Nuclear Materials and Energy 000 (2016) 1–7

Contents lists available at ScienceDirect

Nuclear Materials and Energy

journal homepage: www.elsevier.com/locate/nme

Optimization of mechanical alloying and spark-plasma sintering regimes to obtain ferrite–martensitic ODS steel

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ARTICLE INFO

Article history:
Received 13 November 2015
Revised 29 August 2016
Accepted 31 August 2016
Available online xxx

Keywords:
Ferritic/martensitic steel
Dispersion hardening
Mechanical alloying of powders
Spark-plasma sintering

ABSTRACT

The results of structure investigation, distribution uniformity of dispersed particles of Y_2O_3, porosity and density of the ferritic/martensitic reactor steel EP-450 (0.12C–13Cr–2Mo–Nb–V–B, wt%) produced by spark-plasma sintering (SPS) are presented. More than 140 samples were produced using different combinations of mechanical alloying (time, speed of attritor rotation) and SPS parameters (temperature, speed of reaching preset temperature, pressure and time of exposure under pressure, concentration of strengthening particles). It is determined that the absence of strengthening Y_2O_3 nano-particles in local volumes of sintered specimens is connected with the imperfection of mechanical alloying, namely, the formation of agglomerates of matrix steel powder containing no oxide nano-particles. It has been determined that the time of mechanical alloying should not exceed 30 h to provide minimum powder agglomeration, uniform distribution of Y_2O_3 particles in the powder mixture and minimum porosity of sintered samples. Spark-plasma sintering should be performed at the lowest possible temperature. As a result it was found that samples with 99% theoretical density can be obtained using the following optimized SPS-parameters: sintering temperature is 1098 ÷ 1163 K; speed for reaching the preset temperature is > 573 K/min; load is 70 ÷ 80 MPa; time of exposure under pressure – either without isothermal exposure, or exposure during ≥ 3 min; optimum quantity of Y_2O_3 is 0.2 ÷ 0.5 wt%.

1. Introduction

The main problem of achieving high-fuel burnout in fast reactors lies in the absence of radiation-resistant and at the same time heat-resistant structural materials for the active zone. With the currently achieved nuclear fuel burnout range in the reactor BN-600 of approximately 12% h.a. (about 80 dpa), the basic shell-type austenitic steel ChS-68 does not comply with requirements on radiation resistance (first of all – resistance to irradiation swelling). Intensive research and development activities are being conducted in the last decade in Russia and the world with the aim of creating chrome steel, because its irradiation swelling is much less than those of austenitic steel. The main disadvantage of chrome steel is a low heat-resistance as compared to austenitic steel when exposed to conditions occurring in active zones of fast reactors. Research focused on the creation of oxide dispersion strengthened (ODS) heat- and radiation-resistant chrome steel based on martensitic, ferritic/martensitic or ferrite structures [1–10].

One method for ODS steel creation is spark-plasma sintering (SPS) of powders which provides specific advantages (short time of obtaining high-density samples, lower temperature of compaction as compared to other methods with commensurate density and porosity parameters, relatively low applied pressure, etc.). However, this method has also a number of disadvantages: immaturity of ODS steel compaction technology; complexity of massive bodies formation on existing installations; hard and insufficient plastic compaction requiring additional thermal or any other type of processing to increase technological effectiveness of obtaining finished products, etc. [4–7].

The work in [7] shows the outcome of research on the microstructure of two ODS steels produced by hot isostatic pressing (HIP) and points out that both steels were characterized by areas without Y_2O_3 nano-particles, i.e. strengthening oxide particles in steels are distributed non-homogeneously. The authors suggested that non-homogeneous distribution of strengthening particles in

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http://dx.doi.org/10.1016/j.nme.2016.08.020

steels can be related to an imperfection of mechanical alloying (in spite of the milling time reached up to 100 h) and HIP. With mechanical alloying of 9Cr steel powder and yttrium oxide Y_2O_3 it was established [8] that for a milling time exceeding 8 h the size of powder particles did not reduce further and according to the authors the optimum milling time is approximately 20 h. According to another data [7], the optimum time of steel powder milling is about 40 h. The work presented in [9] showed the influence of the powder shape, i.e. spherical particles or brittle flakes, on the structure of sintered samples. Furthermore, it showed that during 15 h mechanical alloying steel in the form of flakes achieved better results in terms of chemical composition and yttrium homogeneity (particles of Y_2O_3). However, during selected mechanical alloying regimes (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 [10]. As conclusion it was stated that the achievement of a more uniform and dispersed powder structure required an increased mechanical alloying time and optimized milling regimes.

Therefore, for obtaining high-density compacts with uniformly distributed strengthening nano-particles two steps are required: optimizing of mechanical alloying regimes (time, attritor rotation speed, elimination of powder overheating) and spark-plasma sintering in particular.

Because of that, the purpose of this work was to determine the effect of mechanical milling and SPS parameters on the uniform distribution of dispersed Y_2O_3 particles and the structure of reactor ferritic/martensitic ODS steel.

2. Materials and experimental procedure

Reactor ferritic/martensitic steel EP-450 (0.12C–13Cr–2Mo–Nb–V–B, wt%) in the form of brittle flakes after pre-milling for 2 h in a planetary ball mill MTI SFM-1 was mixed with the yttrium oxide powder. Mechanical alloying of the powder mixture was carried out in a planetary ball mill Pulverisette-5 in argon atmosphere. To ensure maximum coverage range of possible suitable sintering conditions and to receive maximum density of samples, all main parameters of the process were varied over a certain range: milling time ($\tau = 30$, 40 and 50 h), temperature (T = 1023, 1098 and 1163 K), pressure (p = 60, 70 and 80 MPa), heating rate (v = 100, 350 and 600 K/min) and isothermal exposure time under load ($\tau = 0$, 1, and 3 min). In addition, the content of Y_2O_3 changed from 0 to 1 wt % to determine the effect of steel composition on kinetics of the powder sintering.

Spark-plasma sintering was performed in the facility LABOX-625™ of Sinterland© company working in a vacuum of 5−10 Pa with a maximum pressure force up to 6 tons and power of the transmitted current up to 2500 A. Temperature was controlled by a thermocouple and infrared pyrometer. The heating of powder started out simultaneously with the application of electric current pulse and the correlated heating of the powder was done by applying pulses of 7 ms with a pause of 40 ms between pulses. There were produced more than 140 samples with dimensions of ~15 mm in diameter and 5 mm in height in various combinations of milling time and sintering parameters. The fabrication time for a specimen is 40–45 min including loading of powder and unloading of the sample.

The density and porosity of the sintered samples were measured by hydrostatic weighing using the high-precision (± 0,0002 g) analytical scale Ohaus Pioneer PA214. A scanning electron microscope (SEM) Quanta 600 FEG with energy dispersive microanalysis attachment for EDAX Trident was used to study the morphology of the powders and microstructure of sintered samples, as well as for elemental analysis. The surface structure of samples and the chemical composition of the steel after sintering were investigated at the wave Axios XRF X-ray spectrometer and SEM Zeiss EVO-50 with microprobe system. Electron microscopic studies of the fine structure of the samples were carried out in a transmission electron microscope LIBRA-120.

3. Results and discussion

Fig. 1 shows the morphology of powders with different content of Y_2O_3 after milling for 50 h. It is found that the composition of the starting powders of EP-450 steel (0.3 or 1% Y_2O_3) does not affect the size of the activated particles, the degree of homogeneity of milling and powder agglomeration. Despite the use of previously established optimized regimes of mechanical alloying (Table 1), after milling for 30 h the powder agglomerates still had a maximum size up to 30 µm. With increasing milling time to 40 and 50 h the degree of agglomeration practically did not change compared to milling for 30 h, but the uniformity of powder slightly increased.

As shown by the work done in [9], after milling for 15 h the distribution of Y_2O_3 oxide in powder is already quite homogeneous and its content practically complies with a target one. The yttrium distribution determined via SEM showed that after 30 h of milling Y_2O_3 oxide was distributed completely uniformly on the steel powder surface (Fig. 2). Therefore, from the perspective of minimum agglomeration and Y_2O_3 oxide distribution homogeneity in the powder 30 h of mechanical activation is found to be an optimum.

Fig. 3(a) shows the general view of the sintered steel structure with 1 wt% Y_2O_3, where ferrite and martensitic grains are observed. The area with oxides is represented in Fig. 3(b). Microstructure in Fig. 3 contains large particles being the $M_{23}C_6$ type carbides, yttrium oxides with a maximum size of the oxide particles up to 40 nm and double oxides of yttrium and silicon. Silicon oxide was found in the work [10] as well.

In general, the microstructure of the surface of sintered samples is quite homogeneous. However, local areas provide a specific structure which is exemplarily shown in Fig. 4. One can see a large elongated grain situated in a highly dispersed structure that formed from a powder agglomerate during the SPS process. The grain orientation corresponds to the direction perpendicular to the sample pressing axis. Such grains are consisting of smaller equiaxial grains with the size 5 ÷ 7 µm (Fig. 5) formed from steel powders being a part of the agglomerate. Such substructure is characteristic for all grains formed from powder agglomerates. Fig. 4 shows open porosity along boundaries of small grains, while a large grain formed from the powder agglomerate shows no porosity. With the increase of mechanical alloying time from 30 to 40 and 50 h the porosity increases.

Chemical composition of different areas of sample with 0.3 wt% of Y_2O_3 is shown in Table 2. Analysis of Fig. 4 and data in Table 2 shows that in view of the main elements the compact complies with the composition of matrix steel. In spectrum 2 an increased content of Si, O are observed and with the presence of Y the formation of double yttrium and silica oxides can be deduced. The content of yttrium of approximately 0.18 wt% corresponds to the content of 0.3 wt% Y_2O_3, that was introduced into steel. In spectrum 1 taken from the large grain formed from the agglomerate, no yttrium was found.

Accordingly, above results verify that in case of powder agglomerates formation in the process of mechanical alloying, grains formed from these agglomerates during the subsequent SPS process do not contain yttrium (yttrium oxide) or at least do not contain it in sufficient quantity for experimental detection. Data received about the inhomogeneity of oxide particles in ODS steels produced by SPS were similar to results of HIP produced materials obtained in the work [7].

Please cite this article as: M.S. Staltsov et al., Optimization of mechanical alloying and spark-plasma sintering regimes to obtain ferrite–martensitic ODS steel, Nuclear Materials and Energy (2016), http://dx.doi.org/10.1016/j.nme.2016.08.020