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CEA developments of new ferritic ODS alloys for nuclear applications

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ABSTRACT

During the last fifteen years, CEA has acquired much experience in the control of the microstructure and the mechanical properties of ODS alloys for nuclear applications. Each major step of the production process has been studied to get the best compromise for the fabrication route of ODS materials. From this scientific background, two new Fe–13/18CrWTi ferritic ODS alloys have been designed to meet the needs of the fusion or GEN-IV programs. These new materials have been investigated at a semi- industrial scale with different industrial partners and consolidated as small plates.

The aim of this paper is to present the recent CEA developments on ODS materials, and to show the first results obtained on the Fe–18Cr1WTi new ferritic ODS alloy. The fabrication route for these new materials is presented, along with the measured mechanical properties and the preliminary microstructure characterizations. These new materials look promising for nuclear applications and are considered by CEA as reference materials for the development of new ODS alloys.

1. Introduction

Advanced nuclear energy systems require improved cladding and core structural materials. The requirements for fusion reactors, sodium fast reactors (SFR), very-high temperature reactors (VHTR), super critical water reactors (SCWR) or other GEN IV nuclear energy systems are different but generic development can be considered for the materials. Due to their high creep rupture strength and excellent swelling resistance, ferritic/martensitic oxide dispersion strengthened (ODS) materials can be used in several types of reactors and many developments concerning this type of alloys are in progress [1–6].

CEA has an important experience in ODS materials. It has investigated, for example, the mechanical alloying [7], the consolidation process [8,9], the control of the texture [10] and the characterization of the nano-clusters in the material [11]. For the cladding tubes of sodium fast reactors, ODS materials are good candidates and CEA has decided to develop new ferritic ODS materials. These developments are mainly dedicated to the SFR program but these new Fe–13/18CrWTi ODS materials could be adapted for fusion or other GEN IV reactors.

2. Design and fabrication route of the new ODS ferritic materials for sodium fast reactors

The assessment of these new ferritic ODS materials for cladding tubes for SFRs is in progress. A bcc structure (ferritic or martensitic) was chosen. It is known to perform well under irradiation and to avoid the swelling problems which can be met in the austenitic steels. The choice of high chromium ferritic ODS material results from different compromises. An ODS material, martensitic or ferritic, can exhibit excellent creep properties and both types of material could be retained for the application. For application at temperatures below 800 °C martensitic steels can be used but at higher temperature they exhibit a phase transformation. That is not the case for high chromium ferritic ODS materials which can be used at temperatures in excess of 1100 °C. The microstructure of a martensitic steel is usually isotropic with a low ductile to brittle transition temperature (DBTT), so a Fe–9Cr martensitic material can be interesting. However, the corrosion resistance in service and especially inside the cladding tube seems correlated to the chromium content of the material. From that point of view, a ferritic material with high chromium content is preferred. A critical point could be also the spent nuclear fuel refining which requires the dissolution of the uranium or the plutonium oxide in the nitric acid. During this stage, it is important to maintain the integrity of the cladding as much as possible. High chromium alloys are then of interest to resist to the corrosion by nitric acid. Conventional ferritic steels exhibit generally higher DBTT compared to martensitic

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Table 1
Chemical composition of the ODS materials from the powder after mechanical alloying.

Material	Fe	Cr	W	Ti	Mn	Si	Ni	C	N	O	Y_2O_3
Fe–13Cr1W	Bal.	12.75	1.08	0.26	0.34	0.3[a]	0.21	0.03	0.018	0.12	0.3[a]
Fe–18Cr1W	Bal.	18.05	0.95	0.26	0.31	0.3[a]	0.19	0.027	0.02[a]	0.11	0.56

[a] Expected values, not yet available.

ones. In the case of a ferritic ODS material consolidated by hot extrusion and unrecrystallized with a very fine microstructure, the DBTT can be similar to one of a good martensitic material (around −50 °C) [12]. Thus, ferritic ODS materials could display the advantages of both classes of materials. The choice was made to keep two ferritic ODS materials as references: one alloy with 13% of chromium and the other one with 18%. The other main alloying elements are standard for martensitic/ferritic steels. Table 1 presents the chemical composition of the powders of the two alloys after the mechanical alloying. The tungsten was preferred to the molybdenum due to activation properties. The final chemical compositions after the consolidation process are not yet available.

The mechanical alloying can be performed using pre-alloyed powders or elementary powders. In our case we ordered pre-alloyed powders from the Aubert & Duval Society and the mechanical alloying, to add the yttria, was performed by the Plansee Society in an attritor. It has been shown that during the mechanical alloying, there is a dissolution of the oxides, the yttrium and the oxygen are put in solid solution in the powders [7,11,13]. One 10 kg batch of each alloy was prepared and, after mechanical alloying, the powders were sieved at 150 μm. The precipitation of the nano-clusters occurs during the consolidation process. This process also controls the final microstructure and to get very fine structures it is necessary to use the hot extrusion process instead of the hot isostatic pressure. The aim of these developments is to produce ODS tubes as cladding materials. The fabrication route for tubes has to be determined carefully and so, before going to a finished product which will be difficult to produce and characterize, thin plates about 4 mm thick, 30 mm wide and 2000 mm long were made at CEA/SRMA. These materials were hot extruded at 1100 °C, hot rolled 20% at 650 °C and annealed for 1 h at 1050 °C. For basic studies this type of semi-final products are very convenient because they permit machine tensile and small impact testing of specimens in different directions in order to study the anisotropy of the material.

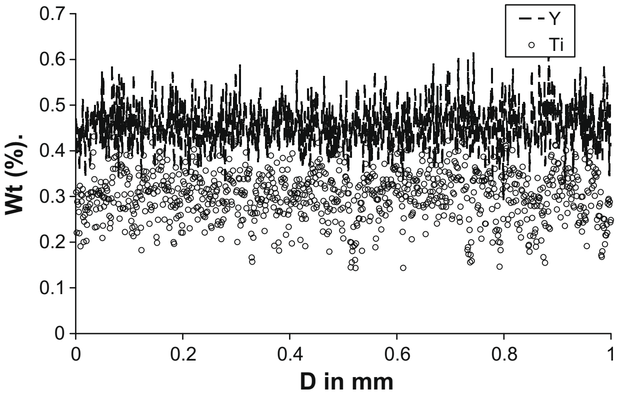

Fig. 1. Microprobe analysis of the Fe–18Cr1W ODS alloy showing profiles of the yttrium and titanium within the matrix.

3. Characterization of the microstructure and the mechanical properties of the new Fe–18CrWTi ferritic ODS alloy

The main reasons for the characterization of the microstructure are to check the homogeneity of the material, to verify the size of the grains or laths and to confirm the presence of an homogeneous dispersion of nano-clusters. Different line scans using a standard wavelength dispersive spectrometer (WDS) micro-probe, were

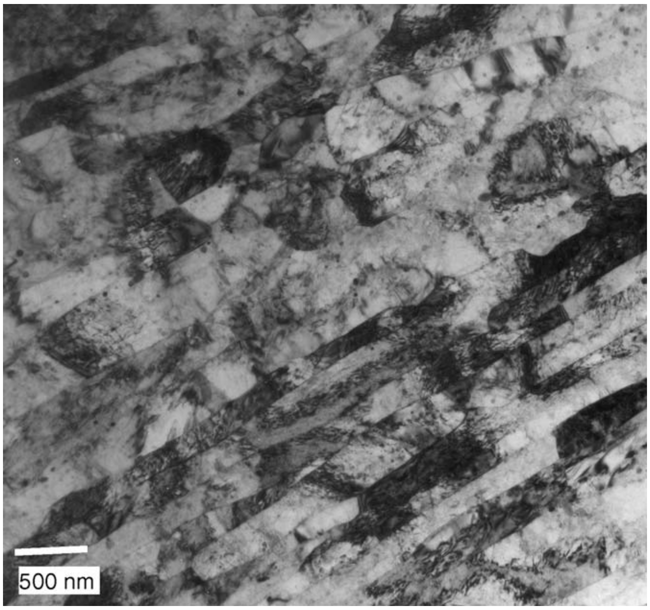

Fig. 2. Microstructure of the Fe–18Cr1W ODS material from the TEM micrograph.

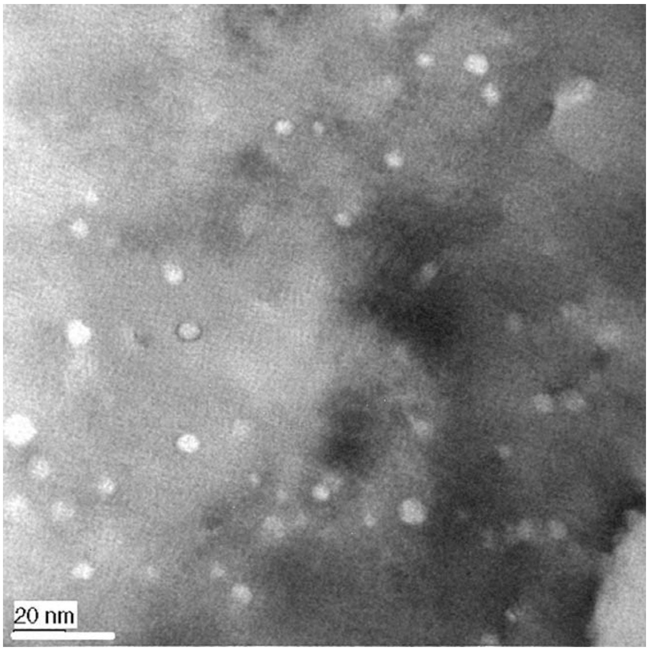

Fig. 3. Nano-clusters within the Fe–18Cr1W ODS material from the TEM micrograph.

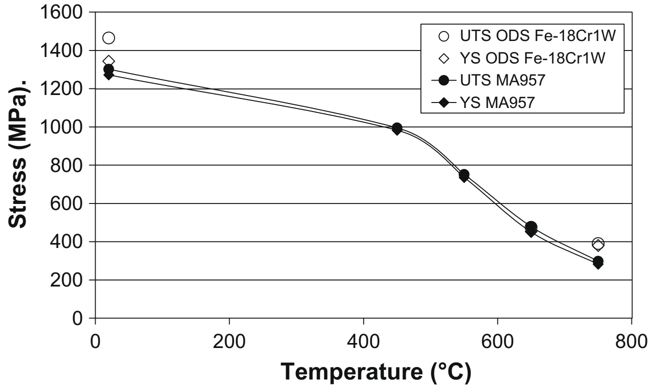

Fig. 4. Yield strength and ultimate tensile strength of the ODS Fe–18Cr1W compared to those of the MA957 alloy.

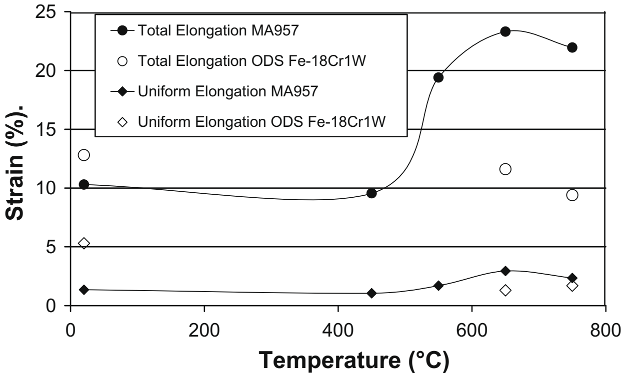

Fig. 5. Total and uniform elongation of the ODS Fe–18Cr1W compared to those of the MA957 alloy.

performed on the alloys. Fig. 1 shows the profiles of the yttrium and titanium in the Fe–18Cr1W ODS material. Despite some fluctuations, they are homogenous at this scale and it illustrates the good quality of the mechanical alloying performed by Plansee. The analysis step was 1 μm and no depleted zones were observed as is usual when the mechanical alloying is not sufficiently efficient. The examinations by transmission electron microscopy (TEM) were performed using a Jeol 2010 F (200 kV) microscope with a field emission gun. Figs. 2 and 3 present the TEM micrographs of the Fe–18Cr1W ODS material. The microstructure is made of very fine grains or "fibres" which are elongated along the hot extrusion direction. Different classes of oxides are observed, the size of the largest is few hundred nanometers whereas nano-clusters are also observed all around the material (see Fig. 3). They are spherical with diameters smaller than 10 nm.

Mechanical property investigations of both alloys are in progress. Only the tensile properties of the Fe–18Cr1W ODS alloy are presented here in Figs. 4 and 5 and in Table 2. The tensile specimens were thin plates of 2 mm width and 8 mm gauge length with a thickness of 1 mm. They were machined parallel to the extrusion direction. The tensile tests were performed under air with a strain rate of $7 \times 10^{-4}\ s^{-1}$ and the test temperatures ranged from 20 to 750 °C. The tensile properties are compared to the ones of the MA957 ODS alloy (Fe–14Cr–1Ti–0.3Mo–0.25Y_2O_3) hot extruded and drawn by 25%.

Table 2
Yield strength and ultimate tensile strength (MPa) of the MA957 and Fe–18Cr1W alloys at 650 °C.

	YS	UTS
MA957	450	479
Fe–18Cr1W	453	475

The behaviour of the Fe–18Cr1W ODS is similar to the one of the MA957. The tensile strength is very high at room temperature and reaches almost 400 MPa at 750 °C. The ductility reaches a few percent at high temperature which is usual with this type of material.

4. Conclusion

CEA has decided to develop new high chromium ferritic ODS materials for high temperature nuclear applications. The chemical composition of these new Fe–13/18CrWTi ODS can be slightly modified to reach the specifications of the materials used for fusion reactors. These materials were investigated in collaboration with A&D and Plansee with a consolidation performed at CEA/SRMA at a semi-industrial scale. The production was near 10 kg per batch. Preliminary characterizations of the materials are encouraging. The microstructure is homogeneous and constituted by very fine grains elongated in the hot extrusion direction. Nano-clusters, not yet identified, are observed within the matrix. The mechanical properties show a high tensile strength up to 750 °C with the expected ductility for this type of material. The assessment of these new materials for nuclear applications is in progress. Different studies concerning the microstructure, the workability of the material to form thin tubes or plates and the mechanical behaviour (tenacity, creep, etc.) will start in 2008. Corrosion tests, welding studies and irradiations with tensile and impact specimens in Phenix reactor up to 17 dpa and between 380 °C and 560 °C are already planned for 2008.

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