NDT study of oxide dispersion strengthened steels

Vladimir Krsjak¹, Zoltan Szaraz¹, Jarmila Degmova² and Peter Hähner¹

¹Joint Research Centre, Institute for Energy, European Commission, P.O. Box 2, 1755 ZG Petten, Netherlands
²Slovak University of Technology, FEI, Ilkovicova 3, 81219 Bratislava, Slovakia

E-mail: vladimir.krsjak@ec.europa.eu

Abstract. Various oxide dispersion strengthened (ODS) steels (PM2000, MA956, ODM751 and ODS Eurofer) have been investigated using positron annihilation lifetime spectroscopy. Preliminary characterization of the vacancy type defects and the yttria nanoparticles are reported in this paper. The interpretation of the experimental data considers also the results of magnetic Barkhausen noise (BN) measurements as well as SEM and TEM investigations. Significant differences due to the presence of the yttria oxides (namely Y2O3) were observed in the studied materials in comparison to conventional ferritic/martensitic steels (e.g. Eurofer). Higher positron mean lifetime in ODS steels is, however, not only due to the presence of dispersoids, but also a result of vacancy agglomeration (clusters of 6-8 vacancies) which have been confirmed in recrystallised ODM751 and MA956 materials. On the other hand, positron trapping at dislocations was observed in the as-extruded ODS Eurofer in contrast to the other, recrystallised, materials where the high temperature treatment had led to the static recovery of these defects. It is suggested that some defects which are present (dislocations, vacancy clusters and dispersoids) and affect positron trapping in the materials are also important pinning sites for the magnetic domains. This is reflected by a shift of the signal peak in the BN spectra. The present complementary study provides more comprehensive information about materials microstructure and can support the interpretation of the physical/mechanical testing results (hardness, fracture mechanics etc.) obtained on these materials.

1. Introduction

The performance of currently available classes of structural materials qualified for various applications in present nuclear reactors is insufficient for many applications envisaged for next generation nuclear systems (so-called GenIV), which is why extensive R&D is being carried out into the development and qualification of new structural materials. Higher temperatures and fuel burn-up, longer service lifetimes, as well as new coolant environments represent important material issues for the safe and economic operation of GenIV reactor systems. Good radiation and corrosion resistance as well as improved creep properties in an extended range of temperatures have been achieved with ferritic steels strengthened by dispersion of nano-sized yttria particles. Nevertheless, the particular effects of the mechanical alloying process and of the specific service conditions (neutron flux and fluence, thermo-mechanical loads, chemical environment of the coolant etc.) on the performance of these oxide dispersion strengthened (ODS) steels need further qualification.
Positron annihilation lifetime spectroscopy (PALS) is a technique which is widely used in the field of radiation embrittlement studies [1, 2]. Its unique sensitivity to radiation induced defects provides information which cannot be obtained by any other technique in a non-destructive way. Published studies on the ODS steels show the capability of positron annihilation spectroscopy techniques to elucidate the nature, localization and thermal stability of the defects, which are responsible for the dimensional (swelling) and the mechanical properties stability under neutron irradiation [3].

Barkhausen Noise (BN) analysis is based on the inductive measurement of a noise-like signal, which is associated with the stochastic re-arrangement of magnetic domains, and generated when a varying magnetic field is applied to a ferromagnetic sample. This technique is known to be very sensitive to microstructural features such as precipitates and lattice defects in materials, because it probes the discontinuous motion of domain walls caused by the presence of any type of pinning centers [4]. Since many of these defects (dislocations, grain boundaries, voids etc.) are also possible trapping sites for positrons, we can expect a correlation to exist with the findings by PALS.

An application of both described techniques in a common study of iron-based model alloys has been published earlier [5, 6], but without specific interpretation of the results obtained. The present paper proposes a possible interpretation of particular characteristics obtained from the ODS steels under investigation and confirms the feasibility of the combination of these techniques for monitoring microstructural changes caused by service exposure (radiation and/or thermal treatment).

2. Experimental

Three commercial ferritic ODS steels (PM2000, MA956 and ODM751) and an ODS variant of ferritic-martensitic Eurofer steel were chosen for this complementary study. Nominal chemical compositions of the materials are compiled in the Table 1. The ODS alloys were produced by mechanical alloying, i.e., matrix powders were mixed and milled together with yttria particles to form solid solutions with uniform dispersion of oxide particles, and the mixtures were then consolidated using hot isostatic pressing and extrusion. The PM2000 and MA956 alloys were supplied as rods in the fully recrystallised condition for improved creep strength. The recrystallisation heat treatment resulted in a coarse columnar grain structure. The ODM751 alloy was received as tubes in recrystallised form as well, whereas the as-extruded ODS Eurofer alloy exhibited a fine-grained microstructure. The distribution and the sizes of the oxide particles were investigated by SEM and TEM. The diameter of the oxide particles was found to vary from 10 to 70 nm.

| Material   | Manufacturer | Cr  | Al  | Ti  | W   | Mn | Mo | C | Y₂O₃ |
|------------|--------------|-----|-----|-----|-----|----|----|---|------|
| PM2000     | Plansee      | 20  | 5.5 | 0.3 | -   | -  | -  | 0.01 | 0.5  |
| MA956      | Incoloy      | 20  | 4.5 | 0.4 | -   | -  | -  | 0.04 | 0.5  |
| ODM 751    | Dour Metal   | 16  | 4.5 | 0.6 | -   | -  | 1.5| 0.01 | 0.5  |
| ODS Eurofer| Plansee      | 8.9 | -   | -   | 1.1 | 0.4| -  | 0.07 | 0.2  |

Microstructural studies often face the problem of variations in the microstructure of different samples, due to not fully uniform fabrication, heat treatment or irradiation processes. An advantage of non-destructive testing (NDT) resides in the fact that specific information can be provided by different experimental techniques applied on the same sample. This offers the opportunity to correlate measurements from different experimental techniques while making sure that the results refer to identical conditions of the material microstructure. With respect to this, the present sample size was chosen as 10x10x0.5 mm³, which is a typical size for PALS, but also suitable for a number of other NDT techniques including BN measurements.
PALS measurements were performed in conventional fast-slow setup of the apparatus, with the use of BaF$_2$ scintillator detectors and Ortec electronics. The used $^{22}$Na positron source with an activity of 3.6 MBq and encapsulated in kapton foil, enabled quick measurements (~ 4 hours) with reasonable FWHM (< 220ps with the used detectors) and source contribution (~ 18%). Analytical data processing was performed using the LT 9.0 program and two-components decomposition of the spectra.

Magnetic BN analyses have been performed using the commercial BN analyzer Stresstech Rollscan200 with an external magnetizing unit and pen-type sensor with ferrite core diameter of 3mm. Magnetizing fields were induced by an alternating current of 1A amplitude and frequency of 10Hz. The picked-up signals were amplified and filtered to discriminate frequencies below 500Hz. Signals were acquired and analyzed by ViewScan software from Stresstech. The BN parameters were determined by averaging 10 measurements (five in longitudinal direction and five in transverse direction to the material extrusion). To minimize the effect of residual magnetism, individual samples were demagnetized after each measurement.

3. Results and discussion

3.1. Positron annihilation lifetime spectroscopy

Two-component decomposition (Table 2) of the positron lifetime spectra was found to be most suitable for all materials studied. With this approach we can attribute the first component to the material bulk properties (reduced due to positron trapping at defects) while the second component comes from positrons trapped in defects. Higher $\tau_1$ value in the as-extruded ODS Eurofer is attributed to the presence of dislocations, as high dislocation densities are common for the steels produced by mechanical alloying [7]. High temperature recrystallization leads to the recovered microstructure with large, almost dislocation free grains which results in shorter positron mean lifetime (MLT).

The effect of the yttria particles on the positron lifetime can be seen in a considerably higher (> 10%) MLT values in comparison to conventional (non-ODS) ferritic/martensitic steels reported earlier [8]. The relatively small content of yttria oxides plays a role here due to significant positron affinity of yttrium (-5.31). Thus, for example, a positron would be trapped in a pure Y phase in an iron (positron affinity = -3.84) matrix with a binding energy of 1.5eV [9]. Positron lifetime in the Y$_2$O$_3$ bulk, experimentally reported as 239ps [10], together with the positron lifetime in small vacancy clusters, is described by the component $\tau_2$. As can be seen in Fig.1, there is an overlap of the positron lifetimes in those defects, which is why the different trapping sites cannot be unambiguously distinguished. Nevertheless, some specific microstructural techniques (e.g. small angle neutron scattering, SANS) can provide additional information about the size, distribution and volume fraction of yttria nanoparticles, which may then be used as an additional input, in order to reveal the information about density and type of vacancy clusters.

| Material    | $t_1$ [ps] | $I_1$ [%] | $t_2$ [ps] | $I_2$ [%] | MLT [ps] | Annihilation rate in trapping sites [s$^{-1}$] | Trapping rate in defects [s$^{-1}$] |
|-------------|------------|-----------|------------|-----------|----------|-----------------------------------------------|-------------------------------|
| PM2000      | 79         | 45        | 226        | 55        | 160      | 4.40E+09                                      | 5.70E+09                      |
| MA956       | 78         | 47        | 246        | 53        | 167      | 4.10E+09                                      | 5.67E+09                      |
| ODM751      | 78         | 49        | 259        | 51        | 171      | 3.90E+09                                      | 5.44E+09                      |
| ODS Eurofer | 129        | 43        | 241        | 57        | 193      | 4.10E+09                                      | 6.55E+09                      |
The highest value of the $\tau_2$ component (259 ps) was found in the ODM751 steel, indicating the presence of vacancy agglomerations (6-7 vacancies) in the material. The range of the vacancy cluster sizes in the materials studied here (4-7 vacancies) is in agreement with published work of Xu et al [11], who observed similar features (4-6 vacancies) in nanocluster-strengthened ferritic steel and described the essential role of vacancies in the formation and stabilization of nanoclusters in this material. A quantitative analysis of the vacancy type defects, however, cannot be carried out without additional characterization of the yttria nanoparticles of the present ODS steels, e.g. by the SANS technique.

3.2. Magnetic Barkhausen noise measurements
The results of the BN spectra analysis are summarized in Table 3. Considering the values of signal amplitudes (signal strengths of the events described in terms of the RMS and the peak envelop height), and relative position of the peak (characteristic of the coercive field for domain wall motion), we can recognize three different types of signals. While ODS Eurofer and ODM751 steels show distinct behaviours, the other two materials, PM2000 and MA956, exhibit very similar features. We assume that this is due to the differences and commonalities in the chemical compositions of the materials (see Table 1).

![Figure 1. Measured positron lifetimes in open volume defects, together with theoretical values for different vacancy clusters (single vacancies, five- and eight- vacancy clusters, respectively, calculations for bcc Fe) and yttria oxide.](image)

**Table 3.** The results of the BN measurements on the ODS steels.

| Material    | RMS [a.u.] | Peak height [a.u.] | FWHM [ms] | Peak position [ms] |
|-------------|------------|---------------------|-----------|--------------------|
| PM2000      | 3±0.2      | 6.6±0.3             | 21.5±1.6  | 4.5±0.2            |
| MA956       | 3.1±0.4    | 6.3±0.6             | 16.9±1.8  | 4.9±0.3            |
| ODM751      | 4.2±0.3    | 9.1±0.6             | 18.3±0.9  | 6.6±0.2            |
| ODS Eurofer | 2.8±0.2    | 6.2±0.3             | 18.5±1.9  | 9.9±0.2            |
According to theory and published works [12], one can expect a decreasing BN signal amplitude and a shift of the peak to the higher values of magnetizing field, when magnetic domain wall pinning is stronger. Although the results of the BN peak and signal RMS are scattered, the comparison of recrystallized (PM2000, MA956, ODM751) and non-recrystallized (ODS Eurofer) materials indicates agreement with this assumption as regards domain wall pinning by grain boundaries. However, the higher carbon content of the ODS Eurofer can also play a role in decreasing the signal amplitude of ODS Eurofer [12].

Recalling that a stronger pinning of the magnetic domain walls induced by the presence of defects in the microstructure, is revealed by a shift of the signal peak to higher values of the coercive magnetic fields (here recorded as a time shift of the peak position), the BN peak position can therefore serve as a quantitative feature of the defects acting as pinning sites for magnetic domains. It is natural to assume that some of these defects can act as trapping sites for positrons as well, and therefore a correlation with positron lifetime technique is suggested. The overall positron trapping kinetics in a material is characterised by the positron mean lifetime (MLT). As can be seen in the Fig.2, there is indeed a correlation between positron trapping and magnetic domain wall mobility.

![Figure 2. Correlation between positron mean lifetime and relative shift of the BN peak.](image)

Both techniques, positron annihilation lifetime spectroscopy and magnetic Barkhausen noise analysis, show similar characteristics of the microstructural features of the individual ODS steels. Recrystallisation and the concomitant recovery of lattice defects influence the parameters measured by the distinct NDT techniques (See Fig.2.). We assume that the significant increase of the positron MLT and the shift of the BN signal towards higher magnetic fields in ODS Eurofer, as compared to the three recrystallised materials investigated, are both due to the higher dislocation density in that material. This can be seen in the Fig.1, where the $\tau_1$ component related to the reduced bulk lifetime is considerably higher for ODS Eurofer, apparently due to positron trapping at dislocation lines. On the other hand, variations in the BN and PALS values of the recrystallised materials are supposed to be due to different sizes of vacancy clusters present in these materials.
4. Conclusions

Material defects (vacancy clusters, dislocations, grain boundaries yttria particles,) which act as positron trapping sites of different dimensions also contribute to the pinning of magnetic domains and impede the mobility of domain walls. In the present paper this situation has been explored by a complementary study combining the PALS and BN techniques, in order to identify a correlation between the distinct techniques. The experimental results provide evidence for the existence of that correlation, which is going to be further explored by studies of the thermal ageing behaviour of the ODS steels ($\alpha'$ precipitation at intermediate temperatures). More detailed information about size and density of defects will be available from on-going SANS experiments, which will provide the characteristics of the yttria nano-particles and the $\alpha'$ precipitates.

5. References

[1] Brauer G, Liszkay L, Molnar B, Krause R 1991 Nucl. Eng. Design 127 47
[2] Sugen V, Segers D, de Bakker P M A, de Grave E, Magula V, van Hoecke T, van Waeyenberge B 1999 J. Nucl. Mater. 274 273
[3] Ortega Y, de Castro V, Monge M A, Muñoz A, Leguey T and Pareja R 2008 J Nucl. Mater. 376 222–228
[4] Yamaura S, Furuya Y and Watanabe T 2001 Acta mater. 49 3019–3027.
[5] Debarberis L, Acosta B, Sevini F, Pirfo S, Hyde J M, Hutchings M T and Ortner S 2004 NDT&E International 37 19–22
[6] Dobmann G, Debarberis L and Coste J F, 2001 Nucl. Eng. Design 206 363–374
[7] Klueh R L, Hashimoto N and Maziasz P J 2005 Scripta Materialia 53 275-280
[8] Zeman A, Debarberis L, Kocik J, Sugen V and Keilova E 2007 J Nucl. Mater. 362 259–267
[9] M.J. Alinger, S.C. Glade, B.D. Wirth, G.R. Odette, T. Toyama, Y. Nagai, M. Hasegawa, 2009 Mat. Sci. and Eng. 518 150-157
[10] Damonte L C, Taylor M A, Desimoni J and Runco J 2007 Rad. Phys. Chem. 76 248
[11] Xu J, Liu C T, Miller M K and Chen H 2009 Phys. Rev. B 79, 020204
[12] Hug-Amalric A, Meiland P, Kleber X and Merlin J, Magnetic Barkhausen noise measurement potentialities for metallurgical transformations characterization in multi-phase High Strength steels, proc. 9th Europ. Conf. on NDT, September 2006, Berlin (Germany)