Hyperfine Interact
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Mössbauer study of EUROFER and VVER steel reactor materials

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Abstract ^{57}Fe Mössbauer spectroscopy and X-ray diffractometry were used to study EUROFER or VVER ferritic reactor steels mechanically alloyed with TaC or NbC. Significant changes were found in the Mössbauer spectra and in the corresponding hyperfine field distributions between the ball milled pure steel and that alloyed with TaC or NbC. Spectral differences were also found in the case of use of same carbides with different origin, too. The observed spectral changes as an effect of ball milling of the reactor material steels with carbides can be associated with change in short range order of the constituents of steel.

Keywords ^{57}Fe Mössbauer spectroscopy · X-ray diffractometry · EUROFER · 15H2MFA · Steel · Reactor material

1 Introduction

Future nuclear (fission or fusion) reactors are designed to operate at significantly higher temperature (>500 °C) than the present fleet of light water reactors, in

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Table 1 Milling conditions used for alloy mixing in the high energy planetary ball mill

Ball mill model: Fritsch Pulverisette 7	Total ball mass: 150 g
Milling time: 5 h	Fluid: Cyclohexane
Ball to powder mass ratio: 15:1	Grinding media: Hardmetal (WC-Co)
Ball diameters: 15 mm	

order to meet sustainability requirements. Nanoscale modifications of the existing ferritic steels offer the best opportunity to improve the radiation resistance and allowable operating temperature window for structures. Although capability of steels has been improved in the past by thermomechanical treatment, utilization of powder metallurgy provides more controlled microstructure and tailored properties in terms of strength and radiation resistance [1]. For further improvement of the superior mechanical properties, fundamental understanding of the influence of composition and heat treatment on the microstructural transformations is necessary.

The aim of our study was to investigate the effect of the different carbide (NbC and TaC) particles on the structure of two different ferritic steels used as reactor materials via a powder metallurgy process. For the characterization of the steels ^{57}Fe Mössbauer spectroscopy and XRD were applied.

2 Experimental

Ferritic steels bars, EUROFER (Fe-0.11C-9Cr-1.1W from Villares Metals) and VVER (Fe-0.16C-2.7Cr-0.7Mo, also known as 15H2MFA type; the pressure vessel material of VVER440 reactors), were supplied to produce chips through an end-mill machine with a cutting speed of 28 mm/min, pass of 0.02 mm and rotation velocity of 64 rpm without refrigerant fluid. A high energy planetary ball mill was used to produce chips in 10 min. Then a second milling process was used to produce composite powders of these two kinds of metals with 3 wt. % of Niobium Carbide (from Alfa Aesar Company with particle size <10 μm) and 3 wt. % of Tantalum Carbide (from Alfa Aesar Company and made at Federal University of Rio Grande do Norte with particle size <10 μm). Table 1 shows the milling conditions:

Powder X-ray diffractograms of the samples were measured by a computer controlled DRON-2 X-ray diffractometer using Co_{Ka} radiation and a β filter. The diffractograms were recorded between 5° and 120° in 2θ, with a goniometer speed of 0.2° min^{-1} at room temperature. The evaluation of the XRD patterns was made by the EXRAY code. For identification of the phases the ASTM X-ray diffraction data were used.

^{57}Fe Mössbauer spectra of powder samples were recorded in transmission geometry with conventional Mössbauer spectrometers (WISSEL, KFKI) working in constant acceleration mode. The γ-rays were provided by a 3×10^9 Bq ^{57}Co/Rh source. The measurements were performed at 300 K and sometimes at 78 K. Isomer shifts are given relative to α-iron. The Mössbauer spectra were analyzed by least-square fitting of Lorentzian lines by the help of the MOSSWINN code.

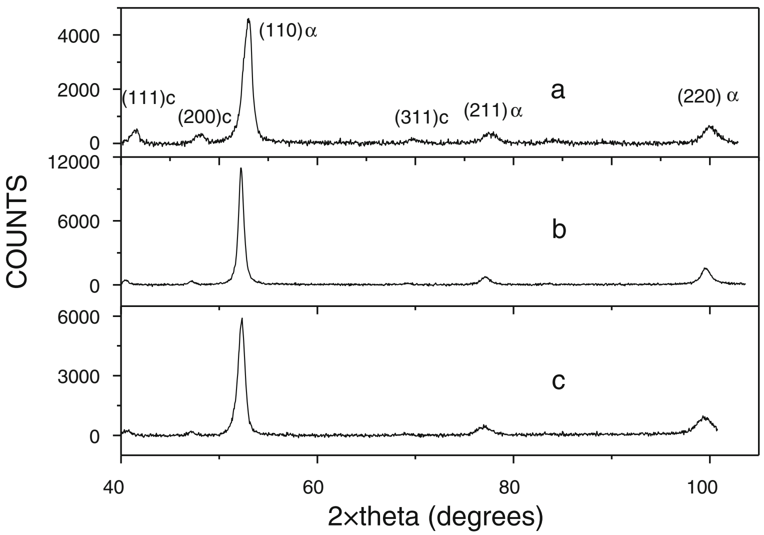

Fig. 1 XRD patterns of the ball milled steel powders **a** VVER+TaC, **b** VVER+NbC, **c** EUROFER +NbC

3 Results and discussion

Typical XRD patterns of the fine powder samples (Fig. 1) show only the reflections of ferritic steels and main lines of the corresponding TaC and NbC carbides.

Typical ^{57}Fe Mössbauer spectra, taken at room temperature, of commercial and home made TaC containing ball milled steels (Fig. 2) show magnetically split patters. It is clear that the fingerprint of EUROFER and VVER ball milled samples can be diagnostically identified. This is based, first of all, on the effect of alloying elements on the hyperfine fields of iron atoms being in different coordination environments, depending on the actual composition of the steel. We have found small but significant differences both between the spectra and between the hyperfine field distributions of the samples milled under the same conditions with carbides of different origins (i.e., commercial or home made). Our results are consistent with microhardness tests showing that EUROFER reinforced with commercial TaC is harder than that reinforced with home made TaC [2].

The model dependent evaluation revealed that the spectra of VVER steel samples can be decomposed into three sextets while the spectral envelope of EUROFER samples can be fit with four sextets. In the case of the pure EUROFER ball milled steel the relative occurrences of the spectral components and of the components of hyperfine field distributions (Fig. 3a) are not in exact correspondence with those calculated taking into account the multinomial distribution of alloying elements [4, 5]. This is mainly due to the creation of several nonregular or defected Fe microenvironments by the ball milling. Even though, it seems, that the model based on the multinomial distribution of the alloying elements can describe the spectral changes we observed upon mechanical alloying of this steel with commercial TaC. The well observable changes in the relative occurrences of both spectral and hyperfine field distribution components (see e.g. the decrease in the relative intensity of component

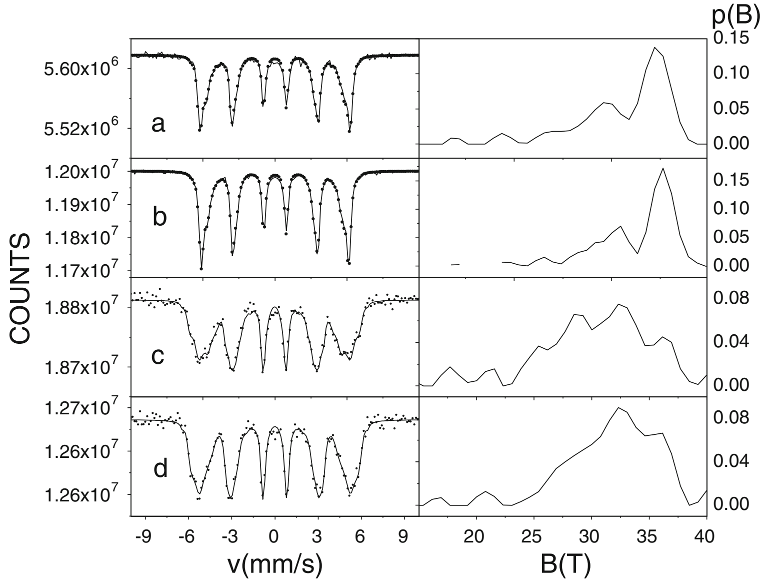

Fig. 2 Typical room temperature ^{57}Fe Mössbauer spectra and the corresponding hyperfine field distributions of different origin TaC containing ball milled steel powders **a** VVER+ commercial TaC, **b** VVER+ home made TaC, **c** EUROFER+ commercial TaC and **d** EUROFER+ home made TaC

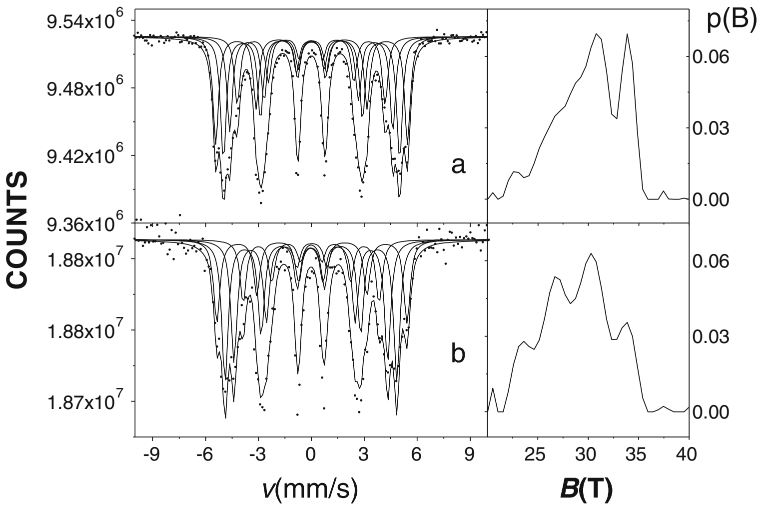

Fig. 3 ^{57}Fe Mössbauer spectra (decomposed into four sextets) and hyperfine field distributions of pure EUROFER ball milled steel **a** and its state after mechanical alloying with commercial TaC **b**

around 33 T and the increase in the relative intensity of component around 27 T) (Fig. 3b) of the steel ball milled with commercial TaC in comparison with those (Fig. 3a) of pure ball milled steel can be understood as changes of the number of alloying elements in the iron coordination spheres, corresponding well due to the change in the concentration of alloying elements in the frame of the model. These changes can be associated with an increase of the concentration of alloying elements in the steel. This may indicate that some amount of Ta may be incorporated in the steel matrix under the applied ball milling non-equilibrium conditions. This may be supported by the XRD results [3], which showed much less relative occurrence of carbides after 5 h ball milling than at the beginning of the milling, however, these XRD results can also be explained by lattice distortions, grain refinements and decreasing the crystallite size.

The observed spectral changes as an effect of ball milling of the reactor material steels with carbides can be associated with change in short range order of the constituents of steel. The lack of matching with multinomial distribution models confirms the presence of non-equilibrium systems with in-grain heterogeneity in the concentrations of alloying elements.

4 Conclusions

TaC or NbC were successfully alloyed into EUROFER or VVER ferritic reactor steels by ball milling method. Significant differences were found between the hyperfine field distributions derived from ^{57}Fe Mössbauer spectra of ball milled pure steels and those alloyed with TaC or NbC carbides. These can be associated with changes in the short range order of the steels upon mechanical alloying with carbides. The effect of the incorporation of the commercial and home made carbides on the short range order of steels were found to be slightly different.

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