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Void formation in ODS EUROFER produced by hot isostatic pressing

Y. Ortega [a,*], M.A. Monge [a], V. de Castro [b], A. Muñoz [a], T. Leguey [a], R. Pareja [a]

[a] *Departamento de Física, Universidad Carlos III de Madrid, 28911 Leganés, Spain*
[b] *Department of Materials, University of Oxford, Oxford OX1 3PH, United Kingdom*

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ABSTRACT

Positron annihilation experiments were performed on oxide dispersion strengthened (ODS) and non-ODS EUROFER prepared by mechanical alloying and hot isostatic pressing. The results revealed the presence of small voids in these materials in the as-HIPed conditions. Their evolution under isochronal annealing experiments was investigated. The coincidence Doppler broadening spectra of ODS EUROFER exhibited a characteristic signature attributed to positron annihilation in Ar-decorated voids at the oxide particle/matrix interfaces. The variation of the positron annihilation parameters with the annealing temperature showed three stages: up to 623 K, between 823 and 1323 K, and above 1323 K. In the temperature range 823–1323 K void coarsening had effect. Above 1323 K some voids annealed out, but others, associated to oxide particles and small precipitates, survived to annealing at 1523 K. Transmission electron microscopy observations were also performed to verify the characteristics of the surviving defects after annealing at 1523 K.

1. Introduction

An obstacle in the development of oxide dispersion strengthened (ODS) steels for structural applications in fusion reactors is the toughness lack of the material produced by powder metallurgy and consolidated by hot isostatic pressing (HIP). In particular, ODS EUROFER steel with Y_2O_3 particles appears to exhibit poor impact properties and a high ductile–brittle transition temperature [1–3]. To asses the capabilities of this material, it is necessary to elucidate if its failure is an inherent characteristic of the production process that can not be mitigated by normalizing and tempering treatments. In order to investigate this particular point, the evolution of the structural defects in the ODS material during isochronal annealing has been investigated by positron annihilation spectroscopy.

Positron annihilation spectroscopy (PAS) is a very powerful technique to investigate vacancy-type defects in metals because these defects are strong traps for thermal positrons in the crystal lattice. Positron lifetime and coincidence Doppler broadening (CDB) measurements of the annihilation radiation measurements have been performed. The first give information about the size of the positron traps, and the second can reveal the chemical environment of the traps [4]. Thus, concurrent positron lifetime and CDB measurements in ODS and non-ODS EUROFER can contribute to elucidate the nature, localization and thermal stability of the defects responsible for the swelling resistance and the detrimental effects on the mechanical properties.

2. Experimental

Gas-atomised EUROFER 97 powder with particle sizes <45 μm was milled with 0.25 wt% Y_2O_3 for 24 h under an Ar atmosphere. Details of the milling procedure are reported elsewhere [5]. Y_2O_3 free EUROFER powder was also milled under identical conditions. Milled Y_2O_3/EUROFER powder, and un-milled and milled Y_2O_3-free powders were canned and degassed at 673 K for 24 h in vacuum, and then the can sealed. These materials were labeled by ODS, UM and M, respectively. The powders were consolidated by HIP at 1373 K for 2 h under a pressure of 200 MPa. The densities measured in a He pycnometer resulted in $(7.76 \pm 0.06)\ g/cm^3$ for ODS EUROFER, and (7.77 ± 0.03) and $(7.79 \pm 0.02)\ g/cm^3$ for un-milled (UM) and milled (M) EUROFER, respectively, compared to a theoretical density of $7.82\ g/cm^3$. A pair of samples cut from a plate of original EUROFER 97 was used as reference. In addition, the CDB spectra from samples of pure Fe and Y_2O_3 were obtained for comparison.

Positron annihilation experiments were performed on pairs of samples in as-HIP state and after isochronal annealing. The samples were annealed for 90 min up to 1523 K in 100 K steps in a vacuum of $<10^{-6}$ Pa. Experiments in parallel were also made with a pair of samples of original EUROFER 97. A fast–fast coincidence spectrometer was used for positron lifetime measurements. CDB measurements were carried out using two HP Ge detectors in timing coincidence following the procedure described elsewhere [6]. To

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* Corresponding author. Tel.: +34 91 6248734; fax: +34 91 6248749.
E-mail address: yanicet@fis.ucm.es (Y. Ortega).

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emphasize the difference between the CDB spectra, the intensity is normalized by dividing the counts at a given γ momentum by the corresponding for the reference samples of EUROFER.

Transmission electron microscopy (TEM) observations were performed on the same pairs of samples used in the positron annihilation experiments, after annealing at 1523 K. Discs of 3 mm punched from the thinned samples were electropolished at 243 K and 20 kV in a electrolyte solution of 5% $HClO_4$ + 95%CH_3OH. The observations were carried out in a Philips CM20 at 200 kV equipped with energy dispersive X-ray spectrometer (EDS).

3. Results and discussion

Reference samples of EUROFER and UM EUROFER exhibited a single-component lifetime spectrum characterized by a lifetime that varied between 140 and 155 ps, irrespective of the annealing temperature. The lifetime spectra for ODS- and M-EUROFER were properly fitted to a sum of two exponential components, and characterized by a mean positron lifetime defined by $\bar{\tau} = I_1\tau_1 + I_2\tau_2$, where τ and I represent the lifetime and relative intensity of the corresponding spectral component, respectively. Fig. 1 shows the $\bar{\tau}$ values as a function of annealing temperature for both materials along with the single lifetime component for base- and UM EUROFER.

Fig. 2 shows the CDB ratio spectra for pure Fe, Y_2O_3, and EUROFER in the as-HIPed condition. The high concentration of Cr in the EUROFER materials is responsible for the depletion in the high-momentum region, compared to the Fe CDB spectrum. This is the expected effect for Cr in the Fe matrix. It is also observed that the three EUROFER materials in the as-HiPed condition present less annihilation events with core electron of high-momentum than the base EUROFER, as Fig. 2 reveals. The spectra for the non-ODS materials, i.e. for UM- and M-EUROFER, are alike each other and qualitatively different from the one for ODS EUROFER. The discrepancies become more evident increasing the annealing temperature as Figs. 3 and 4 show. After annealing at $T \geqslant 1123$ K the shape of the curves for ODS EUROFER is equal to that for Y_2O_3 in the high-momentum range ($p_L \geqslant 15 \times 10^{-3}\, m_0c$), and the differences with the reference spectrum increase.

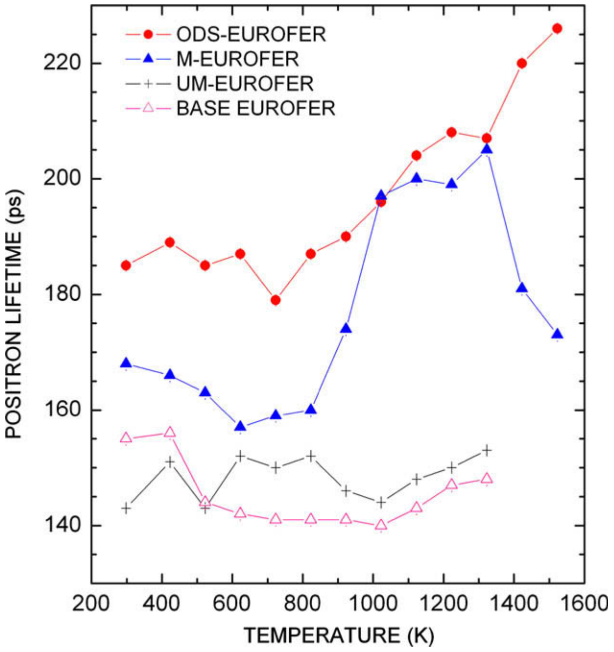

Fig. 1. Positron lifetime for base, un-milled (UM), milled (M) and ODS EUROFER as a function of annealing temperature.

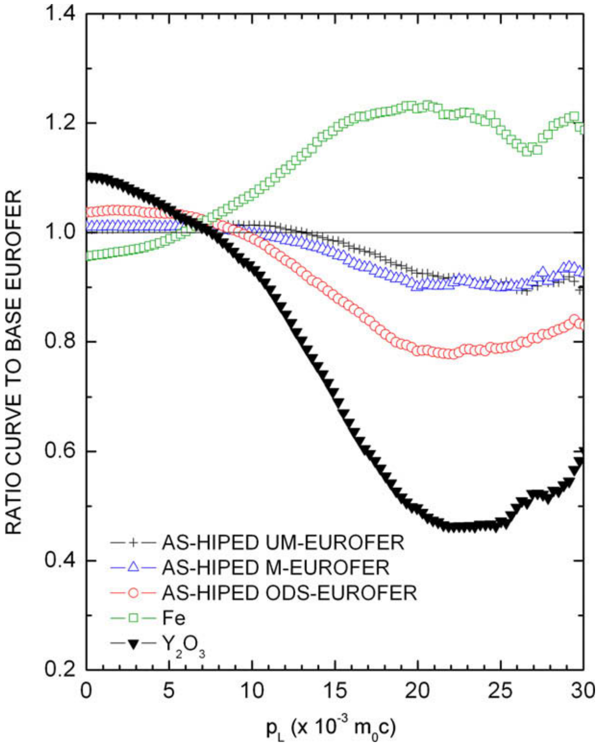

Fig. 2. CDB ratio spectra for un-milled (UM), milled (M) and ODS EUROFER in the as-HIPed condition and for pure Fe, Y_2O_3.

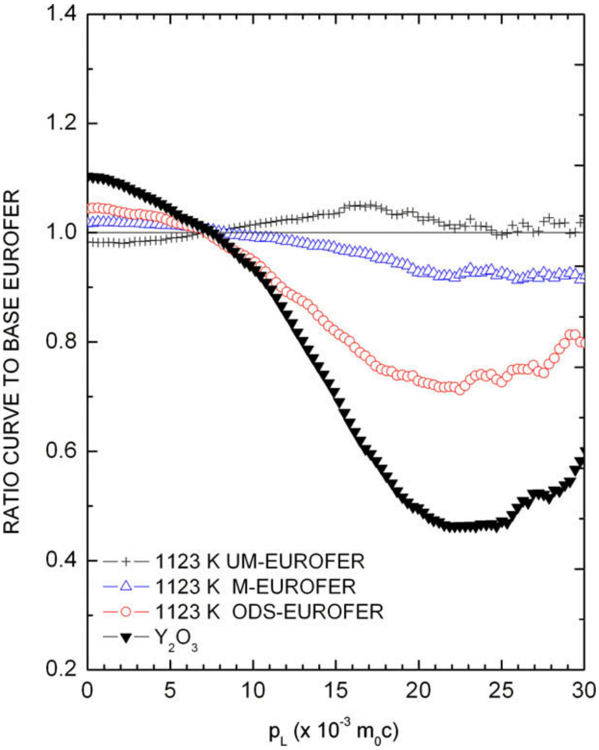

Fig. 3. CDB ratio spectra for un-milled (UM), milled (M) and ODS EUROFER after annealing at 1123 K and for pure Y_2O_3.

Through-focal TEM observations, performed on samples of M- and ODS-EUROFER after annealing at 1523 K, revealed the presence of voids with sizes up to ~25 nm as Figs. 5 and 6 show. These voids are located on grain boundaries, dislocations and randomly

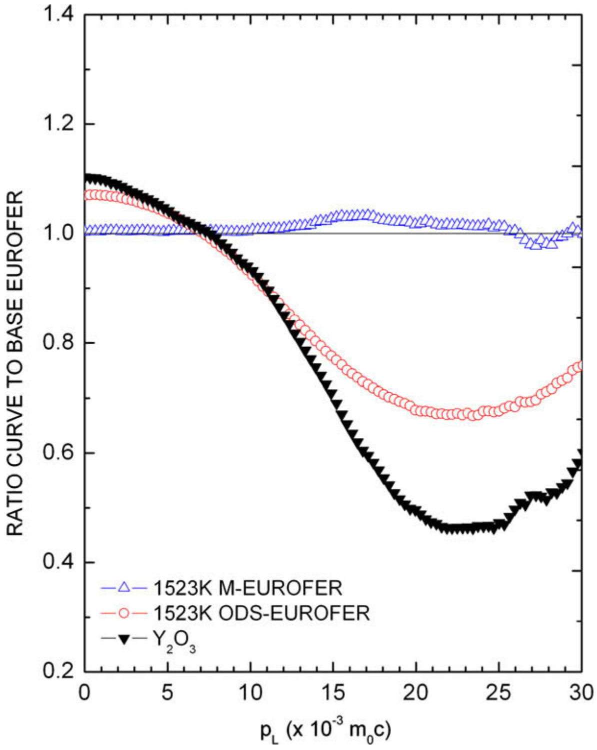

Fig. 4. CDB ratio spectra for milled (M) and ODS EUROFER after annealing at 1523 K and for pure Y_2O_3.

in the matrix. Moreover, in the case of ODS EUROFER the EDS and selection area electron diffraction analyses revealed that the cavities are mostly associated to the Y_2O_3 dispersoids. These cavities exhibited contrast characteristics like those reported for Ar-decorated cavities in ODS-9CrWVTaTi steel mechanically alloyed with 0.5 wt% of Y_2O_3 and Ti [7]. In M EUROFER nanovoids are mainly found associated to very small particles. These particles have not been identified.

Either of the milled materials ODS and non-ODS exhibit very different behaviour respect to the un-milled EUROFER. The presence of a long-lived lifetime component, τ_2, ranging between 300 and 370 ps in M-EUROFER, and between 240 and 340 ps in ODS EUROFER, indicates the formation of three-dimensional vacancy clusters, i.e. small voids or cavities. According to calculations and experimental results, the lifetime for positron trapped in voids containing between 3 and 15 vacancies ranges from 232 and 386 ps in α-Fe [8]. The I_2 values of 10% and 15% for as-HIPed M- and ODS-EUROFER, respectively, indicate the presence of a high density of voids as the TEM observations confirmed after annealing at 1523 K. Since a lifetime component attributable to this type of defects has not been found in the un-milled material, these defects in as-HIPed M- and ODS-EUROFER have to form during the HIP process due to the high density of structural defects created by the milling process.

The shape likeness between the high-momentum regions ($p_L \geqslant 15 \times 10^{-3}\, m_0c$) of the CDB ratio spectra for ODS-EUROFER and the one for Y_2O_3 discloses the effect of the Y_2O_3 dispersion on the positron trapping characteristics of this type of steel. Calculations for positrons in inert-gas bubbles in metals have shown that positrons are trapped at the bubble surface, i.e. at the gas/matrix interface, and the corresponding positron lifetime τ_{bub} is given by [9].

$$\tau_{bub} = (\lambda_{surf} + \lambda_{gas})^{-1} \tag{1}$$

where λ_{surf} represents the annihilation rate of the surface state for positrons at the bare surface of the host metal, and λ_{gas} annihilation rate with gas atoms. If this model is applied to the present experiments, one would expect that CDB spectrum shows signs of the contribution of the matrix surface to the positron annihilation at the gas/matrix interfaces. This is consistent with the present CDB results that evidence positron trapping at Y_2O_3/cavity interfaces in ODS EUROFER, and not in M EUROFER. It has to point out that Y

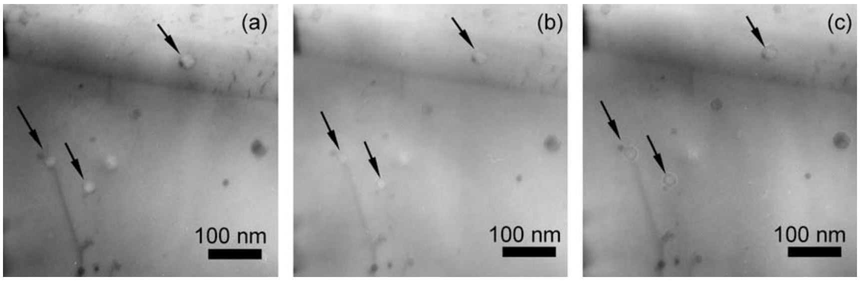

Fig. 5. TEM through-focal series of voids (arrowed) located next to small precipitates in the M-EUROFER annealed at 1523 K. (a) Underfocused by 1 μm, voids appear as white dots surrounded by a dark Fresnel fringe, (b) in-focus, voids show almost no contrast and (c) overfocused by 1 μm, voids appear as black dots surrounded by a bright Fresnel fringe.

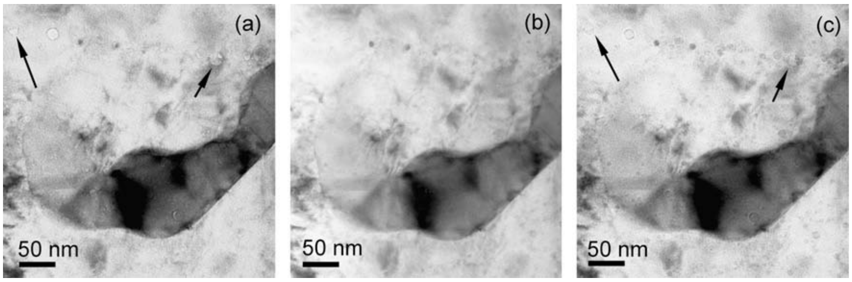

Fig. 6. TEM through-focal series of voids in the ODS EUROFER annealed at 1523 K. Some of the voids associated with Y_2O_3 particles are shown with arrows. (a) Underfocused by 1 μm, (b) in-focus and (c) overfocused by 1 μm.

has a very high positron affinity, −5.31 eV against −3.84 eV for Fe. This can explain that the contribution of Y_2O_3 surface inhibit or hide the possible contribution of the metal matrix surface.

These results agree with the TEM observations, and evidence that the oxide particle/matrix interfaces act as strong sinks for vacancies and Ar atoms providing very favorable sites for clustering of vacancies and gas impurities.

4. Conclusions

Ar atoms absorbed during the MA process of EUROFER are active nucleant agents for vacancy clusters irrespective of the presence of oxide dispersion in the material. Y_2O_3 particle dispersion appears to favor the nucleation, coarsening and stabilization of the voids in EUROFER produced by MA and HIP.

The positron annihilation experiments reveal that the Y_2O_3/matrix interfaces act as very strong and stable sinks for Ar and vacancies. Void coarsening starts at ~800 K when first order Ar-vacancy clusters diffuse towards pre-existing voids. Some voids, likely those not associated to particles, becomes unstable and annealed out for $T \geqslant 1323$ K, while those gas-decorated and associated to particles remain stable after annealing at 1523 K. TEM observations confirm this point. The present results point to these voids as one of causes of embrittlement and poor impact toughness of ODS EUROFER.

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