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S/TEM examination and nanomechanical response of W-Eurofer joints brazed with Cu interlayers

I. Izaguirre [a,*], M. Roldán [b], J. de Prado [a], V. Bonache [a], M. Sánchez [a], A. Ureña [a]

[a] *Materials Science and Engineering Area, ESCET, Rey Juan Carlos University, C/Tulipán s/n, 28933 Móstoles, Madrid, Spain*
[b] *Division of Fusion Technologies, National Fusion Laboratory, CIEMAT, Avenida Complutense, 40, Madrid, Spain*

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ABSTRACT

In this article, a preliminary microscale study of a brazed joint of two materials that will conform the future fusion reactors is carried out. Tungsten will act as plasma-facing material attached to a structure made of some reduced activation ferritic-martensitic steel (Eurofer-like steel). The proposed brazing process introduces copper as filler material and develops the thermal process in a high vacuum atmosphere at 1135 °C for 10 min. The resultant microstructure is characterised by forming a diffusion layer in contact with tungsten base material constituted by W, Fe and Cr. In addition, an iron-rich phase is formed between the diffusion layer and Cu braze region. This steel band presented two different structures: a typical martensite lath structure and another without it. At the centre of the steel band, the laths are replaced by a more homogeneous matrix where copper precipitates nucleated due to its enrichment in this element during the brazing process. It is worth highlighting the presence of dislocations and residual stresses in all the different phases that appear associated with the brazing process. This presence of dislocation stresses shows how the nanomechanical analysis increases the modulus and hardness values of the steel band concerning the Eurofer base material. The diffusion layer presents the highest values in the mechanical characterisation due to its morphology and the components that constite the phase.

Introduction

The construction of a European demonstration fusion power plant (DEMO) will require developing and qualification of a wide range of high-performance materials. Within this European strategy to develop fusion energy, new joining technologies capable of withstanding these critical conditions inside the reactor have particular importance [1]. Those technologies need to address several problematic issues associated with the extreme conditions of the nuclear fusion environment and the use of critical materials such as tungsten, that it will provide high sputtering and temperature resistance due to its adequate thermo-physical properties, along with Eurofer97, as selected structural steel material [2] to form the so-called first-wall of the future machine.

Many authors have studied W-Eurofer joints with various fillers and manufacturing processes [3–5]. Within those technologies, brazing allows to join the components using lower temperatures in comparision with fusion welding techniques [6] or shorter times concerning solid-state ones [7]; therefore, it has high applicability for industrial production. Besides, it allows performing post-weld heat treatment in the whole component inside the furnace. Using a Cu filler for its application in the first wall joints of the fusion reactor, ensure, according to the macroscopic charcterizationn, the consequtión of high continuity joints with high strength, which supposed a potential solution for this component [8–11]. This paper aims to perform an initial but necessary study of the interface W-Eurofer in a micro/nano-characterisation with S/TEM and nanoindentation. Both techniques allow us to evaluate the mechanical properties of the phases that constitute the whole joint, including the softening effect of particular phases, grain and phase distribution, showing the dilution process after applying the brazing treatment.

Experimental details

Materials

The base materials used for the bonding were: i) tungsten (>99.97%, Plansee); and ii) a reduced activation ferritic/martensitic steel (Eurofer) with a chemical composition in wt.% of 0.11C, 8.90Cr, 0.42Mn, 0.19 V, 1.10 W, 0.14Ta balanced Fe [12,13]. The sizes of the base materials, tungsten and Eurofer, were blocks of 6 × 6 × 4 mm. The intermediate

* Corresponding author.
E-mail address: ignacio.izaguirre@urjc.es (I. Izaguirre).

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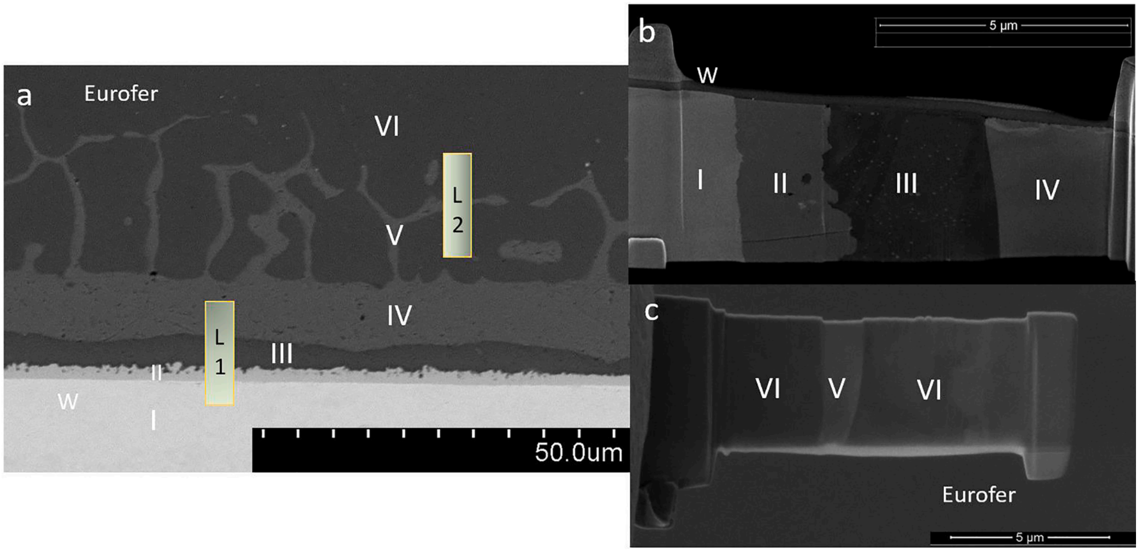

Fig. 1. a) SEM micrograph of the W-EUROFER brazed joint using copper as filler material where the exact location of extraction area of both lamellae is marked as lamella 1 and 2, b) overview micrograph showing the different phases of lamella 1 (L1) and c) lamella 2 (L2).

material used as filler was pure Cu (>99.9%) supplied by Lucas Milhaupt in strip form of 50 μm thick. The strip was cut with the exposed base material surface dimensions and placed between both specimens.

Brazing process

A high vacuum furnace (Nabertherm P330) was used for the brazing tests at a residual pressure of 10^{-6} mbar. Before the brazing tests, exposed surfaces of both base materials were ground down with 4000 grit silicon carbide paper. Brazing conditions were chosen according to previous studies carried out by the group where temperature, dwell times, and filler thickness were optimised [14]. Brazing was performed by applying only one cycle in a high vacuum furnace at 1135 °C, dwell times were 10 min at the brazing temperature, and heating and cooling rates were 5 °C/min. The only load applied is that of the Eurofer base material placed on top, which is 10 N approximately.

Characterisation techniques

Two FIB lamellae containing the whole W-Eurofer brazed joint were extracted using the conventional lift-out technique, allowing us to study the microstructure. The samples were characterised by a field-emission STEM (scanning transmission electron microscopy, JEOL300F) equipped with an Energy-dispersive X-ray Spectroscopy (EDS) detector.

The mechanical properties were evaluated by nanoindentation technique using a pyramidal Berkovich tip using a Continuous Stiffness Measurement control (CSM), which calculates the hardness and elastic modulus during the loading up to a penetration depth of 150 nm, using 5 nm harmonic oscillation amplitude. The results of each indentation are continuous values of H and E as a function of penetration. In addition, average nanohardness values and young modulus from 100 to 120 nm have been considered. To study all the phases that constituted the braze, several indentation lines crossed both interfaces with a low angle concerning the interface were carried out.

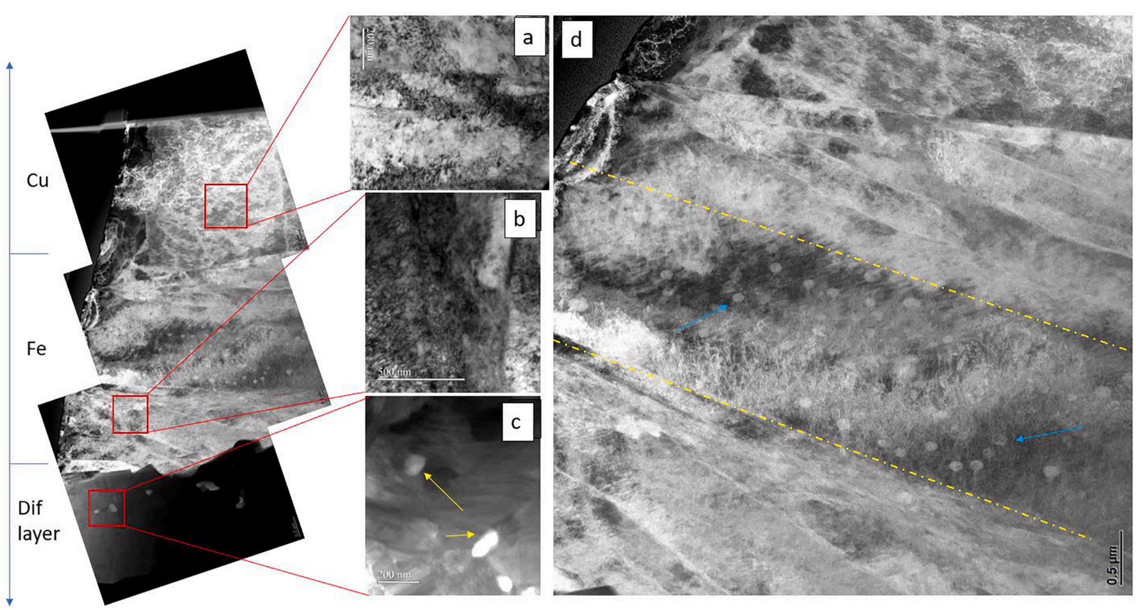

Fig. 2. Lamella 1 reconstruction using S/TEM with detailed micrographs of the different regions. Notice that the main composition and figures a, b and c with TEM mode and d were obtained with STEM mode.

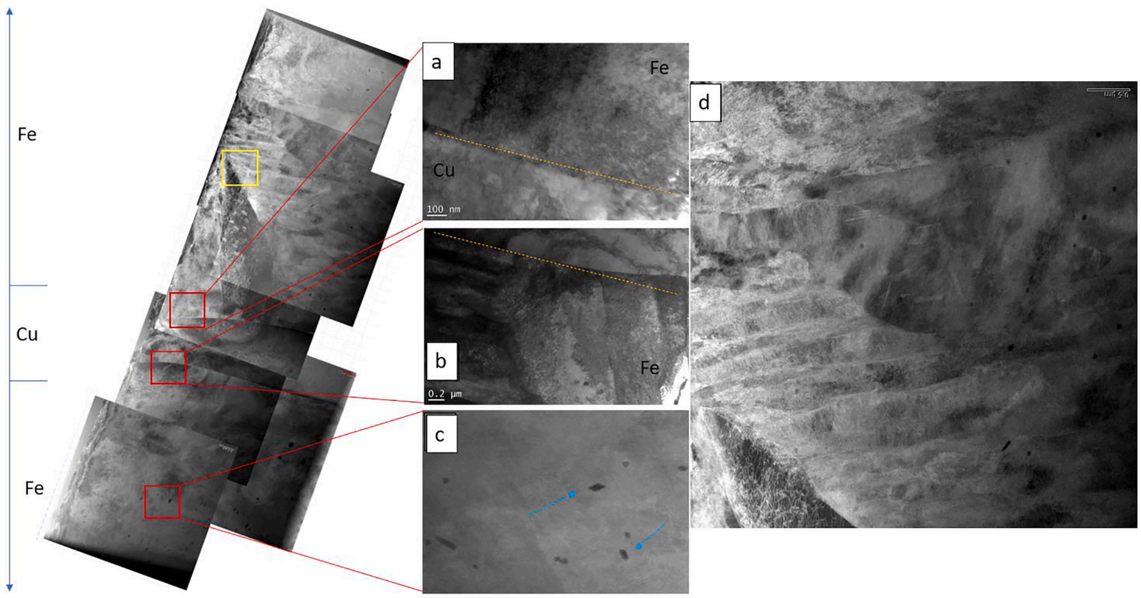

Fig. 3. Reconstruction of the second lamellae using STEM. a), b), and c) details of TEM characterisation of the different regions analysed and d) high magnification image of the Fe region marked in the yellow box where copper penetrates through the Eurofer grain boundary. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Results

Microstructural characterisation

The general inspection of the W-Eurofer brazed joint shows how the brazing process gave rise to the formation of different phases associated with their interaction. The overall microstructure of the joint shown in Fig. 1 is formed by the tungsten base material (phase number I) in contact with a diffusion layer at the braze interface of approximately 2 µm (phase number II). Above this layer, the formation of oversaturated steel band in contact with W of approximately 4–5 µm has been reported, followed (phase number III) by a copper band formed by the residual copper filler (phase number IV). Finally, during the brazing process, copper melts, penetrates and incorporates into the steel following the austenite grain boundaries (phase number V), giving rise to copper paths penetrating in the nearest Eurofer base material (phase number VI) in contact with the copper band.

The study of the first lamella, reconstructed with STEM images in Fig. 2, showed the formation of the W-Fe-Cr diffusion layer in contact with tungsten base material, showing a distorted microstructure constituted by needle-like grains as observed in Fig. 2c), which nucleated following the diffusion direction because of the solid-state diffusion nature, where the majority elements of the brazing system interdiffuses. In addition, precipitates have been detected inside this layer with composition 53W25Fe20Cu2Cr wt% according to the EDS analysis carried out. Some precipitates have been highlighted with yellow arrows in Fig. 2c.

The formation of a steel band above this layer contrast with the initial configuration of the brazing system, where copper is situated between tungsten and Eurofer. This formation is attributed to the Cu dissolution of Fe, which solidified in contact with W forming the steel band (with Eurofer-like composition plus Cu). The S/TEM examination of this steel band has reported the presence of a former martensitic lath microstructure typical of this steel, but also the formation of an intermediate zone where the presence of the martensitic laths was not observed. The mentioned microstructure distribution is shown in Fig. 2d). Both two yellow dashed lines in Fig. 2 indicated the region with no lath, which is characterised by the presence of Cu-rich precipitates with composition 60Fe34Cu6Cr wt. % (blue arrows in Fig. 2d). Then, at both sides of this region so-called martensitic lath steel bands formed during the cooling stage of the brazing cycle where the copper solubility in iron decreases. Besides, the concentration of copper in the steel band increases due to the higher solubility of copper in iron at the high temperatures of the cycle, giving rise to this high density of precipitates during the cooling stage, where the solubility decreases. Therefore, the increase of copper concentration in the steel band could affect the evolution of the microstructure and the formation of this intermediate zone in the band. In addition, the most significant distribution density of Cu-rich precipitates within the steel band was detected within the no-lath steel band microstructure, which may indicate a possible effect of trapping Cu atoms along subgrain boundaries or dislocations.

In general, this steel band is characterised by the presence of a high dislocation density, as shown in Fig. 2b, generated by the strain produced during the cooling stage, as a consequence of the mismatch in the thermal expansion coefficient between Eurofer and tungsten and contrast with the typical microstructure of the Eurofer97 in as-received conditions [15]. Besides, Eurofer base material needs a tempering treatment to relieve the residual stress, reduce the dislocation density and enhance precipitation.

Finally, the study of the copper band shows a sizeable single copper crystal constituted by sub-grain structures that maintain the crystal orientation, as can be identified in Fig. 2a, where the Cu band was oriented close to a specific zone axis, most of the band presents a dark grey colour due to the orientation contrast. The mentioned sub-grain boundaries were nucleated by a dislocation arrangement that created a low-angle grain boundary. However, a very high dislocation density is found in both Cu and Fe-rich bands (Fig. 2 a and b).

The second lamella was extracted in the Eurofer-Cu interface. The incorporation of the copper filler characterises this area of the brazed joint through the PAG (Prior Austenitic Grain boundary) during the brazing process. The steel band, which is closer to the Cu band, is characterised by the presence of several precipitates (some marked with blue arrows in Fig. 3c), possibly MX, coming from carbides forming elements presented in the Eurofer base material, which could grow due to the high temperatures reached during the brazing. Above this region, copper diffused to the Eurofer grain boundaries. It seems that it has penetrated following the austenitic grain boundaries during the brazing cycle (the region between yellow dashed lines in Fig. 3 a and b). Those

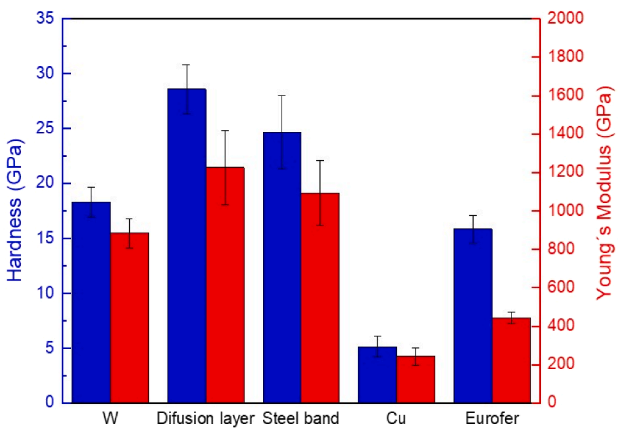

Fig. 4. Hardness and Young modulus of the phases at the Euofer-braze interface.

regions of the steel are less affected by the braze zone since it is less influenced by the braze area. Furthermore, it can be observed the typical microstructure of the Eurofer steel formed by martensitic laths, although there are others with no well-defined lath microstructure (Fig. 3d). In addition, within these no lath structure bands, generally speaking, the amount of secondary phases is higher than those that maintain Eurofer -like precipitates. With no regard to the phase, all of them showed high dislocation density because of the residual stress generated by the brazing process.

Mechanical characterisation

Regarding the nanomechanical characterisation, it should be noted that continuing with what was explained in the microstructural characterisation, the brazing process induced the formation of a high dislocation density both in the Eurofer and braze material. As a result, the nanohardness of the different phases that constituted the braze joint (Fig. 4) diffusion layer and the steel band show the highest hardness in the joint. The complex composition of the diffusion layer, where the incorporation of W, Fe and Cr by solid-state diffusion mechanism produced a high strain lattice richer in W and the intermetallic nature of this phase, gave rise to high hardness and stiffness with 62W23Fe11Cu3Cr composition. Regarding the steel band, the high dislocation density showed in the S/TEM characterisation and the copper precipitates that distorted the network gave rise to the increase of the hardness with respect to Eurofer base material. Accordingly, copper as soft material showed the lower studied mechanical properties but an increased with respect to the as received properties was detected (3,51 GPa and 154 GPa hardness and young's modulus, respectively). These results agree with the microstrcutural studied where the presence of a high dislocation density in copper was detected. On the other hand, tungsten maintains its properties after brazing (17 GPa and 900 GPa hardness and young's modulus, respectively), keeping the values upper than Eurofer base material, and copper presents the lowest hardness of all phases of the joint.

Fig. 5 shows the hardness and stiffness profile of the braze area. This figure shows two dotted lines that are the lines in which the indentations have been done. It crossed both interfaces with a small angle with regard to the interface to ensure that all phases are covered. According to the results presented in the figure, the area where the diffusion phase and steel band is located at the interface has the highest hardness, and it can be assumed a low toughness area that, during the application of stress, cracks could propagate following this zone.

Regarding the copper/Eurofer zone, one of the objectives of selecting copper as the filler material is its capacity to relieve the residual stress through plastic deformation mechanisms generated during the cooling stage of the brazing process. Therefore, the generation of high-stress zones in brittles phases that could affect the mechanical integrity of the joint is reduced. This area is dominated by the intercalation of copper and Eurofer phases, generating peaks and valleys in the hardness profile.

Conclusion

Applying the brazing technique to joint W to Eurofer using copper filler material gave rise to the formation of several phases that might be characterised to understand the mechanical and service behaviour of the joint.

The TEM/STEM examination showed that the copper phase and the steel band generated are highly distorted and dislocated. A deeper examination of this steel band has reported a martensitic laths microstructure typical of this steel and the formation of an intermediate zone, where the presence of the martensitic laths is not observed, and copper-rich precipitates characterises it.

The examination of the Eurofer material close to the copper band revealed the presence of precipitates possibly formed by carbides of carbide forming elements. Still, the region, as the distance increases from the braze zone, presents, a more martensitic like microstructure is typical of this steel.

The mechanical characterisation showed an increase of hardness associated with a high dislocation density and, therefore, a decrease in the toughness is expected.

Tungsten is not mechanically affected by the brazing process keeping the values similar to in as-received conditions.

Due to the diffusion processes that have occurred, the tungsten interface is the area with the highest hardness, and it could lead to an easy propagation of a crack during the fracture of the joint. Therefore, future efforts should be focused to avoid the formation of the diffusion layer and the steel band, which have shown the highest hardness of all phases.

CRediT authorship contribution statement

I. Izaguirre: Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Visualization. **M. Roldán:** Methodology, Validation, Formal analysis, Investigation, Data curation,

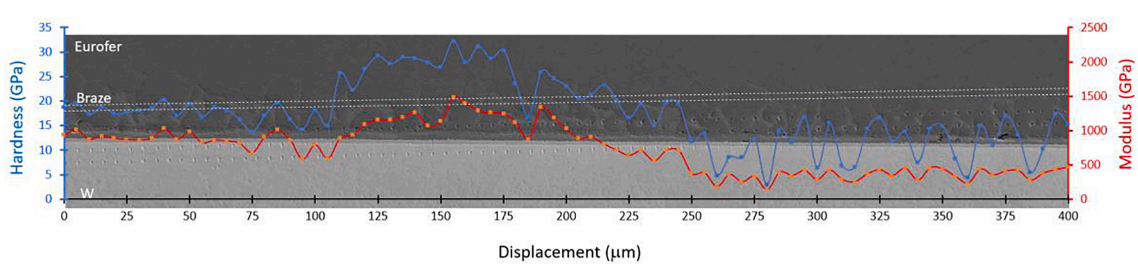

Fig. 5. Hardness (blue) and modulus (red) profiles of the phases that constitute the brazed joint. The dotted white line refers to the matrix indentation used to get the values. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Writing – original draft, Visualization. **J. de Prado:** Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Visualization. **V. Bonache:** Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Visualization. **M. Sánchez:** Conceptualization, Formal analysis, Investigation, Resources, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition. **A. Ureña:** Conceptualization, Formal analysis, Investigation, Resources, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Ignacio Izaguirre reports financial support was provided by Rey Juan Carlos University.

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