EFDA TECHNOLOGY WORKPROGRAMME 2005

TT-TRITIUM BREEDING AND MATERIALS
TV - VESSEL/ In-VESSEL

TASK: TW5-TVM-BRAZE
DEVELOPMENT OF A SILVER FREE INDUCTION BRAZING ALLOY

Deliverable: Production of nanocrystalline braze alloy by splat melting and annealing for range of appropiate compositions. The braze alloy will also be characterised.

T. Petrisor, Lelia Ciontea

Technical University of Cluj-Napoca, Cluj-Napoca

1. Introduction

Brazing is the most used materials joining technique (metal-ceramic assembly, Si/SiCf composite, beryllium, refractory metals, etc.) for plasma facing components in the fusion reactor. Lately, considerable efforts have been devoted to the joining of SiC/SiCf composites and beryllium. The brazing material has to exhibit the following general properties [1,2]:

- capacity to wet the material to be brazed
- physical and chemical compatibility with the brazed material
- ensurance of reliable mechanical and thermal properties
- good flow characteristics at the brazing temperature
- capacity to form a diffusion layer without forming brittle intermetallic compounds
- narrow temperature range between the liquids and the solidus line

In particular, the brazing material for the fusion reactor should contain only low atomic number elements, to avoid the contamination of the plasma by the high Z elements. For example, silver has the property to transmute to cadmium, a volatile element with a high atomic weight that poisons the plasma. Therefore, the silver based brazing alloys are unacceptable for plasma facing components.

Lately, the Si based (Ti,Cr) eutectic alloys have been successfully used for the brazing of SiC/SiCf composites [3-5]. The main advantage of the eutectic alloys are related to the eutectic temperature, which is the lowest melting temperature in the system and, on the other hand, to the liquids and solids line which are superposed. Therefore, in the first part of the task, several silver free eutectic alloys have been studied.

2. Experimental

2.1 Alloys preparation

The silver free alloys have been prepared starting from 99,99% pure elements. Stoichiometric mixtures of the pure metals were melted in an argon plasma furnace with water cooled copper hearth. In order to obtain a homogeneous eutectic microstructure, the samples were remelted several times. To study the role of manganese on the wettability, the above eutectic alloys were doped with 0.5, 1 and 2at% Mn.

2.2 Wetting experiments

The wetting experiments have been investigated on an ITER-GRADE ELBRODUR Cu-Cr-Zr alloy. For the wetting experiments bulk pieces of alloys were put on CuCrZr plates without applying any external pressure. Prior, both the pieces of the alloy and the CuCrZr plates were ultrasonically cleaned in acetone and 2-isopropanole. The general thermal treatment used for the wetting experiments is presented in Figure 1. The samples were treated in a quartz tube furnace in high vacuum (10^{-7} Torr) to avoid the oxidation.

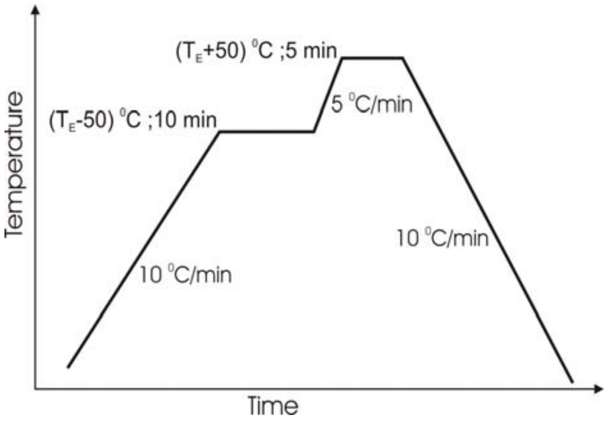


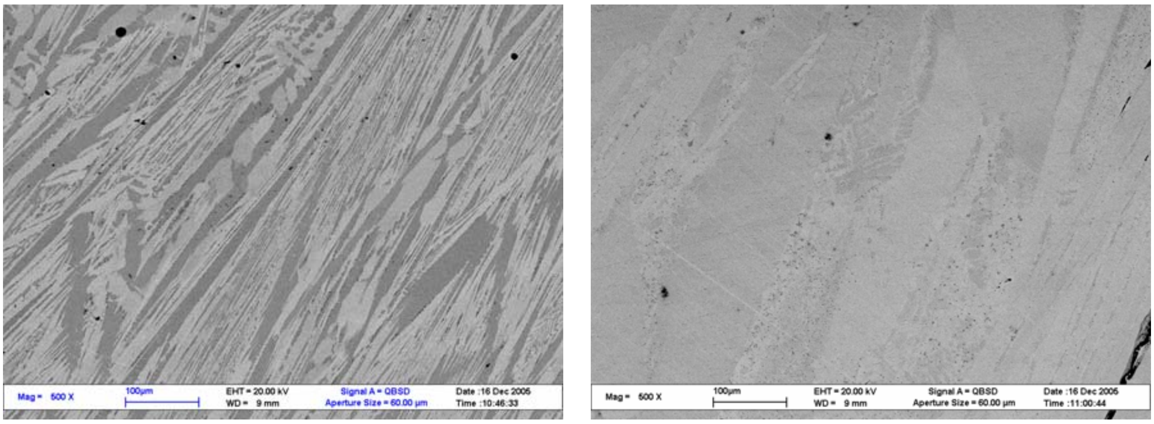
Figure 1. Temperature diagram of the wetting process.

3. Results

3.1. Microstructural, crystalline and thermal properties of the eutectic alloys

3.1.1. (Ti-43%at.Cu)-x %at.Mn (x=0, 0.5, 1, 2) eutectic alloys

The SEM (Scanning Electron Microscopy) image of the Ti-43%at.Cu alloy with different manganese concentrations is presented in Figure 2. As can be observed, the alloy has a lamelar microstructure consisting in alternate layers of the two crystalline phases. From the EDXS (Energy Dispersive X-ray Spectroscopy) it was determined that the dark and light phases corresponds to Ti_2Cu and TiCu intermetalics, respectively. The Mn singnificantly influences the eutectic microstructure in such a way that the increase of the Mn concentration modifies the volume ratio between the two phases, reducing the amount of Ti_2Cu. Therefore, for 1 and 2 at.%Mn, the lamelar character of the microstructure is not preserved. Neverthless, the X-ray diffraction measurements (Figure 3) have revealed that even for 2at.%Mn the alloy preserves the eutectic composition of the Ti-43%at.Cu pure alloy.



(a) (b)

Figure 2. SEM image of (a) (Ti-43%at.Cu)-0.5 %at.Mn and (b) (Ti-43%at.Cu)-2 %at.Mn

The differential thermal analysis (DTA) have revealed that the eutectic temperature monotonously decreases with the manganese content from 950 ^{0}C for 0 at.%Mn to about 915 ^{0}C for 2at.%Mn.

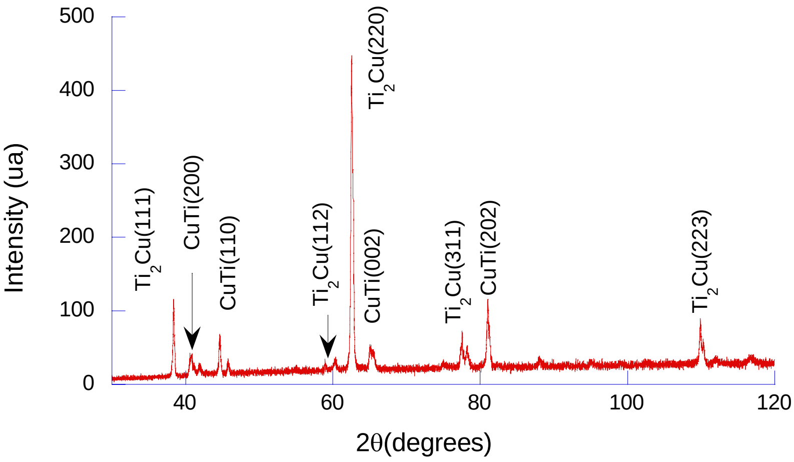
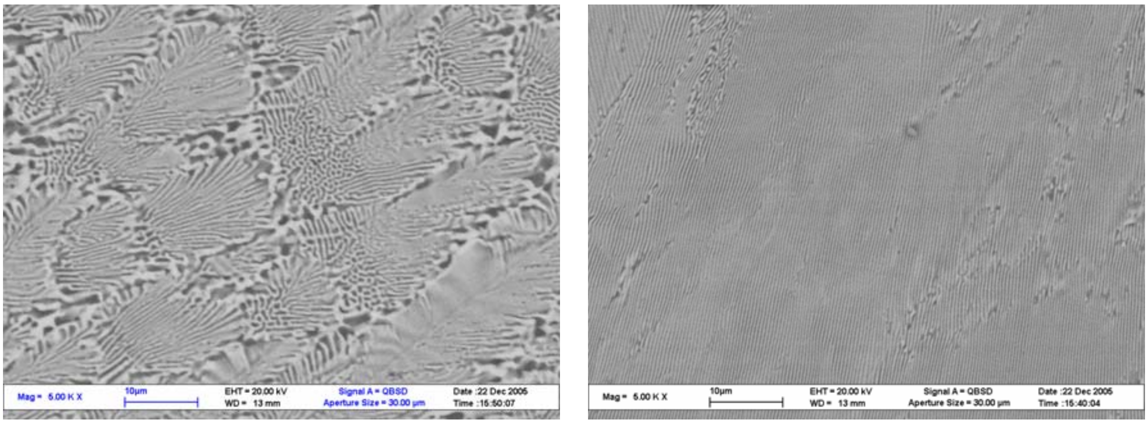


Figure 3. X-ray diffraction pattern of (Ti-43%at.Cu)-2 %at.Mn alloy.

3.1.2 (Al-17,1%at.Cu)-x at.%Mn (x=0, 0.5, 1, 2) eutectic alloys

As presented in Figure 4, the alloying with manganese results in a very fine and uniform eutectic structure with respect to the pure Al-17.1%at.Cu alloy. It is to be noted that the manganese free alloy has a domain structure of about 10 µm. Inside the domains the eutectic exhibits a quasi-lamelar structure. EDXS analysis have demonstrated that the domain boundaries mainly consist in Al-Cu solid solutions (light phase). The (Al-17,1%at.Cu)-2 %at.Mn alloy has a nanometric uniform lamelar structure. The cross dimension of a lamella is of about 40 nm.



(a) (b)

Figure 4. SEM image of (a) (Al-17,1%at.Cu) and (b) (Al-17,1%at.Cu)-2 %at.Mn

The X-ray diffraction patterns (Figure 5) are in agreement with the SEM and EDX analysis, as well as with the phase diagram of the Al-Cu system, containing only the peaks ascribed to Al_2Cu intermetallic compound and to Al-Cu solid solution. The variation of the peak intensities is rather arbitrary. This can be mainly explained by the texturing of the samples during the preparation process in a high temperature gradient. Nevertheless, the intensity of the Al-Cu solid solution peaks tends to decrease with Mn concentration. This can be correlated with the disappearance of the domains' boundaries, which are rich in Al-Cu solid solution.

The eutectic temperatures, determined from DTA analysis, monotonously increase with the manganese content from 448 ^{0}C for 0 at.%Mn to about 570 ^{0}C for 1at.%Mn.

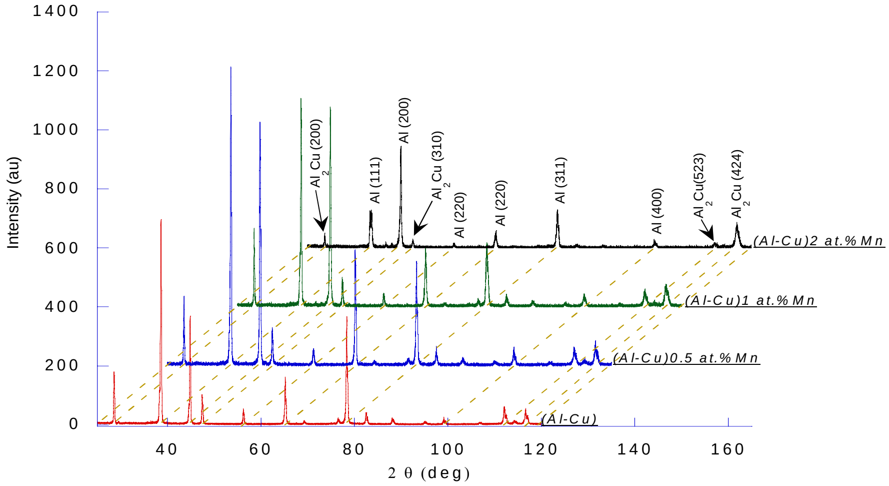
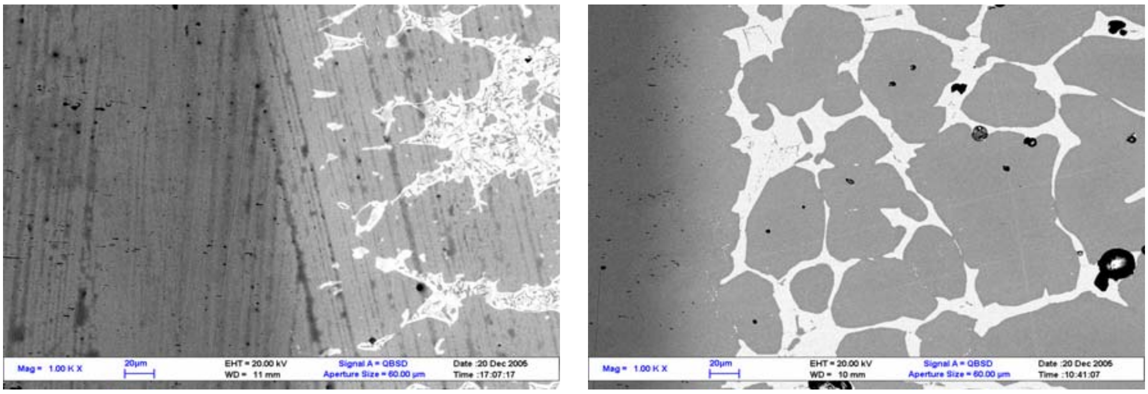


Figure 5. X-ray diffraction pattern of (Al-17.1%at.Cu) -x %at.Mn alloy.

3.1.3 Cu-Sn based brazing alloys

Several Cu-Sn based alloys have been studied. The most promising candidates for the brazing alloys are: Cu-30at.%Sn-2at.%Mn-6at.%Ti and Cu-13at.%Sn-2at.%Ni-6at.%In. The melting temperature, determined from the DTA analysis, is 736 ^{0}C and 765 ^{0}C, respectively. The SEM images of these alloys are presented in Figure 6. The microstructure of both alloys is the result of a mixture of two phases, much alike to that of an eutectic structure.

EDXS analyses have revealed that in both cases the light phase is Sn rich, while the dark one is Cu rich. The phases have the following composition: for Cu-30at.%Sn-2at.%Mn-6at.%Ti alloy, the dark phase has Cu-8.8at.%Sn-1.88at.%Mn-0at.%Ti and the light phase has Cu-21.4at.%Sn-7.16at.%Mn-9.3at.%Ti and for Cu-13at.%Sn-2at.%Ni-6at.%In, the dark phase has Cu-6at.%Sn-1.8at.%Ni-2.6at.%In and the light phase has Cu-14.9at.%Sn-4.2at.%Ni-6.7at.%In



(a) (b)

Figure 6. SEM image of the cross section of samples prepared for the wetting experiments (a) Cu-30at.%Sn-2at.%Mn-6at.%Ti and (b) Cu-13at.%Sn-2at.%Ni-6at.%In. In both images the regions with light features represent the brazing alloys.

3.2 Wetting experiments

The samples for the wetting experiments were prepared using a temperature-time diagram shown in Figure 1. The experimental procedure for the determination of the wetting angle and the diffusion depth using the optical microscopy is presented in Figure 7 for the (Ti-43%at.Cu)-x %at.Mn eutectic alloys. It is to be noted that, in the region of the junction, the brazing material is quite compact, uniform and free of cracks. This aspect is very important for a high quality brazing. The diffusion front can also be observed. Our study has revealed that for all the alloys the thickness of the diffusion layer is strongly dependent on the wetting temperature and time.

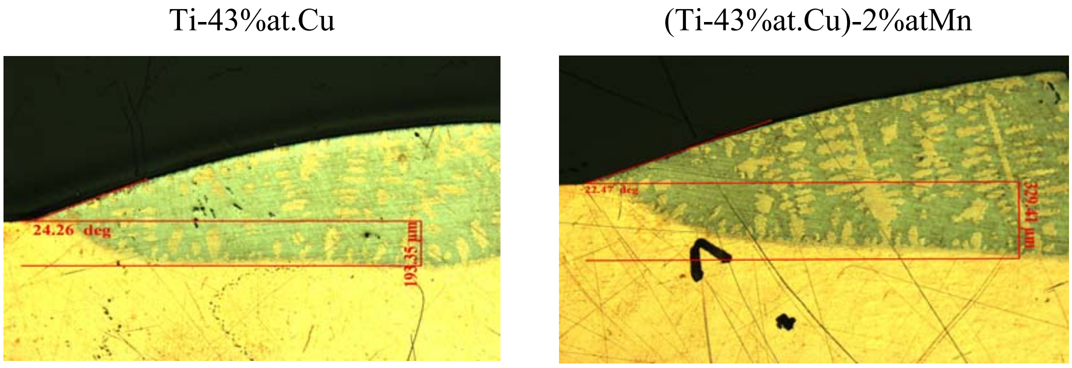

Ti-43%at.Cu (Ti-43%at.Cu)-2%atMn

Figure 7. The optical cross section of wetting sample

Due to the coexistence of the diffusion and spreading behaviour, it is difficult to make a comparison between the two alloys. The results of the wetting experiments are presented in Table 1.

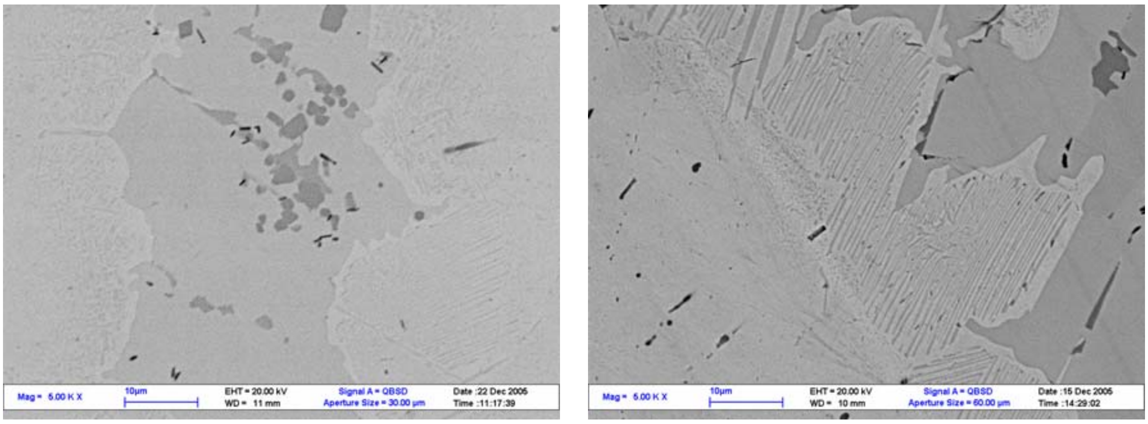
Table 1. The diffusion depth and the wetting angle for the studied brazing alloys.

BRAZING ALLOY	DIFFUSION DEPTH	WETTING ANGLE
Ti-43%at.Cu	193.35µm	22.26 º
(Ti-43%at.Cu)0.5%atMn	449.78 µm	12.79 º
(Ti-43%at.Cu)1%atMn	353.46 µm	16.49 º
(Ti-43%at.Cu)2%atMn	329.41 µm	22.47 º
(Al-12.2%at.Si)0.5Mn	7.01 µm	39.73 º
(Al-12.2%at.Si)1Mn	44.93 µm	22.49 º
(Al-12.2%at.Si)2Mn	18.44 µm	46.88 º
Cu-13%at Sn2%at Ni6%atIn	< 5 µm	19.6 º
Cu-30%at Sn2%atMn6%atTi	17.11 µm	28.5 º
Cu-32%at Sn6%at Ti	19.44 µm	21.08 º

3.3 Brazing experiments

For the preliminary testing of the studied brazing alloys ITER-GRADE ELBRODUR Cu-Cr-Zr plate like samples (10x10x3 mm^3) have been brazed. The results presented in this report regard only the eutectic alloys. The joints have been prepared using a fine powder of eutectic alloys obtained by milling. After overlapping, the samples were loaded with an axial load of about 1N to keep them fixed during the thermal cycle. The joinings were performed in vacuum 10^{-7} Torr, following the same temperature-time diagram as that for the wetting experiments (Figure 1). The as obtained joinings have been characterized from a microstructural, chemical and mechanical point of view by SEM, EDXS and shear test, respectively.

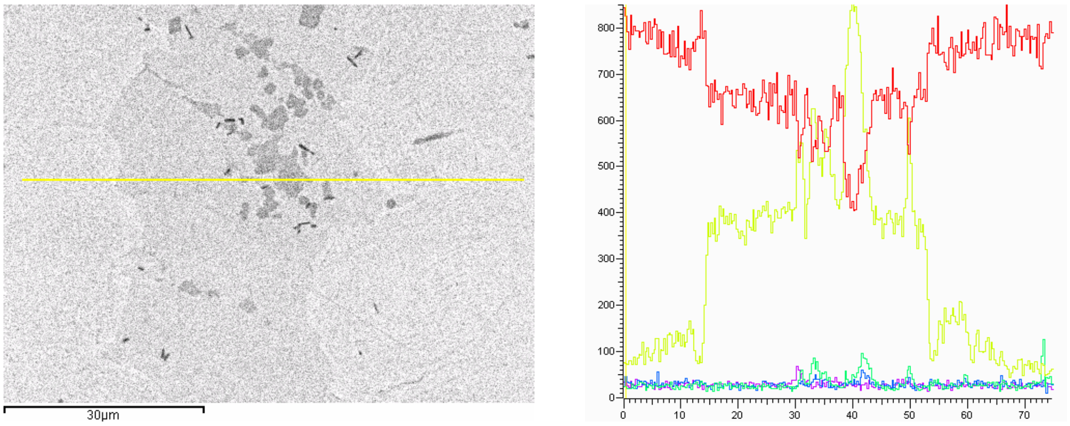
In Figure 8 a SEM cross section of the CuCrZr/CuTiMn/CuCrZr junction is presented. The thickness of the joint is of about 20-50 µm, but a variation in thickness can be observed depending on the surface conditions. The joint layer shows the absence of the discontinuities or cracks as a result of a complete melting of the brazing powder. At the interface between CuCrZrand CuTiMn brazing material a diffusion layer can be noticed (Figure 8b).



(a) (b)

Figure 8. SEM image of the junction using (Ti-43%at.Cu)-2 %at.Mn eutectic alloy (a) cross section of the junction and (b) the interface CuCrZr/TiCuMn.

The diffusion layer determined by EDXS analysis (Figures 9a,b) is of about 10 µm. Due to the diffusion of Ti in the brazed material and, on the other hand, the diffusion of Cu in the brazing material in the diffusion layer, the eutectic structure is modified. Anyway, the diffusion layer seems to be compact and crack free, relevant for the quality of the adherence.



(a) (b)

Figure 9. EDXS analysis of the CuCrZr/TiCuMn/ CuCrZr junction (a) scanning line and (b) element distribution along the scaning line (Cu-red and Ti-green)

The mechanical performances of the joints were determined by means of shear tests using a modified ASTM D905-89 test procedure [6]. Even if the presence of a pure shear stress field was not assured by this procedure, it was however a suitable method to obtain a rather good estimation of the shear strength and a good mean for comparative evaluation of the performances of specimens obtained with different process parameters. In Figure 10 is presented the shear strength of the CuCrZr/TiCuMn/ CuCrZr junctions versus Mn concentration. The shear strength increases with mangenese concentration reaching the maximum of 270 MPa for 2at.%Mn [7].

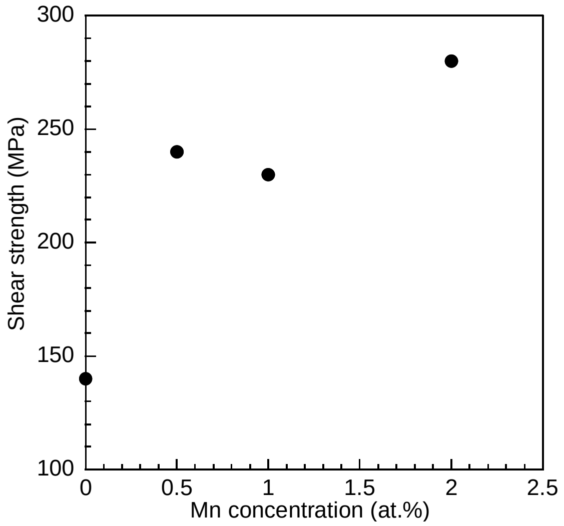
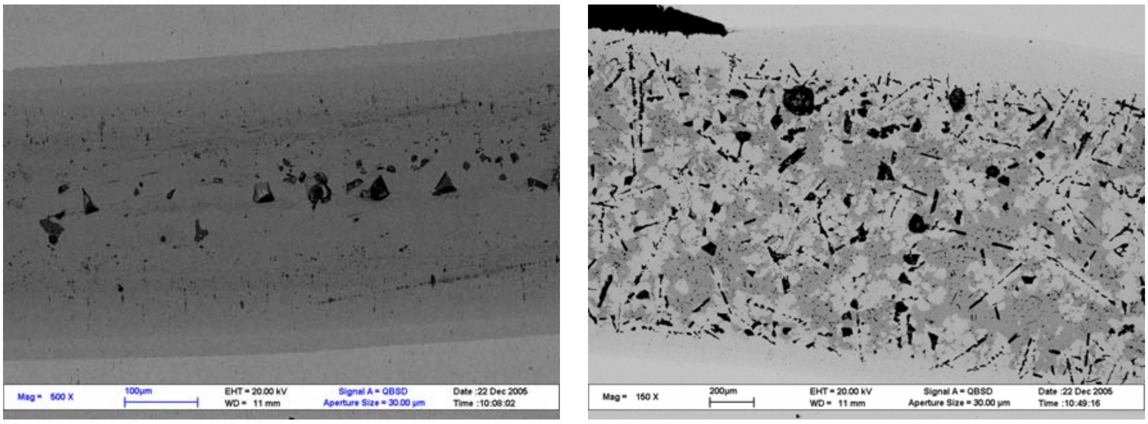


Figure 10 Shear strength of the junction versus manganese concentration of the Cu-Ti brazing alloys

The CuCrZr/Al-17.1at.%Cu/ CuCrZr and (b) CuCrZr/Al-12.2at.%Si/CuCrZr junctions were prepared under the same conditions as the CuCrZr/TiCuMn/ CuCrZr junctions.

The SEM cross section of the juctions are presented in Figure 11. For both junctions the brazing material exhibits a relatively high density of voids (dark regions). Unlike the Al-17.1at.%Cu, the Al-17.1at.%Cu presents cracks in a region closed to the diffusion layer. Anyway, both cracks and voids are expected to have a negative influence on the mechanical properties of the junctions. Another drawback of these junctions consists in the high thickness of the brazing layer, several hundreds of microns. Therefore, further studies to optimize these brazing alloys are still in progress.



(a) (b)

Figure 11. SEM cross section image of (a) CuCrZr/Al-17.1at.%Cu/ CuCrZr and (b) CuCrZr/Al-12.2at.%Si/ CuCrZr

4. Conclusions

The activity performed in 2005 in the frame of the task TW5-TVM-BRAZE, can be summarised as follows:

- (Al-17,1%at.Cu)-x at.%Mn , (Ti-43%at.Cu)-x %at.Mn (x=0, 0.5, 1, 2) eutectic alloys and Cu-30at.%Sn-2at.%Mn-6at.%Ti and Cu-13at.%Sn-2at.%Ni-6at.%In alloys were manufactured.
- Structural, morphological and thermal characterization of the above mentioned brazing materials has been performed by SEM, EDXS, X-ray diffraction and DTA analysis.
- The wetting study has been carried out on ITER-GRADE ELBRODUR Cu-Cr-Zr alloy.
- Brazing experiments on ITER-GRADE ELBRODUR Cu-Cr-Zr plates using the eutectic alloys have been performed.
- Microstructural, chemical and mechanical characterization by SEM, EDXS and shear test, respectively, have been also made.
- Manufacturing of both amorphous and nanocrystalline Cu-Sn-Mn-Ti and Cu-Sn-Ni-In brazing alloys and foils (thickness of minimum 50 µm and 10 mm wide).

5. Foreseen activities and results for 2006

The following activities are to be performed in 2006:

- Wetting study on Be of the brazing alloys and foils prepared in 2005.
- Brazing experiments on Be plates using both the eutectic alloys and Cu-Sn-Mn-Ti and Cu-Sn-Ni-In brazing alloys and foils.
- Microstructural, chemical and mechanical characterization by SEM, EDXS and shear test of the Be and Be/CuCrZr junctions

References

[1 **Odegard B.C, Kalin B.A**, *“A review of the joining techniques for plasma facing components in fusion reactors*” Journal of Nuclear Materials, (1996), 44.

[2] **Lorenzetto P., Boireau B., Boudot C., Bucci P., Furmanek A., Ioki K., Liimatainen J., Peacock A., Sherlock P., Tahtinen S.**, *“Manufacture of blanket shield modules for ITER”,* Fusion Engineering and Design, 75-79 (2005), 291

[3] **Riccardi B., Nannetti C.A., Petrisor T., Sachetti M.**, “*Low activation brazing materials an techniques for SiC/SiCf composites”*, Journal of Nuclear Materials, 307-311 (2002) 1237

[4] **Riccardi B., Nannetti C.A., Woltersdorf J., Pippel E., Petrisor T.**, ”*Brazing of SiC and SiCf/SiC composites performed with 84Si-16Ti eutectic alloy: microstructure and strength”*. Journal of Material Science 37 (2002) 5029

[5] **Riccardi B., NannettiC.A., Petrisor T., Woltersdorf J., Pippel E., Libera S., Pilloni L.**, “*Issues of Low Activation Brazing of SiC_f/SiC Composites by Using Alloys Without Free Silicon*” Journal of Nuclear Materials, 329-333, Part A AUG 1 (2004) 562

[6] **Iseki T., Arakawa K., Suzuki H.**, “*Joining of dense silicon carbide by hot pressing”* J. Mater. Sci. Lett. 15 (1980), 149.

[7] **Petrisor T., Neamtu B., Rauca M., Brandusan L.**, “*Synthesis of silver free eutectic alloys for Be and $Cu_{99.32}Cr_{0.6}Zr_{0.08}$ brazing”* accepted for presentation at MATEHN 06, 4th International Conference on Materials and Manufacturing Technologies, Cluj-Napoca, Romania, 21-23 September, 2006.