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Cleaning surface treatments for the fabrication of ITER First Wall panels by HIP

P.-E. Frayssines [a,*], P. Bucci [a], E. De Vito [a], E. Rigal [a], P. Lorenzetto [b]

[a] DRT/LITEN/DTH/LTH, CEA – Grenoble, 17 Rue des Martyrs, F-38054 Grenoble cedex 9, France
[b] EFDA, Close Support Unit, 85748 Garching, Germany

ABSTRACT

This paper presents our investigations to find an industrial route to clean copper alloy and stainless steel in order to manufacture high-strength joints for ITER Primary First Wall panels. Products investigated are chemical liquids, and a more advanced technique that uses a plasma process is also investigated. HIP joints have been tested by performing impact toughness and tensile tests. Surface cleanliness has been assessed thanks to XPS measurements.

1. Introduction

The Primary First Wall (PFW) panels are one of the main components of the ITER. They are made with two bi-metallic structures. The first structure is an assembly of 316LN stainless steel and CuCrZr alloy that acts as a heat sink. The CuCrZr part is divided into two plates that imbed stainless steel cooling tubes. Thus, both CuCrZr/316LN and CuCrZr/CuCrZr joints are present. The second bi-metallic structure is obtained by welding beryllium tiles onto the CuCrZr/316LN support. In both the cases, the fabrication of the bi-metallic structures is done by diffusion welding (two different temperatures are used).

Mechanical properties of the joints are highly affected by the cleanliness of the materials. Pollution layers on the metallic surfaces may block the diffusion process, and result in interfacial inclusions and drastically reduce the joint mechanical strength. Laboratory processes developed up to now on small-scale mock-ups give satisfactory results, and 316LN/CuCrZr joints prepared with our own cleaning route have successfully passed the fatigue tests under ITER relevant operating conditions. However, the fabrication of the ITER will need the manufacture of numerous large parts, and it is absolutely necessary to evaluate industrial cleaning processes to insure the industrial relevancy of PFW fabrication.

The main objective of this paper is to present our investigations to find industrial cleaning processes as well as perform our own cleaning route. CuCrZr/CuCrZr and CuCrZr/316LN joints have been considered (Tables 1 and 2). Two ways have been studied: the use of selected industrial chemical liquids and the use of a low pressure plasma. The efficiency of the cleaning treatments has been studied by performing joint mechanical testing and by making XPS analyses to measure the residual carbon and oxygen concentrations on the metallic surfaces. Impact toughness and tensile results are compared to those obtained with our reference joints.

2. Industrial chemical liquid cleaning

Two industrial companies specialized in metal cleaning have been contacted. Both the companies use solvent or detergent liquids to first degrease the metallic pieces. Then, slight or strong acid liquids are used to etch the surface of the alloys. In the case of CuCrZr, slight acid liquid does not allow to totally remove the finger marks that come from their handling. This shows that slight acid liquid has a cleaning action which is limited to the extreme surface of the metal. The use of a strong acid liquid enables to totally remove the finger marks, but it significantly modifies the mean roughness of the copper alloy. So, the strong acid liquid should be used under high control to stop the etching process when the final marks on the metallic surface disappear. In the case of stainless steel, the pollution on the metallic surface is less visible and the process efficiency depends largely on the Chemical society know-how. To create a thin and a strong protective oxide layer on 316LN surfaces after the etching process, the pieces can be passivated.

3. Plasma cleaning treatment

To avoid the hazards of the chemical products and their reprocessing difficulties, we have tested the use of a plasma treatment [1]. It was divided into two steps. During the first step, metallic materials are degreased with the help of an oxygen plasma. The high oxidizing potential of this plasma enables to efficiently remove most of the organic pollution such as greases. However, this treatment favours the growth of an oxide layer. The best working parameters have to be found in order to obtain a very low carbon concentration without a thick oxide layer. The second step uses a hydrogen plasma to reduce the oxide layer.

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* Corresponding author.
E-mail address: pierre-eric.frayssines@cea.fr (P.-E. Frayssines).

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Table 1
Chemical composition of CuCrZr alloy.

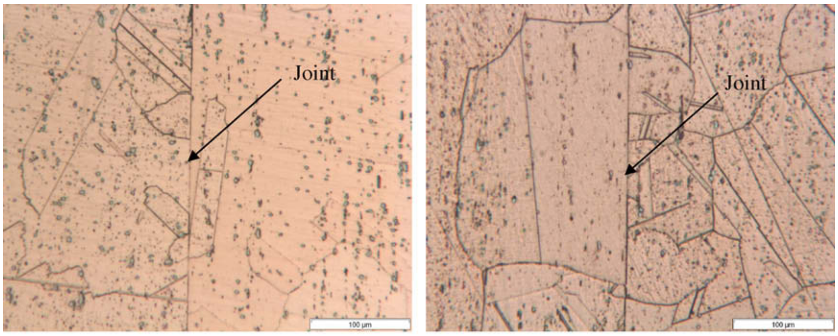
wt%	Cu	Cr	Zr
CuCrZr	98.97	0.84	0.14

4. Mock-ups fabrication

Several joints have been made with CuCrZr and 316LN materials cleaned with chemical liquids or with plasma. CuCrZr/316LN and CuCrZr/CuCrZr joints have been made at 1040 °C under 140 MPa

Table 2
Chemical composition of 316L(N) stainless steel used in this study.

wt%	C	Ni	Cr	Mo	S	P	Si	Mn	N2
ITER	<0.03	12–12.5	17–18	2.3–2.7	<0.025	<0.035	<0.5	1.6–2	0.06–0.08
T6974	0.027	12.210	17.530	2.455	0.001	0.024	0.305	1.845	0.069



Solvent or detergent chemical liquid cleaning Plasma cleaning

Fig. 1. Micrographs of CuCrZr joints achieved with pieces cleaned with chemical liquids and plasma (etching with ammonia and hydrogen peroxide).

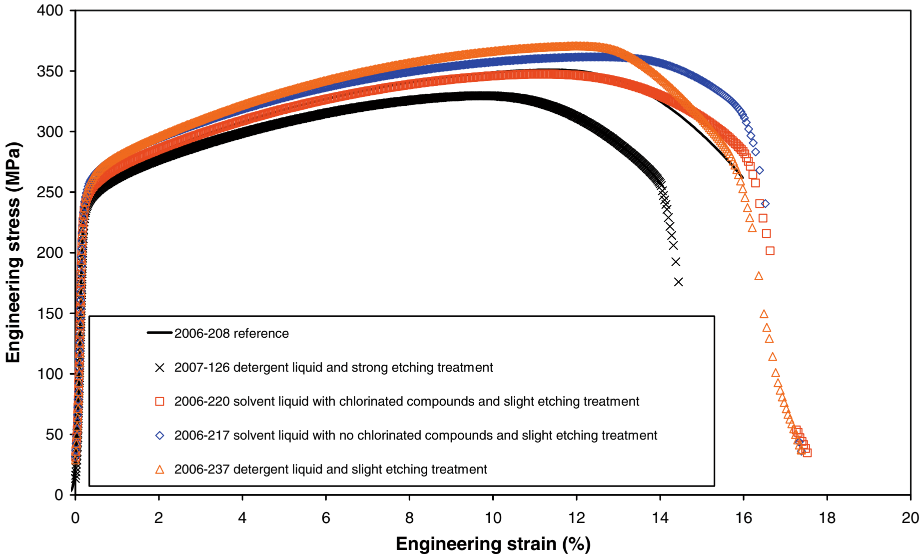


Fig. 2. Tensile behaviour of CuCrZr joints (room temperature).

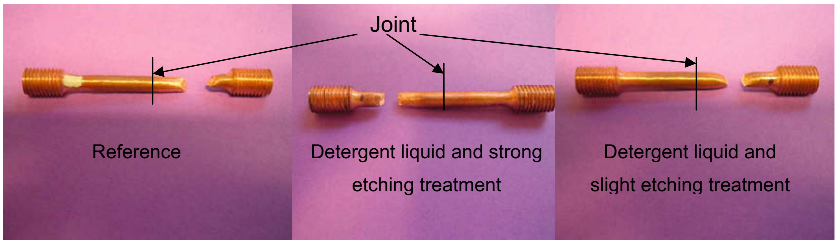


Fig. 3. Photographs of broken tensile CuCrZr specimens.

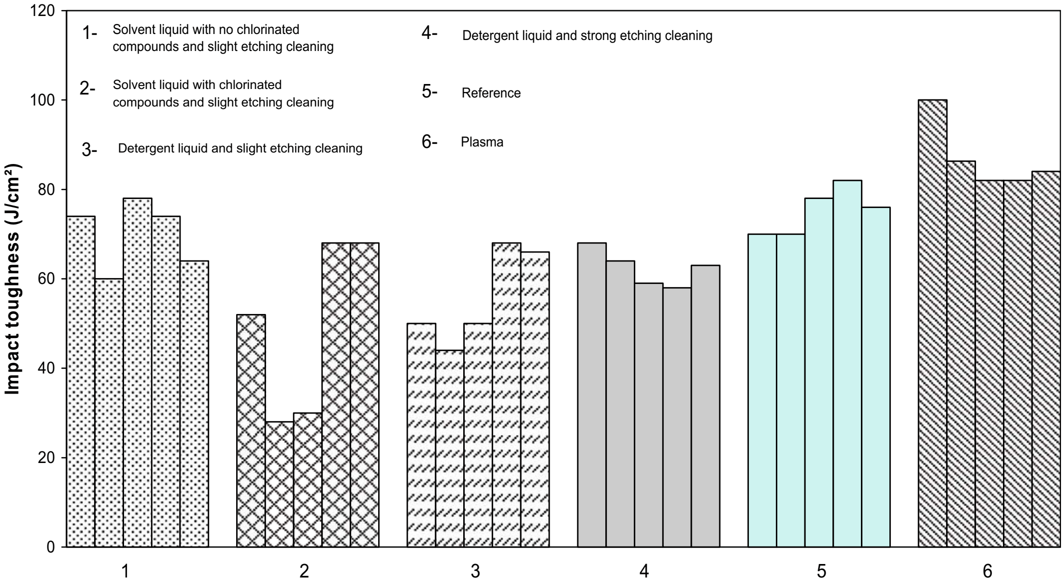


Fig. 4. Impact fracture toughness of CuCrZr joints.

Fig. 5. Fractography of CuCrZr joint impact specimens. Surfaces cleaned with (a) solvent liquid and slight etching cleaning, (b) detergent liquid and strong etching cleaning, and (c) reference route.

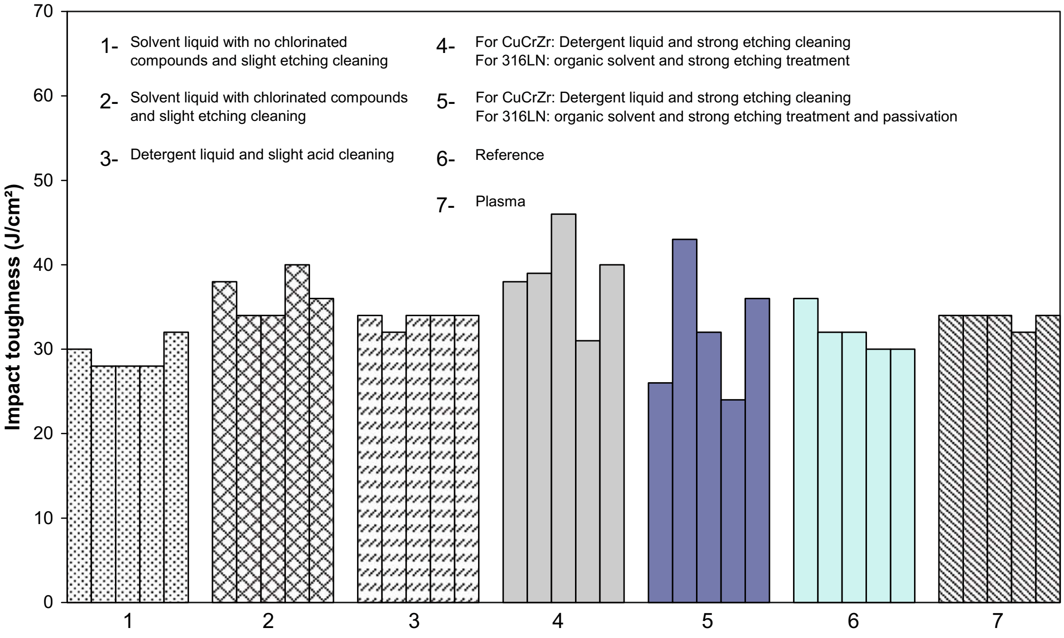


Fig. 6. Impact toughness of CuCrZr/316LN joints.

for two hours. To partially recover the as-received mechanical properties of CuCrZr, a 980 °C solutioning heat treatment has been applied to the joints. Then, the joints were rapidly cooled by gas quenching at a rate higher than 60 °C/min. After the solutioning heat treatment, the joints were aged at 480 °C for 2 h as specified as a reference treatment for ITER use [2].

5. Mechanical results

The mechanical properties of the joints have been studied by performing impact and tensile tests. Impact specimens were 10 × 10 × 55 mm with a U notch centred on the joint. A 150 J pendulum was used. The tensile specimens were 4 or 6 mm in diameter and 30 mm in gauge length. The joint was always located at the middle of the tensile specimens. The deformation rate was $10^{-4}\ s^{-1}$.

5.1. CuCrZr/CuCrZr joints

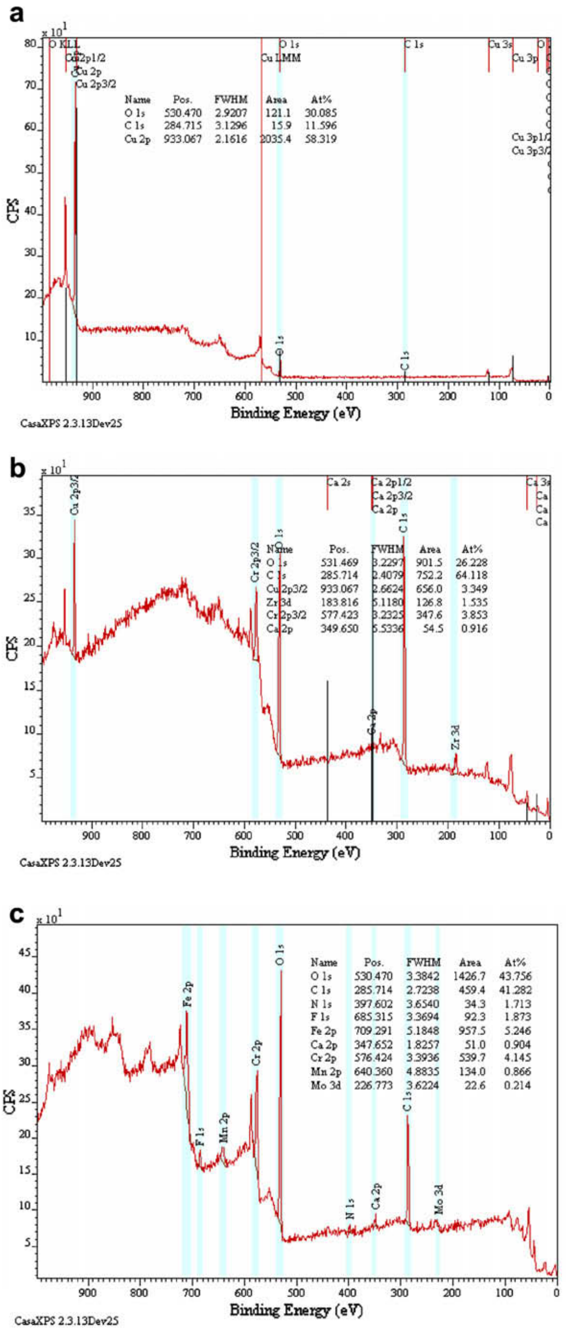
Micrographs of CuCrZr joints presented in Fig. 1 show that no recrystallisation occurs through the interface whatever the cleaning treatment. Tensile tests present similar results (Fig. 2), with similar values of yield strength, ultimate tensile strength and elongation whatever the cleaning treatment. Furthermore, rupture occurred always in CuCrZr and not at the joint (Fig. 3), which indicates that tensile testing is not relevant to characterize the effect of the investigated cleaning treatments. Fig. 4 shows that higher impact toughness values are obtained with plasma cleaning. The worst results are obtained when CuCrZr alloys are cleaned with solvent liquid constituted with chlorinated compounds and are etched by a slight acid liquid. Furthermore, results are highly scattered. The lowest impact values are associated to a bad diffusion welding: machining marks are visible on the broken surfaces (Fig. 5(a)). In the other cases, the crack propagates both through CuCrZr and at the joint (Fig. 5(b)–(c)).

5.2. CuCrZr/316LN joint

Tensile tests performed on CuCrZr/316LN joints gave results that were similar to those obtained in the case of CuCrZr/CuCrZr joints (Fig. 2). Moreover, the ultimate tensile strength of the CuCrZr/316LN joints is similar to that found in [3], where CuCrZr is aged for 4 h at 480 °C. Fig. 6 shows the impact toughness results of CuCrZr/316LN joints. All the joints present about the same impact toughness whatever the cleaning treatment. Slightly lower values were obtained with 316LN material ultimately passivated. This treatment favours the development of a protective chromium oxide layer which probably hinders the diffusion process and reduces the joint impact toughness. Since in all the cases the rupture occurred in CuCrZr, it is difficult to choose a cleaning route based on these results alone.

6. Discussion

Tensile tests were not conclusive because, whatever the cleaning treatment, tensile specimens broke in CuCrZr, not at the joint: the tests give only information about the tensile properties of CuCrZr affected by the manufacturing process. Impact toughness measurements gave more discriminating and interesting results. In the case of CuCrZr/CuCrZr joints, plasma cleaning process is the best cleaning route: the joint impact energy can reach 100 J/cm^2 compared to 80 J/cm^2 for joints manufactured with our laboratory cleaning route. These results are correlated to the cleanliness of the copper surfaces. XPS measurements done on copper samples show that the residual carbon and oxygen concentrations are very low (Fig. 7(a)), 10 at.% and 20 at.%, respectively. Residual pollution associated to chemical liquid processes is higher as shown in Fig. 7(b). Correlatively, impact results are lower. However, cleaning with detergent liquids coupled with a strong etching treatment allows to achieve CuCrZr/316LN joints with mechanical properties as good as those achieved with our own reference route. This is why these products seem to be a good industrial alternative to our reference route. Moreover, XPS measurements show that the surface of austenitic stainless steel cleaned with organic solvent and strong acid liquid presents approximately the same residual pollution as the sample cleaned with plasma (Fig. 7(c)). In this case,



Name	Pos.	FWHM	Area	At%
O 1s	530.470	2.9207	121.1	30.085
C 1s	284.715	3.1296	15.9	11.596
Cu 2p	933.067	2.1616	2035.4	58.319

Name	Pos.	FWHM	Area	At%
O 1s	531.469	3.2297	901.5	26.228
C 1s	285.714	2.4079	752.2	64.118
Cu 2p3/2	933.067	2.6624	656.0	3.349
Zr 3d	183.816	5.1180	126.8	1.535
Cr 2p3/2	577.423	3.2325	347.6	3.853
Ca 2p	349.650	5.5336	54.5	0.916

Name	Pos.	FWHM	Area	At%
O 1s	530.470	3.3842	1426.7	43.756
C 1s	285.714	2.7238	459.4	41.282
N 1s	397.602	3.6540	34.3	1.713
F 1s	685.315	3.3694	92.3	1.873
Fe 2p	709.291	5.1848	957.5	5.246
Ca 2p	347.652	1.8257	51.0	0.904
Cr 2p	576.424	3.3936	539.7	4.145
Mn 2p	640.360	4.8835	134.0	0.866
Mo 3d	226.773	3.6224	22.6	0.214

Fig. 7. XPS spectra after a brief etching (120 s) of the metallic surface with 2 keV argon ions. (a) CuCrZr after a plasma cleaning treatment, (b) CuCrZr degreased with detergent liquid and etched with a strong acid liquid, (c) 316LN sample degreased with an organic solvent and deoxidized with a strong acid liquid.

the observation of the Fe2p peak associated to the substrate indicates that the residual pollution layer is less than 10 nm thick.

7. Conclusion

Our study has investigated some industrial chemical liquids and processes to clean CuCrZr and 316LN materials in order to propose an industrial way for the fabrication of the CuCrZr/316LN joints of ITER First Wall Panels. According to the impact toughness measurements, plasma cleaning appears as the best way to clean CuCrZr and 316LN materials before their diffusion welding. As this process has not yet been tested under relevant industrial conditions (large-scale, pulse discharge conditions), a chemical liquid process has been proposed instead.

Acknowledgement

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