only the operative brazeability but also the metallurgical brazeability..

Acknowledgments

This work has been carried out within the framework of the EUROfusion Consortium and has received funding from the Euratom research and training programme 2014-2018 under grant agreement No 633053. The views and opinions expressed herein do not necessarily reflect those of the European Commission. The authors would like to acknowledge to MULTIMAT-CHALLENGE program (S2013/MIT-2862).

References

[1] H. Bolt, V. Barabash, G. Federici, et al., Plasma facing and high heat flux materials – needs for ITER and beyond. J. Nucl. Mater. 307-311 (2002) 43-52.

[2] A. Calvo, K. Schlueter, E. Tejado, et al., Self-passivating tungsten alloys of the system W-Cr-Y for high temperature applications. Int. J. Refract. Met. Hard Mater. 73 (2018) 29-37.

[3] J. Aktaa, W.W. Basuki, T. Weber, et al., Manufacturing and joining technologies for helium cooled divertors. Fusion Eng. Des. 89(7–8) (2014) 913-920.

[4] P. Norajitra, R. Giniyatulin, T. Hirai, et al., Current status of He-cooled divertor development for DEMO. Fusion Eng. Des. 84(7–11) (2009) 1429-1433.

[5] W.W. Basuki, J. Aktaa, Diffusion bonding between W and EUROFER97 using V interlayer. J. Nucl. Mater. 429(1–3) (2012) 335-340.

[6] P. Fernández, A.M. Lancha, J. Lapeña, M. Hernández-Mayoral, Metallurgical characterization of the reduced activation ferritic/martensitic steel Eurofer'97 on as-received condition. Fusion Eng. Des. 58–59 (2001) 787-792.

[7] J. de Prado, M. Sánchez, A. Ureña, Development of brazing process for W–EUROFER joints using Cu-based fillers, Phys. Scr. T167 (2016) 014022.

[8] W.W. Basuki, J. Aktaa, Investigation of tungsten/EUROFER97 diffusion bonding using Nb interlayer. Fusion Eng. Des. 86(9–11) (2011) 2585-2588.

[9] J. de Prado, M. Sánchez, A. Ureña, Wettability study of a Cu-Ti alloy on tungsten and EUROFER substrates for brazing components of DEMO fusion reactor. Mater. Des.99 (2016) 93-101.

author's email: maria.sanchez@urjc.es