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Peculiarities of helium porosity evolution in the ferritic–martensitic steels produced by spark plasma sintering

I.I. Chernov[a], M.S. Staltsov[a,*], B.A. Kalin[a], I.A. Bogachev[a], S.N. Korshunov[b]

[a] National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Moscow 115409, Russia
[b] National Research Center "Kurchatov Institute", Moscow 123182, Russia

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ABSTRACT

Oxide dispersion strengthened (ODS) ferritic–martensitic steels are considered as promising structural materials for fusion reactors, as well as for active zone of new generations fast reactors. In this connection, peculiarities of helium porosity formation and gaseous swelling have been investigated in the dispersion-strengthened EP-450 ODS steel with 0.3 and 1 wt.% Y_2O_3 dispersant produced by spark plasma sintering (SPS) as compared with the matrix EP-450 steel, EP-450 ODS steel produced using a hot extrusion (HE) as well as reactor austenitic ChS-68 steel. The samples were irradiated by 40-keV He^+ ions at 923 K up to fluence of 5×10^{20} ion/m^2. Microstructural investigations of irradiated samples were performed using a transmission electron microscope. It is found that plurality of zones with a very different type of helium porosity and different character of their distribution is developed in steel with 1 wt.% Y_2O_3. Such zones are less in steel with 0.3 wt.% Y_2O_3 as opposed to matrix EP-450 steel, EP-450 ODS steel obtained by HE, and austenitic ChS-68 reactor steel. It is found in comparing the character of helium porosity formation in the matrix steel EP-450, steel EP-450 ODS (HE) and EP-450 ODS (SPS) that bubbles are developed with a smaller average sizes and, therefore, helium swelling is lower in all ODS steels than that in steel EP-450, but for ODS steel made by SPS, swelling is significantly higher than in ODS steel produced by hot extrusion. At the same time, austenitic steel ChS-68 shows a minimum gaseous swelling for the used conditions of helium ion irradiation. An assumption is made that the extremely nonuniform distribution of helium bubbles (gas filled pores) both in volume and size in SPS steel is associated with the initially highly defect structure, including the residual porosity in 1–3% as well as a result of strong redistribution of chromium between ferritic grains and grains of tempered martensite during manufacturing of samples.

1. Introduction

The increase in the capacity of the new generation fast breeder reactors (FBR) requires the use of new structural materials. For example, austenitic steels used as a fuel cladding material are prone to high swelling at large damaging doses. Therefore, the use of new heat-resistant and low-swelling chromium steels is a material of choice. Heat resistance of such steels generally increased by dispersion hardening using nanoscale oxide particles (ODS) such as yttrium oxides. These steels are made of powder metallurgy methods, one of which is a spark-plasma sintering (SPS) process [1–6]. In addition, reduced activated chromium steels are considered as promising structural materials for future energy FBR and fusion reactors (FR) [7,8].

Two requirements are of paramount importance in the manufacture of ODS steel by powder metallurgy methods: the uniformity of hardening particles distribution by volume and the maximum possible density of the compact. Obviously, the particles of the strengthening phase may completely not be not uniformly distributed in the powder filling even after rough mechanical mixing prior to mechanical alloying. At the same time, if the agglomerates of matrix steel powder are formed during the subsequent mechanical alloying, these particles of the strengthening fraction can never get inside of the agglomerates, as for example, large grains are formed from these agglomerates during SPS of powders under pressure. These large grains consist of fine subgrains each of which is formed from a single powder particle of matrix steel in turn [6,9]. As shown in [6,9], there are no particles of the strengthening phase in these coarse grains. Previous work [4] shows the outcome of research on the microstructure of two ODS steels produced by hot isostatic pressing (HIP) and points out that both steels consisted of areas without Y_2O_3 nano-particles, i.e. strengthening oxide particles in steels

* Corresponding author.
E-mail address: m.staltsov@gmail.com (M.S. Staltsov).

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are distributed non-homogeneously. The authors suggested rightly that non-homogeneous distribution of strengthening particles in steels can be related to an imperfection of mechanical alloying (in spite of the milling time reaching up to 100 h) and HIP.

With mechanical alloying of 9Cr steel powder and yttrium oxide Y_2O_3 it was established [10] that for a milling time exceeding 8 h the size of powder particles did not reduce further. According to these authors the optimum milling time is approximately 20 h. According to another data [4], the optimum time of steel powder milling is about 40 h. In addition, the work [11] showed the influence of the particle shape, i.e. spherical particles or brittle flakes, on the structure of the sintered samples. Furthermore, it was shown that during 15 h of mechanical alloying steel in the form of flakes achieved better results in terms of chemical composition and homogeneity of yttrium distribution (particles of Y_2O_3). However, during selected mechanical alloying regimes (speed of mill rotation 400 min^{-1}, time of one milling cycle 1 h, container cooling down 1 h, total time of milling 5 and 15 h) the formation of powder agglomeration was observed, similar to the results obtained in [9,12]. It was concluded that the achievement of a more uniform and dispersed powder structure requires an increased mechanical alloying time and optimized milling regimes [9,12]. Moreover, as was shown in [6] the compaction rate of the samples does not depend monotonically on the concentration of the strengthening particles reaching a maximum at a content of about 0.3 wt.% Y_2O_3 during SPS. Therefore, two steps are required for obtaining of high-density compacts with uniformly distributed strengthening nano-particles: optimization of mechanical alloying regimes (time, attritor rotation speed, elimination of powder overheating) as well as spark-plasma sintering regimes.

In this connection, a cycle of experimental studies was carried out varying all possible indicated parameters. In the study, over 140 samples of EP-450 ODS ferritic–martensitic steel strengthened by yttrium oxide particles were produced. These investigations lead to the establishment of the optimal parameters of mechanical alloying and spark-plasma sintering for fabrication of EP-450 ODS steel samples with minimal porosity and maximal density. These parameter: time of 1 milling cycle is 2 h; cooling time of container is 1 h; number of turns of the mill is 200 min^{-1}; total time of milling is 30 h; optimum amount of Y_2O_3 is 0.2 ÷ 0.5 wt.%; the heating rate to a predetermined temperature is >300 K/min; pressure is 70 ÷ 80 MPa; exposure time under load is 0 or ≥3 min; sintering temperature is 1098 ÷ 1163 K [6,11−13].

The problem of structural materials radiation resistance is aggravated by the accumulation of significant concentrations of helium and hydrogen due to various nuclear reactions in structural materials with deep fuel burnup in future FBRs. In addition, there will also be a direct introduction of helium and hydrogen isotopes by radiation from the plasma in FR first wall materials. Helium affects the kinetics of vacancy porosity development and void swelling [14], and it causes gas swelling at high concentrations [15,16]. In addition, helium and hydrogen dramatically increase the radiation swelling of BCC materials showing a synergistic effect [17,18] in contrast to their lower influence on the swelling of FCC steel [19].

The purpose of this work is to establish the peculiarities of the helium porosity development and gas swelling in reactor EP-450 and EP-450 ODS ferritic–martensitic steels obtained using different technologies (hot extrusion – HE, spark-plasma sintering – SPS) as compared with helium swelling of the well-studied reactor austenitic ChS-68 steel [16].

2. Materials and experimental procedure

The compositions of the investigated materials and the content of dispersed Y_2O_3 particles in ODS steels are given in Table 1.

A standard heat treatment was applied for each class of steel: to ferritic–martensitic steels EP-450 and EP-450 ODS (HE) – normalization at 1423 K / 1 h, air cooling + tempering at 993 K / 2 h, air cooling; austenitic steel–water quenching from 1323 K / 1 h; the exposure time for normalization was increased up to 3 hours for better stress removal and neutralization of residual porosity in the samples of EP-450 ODS (SPS) steel. Table 2 presents the information on the manufacturing conditions of samples by spark-plasma sintering.

Table 1
Chemical composition of investigated steels, wt.%.

Steel	C	Cr	Ni	Mn	Mo	Nb	V	B	Others
EP-450	0.12	13	≤0.3	0.6	2.0	0.3	0.2	0.004	–
EP-450 ODS (SPS)	0.12	13	≤0.3	0.6	2.0	0.3	0.2	0.004	1 Y_2O_3
EP-450 ODS (SPS)	0.12	13	≤0.3	0.6	2.0	0.3	0.2	0.004	0.3 Y_2O_3
ChS-68	0.06	16.3	14.8	1.6	2.2	-	0.2	0.004	0.35 Ti

Table 2
Information on the manufacturing conditions of samples by spark-plasma sintering.

Sample marking	The content of Y_2O_3, wt.%	Time of mechanical alloying, h	Sintering temperature, K	Pressure, MPa	Exposure time, min
B1-2	1	30	1163	80	1
A3-3	0.3	50	1163	80	1
A1-4	0.3	30	1098	70	1
A1-5	0.3	30	1098	80	1
A2-10	0.3	40	1163	70	0

The samples were collected in special cassettes containing up to 8 samples and irradiated under identical conditions with 40 keV He^+ ions up to a fluence of 5×10^{20} m^{-2} at T_{irr} = 923 K in the ILU-3 ion accelerator of the Kurchatov Institute. The fluence corresponds to about 2 dpa at the peak of damage and concentration of helium is about 0.4 at.% (4000 appm) at the peak of its depth distribution.

Thin foils for the transmission electron microscope (TEM) were prepared by means of FIB technology applied perpendicularly to the irradiated surface or in the Tenupol-5 device by electropolishing from the unirradiated side. A study of the irradiated samples microstructure was carried out usingLIBRA-120 TEM with a resolution of at least 0.5 nm using an accelerating voltage of 120 kV. Chromium concentration was determined by means of energy-dispersive X-ray spectroscopy (EDS) selectively in the samples areas with different character of porosity development (low or very high gaseous swelling).

3. Results and discussion

The initial microstructures of steels and distribution of dispersed particles were studied in our previous works [6,9,11−13,21].

Several zones with a very different character of helium porosity development are observed in the steel sample B1-2 with 1 wt.% Y_2O_3 (Fig. 1), which is not peculiar to steels made by the classical technology (melting + rolling or HE) (Fig. 2). The bubbles of a parallelepiped or cube shape typical for ferritic–martensitic steel are found in zone 1 (see Fig. 1(a)). They are mostly located in chains along the grain boundaries or probably subgrains hereinafter, the surface of the sample is indicated by a red dashed line. Table 3 presents the porosity parameters calculated from the depicted micrographs and other micrographs of regions with a similar bubble distribution.

The swelling of the irradiated layer of the material was ~0.9% at a bubble density of 2.5×10^{22} m^{-3} and an average size of 5.2 nm in the region 1 of the foil (see Table 3). Such a low swelling value is due to the presence of large bubble-free areas despite the rather large bubble size (see Fig. 1(a)).

The individual grains with very large bubbles of spherical shape up to 60 nm in size were found against a background bubbles of smaller