Journal of Nuclear Materials 385 (2009) 308–311

Contents lists available at ScienceDirect

Journal of Nuclear Materials

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

Development of oxides dispersion strengthened steels for high temperature nuclear reactor applications

K. Verhiest [a,c,*], A. Almazouzi [a], N. De Wispelaere [b], R. Petrov [c], S. Claessens [b]

[a] Belgian Nuclear Research Centre, Centre d'Etude de l'Energie nucléaire (SCK·CEN), Boeretang 200, Mol 2400, Belgium
[b] ArcelorMittal Research Industry Gent (OCAS), J.F.Kennedylaan 3, Gent 9060, Belgium
[c] Ghent University, Department of Metallurgy and Materials Science, Technologypark 903, Zwijnaarde, Gent 9052, Belgium

ARTICLE INFO

PACS:
62.23.Pq
81.05.Ni
83.80.Iz
81.05.Bx
68.55.Nq

ABSTRACT

By introducing a dispersion of nanosized yttrium oxides particles into a steel matrix, the upper temperature limit in mechanical creep strength can be enhanced in temperature by 100 K at least. Production routes for the production of a new class of oxides dispersion strengthened (ODS) steels are investigated within this work. Preliminary results obtained when doping pure iron matrix phase with two types of yttrium oxides (Y_2O_3) nanoparticles (commercial as well as laboratory fabricated nanopowder) are presented. The twofold purpose of this work is firstly to obtain a comparative analysis between the commercial and the laboratory fabricated Y_2O_3 nanopowder used to produce the doped iron, and secondly to demonstrate the feasibility of new production route by observing the nanostructure of the first test batches with pure iron. Observations are carried out with transmission electron microscopy (TEM) to determine the size distribution of the particles in the powder, while glow discharge optical emission spectroscopy (GDOES) and high resolution-scanning electron microscopy (HR-SEM) are used to analyze the chemical composition and the homogeneity of the produced doped iron. It is demonstrated, that even with small size particles nanopowder fabricated in the laboratory, the distribution is fairly homogeneous compared to the one obtained with a relatively large particles commercial nanopowder, confirming the feasibility of the new production route.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

In the nuclear field, high-chromium steels are considered as the major promising candidates for the structural components of next generation power plants such as fusion, accelerator driven systems (ADS) or the so-called fission generation IV reactors. Currently T/P91 steel, an industrial and commercial available high-chromium ferritic/martensitic steel is considered as a good candidate structural material applicable for such advanced nuclear systems. The reason for this can be found in its superior swelling resistance and better mechanical properties at high temperatures compared to austenitic stainless steels. However, these steels suffer from corrosion when in contact with lead-alloys especially at high temperature. Their creep resistance is also limited to moderate temperature level (<850 K). Thus, to increase the efficiency of the next generation of nuclear power plants, it is mandatory to develop a new material, steel-based, capable of sustaining the expected harsh conditions.

Therefore, a substantial effort is being set nowadays for the development and investigation of new high-chromium steels doped with a defined dispersion of oxide nanoparticles in the matrix as these composite steels have been demonstrated to exhibit superior performance compared to their non-doped ones. Indeed, it is demonstrated that by a dispersion of oxide nanoparticles in the matrix, it is possible to enhance the creep strength and to extend the applicability of the material with an average value of 100 K, from 850 to 950 K [1]. Oxides dispersion strengthened (ODS) steels are being developed by powder metallurgy (PM) and investigated for fission and fusion applications in Europe [2–4], Japan [5,6] and the United States [7,8]. However, until now, PM was the only technique proposed as the ultimate production route to obtain a dispersion of nanoparticles in a steel matrix. But this method, although universal, does not allow the production of large quantities exhibiting excellent quality in terms of microstructural and mechanical properties homogeneity [9]. Some of the problems involved with ODS productions based on powder metallurgy are the anisotropy of the mechanical properties, the impossibility to produce large batches (tonnage), the difficulty of joining/welding ODS steels with large structures and the high production costs. On the other hand, the classical and conventional casting methods have failed to produce uniformly dispersed oxides in the casted steels due mostly to the difficulties in preventing the accumulation of the oxides particles at the surface of the ingots [10].

---

* Corresponding author. Tel.: +32 14333059; fax: +32 14321216.
E-mail address: Katelijne.Verhiest@sckcen.be (K. Verhiest).

0022-3115/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2008.12.006

Thus, new production routes being different and potentially more advantageous compared to powder metallurgical techniques are investigated with the aim to fabricate an important homogeneous quantity of this type of material keeping its attractive properties for high temperature applications including the nuclear ones. Moreover, in order to produce high quality ODS steel, the nanopowder used to dope the matrix material has to be proficient in size and quality: small particle size distribution as well as powder purity are preliminary requirements.

This paper reports on the preliminary results obtained when doping iron as matrix phase with two types of Y_2O_3 nanoparticles (commercial as well as laboratory fabricated powder). The first aim is to analyze a commercial and a laboratory fabricated nanopowder used to fabricate a doped iron matrix and secondly to demonstrate the feasibility of a new production route, that is industrially scalable, by observing the microstructure. The nanopowders are investigated using transmission electron microscopy (TEM), while the analysis of the fabricated nanoparticles doped iron matrix is performed using high resolution-scanning electron microscopy (HR-SEM) for surface chemical mapping and glow discharge optical emission spectroscopy (GDOES), a depth profiling method to check the chemical homogeneity.

2. Experimental

2.1. Materials

In order to assess the oxides dispersion strengthened (ODS) steel, two types of nanopowders serve as the phase to disperse artificially in the matrix. For this, commercial yttrium oxides nanopowder was purchased from Sigma–Aldrich with a pre-specified chemical composition, and a laboratory fabricated Y_2O_3 nanopowder was produced by means of a solution combustion synthesis (SCS). This inorganic synthesis procedure is based on the method developed by Igarashi et al. [11]. The chemical synthesis is given by the reaction:

$$2Y(NO_3)_3 + 2CO(NH_2)_2 + 5.5O_2 \rightarrow Y_2O_3 + 4H_2O + 10NO_2 + 2CO_2. \quad (1)$$

The reagent solution consists of an ‘explosive’ mixture processing by the oxidation of urea (U_r) with the yttrium-nitrate (N_t) as oxidizer. Y_2O_3 is the desired reaction product generated together with water vapor, nitrous gas (NO_2) and carbon dioxide (CO_2). The nitrates and the urea are dissolved in a vial containing the reaction medium according to an appropriate order of mixing to avoid any exothermic explosion. The characteristics of the particles can be controlled by changing the reaction parameters. The strict control of final powder size, crystallinity and reaction yield is obtained by modifying the stoichiometric molecular ratio of the two reagents, urea to nitrate molecular ratio, temperature of the combustion flame, precursor solution, type of fuel, reaction medium and possible post-production heat treatments [12]. After combustion, the particles are collected in a vial in which the synthesis is performed at high temperature. A foamy white powder is the resulting reaction product after synthesis. As post-production heat treatment, a calcination at varying temperatures and at varying durations of heating time can be performed to stabilize the final product.

Pure iron is used to qualify the production methods under development and permits to identify clearly the interaction between the oxides particles and the iron-based matrix without additional influence of other alloying elements. The details of the production route of the materials under investigation are not the subject of this paper due to the industrial confidentiality. However, and for clarity, the method consists on adding the powder in the molten metal without any contact with a crucible followed by a rapid quench in a controlled atmosphere. At the first stage, pure iron is used instead of the steel in order to optimize the fabrication parameters.

2.2. Microstructural analysis techniques

First of all the composition and the size distribution of the nanopowder are investigated. TEM samples out of the laboratory fabricated powder are prepared by dissolving the as-prepared powder (i.e. without any post-production heat treatment) in ethanol followed by ultrasonic cleaning. In contrary to drop casting (in which a drop of the dissolved particles is put on a copper grid), dip casting is used by dipping a copper grid into the dispersion solution followed by evaporation in air. Because of the hydrophilic nature of the powder, the particles are dissolved only after cleaning in an alcohol bath. The dipping of the copper grid is performed immediately after cleaning. In parallel, XRD analysis is performed on the commercial as well as on the laboratory scaled powder in order to have a confirmation in particle size evaluation based on peak broadening analysis. The particle observation is made using TEM JEOL JEM 3010 equipment. For X-ray powder diffraction a Philips X’Pert Pro system (PreFix) is used. To determine the distribution curve in which the fraction of particles (%) in function of particle size (nm) is presented, a statistical pool with a minimum of 200 individual particles was evaluated based on bright-field TEM observations. The fraction (%) is determined by the ratio in which the amount of particles with a particular size is divided by the complete window of particles evaluated.

GDOES is used to evaluate dispersions in pure iron fabricated with specific production routes based on both the conventional casting procedure and the thermo-mechanical alloying methods of industrial steels. GDOES is a spectroscopic tool combining sputtering and atomic emission to provide an extremely rapid and sensitive method for element depth profiling analysis. This method is used in this case as a quick tool to survey the chemical composition and thus the homogeneity of the produced batches. In fact, for this method the sample preparation involves simply cutting of the sample followed by grinding in order to obtain a flat surface. The measurements with a Spectruma ‘GDA 750’ device are performed using argon ions for sputtering with a beam spot size of 2.5 mm.

HR-SEM observations are done complementary to the GDOES analysis by means of a NOVA 6OO dual beam microscope. The microscope is equipped with a FEG-SEM column which allows ~2 nm and better resolution at 30 keV. The same samples that are analyzed by GDOES, were used for these observations but care was taken to remove any residues using electrolytic polishing with A2 Struers® electrolyte, at a tension of 40 V, a flow rate of 7 and a process time of 20 s. Images in secondary electron mode from the same surface as the one analyzed by GDOES are collected at respectively 10 and 5 keV; beam currents at respectively 2.1 and 0.40 nA; a working distance of 5.2 and 5 mm using the Everhart–Thornley detector (ETD) and the trough lens detector (TLD).

3. Results and discussion

3.1. Synthesis and characterization of nanocrystalline yttrium oxides

As stated earlier, the production of the oxide particles was optimized to obtain high purity oxide nanometric particles with as narrow as possible size distribution. In Fig. 1(a) the distribution of commercial yttrium oxide powder is presented, and compared to an example of the laboratory fabricated Y_2O_3 oxides particles as function of particle size in Fig. 1(b). The particle size distribution

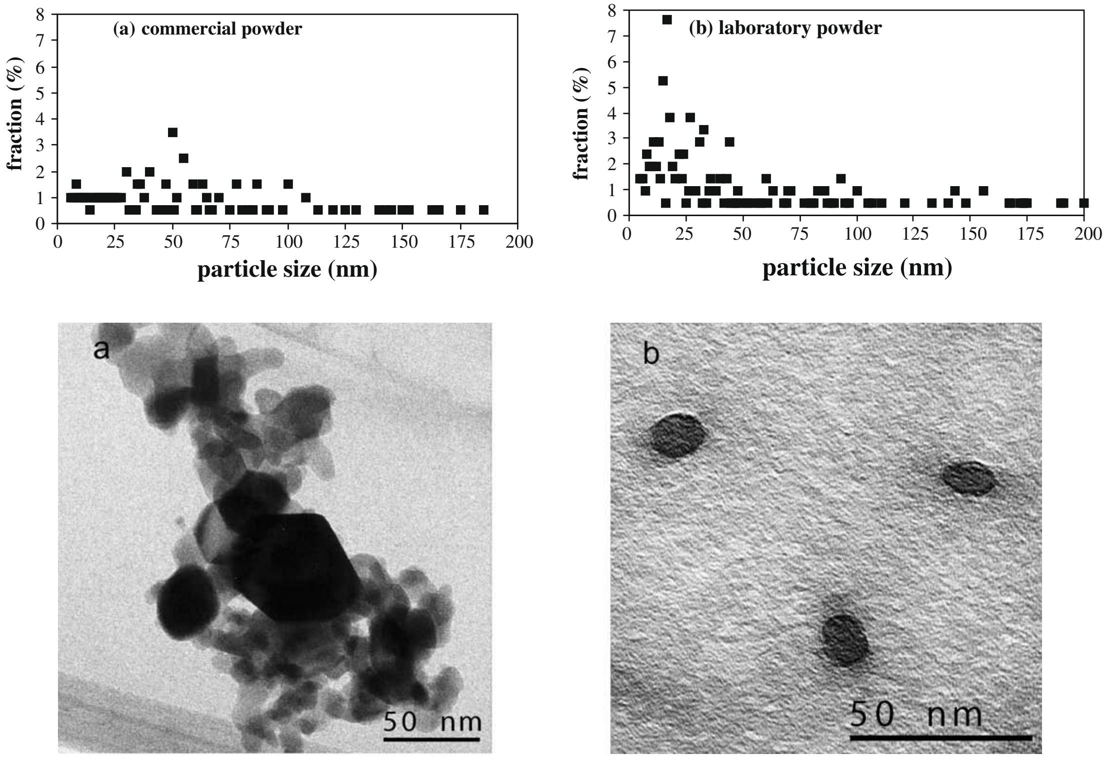

Fig. 1. Size distribution and bright-field TEM image of commercial nanosized Y_2O_3 particles: (a) compared to a laboratory fabricated Y_2O_3 nanopowder and (b) in the as-prepared state.

presented is of powder in the as-prepared state production with an yttrium-nitrate to urea molecular ratio of 1. A bright-field TEM image of both powders are presented complementary to each distribution curve.

Fig. 1 shows that the laboratory produced Y_2O_3 powder has a relatively narrow size distribution with an average particle size of about 17 nm while the commercial yttrium oxides powder distribution is somewhat broader and the average size was estimated to be about 50–55 nm. TEM observations reveal that the particles in the laboratory produced powder are spherical in contrast to the commercial ones that appear more elliptical. Further examinations with X-ray diffraction confirmed the average sizes obtained from TEM image analysis. In addition, the electron diffraction patterns show that the particles have a predominantly cubic structure in both cases.

It is worth adding that the laboratory production method has been optimized to fabricate a powder with a predefined average size. In fact, by varying the nitrate to urea ratio in a proper way, it is possible to produce a high purity Y_2O_3 powder with average sizes ranging from 2 to about 40 nm, as it can be seen in Table 1, which presents the average size of the produced particles as function of the N_t to U_r molecular ratio (N_t/U_r) and concentrate state of the urea in the production cell.

Table 1

Average size of the produced particles as function of the yttrium-nitrate (N_t) to urea (U_r) molecular ratio (N_t/U_r) and concentrate state of the urea in the production cell.

N_t/U_r (mol. ratio)	U_r (conc. state)	Size (nm)
0.4	lean	2
0.4	rich	38
1	lean	19
2.5	stoichiometric	28
3.03	rich	28

3.2. Analysis of oxide doped iron

To qualitatively control how yttrium oxides particles are dispersed into the iron matrix, GDOES is used for the in-depth elementary analysis of yttrium (Y). Consequently, it was possible to estimate roughly and quickly the distribution of yttrium in samples taken out from several positions of the fabricated batch. Fig. 2, where the intensity of Y signal (measured in arbitrary units) are displayed as a function of the sputtering depth, for (a) commercial powder and (b) laboratory powder, shows some typical depth profiles that were obtained. In addition, and for the sake of comparison the GDOES signal (∗) obtained from an experimental ODS made by the conventional powder metallurgy, namely ODS-EUROFER, is also plotted. It can be stated at this point, that the produced

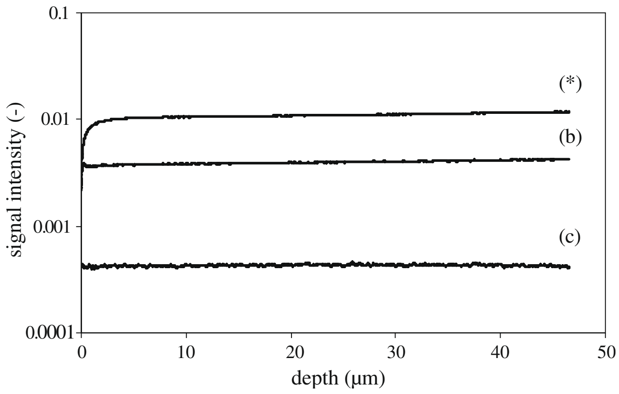

Fig. 2. GDOES intensity signal of the yttrium element in arbitrary units (–) as function of the sputtering depth (μm) obtained from the analysis of an ODS steel (∗), a commercial (a) and the laboratory (b) powder doped iron in the condition of a 2.5 nm beam spot size.

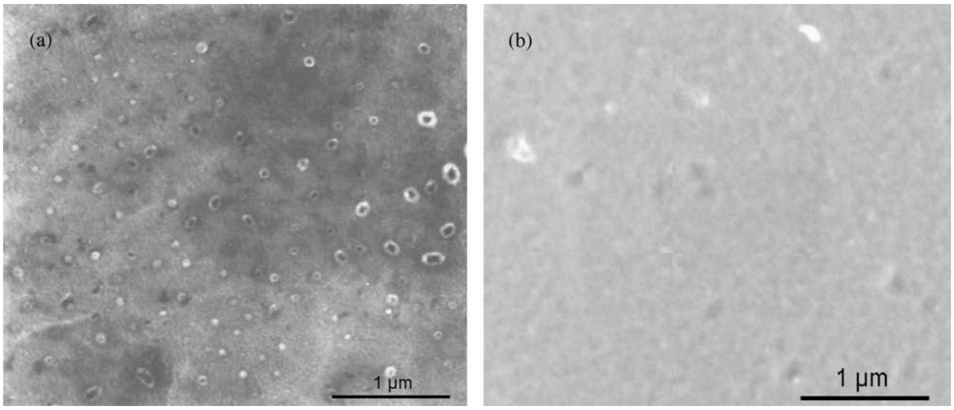

Fig. 3. High resolution-scanning electron micrographs revealing a nanometer scaled dispersion obtained with one of the new production method based on a casting method using: (a) commercial powder and (b) laboratory fabricated yttrium doped particles.

materials appear as homogeneous as the ODS steel, indicating that the yttrium was indeed quite randomly dispersed in the matrix despite the small size of the laboratory produced powder used in this case ($N_t/U_r = 1$, see Table 1).

However, in order to complement GDOES analysis and to check if the particles are homogeneously dispersed, a more powerful analysis technique was employed. This direct method reveals un-ambiguously the particle size distribution although in a small region (few 10's of nm^2).

Consequently, HR-SEM was used to observe and evaluate the homogeneity of the dispersion, the average particle size and the inter-particle distance in the iron matrix. Fig. 3 displays two typical HR-SEM images obtained from the same area where the GDOES was performed.

Fig. 3(a) shows a homogeneous dispersion for the iron doped with commercial powder, being representative for different spots analyzed. The estimated average size of the dispersed Y_2O_3 nanoparticles is in the range of 60 nm in accordance with the initial size. The inter-particle distance in the range of about 100 nm at most, proves that the particles are randomly distributed indeed. Fig. 3(b) depicts a HR-SEM image obtained from material doped with the laboratory produced powder. It reveals somewhat inhomogeneous dispersion at few spots, which is probably due to the very small scaled particle size. However, the coherency of the particles with the matrix causes their non-detection even at much higher magnifications. It is nevertheless believed that the obtained distribution is quite encouraging and further work on the optimization of the production route is still ongoing.

4. Conclusion

A new production route is developed to produce nanosized yttrium oxides doped-ferro-alloys using advanced casting and thermo-mechanical treatments. Preliminary results demonstrate that the new production method is promising based on the analysis of pure iron doped with different type (laboratory fabricated vs. commercial) of yttrium oxide particles. The laboratory Y_2O_3 nanopowder has been produced with Solution Combustion Synthesis, which is a successful and relative simple inorganic reaction system for the production of small oxides particle size, crystalline homogeneous ceramics and this at low reaction temperatures and within reduced reaction time.

The future work involves the assessment and investigation of nanooxides doped steels including a further optimization of the envisaged production routes in terms of product performance and industrial production. Furthermore, the investigation of the interrelationship microstructure/mechanical properties tensile, toughness and creep will be the subject of detailed studies in order to increase the performance of the doped matrix.

Acknowledgements

The partial support in the FP7-GETMAT project (Contract No. FP7-212175) is carried out by one of the partners SCK CEN and is gratefully acknowledged. OCAS (ArcelorMittal Research Industry Gent) as well as the University of Ghent is gratefully thanked for industrial and academic support.

References

[1] R. Lindau, A. Môslang, M. Schirra, P. Schlossmacher, M. Kliminakou, J.Nucl. Mater. 307–311 (2002) 769.
[2] Z. Oksiuta, N. Baluc, J. Nucl. Mater. 374 (2008) 178.
[3] A. Alamo, J.L. Bertin, V.K. Shamardin, P. Wident, J. Nucl. Mater. 367–370 (2007) 54.
[4] C. Degueldre, S. Conradson, W. Hoffelner, Comp. Mater. Sci. 33 (2005) 3.
[5] S. Ukai, T. Nishida, H. Okuda, M. Fujiwara, K. Asabe, J. Nucl. Sci. Technol. 34 (1997) 256.
[6] S. Ukai, T. Yoshitake, S. Mizuta, Y. Matsudaira, S. Hagi, T. Kobayashi, J. Nucl. Sci. Technol. 36 (1999) 710.
[7] R.L. Klueh, J.P. Shingledecker, R.W. Swindeman, D.T. Hoelzer, J. Nucl. Mater. 341 (2005) 103.
[8] I.S. Kim, J.D. Hunn, N. Hashimoto, D.L. Larson, P.J. Maziasz, K. Miyahara, E.H. Lee, J. Nucl. Mater. 280 (2000) 264.
[9] C. Capdevilla, H.K.D.H. Bhadeshia, Advanced Engineering materials 3 (2001) 9.
[10] V.K. Sikka, D. Wilkening, J. Liebertau, B. Mackey, Mater. Sci. Eng. A 258 (1998) 229.
[11] T. Igarashi, M. Ihara, T. Kusunoki, K. Ohno, T. Isobe, M. Senna, Appl. Phys. Lett. 76 (2000) 1549.
[12] L.E. Shea, J. McKittrick, O.A. Lopez, J. Am. Ceram. Soc. 79 (12) (1996) 3257.