Association EURATOM – MEdC Romania

MATERIALS 2010

Year	*Work Description*	*Associate*	*BS Manpower (ppy)*	*BS Hardware, Cons., Other Expenditure (kEuros)*	*PS Manpower (ppy)*	*PS Hardware, Cons., Other Expenditure (kEuros)*	
ODSFS	**WP10-MAT-ODSFS-01-01/MEdC/BS** Microstructure characterization of ODS ferritic steels (ODSFS) by (HR)TEM, X-EDS, EELS and APT.	MEdC (Sarbu)	0.50	1.00	0.00	0.00	Ok
REMEV	**WP10-MAT-REMEV-01-01/MEdC/BS** Transmission and backscattering Mössbauer Spectroscopy studies of the short range order, structure and magnetic properties in α-Fe and binary Fe-Cr model-alloys.	MEdC (Diamandescu)	0.50	1.00	0.00	0.00	Ok

REMEV	**WP10-MAT-REMEV-06-01/MEdC/BS** In-situ TEM observation of dynamics of screw & edge dislocations and He bubbles in alpha-Fe and binary Fe-Cr model-alloys subjected to ion irradiation versus temperature.	MEdC (Teodorescu)	0.50	2.00	0.00	0.00	Ok

WWALLOY	**WP10-MAT-WWALLOY-01-01/MEdC/BS** Functional gradient W-steel materials by unconventional co-sintering Routes	MEdC (Galatanu)	0.80	5.00	0.00	0.00	ok

OK means: Report sent as Slides, Extended Text or by participation at Reporting Meeting.

EFDA Fusion Materials Topical Group Deliverable under Base- Line Support	
Reference:	Topical Group: **Fusion materials** Area: **ODSFS** and **W-WALLOYS Development** Task: **WP10-MAT-ODSFS-01-01/MEdC/BS and** **WP10-MAT-WWALLOY-01-01/MEdC/BS**
	Task Title : **Microstructure characterization of ODS ferritic steels (ODSFS) by (HR)TEM, X-EDS, EELS and APT** Task Coordinator: **S. González de Vicente**
Author(s):	Name and Association(s) of the Author(s) **Corneliu Sarbu**, Association EURATOM-MEdC, Romania
Date:	**December 31st 2010**
Distribution list:	Task Co-Ordinator: **S. González de Vicente** Task Force Leader: S**erguey Dudarev and Michael Rieth** (CSU Responsible Officer) (CSU Group Leader)

EFDA Fusion Materials Topical Group Deliverable under Base- Line Support	
Reference:	Topical Group: **Fusion materials** Area: **ODSFS** and **W-WALLOYS Development** Task: **WP10-MAT-ODSFS-01-01/MEdC/BS and** **WP10-MAT-WWALLOY-01-01/MEdC/BS**
Content:	**The ODSFS materials microanalysis.** The initial intent of the present research was the analysis by means of XRD, Moessbauer spectroscopy, TEM electron diffraction and X-EDS of the following materials: (A) two powders prepared by mechanical alloying (MA) starting with pure elements [Fe(99%, 44μm), Cr(99.95%, <25μm) and Y(99.9%, median size 500μm), Ti(99.9%, <105μm)], and having the following compositions: (a) alpha-Fe + Y2O3 [the targeted compositions of the MA prepared alloy being 85.2wt%Fe – 14.1wt%Cr – 0.3wt%Y] (b) alpha-Fe + Y2O3 +Ti [the targeted composition of the MA prepared alloy being 85.2wt%Fe – 14.1wt%Cr – 0.3wt%Y – 0.3wt%Ti]; (B) the consolidated material resulting from the two powder compositions; (C) the final ODSFS materials obtained by extrusion from the two consolidated materials. Because the Association in charge to make the above mentioned materials cancelled the continuation of making ODSFS immediately after the production of the MA powders, we got and did analyse only the two above mentioned (see (A)) MA powders, which were analysed by XRD, Moessbauer spectroscopy and TEM-XEDS. The main results are: (1) the average dimensions of the powder particles prepared by MA is around 8nm, so they were nanopowders; (2) no amorphous phase was observed by transmission electron diffraction, (3) the Y was not completely alloyed with the α-FeCr phase as a result of MA preparation. Particles containing exclusively Y and O were identified by X-EDS. The large majority of analysed powder particles were containing all the

elements: Fe, Cr, Y and, if the case, Ti.

(4) significant amounts of impurity elements were detected in most of the analysed particles.

(5) The Moessbauer spectroscopy has shown that the proportion of Cr presence in the b.c.c. lattice of Fe-Cr solid solution is of about 15%.

The final conclusion concerning the two analysed MA prepared powders was that the parameters of MA process should be modified in order to get the final desired composition and the purity of preparing conditions carefully watched.

The work on consolidated and on finally prepared by extrusion materials having the two above mentioned compositions was not done because of lack of supplied samples.

The ODS W+Y2O3 (1 and 5 vol% Y2O3) alloys microanalysis. This task exceeds the frame of the **WP10-MAT-ODSFS-01-01/MEdC/BS** initially settled task. It was done because of the interest of NRG Dutch Association in microanalysis of samples produced by PIM technology. Initially we had in view also **Walloy+Ta** samples prepared by PIM technology but our partners didn't succeed to produce samples in due time. We investigated:

(A) W+1vol%Y2O3 sample of final material prepared by PIM technology;

(B) W+5vol%Y2O3 sample of final material prepared by PIM technology;

(C) pure W-alloy, prepared in the same way, as standard.

TEM (TED) and X-EDS analysis methods were used. The main results are:

(1) pores are present inside the grains in all three kinds of materials;

(2) inclusions containing Y and O are present inside grains, as single or multiple inclusions in one grain. Grains containing no inclusions were also

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	observed, but seldom; (3) in most cases these Y and O containing inclusions are in crystalline state, presumably as Y2O3 micro or nano-crystals, but it was observed also an amorphous filling of such inclusions (the elemental composition of which couldn't be analysed elementally); (4) we made the special observation of the presence of inclusions made of crystalline Y2O3 (of varying size) which contain inside them very small and dispersed inclusions of crystalline W. The number of such inclusions in the sample prepared with 5vol% Y2O3 is significantly higher than in the sample prepared with 1vol% Y2O3. These inclusions are present either inside the W-matrix grains (alone or in company of one or more "normal" Y containing inclusion(s) in the same W grain) or in between the normal W-matrix grains, playing the role of "abnormal" grains of the W-matrix. We don't know their influence on the thermal and mechanical properties of the bulk material.		
Revision No: X	Changes: Y		
	Written by:	Revised by:	Approved by:
	Corneliu Sarbu	Name	**F. Spineanu** HRU – MEdC Association

Objectives

The objective was to assess the formation of ODS-type alloys in both alpha-FeCr-based samples (ODSFS) and W-based ones.

No results could be produced by us for any of the ODSFS materials in view, because of lack of samples which were to be supplied by the collaborating Association.

Achievements

Concerning the W-based ODS alloys prepared by PIM with 1vol%Y2O3 and 5vol%Y2O3, we did assess the presence of Y2O3 inclusions inside the W grains, therefore the successful formation of ODS W-based alloys by PIM technology in the final material made by NRG Dutch Association.
In the studied W-based ODS alloys we have observed the presence of inclusions of crystalline Y2O3 matter containing inside very small inclusions of W, which are located both inside W-matrix grains and in between them (i.e. playing the role of matrix grains of abnormal elemental composition).
Our microanalysis was done by using an old analytical TEM instrument which was nevertheless able to produce good results. A top-level TEM instrument (analytical HRTEM, with FEG, filtered energy electrons and aberrations corrected optical system) is just going to be installed in our institute, so that in the next future we will be able to get even better results in the microanalysis of materials of interest.

Shortcomings

The lack of samples was the only difficulty we encountered. That is why we were not able to produce microanalysis results on ODSFS (on schedule to be produced by our Portuguese collaborating Association) and on W+Ta alloys.
We propose an action to be taken by EFDA for the settlement of a firm schedule of samples supply and analysis to be done after the collaboration intention between different Associations was expressed. The lack of a commitment to supply samples in due time can lead to difficulties as mentioned here.

Conclusions and General perspectives

The detailed analytical TEM micro/nano-analysis of the materials of interest for fusion (mainly of the ODS ones) is able to supply structural infos which could be important in the evaluation of the thermal and/or mechanical properties. We will be able in the immediate future to perform such analyses by using a top=level analytical (HR)TEM going to be installed in our institute.
We have already settled a firm collaboration with the NRG Association from Holland in this respect for 2011. We hope we will be able to settle such collaborations also with other Euratom Associations in charge with production of fusion materials. It is our proposal that this kind of work (micro/nano-analysis by using (HR)TEM attached analysis devices) should be continued and considered as vitally important mainly in view of the production of nano-grained ODS materials. The main condition for successful achievements is the settlement of a firm collaboration schedule between teh collaborating Associations.

References (to Conference paper/poster, Meeting, Publication)

- Presentation at the monitory meeting held in San Sebastian on June-30th – July-4th 2010
- Presentation at the monitory meeting to be held in Garching bei Muenchen on Feb 9-10, 2011

EFDA Fusion Materials Topical Group Deliverable under Base- Line Support	
Reference:	Topical Group: **Fusion Materials** Area: **MAT-REMEV** Task: **WP10-MAT-REMEV-01-01/MEdC/BS_2010**
Document:	Task Title : Transmission and Backscattering Mössbauer Spectroscopy Studies of the Short Range Order, Structure and Magnetic Properties in α-Fe and Binary Fe-Cr Model-Alloys Task Coordinator
Author(s):	Name and Association(s) of the Author(s) : Lucian Diamandescu, Association EURATOM – MEdC Romania
Date:	**15, December, 2010**
Distribution list:	
Content:	FeCrY and FeCrTiY nanoscaled alloys, obtained by planetary ball milling, have been investigated by transmission and backscattering (conversion electron -CEMS and conversion X-ray-CXMS) Mössbauer spectroscopy to study the peculiarities of magnetic hyperfine structure and short range order parameter. In transmission geometry the measurements have been performed at room (RT) and liquid helium temperatures (LHT). Mössbauer spectra of the thermally treated (760 °C under vacuum) samples have been recorded also at room temperature. CEMS and CXMS measurements were performed at RT. Two fitting models were applied in the Mössbauer spectra computing for all recorded data: a hyperfine magnetic fields distribution (Hesse-Rübartsch

model) and the binomial model. In the binomial fit model it is assumed that the Mössbauer areas of magnetic sublattices are proportional with the binomial probabilities for the substitution of Fe by Cr atoms in the bcc structure of α- Fe. For our samples, the average magnetic fields <H> values at iron nucleus given by the two models are very close indicating that both models are appropriate for the study of magnetic interaction in Fe-Cr based alloys. No phase transitions were evidenced between the room temperature and liquid helium temperature. For the FeCrY samples (without thermal treatment) the SRO values are close to zero, revealing a rather random distribution of Cr atoms in α-Fe structure. In the case of FeCrTiY nanoscaled sample, the SRO parameter becomes negative indicating an increase of Fe-Cr pairs in the system. For thermally treated samples (vacuum ~ 760 °C) the best fit with the experimental data in the binomial model was obtained at a chromium concentration of ~ 9% instead of 14.1% (nominal content in the untreated samples). The values of <H> given by the distribution model for the treated samples support the same chromium concentration value. This finding, together with the positive SRO values, indicates a shortage in Fe-Cr pairs after thermal treatments and a possible chromium clustering process. Due to the very small crystallite size of the studied samples, the results by

EFDA Fusion Materials Topical Group Deliverable under Base- Line Support			
Reference:	Topical Group: **Fusion Materials** Area: **MAT-REMEV** Task: **WP10-MAT-REMEV-01-01/MEdC/BS_2010**		
	CEMS and CXMS measurements are similar with those obtained in transmission geometry. The surfaces effects – characteristic information given by these two methods, can't be evidenced, the particle size being much lower than the penetration depths of the conversion electrons and conversion X-rays.		
Revision No: 1	Changes:		
	Written by:	Revised by:	Approved by:
	Name: L. Diamandescu	Name	L. Diamandescu MEdC Association

Objectives

This project aimed to contribute to the achievement of the following one or more issues in Fe-Cr based alloys (potential candidates for blanket structures in fusion reactors) and α-Fe materials by means of Mössbauer spectroscopy: investigation of local structure and short range order, study of magnetic properties 'via' hyperfine magnetic fields in correlation with Cr concentration in the samples. The obtained results were used for a more general and important issue: to realise if Mössbauer spectroscopy could be used to improve the technology for obtaining FeCr based alloys (in particular prepared via ball milling route) in view of applications for fusion reactors.

Achievements

- The SRO parameters were calculated for FeCrY and FeCrTiY nanoscaled samples obtained by planetary ball milling by means of Mössbauer spectroscopy; the average magnetic fields <H> calculated with both *hyperfine magnetic field distribution and binomial* models were considered in the SRO calculations.
- Average hyperfine magnetic fields **<H>** and isomer shifts (**IS**) values given by the hyperfine magnetic fields distribution and binomial fit models are similar for Mössbauer transmission experiments; the theoretical evaluation of hyperfine magnetic fields for different sites is in good agreement with the experimental Mössbauer data;
- No phase transitions were evidenced between RT and liquid helium temperature;
- SRO determination indicates generally a rather random distribution of Cr atoms (the obtained values close to zero). The effect of Ti in the system seems to consist in an increase of the number of pairs, all SRO values being small and negatives;
- In the case of the thermally treated samples the best fit with binomial model was obtained at a Cr concentration of ~ 9 % suggesting a rejection process of Chromium atoms during heating. For both samples, FeCrY and FeCrTiY, the SRO parameters are positives, indicating a shortage in Fe-Cr pairs after thermal treatments.

Shortcomings

The best way to determine the SRO parameter in Fe-Cr based alloys seems to be the Mössbauer Spectroscopy.

Conclusions and General perspectives

Based on the present study we can infer that Mössbauer spectroscopy is a very suitable method to study the magnetic hyperfine interactions and SRO parameter's peculiarities in Fe-Cr based alloys. Due to the fact that Fe and Cr lattices are isostructural, the X-ray diffraction method is not very useful to study Fe-Cr based alloys. The Mössbauer spectroscopy is of particular interest when we need to obtain information about magnetic hyperfine interaction correlated with SRO parameter, information that can be used to improve the production technology of Fe-Cr based materials for fusion reactors.

References (to Conference paper/poster, Meeting, Publication)

Preliminary results concerning Mössbauer measurements on FeCrY and FeCrTiY alloys have been presented at National Physics Conference, September 2010, Iasi-Romania under the title:
Mössbauer Spectroscopy Investigations on FeCr Based Alloys for Fusion Reactors
Authors, L. Diamandescu, S. Constantinescu, I. Bibicu, M. Feder, D. Tarabasanu-Mihaila, T. Popescu.

EFDA Fusion Materials Topical Group Deliverable under Base-Line Support	
References:	Topical group: **Fusion Materials** Area: **MAT-REMEV** Task: **WP10-MAT REMEV-06-01/MEdC/BS_2010**
Document :	Task title: In-situ TEM observation of dynamics of screw & edge dislocations and HE bubbles in alpha Fe and binary Fe-Cr alloys subjected to ion irradiation versus temperature.
Author(s) :	Task Coordinator Name and Association(s) of the Author(s): V.Teodorescu, C. Ghica, L.C.Nistor, A.V.Maraloiu, Association EURATOM-MEdC Romania
Date:	**15, December , 2010**
Distribution list:	
Content :	Samples of pure Fe and Fe-Cr (9%) model alloy have been prepared by the melt-spinning method starting from pure materials (99.995% from Alfa Aesar). TEM specimens were prepared by ion milling method and by electro-polishing method. In situ studies were performed by heating the specimen in the Jeol 200CX electron microscope in a temperature range of RT-500 ^{o}C. In the both samples (Fe and Fe-Cr alloy), a high density of dislocations was observed, most of them decorated with gas nano-bubbles, probably filled with argon, having an average size of 30nm. Practically all observed dislocations are curved, showing a mixed screw & edge nature. The dislocations are generally fixed on bubbles or other pinning points, and become mobile by the specimen heating above 400^{o}C. Some TEM video recording of dislocations motion (jump from a pinning point to the next one) were performed and analyzed. The dislocations are more mobile in the pure Fe samples compared with the Fe-Cr alloy samples. The TEM specimens show a rapid oxidation by heating over 600^{o}C in the microscope vacuum, limiting our in-situ TEM observations at about 500^{o}C. In the second type of experiment, pure Fe ribbons were obtained in helium atmosphere using the same melt-spinning method. By variation of the spinning wheel speed, different cooling rates were obtained for the pure Fe ribbons. By growing the wheel speed, the cooling is faster. In the ribbon samples prepared with wheel speed between 1000 to 2000 rot/min, the average size of the He bubbles decrease from 52 nm to 14 nm. Most of the bubbles are linked to each otherthrough dislocations (Fig. 1.) In the most cases the bubbles are aligned along a dislocation line, suggesting of the nucleation and the bubbles and the growth process are facilitated by the diffusion of the helium atoms along the dislocation line which acts like a pipe line for the helium diffusion In all these samples, a network of dislocations and He bubbles was observed. Practically no movement of the dislocations was observed by

References:	Topical group: **Fusion Materials** Area: **MAT-REMEV** Task: **WP10-MAT REMEV-06-01/MEdC/BS_2010**

insitu TEM heating, inlike the case of the presence of the argon gas bubbles.

However, the bubbles are not observed in the ribbons prepared with wheel speed over 2400 rot/min. This means that over this speed, the cooling rate is too high to allow the bubble formation by helium ion diffusion in the iron matrix. However, helium is still present in the iron matrix and the annealing of the sample at 1000^{o}C in vacuum for 10 minute reveals the presence of a low density of He bubbles with size of 200 nm.

The last type of experiment was performed on pure Fe specimens cut from bulk iron samples, which were prepared for TEM by electro-polishing. The same TEM specimen was observed before and after the He ion irradiation with a perpendicular ion beam with an energy of 10 keV, performed in a modified Gatan Duo Mill apparatus in during15 minute. The TEM specimen is modified only on its surface. No bubbles were observed inside the iron specimen. The modifications can be observed in TEM only at the very thin edges of the specimen. The AFM imaging of the TEM specimen before and after ion irradiation reveals clearly the presence of the surface modifications. A relief of nano-hills with amplitude of about 10 nm and a spatial frequency of about 50 nm, is present on the irradiated surface.

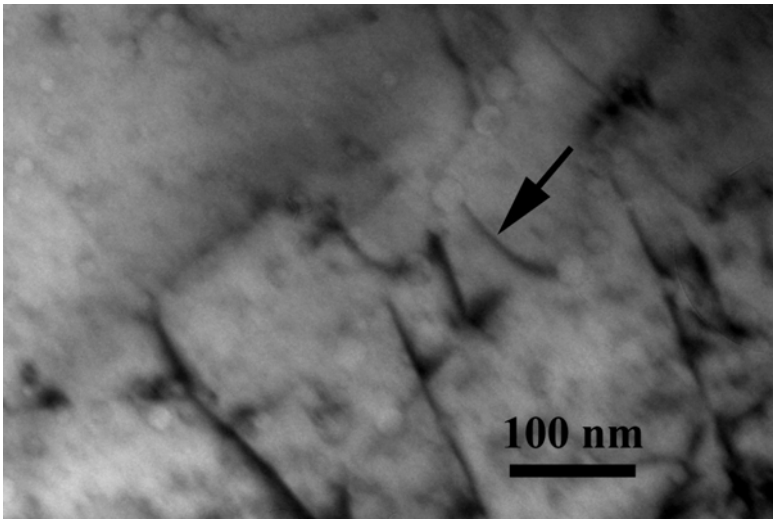

Figure 1. TEM image of the dislocations and He bubbles network in the pure Fe ribbon produced with a wheel speed of 2000 rot/min. The arrow indicates a dislocation line connecting two He bubbles.

Revision No:1	Changes:		
	Written by:	Revised by:	Approved by:
	Name: V. Teodorescu	Name:	V. Teodorescu MEdC Association

Objectives

In situ TEM study of the dislocations dynamics in a-Fe and binary Fe-Cr alloys samples by variation of the TEM specimen temperature during TEM observations. TEM observation of the dislocation& He bubbles network , collecting experimental structural data interesting to be compared with the structural model data obtained in the frame of the MAT REMEV project.

Achievements

- Pure Fe and Fe-Cr(9%) model alloy ribbon samples were obtained by melt-spinning method and prepared as TEM specimens.
- In situ TEM observations of the dislocation movements were performed during heating of the iron specimen in the microscope.
- The TEM studies revealed the presence of gas bubbles in the melt-spinning ribbons. He bubbles with different size were obtained in Fe ribbons produced in helium atmosphere. The dislocations and the He bubbles are connected in a complicate network in the matrix of the Fe ribbons.
- The low energy (10 keV) helium ion irradiation of the TEM specimen prepared from pure bulk Fe samples reveals only surface effects, without any modifications induced in the bulk structure of the specimen.

Shortcomings

Conclusions and General perspectives

The in-situ TEM study of the pure iron ribbons produced by melt-spinning in He atmosphere show the presence of a complicated network of dislocations and He bubbles with nano-metric scale. The dislocations are quite fixed on pining points or on the bubbles and only few jumps were visualized by in situ heating TEM observations.

The size and the density of the helium nano-bubbles present in the melt-spinning pure iron ribbons look similarity with helium bubbles obtained after heavy He ion irradiation.

In perspective, the analyze of the relation between the cooling rate, the He bubbles size and the dislocation movements observed by TEM under in-situ applied stress, can reveals interesting data about the interaction of He bubbles and dislocations elastic field in pure iron samples.

References (to Conference paper/poster, Meeting, Publication)

TEM Observation of dislocations & helium bubbles network in pure Fe ribbons produced by melt-spinning in helium gas atmosphere, V.S.Teodorescu, C.Ghica, L.C.Nistor, A.V.Maraloiu, M.Valeanu, F. Tolea (paper in preparation)

EFDA Fusion Materials Topical Group Deliverable under Base- Line Support			
Reference:	Topical Group: **Fusion Materials** Area: **Emerging Technologies** Task: **WP10-MAT-WWALLOY-01-01/MEdC/BS**		
Document:	Task Title : Functional gradient W-steel materials by unconventional co-sintering Routes Task Coordinator **Sehila Gonzalez de Vicente**		
Author(s):	Name and Association(s) of the Author(s) : Andrei Galatanu, Association EURATOM – MEdC Romania		
Date:	**31, December, 2010**		
Distribution list:	**Sehila Gonzalez de Vicente**		
Content:	FGM W-Fe and W-steel (316) cylindrical samples with 10-20 mm diameters and 1-10 mm heights have been sintered at different temperatures and applied pressures. The samples were realized by spark plasma sintering (SPS) or classical sintering starting with mixtures of powders in 1:0, 1:1, 1:2, 1:3 atomic proportions, placed in up to 9 different layers with thickness from 0.1 to 5 mm. SEM and EDX investigations have been performed for all samples, aiming to investigate the influence of layer thickness and compositions as well as the role of different sintering temperatures and pressures in process optimisation. Important results were obtained concerning the effects of different thermal and electrical conductivities of W and Fe in SPS process, the oxygen influence on sintering process and the diffusion of Fe and W in final materials.		
Revision No: 1	Changes:		
	Written by:	Revised by:	Approved by:
	Name: **A. Galatanu**	Name	F. Spineanu HRU – MEdC Association

Objectives

The objective was to test and optimize the sintering process for W-steel FGM as a precursor step toward a joint between W-steel FGM and W (armour) and ODSFS steel (structural) materials

Achievements

- ► The investigation performed shows that sintering of samples is possible at 1100-1400 C with moderate pressures. For an apparent morphologic gradient 2-4 thin layers toward each margin composition are necessary.
- ► EDX and SEM results show that Fe diffuses more in W than W in Fe. Also we observed that oxygen is more present in W rich layers.
- ► We have also tested and obtained concluding proofs concerning the possibility to join steel plates (steel to steel) and W plates (W to W) using the SPS equipment.
- ► Finally, we also successfully tested the hot press procedures to consolidate W fibbers composites realized by the IPP Garching.

Shortcomings

No tests performed with EFDA certified materials which were not available.

Conclusions and General perspectives

The investigation of process parameters and preparation routes for W-steel FGM performed has lead to SPS process optimization.
The present results will contribute to the development of material science and advanced materials for DEMO. The information and know-how obtained will be a start point for further work concerning property gradient joint between W-Eurofer by unconventional co-sintering.

References (to Conference paper/poster, Meeting, Publication)

EFDA MAT-WWALLOY Group meeting San Sebastian, Spain, 28th June - 2nd July 2010.