ODS steel raw material local structure analysis using X-ray absorption spectroscopy

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Abstract. Oxide dispersion strengthened (ODS) steels are promising materials for fusion power reactors, concentrated solar power plants, jet engines, chemical reactors as well as for hydrogen production from thermolysis of water. In this study we used X-ray absorption spectroscopy at the Fe and Cr K-edges as a tool to get insight into the local structure of ferritic and austenitic ODS steels around Fe and Cr atoms and its transformation during mechanical alloying process. Using the analysis of X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) we found that for austenitic samples a transformation of ferritic steel to austenitic steel is detectable after 10 hours of milling and proceeds till 40 hours of milling; only small amount of α-phase remains after 80 hours of milling. We found that the Cr K-edge EXAFS can be used to observe distortions inside the material and to get an impression on the formation of chromium clusters. In-situ EXAFS experiments offer a reliable method to investigate the ferritic to austenitic transformation.

1. Introduction

Oxide dispersion strengthened (ODS) steels have exceptional thermal conductivity and low thermal expansion while demonstrating high-temperature creep, corrosion and irradiation resistance. Therefore, they have a great potential for an application as structural materials for concentrated solar power plants, jet engines, chemical reactors as well as for hydrogen production from thermolysis of water. Previous developments were focused mainly on nanostructured ODS ferritic (Fe-Cr alloys) steels with very promising applications in, e.g., fusion power reactors up to about 550°C [1].

Recently the use of the austenitic ODS steels for high temperature fusion applications and concentrated solar power plants has been suggested by the group from Karlsruhe Institute of Technology (KIT) in [2]. It is expected that the dispersion of nanoscaled oxide particles with still unknown (x)Y₂O₃-(1-x)TiO₂ structure will possibly suppress the gas bubble growth and related void swelling under neutron irradiation [3, 4]. In addition ODS particles could reduce irradiation hardening and increase high temperature resistance up to 800°C. Moreover, austenitic steels are non-magnetic and do not suffer from a ductile-brittle-transition, which are typical drawbacks of ferritic/martensitic steels [5].

ODS steels have been studied by different characterization techniques, including transmission electron microscopy (TEM), atom probe tomography (APT) and small angle neutron scattering...
Table 1. Nominal chemical compositions of the ferritic (F) and austenitic (A) samples with different milling time.

| Sample | Milling time (h) | Fe  | Cr  | Ni  | W  | Ti  | Y  |
|--------|------------------|-----|-----|-----|----|-----|----|
| F0h    | 0                | 85.7| 13  | -   | 1.0| 0.3 | -  |
| F40h   | 40               | 78.45| 20  | -   | 0.9| 0.25| 0.4|
| A40h   | 40               | 69.8| 16  | 13  | 0.8| 0.1 | 0.3|

[6]. The use of both TEM and APT is strongly restricted to a limited number of particles or by a very small probed region as well as by the challenging requirements for sample preparation. In contrast, synchrotron radiation X-ray absorption spectroscopy (XAS) provides a practical way to study elements of matrix and minority, giving unique and direct information on their chemical and physical state in the sample [7, 8].

The aim of this work was to study powders of ferritic and austenitic ODS steels produced by a mechanical alloying process with X-ray absorption spectroscopy, which gives insight into local structure around Fe and Cr atoms. We have studied the dependence of the local structure on the time of mechanical alloying as well as on the thermal treatment.

2. Experimental and data analysis

In our study we used two groups of samples: ferritic and austenitic ODS steels, which are further labeled with F and A, respectively.

All samples were prepared using a mechanical alloying process in a water-cooled attritor ball mill (Zoz CM02) in argon atmosphere using Zr$_2$O$_3$ as a grinding media. A ball-to-powder ratio (BPR) of 10:1 was chosen. The milling time was in the range of 0 to 40 hours for ferritic steels and from 0 to 80 hours for austenitic steels. After milling (i.e. 10, 40 or 80 hours), the powder was taken out of the container and stored in an Argon-filled glove-box. All powders were packed in argon environment and thus transported to the synchrotron for XAS measurements.

A prealloy with a chemical composition of FeCr13W1T10.3 (F-prealloy, F0h) was used to produce a ferritic ODS steel. Hence, Fe$_3$Y powder was added to this powder and mechanically alloyed for 40 hours to produce the F samples (e.g. F40h). To produce the A-samples, a two-step process is required. In the first step Y$_2$O$_3$ with particle size about 1 μm was added to F-prealloy instead of Fe$_3$Y and milled for 40 hours (A-prealloy, A0h). Afterwards pure nickel powder was added and a subsequent milling treatment was carried out to produce A samples (e.g. A40h for sample mechanically alloyed for 40 hours). The initial particle size of the the A0h is important for the ferrit-austenite transition. With a bigger particle size, the probability of been hit by the grinding medium and consequent mechanical alloying with nickel is increased. Thus assumingly leads to a faster transition of bigger ferrite particles into austenite. For this reason the particle size of ferrite particles used for mechanical alloying with nickel should be uniform and smaller than 150 μm. The nominal chemical composition of the samples given in Table 1 does not change during the mechanically alloying process, e.g. the composition of the samples A0h, A10h, A20h, A40h, and A80h is the same. Please note that the titanium was not added during mechanical alloying, it was present already in the F-prealloy.

The Fe and Cr K-edges x-ray absorption spectra were measured in transmission mode at the ELETTRA storage ring (Trieste, Italy) XAFS bending-magnet beamline [9] in the temperature range from 20°C to 1000°C. The x-ray radiation was monochromatized by a 40% detuned Si(111) double-crystal monochromator, and the beam intensity was measured using two ionization chambers filled with argon and krypton gases. The L'Aquila-Camerino vacuum furnace [9] was used for high temperature measurements. The samples for high temperature measurements
were prepared by pressing the proper amount of the ODS powder well mixed with boron nitride powder into a pellet. The proper amount of the ODS powder was deposited on the Millipore filter for room temperature measurements. In both cases we have paid special attention to sample homogeneity and thickness to optimum conditions at the Fe or Cr K-edge.

The X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) $\chi(k)$ were extracted and analyzed following the conventional procedure [7, 8] using the EDA software package [10]. Theoretical backscattering amplitude and phase-shifts functions, employed in the best-fit EXAFS analysis, were calculated using ab-initio FEFF8 code [11].

3. Results and discussion
3.1. X-ray absorption near edge structure (XANES)
The Fe K-edge XANES spectra are shown in Figs. 1 and 2 and clearly reveal the phase of the matrix. Austenitic steels undergo a phase transition after 40h of milling, which is best seen in the XANES spectra in the region of around 7131 eV, where single white line peak characteristic for $\alpha$ phase splits into two peaks (at about 7129 and 7135 eV) characteristic for $\gamma$ phase. There are no significant changes in the spectra of the austenitic samples with milling times of 40 hours and 80 hours.

At the same time there is no phase transition in the F-steels after 40 hours of milling as seen in Fig. 1. All the features before and after the absorption edge correspond to the reference Fe K-edge XANES spectrum of iron foil.

3.2. Extended X-ray absorption fine structure (EXAFS)
We found that the Fe and Cr K-edges EXAFS spectra of austenitic steel samples show significant dependence on the treatment procedure, therefore we intensified our efforts in studying in detail their behaviour.

The quality of the Fe K-edge EXAFS spectra (Fig. 3) is very good. For the A-series of samples a noticeable change with an increase of the mechanical alloying time can be observed in the EXAFS spectra and respectively in their Fourier transform (Fig. 3). As one can notice, a reduction of the signal amplitude occurs with an increasing of milling time, which is caused by the increase of the disorder in the steel matrix. The second effect is that there are significant structural changes appearing after 40 hours of milling, which are best observed in the regions of 4.5-5.5 Å$^{-1}$ in $k$-space and of 3-6 Å in $R$-space.
Figure 3. The Fe K-edge EXAFS spectra $\chi(k)k^2$ and their Fourier transforms (phase uncorrected) of prealloy (F0) and austenitic samples with mechanical alloying time from 10 to 80 hours.

To study these phenomena in more details we have reconstructed the radial distribution functions (RDFs) for the first coordination shell of iron from the EXAFS spectra using advanced approach described in [10]. The advantages of this method are that it is model free and does not require any assumption on the shape of the RDF. Note that this method allows one to analyse the coordination shells where only single-scattering contributions are present. In our case the method can be used for the analysis of peaks in FTs up to about 3 Å in Fig. 3. This $R$-space range corresponds to 14 atoms in two nearest coordination shells (at about 2.49 Å and 2.87 Å), which appear as a single peak in the Fourier transform, for the pure $\alpha$-phase and to 12 atoms in the first coordination shell for the pure $\gamma$-phase [12].

As one can see in Fig. 4, the reconstructed RDFs confirm findings of the XANES analysis. The second peak at about 2.85 Å decreases strongly for longer milling times. At the same time it does not disappear completely, indicating that a small amount of $\alpha$-phase still remains even after 80 hours of milling, while the majority of the material is transformed into austenitic phase.

Similar results have been obtained from the analysis of the Cr K-edge EXAFS spectra (Fig. 5). Chromium atoms follow the transformation of the matrix, but their local environment is more...
The reconstructed RDFs for the sample A40h (austenitic sample milled for 40 hours), which was heated from 20°C to 1000°C and then cooled back down to 20°C, are shown in Fig. 6. As expected, the RDF peaks become broader during heating due to an increase of thermal disorder. One can observe that A40h sample does not return to the original structure after the complete heat treatment: the final RDF looks more pronounced, and the amount of the $\alpha$-phase indicated by the second peak in the RDF at about 2.85 Å is much smaller than before treatment, which is a clear indication that the material becomes more ordered, and the $\gamma$-phase becomes dominant. This has also been observed by [13, 14].

The conventional analysis, based on the best fit of the first coordination shell EXAFS signals within the single-scattering approximation, revealed more details about the phase transformations (Fig. 7). As one can notice, structural transformation starts at 600°C and is fully finished above 800°C. This transformation is irreversible, because when the samples are cooled back to 20°C the structure does not return into the starting state, but stays in the same phase as at the high temperature.

4. Conclusions

The nanostructure of ferritic and austenitic ODS steels was studied at the Fe and Cr K-edges X-ray absorption spectroscopy as a function of milling time. Also in-situ EXAFS measurements were performed upon thermal treatment of austenitic ODS samples up to 1000°C to get insights about the local structure around Fe and Cr atoms and their transformation in the presence of ODS precipitates.

We found that the Cr K-edge EXAFS can be used to observe distortions inside the material and to get an impression on the formation of chromium clusters.

Before XAS investigation the necessary milling time was uncertain and needed to be determined. The authors sought for the shortest milling time to be economically efficient and the longest time to receive a homogenous distribution of all elements. Also the amorphization process described by [15] should be investigated. After the milling process the mechanically alloyed powder is fabricated via extrusion or hot isostatic pressing to a near-net-shape geometry.
For austenitic samples a transformation of ferritic steel powders to the fcc (austenitic) structure after 10 hours of milling was detected, and its amount increased upon milling up to 40 hours. Between 40 and 80 hours only a small shift of the Fe K-edge was recognizable in the XANES spectra, indicating that the ferritic/austenitic ratio is moving towards an equilibrium ratio during milling. A small amount of α-phase was detected even after a milling time of 80 hours and for a chemical composition which favors the formation of a complete austenitic phase.

To get deeper insights to subsequent fabrication process and the optimal temperature we performed in-situ experiments. A40h was chosen, due to its complete mechanical alloying, which is revealed on the basics of no peak shift compared to A80h in Figs. 2, 4 and 5. The results shown in Figs. 6 and 7 show a complete ferrite to austenite transition after heating up to 900 K. These heating experiments and their results simulate the fabrication process which follows the mechanical alloying and reveal a uniform austenitic steel in a near-net-shape geometry after 40 h of milling time.

So in-situ EXAFS experiments offer a reliable method to investigate the ferritic to austenitic transformation in consideration of pinning effects [4, 16, 17], due to ODS precipitates.

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