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Microstructural and mechanical characterisation of Fe-14Cr-0.22Hf alloy fabricated by spark plasma sintering

M.A. Auger [a, *], Y. Huang [b], H. Zhang [c], C.A. Jones [a], Z. Hong [a], M.P. Moody [a], S.G. Roberts [a, d], P.S. Grant [a]

[a] Department of Materials. University of Oxford, OX1 3PH, Oxford, UK
[b] Hefei University of Technology, Hefei, Anhui, 230009, China
[c] Department of Materials, Loughborough University, Leicestershire, LE11 3TU, UK
[d] Culham Centre for Fusion Energy, Abingdon, Oxon, OX14 3EA, UK

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ABSTRACT

Fe-14Cr pre-alloyed powder and pure Hf powder were mechanically alloyed to produce powder with nominal composition Fe-14Cr-0.22Hf (wt. %) that was consolidated by the spark plasma sintering (SPS) technique in order to investigate the ability of Hf to produce a nanometric dispersion of oxide particles in a ferritic matrix. Comprehensive microstructural and mechanical characterisation of the as-milled powder and the consolidated material was performed using electron microscopy, X-ray diffraction, atom probe tomography and indentation techniques. It was shown that Hf additions can effectively produce, by internal oxidation, a fine scale dispersion of Hf-O nanoparticles in the consolidated material. A uniform grain structure was produced in the alloy. Although the nanoparticle dispersion was not homogeneous at the finest scale, the resulting dispersion strengthening contributed significantly to the hardness. According to these results, internal oxidation of reactive elements rather than direct addition of oxides may offer additional opportunities in the design and development of oxide dispersion strengthened steels.

1. Introduction

In the development of advanced materials for fission and fusion applications, oxide dispersion strengthened (ODS) steels are amongst the most promising structural materials [1–4]. Their microstructural stability under conditions of high temperature and high stress, resistance to radiation damage and creep resistance, have been extensively demonstrated [5–9]. This performance derives from a homogeneous dispersion of stable nanoparticles in the steel matrix that prevents dislocation motion and grain boundary sliding at high temperature [10]. These nanoparticles can also act as sinks for point defects and He bubbles under irradiation conditions in a nuclear reactor environment [11,12], which underpins their excellent radiation resistance.

The manufacturing of ODS steels has been widely studied, with different combinations of processing routes investigated. The most common manufacturing approach usually starts with mechanical alloying of elemental or pre-alloyed powders with a low fraction of oxide particles (typically Y_2O_3) with the aim of providing a homogeneous dispersion of oxide nanoparticles in the final consolidated material [13–19]. The use of the spark plasma sintering (SPS) technique [20] to achieve the final densification of the milled powder, has increased in the last years, as it significantly shortens the time required for consolidation to a few minutes, compared with the several hours required for other sintering techniques such as hot isostatic pressing (HIP). In SPS, high current (1000–5000 A) and low voltage (<10 V) DC pulses and a uniaxial pressure (up to 100 MPa) are applied to a powder constrained in a graphite mould, which is heated at a high rate (up to 2000 °C/min) towards a target holding temperature. Isothermal holding times are typically 3–20 min and, as the current flow stops, the system rapidly cools down. A wide range of alloys, including TaC [21], transparent Y_2O_3 [22], Ni [23], Al_2O_3 [23], Ti-6Al-4V [24] or W-Ni-Fe [25], have been successfully consolidated by SPS. The effectiveness of this technique in the manufacture of ODS alloys has also been confirmed [26–29].

* Corresponding author. Department of Materials, University of Oxford, Parks Road, OX1 3PH, Oxford, UK. Tel.: +44 0 1865 2 73694; fax: +44 0 1865 2 73789.
E-mail address: maria.auger@materials.ox.ac.uk (M.A. Auger).

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Hafnium has diverse potential uses in nuclear power reactors, such as thermal neutron absorber in nuclear energy control rods or as a specialized refractory material in elemental form or as hafnium oxide [30]. There are only limited reports of the production and characterisation of Fe-Cr-Hf powder so far, but the effectiveness of Hf additions in promoting a dispersion of nanoparticles in mechanically alloyed and annealed powder has been suggested [31–33]. A recent study [34] has also reported effective irradiation resistance enhancement of a Fe-Cr-2Hf (wt. %), cold compressed after mechanical alloying and powder annealing, under 200 keV He irradiation at 500 °C by reducing void swelling, which is significant for potential nuclear uses of this alloy type. In this work, Hf powder was added to Fe-14Cr (wt. %) pre-alloyed powder in order to evaluate its capacity to form a fine dispersion of nanoparticles in a ferritic alloy matrix and to consider the resulting performance with respect to more conventional ODS steels that typically contain Y_2O_3 [15,16,35]. A 0.22 wt. % concentration of Hf in the alloy was selected to produce a final oxide fraction comparable with the $0.25Y_2O_3$ (wt. %) content in ODS alloys previously prepared and characterised by authors of the current work [28,36]. Addition of Hf to steel alloys already containing Y_2O_3 has been shown to promote the formation of finer oxides with respect to the original ODS alloy [37]. In this work, the effectiveness of Hf addition in promoting a nanometric dispersion of precipitates in a Fe-14Cr (wt. %) alloy was compared with the widely studied use of direct Y_2O_3 additions.

2. Materials and methods

Argon-atomised Fe-14Cr (wt. %) pre-alloyed powder (<150 μm in diameter, Aubert & Duval, France; composition details in Table 1) and elemental Hf powder (−325 mesh, 99.6% pure, Alfa Aesar, UK, product number 10201) were used as starting materials to produce mechanically alloyed powder with nominal composition Fe-14Cr-0.22Hf (wt. %) (referred to as 14Hf hereafter). The powder mixture was mechanically alloyed in a planetary ball mill (Fritsch Pulverisette 6) for 60 h at 150 rpm in Ar atmosphere. AISI 52100 steel balls were used in the milling process at a ball-to powder ratio of 10:1. The grinding media were contained in a 500 ml chrome-steel bowl. The milled powder was loaded into a graphite mould lined with graphite paper in an Ar-filled glove box for SPS consolidation.

The SPS process was performed at FCT Systeme GmbH (Rauenstein, Germany) using a uniaxial pressure of 50 MPa for 5 min. The hold temperature of 1150 °C was reached at a heating rate of 100 °C/min to produce a consolidated disk of ~20 mm diam. × 5 mm thick. Further details of the SPS process can be found in [28].

The milled powder was characterised by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), nanoindentation and atom probe tomography (APT) techniques. The powder sample was prepared for characterisation by embedding it in a conductive phenolic resin and polishing with SiC paper and colloidal silica suspension. The consolidated sample was characterised by SEM, EDS, synchrotron X-ray diffraction, electron back-scattered diffraction (EBSD), Vickers hardness measurements, transmission electron microscopy (TEM) and APT. Different samples from the consolidated disk were cut, ground and polished with SiC paper and colloidal silica suspension (0.06 μm in size) for direct characterisation or for further TEM and APT sample preparation.

Microstructure and compositional imaging was performed in a JEOL JSM5510 scanning electron microscope equipped with an Oxford Instruments silicon drift detector (SDD). AZtec EDS analysis software was used for data processing. Standard θ-2θ X-ray diffraction measurements were obtained in a Philips PW1710 diffractometer, using Cu Kα wavelength radiation (E = 8.048 keV) at a voltage of 35 kV and a current of 50 mA. The scans were registered in the range $2\theta = 20° - 120°$ in continuous mode using a step size of 0.02° and a scan step time of 1.25 s.

14Hf consolidated by SPS was mounted on an alumina holder and scanned by synchrotron X-ray diffractometry on beamline I11 with a wavelength of 82.5770 pm at the Diamond Light Source (Harwell Science and Innovation Campus, Didcot, UK). EBSD was conducted in a JEOL JSM6500F SEM operated at 20 kV using a probe current of ~10 nA; areas of $8 \times 12.5\ \mu m^2$ were mapped in a square array with a step size of 0.1 μm. TEM was conducted in a JEOL 2100 equipped with STEM-EDS operating at 200 kV and in a JEOL 3000 F operating at 300 kV. Samples suitable for TEM observation were prepared by the FIB lift-out technique combined with flash-polishing [36].

APT analysis was carried out in a CAMECA LEAP® 3000X-HR operating in laser pulsing mode. The specimen base temperature was around 50 K and the laser energy was 0.4 nJ at a repetition rate of 200 kHz. CAMECA IVAS® 3.6.12 commercial software was used

Table 1
Chemical composition of the Fe-14Cr (wt. %) pre-alloyed powder.

Element	Fe	Cr	Si	Mn	C	N	O
wt. %	Bal.	14.13	0.281	0.194	0.004	0.0095	0.052

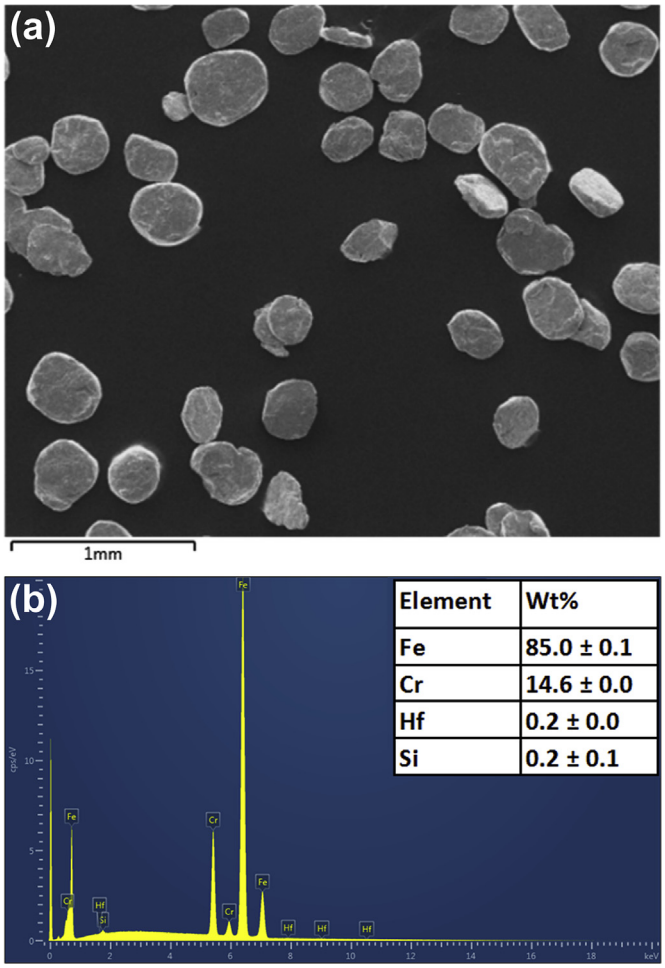

Fig. 1. a) SEM image of as-milled 14Hf powder. b) EDS quantification of one 14Hf powder particle.