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Influence of the duration of high energy ball milling on the microstructure and mechanical properties of a 9Cr oxide dispersion strengthened ferritic–martensitic steel

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ABSTRACT

Oxide dispersion strengthened (ODS) 9Cr steel was prepared by milling atomised steel powder (Fe–0.1C–9Cr–2W–0.2Ti) with nano yttria powder in a high energy horizontal ball mill (Simoloyer CM-08) for 1, 2, 3 and 4 h. Both particle as well as crystallite sizes of milled ODS steel powder reduced with milling time reaching steady state after 3 h. The grain size of the heat treated ODS steel also reduces with milling time reaching a steady state after 3 h. Four hours of milling is sufficient to get the dispersoids of less than 5 nm in heat treated ODS steel. Both yield and tensile strengths increase with milling time up to 673 K and there is no effect of milling on the strength levels beyond 673 K.

1. Introduction

Oxide dispersion strengthened (ODS) ferritic–martensitic steel possesses excellent creep strength and resistance to oxidation; corrosion and neutron irradiation damage [1–5]. Fine grained microstructure, nanosized oxide (Y–Ti–O complex) dispersoids and stability of the microstructure at high temperatures are primarily responsible for attaining such good combination of high temperature properties [6–10]. Though, there exist many processing technologies to produce nanocrystalline materials, mechanical milling is the most extensively used technique. Out of the many high energy milling techniques that are in vogue, high energy horizontal ball milling is the most recent and efficient one with which processing times can be reduced by an order of magnitude [11] when compared to the popular attritor milling. Even though, extensive research has been carried out on the influence of milling parameters on the dispersion of yttria particles in the product using conventional high energy milling methods, there is an ambiguity regarding the effect of milling on Y_2O_3 particles. The reported findings can be classified into three categories viz., (a) fragmentation of the particles to a size of 1–2 nm [12], (b) amorphisation of Y_2O_3 and dissolution [10,13] and (c) fragmentation, dissociation and dissolution [14]. It is also not clear whether these processes are dependent on the energy of milling.

No systematic study has yet been carried out on process optimisation in the development of yttria dispersed titanium containing steels. The present study, therefore, is an attempt to evaluate the influence of milling time on the evolution of microstructure and the structure-dependent mechanical properties of ODS-9Cr steel at various stages of processing.

2. Experimental procedure

Argon atomised steel powder containing 9Cr, 0.1C, 2W and 0.2Ti (the chemical composition of the powder is given in Table 1) in the size range of 20–120 μm with an average size of 68 μm supplied by M/s. Crucible Research, USA and nano yttria powder (30–50 nm size, 99.95% purity) supplied by M/S Inframat Advanced Materials, LLC, USA were used to produce the ODS steel. The steel powder was blended with Y_2O_3 for 10 min at 100 rpm and milling of powder was carried out in a high energy horizontal attritor mill (Simoloyer CM-08, ZOZ GmbH, Germany) for 1, 2, 3 and 4 h at 700 rpm (relative velocity of 7 m/s) using stainless steel container and 5 mm diameter hardened steel balls under argon atmosphere. Ball to powder ratio of 10:1 was maintained for all the milling operations. The milled powders were filled in mild steel cans of 50 mm ⌀ and 75 mm height, degassed at 623 K under 1×10^{-5} kPa of vacuum and sealed.

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Table 1
Chemical composition (wt%) of P_0 and P_4 powders.

Powder	Cr	W	Ti	C	Total O	N	Y_2O_3	Excess O
P_0	9.05	2.02	0.22	0.12	0.008	0.003	–	–
P_4	9.00	2.04	0.22	0.12	0.15	0.016	0.28	0.09

The sealed powder cans were upset at 1323 K in a 250 T hydraulic press. The upset billets were surface machined and extruded to 16 mm diameter rods at 1423 K with an extrusion ratio of 9. The extruded rods were machined to remove the residual can material and were heat treated. The heat treatment consisted of heating to 1323 K, holding for 30 min and cooling in air followed by tempering for 2 h at 1023 K and air cooling to room temperature. For ease of understanding, the ODS steel powder samples are identified as P_0, P_1, P_2, P_3 and P_4 with the subscript indicating the number of hours of milling of powders and the heat treated rods as ODS1, ODS2, ODS3 and ODS4 for milling times of 1, 2, 3 and 4 h respectively.

The chemical composition of the powders was measured using ICP-AES (Teledyne Leeman, Model: Prodigy). The O, N, C and S analysis of the as received and milled powders was carried out using oxygen/nitrogen (LECO, Model: TC436) and carbon/sulphur (LECO, Model: CS444) analysers. The particle size of the milled powders was estimated using Laser diffraction particle size analyzer (CILAS, Model: 920 Liquid). The size and morphology of milled powders as well as the microstructure of heat treated rods were studied using scanning electron microscope (Hitachi, Model: S-3400N). The bulk samples were etched with Vilella's reagent for microstructural examination. X-Ray diffraction studies were carried out on the milled powders in a XRD machine (Bruker AXS, D8 Advance) using CuK_α radiation with a scan rate of 5 s per step of 0.05° (2θ) and the diffraction angle (2θ) range of all the measurements was restricted to $20–110^\circ$. Crystallite sizes were calculated from the full width at half maxima (FWHM) of the most intense line Bragg peak of the sample, using Scherrer formula after subtracting the widths due to instrumental broadening and strain effects using the equation [15]:

$$FWHM_{sample} - FWHM_{LaB6} = \left(\frac{\lambda}{(D_v \cos\theta)} + 4\varepsilon_{str} \tan\theta \right) \qquad [1]$$

where D_v is the volume weighted crystallite size and ε_{str} is a strain factor and λ is wave length of CuK_α radiation (1.541 Å).

Grain size of the heat treated rods in longitudinal direction was estimated by EBSD technique using FESEM (Hitachi, model: S-4300SE/N). Transmission electron microscopic (TEM) investigations of heat treated ODS steels were carried out using a FEI Tecnai G2 200 kV (LaB_6) microscope equipped with Gatan image filter capable of carrying out imaging and electron energy loss spectroscopy. The EDS spectra were collected using an EDAX silicon thin window detector. Bulk samples were initially thinned down to the thickness of about 100 μm and 3 mm diameter discs were punched. These discs were electro polished in a twin jet electro polisher using 10% perchloric acid 90% ethanol solution at −2 °C and 20 V. The electro polished samples were cleaned with an argon ion beam at a low angle in a precise ion polishing system (Gatan, Model: 691). Size of the dispersoids was estimated using image analysis software. Once the frequency distribution of the dispersoid diameter was obtained for each composition, the corresponding volume fraction of dispersoids (f) was estimated using the equation given below [16]:

$$f = \frac{\pi \sum N_i d_i^3}{6At} \qquad [2]$$

In Eq. (2), N_i is the number of dispersoids having a diameter of d_i, A is the total projection area, and t is the foil thickness. The foil thickness was measured using convergent beam electron diffraction (CBED) pattern.

Microhardenss of the milled powder was measured at 100 g load and bulk hardness of the heat treated rods was measured with 5 kgf load using Vickers micro (Walters UHL, Model: VMH-I04) and macro hardness testing machines (LECO, Model: LV-700AT) under standard test conditions. The tensile properties of the heat treated rods were evaluated from room temperature to 1073 K at an initial strain rate of $7.5 \times 10^{-4}\ s^{-1}$ using universal testing machine (INSTRON, Model: 4507), having a capacity of 200 KN with a furnace to heat the sample up to 1273 K. Round tensile test specimens of 3.99 mm ∅ and 22 mm gauge length (ASTM E21) were used. Minimum of two tensile test specimens were used for each test condition and average values are reported.

3. Results

3.1. Characterisation of milled powders

The chemical compositions of the as received argon atomised steel powder (P_0) as well as the powder obtained after 4 h of milling (P_4) are presented in Table 1. From the data it is evident that O and N contents increase with increasing milling time. The increased levels of O and N are the result of minor leakages of air into the container. Considering the fact that excess oxygen content (oxygen more than that locked in Y_2O_3) of 0.085% has been found to be optimum for the formation of the desired volume fraction of Y–Ti–O complex oxide dispersoids [3], the increased oxygen concentration is acceptable. Excess nitrogen can primarily affect the availability of titanium for the formation of the dispersoids. However, the nitrogen pick up is not expected to significantly affect the role played by Ti in the formation of the dispersoids in view of the preferential affinity of titanium for oxygen.

The SEM images of the as-milled ODS-9Cr steel powders P_1, P_2, P_3 and P_4 are shown in Fig. 1a, b, c and d respectively. The variation of particle size of ODS steel powders with milling time is shown in Fig. 2. The results suggest that the particle morphology changes from sphere to disc during early stages of milling and the size increases initially and then decreases. Further milling increases strain accumulation and fracture leading to decrease in particle size with increasing milling time. It is well known that during milling of ductile particles, plastic deformation, welding and fragmentation processes occur concurrently. While welding increases the particle size, fragmentation decreases it. When the particle coarsening caused by welding is matched by the size reduction due to fragmentation, the particle size reaches a steady state. It is evident that steady state particle size of about 66 ± 4 μm was reached after milling for 3 h.

The variation of average crystallite size of ODS-9Cr steel powders estimated from the XRD data as a function of milling time is shown in Fig. 3. The crystallite sizes of P_1, P_2, P_3 and P_4 were 19.7 ± 1.2, 17.5 ± 1.1, 15.7 ± 0.5 and 15.5 ± 1.1 nm respectively. The crystallite size was found to decrease rapidly during initial stages of milling and reaches a near steady state after 3 h of milling. It is an established fact that (a) intense plastic deformation occurs in mechanical milling, (b) cell structures form easily in bcc metals at slight deformation because of the ease of cross slip and (c) the cell size decreases and misorientation angle increases with increasing deformation [17]. The lower rate of decrease in cell size at heavier deformation (increased milling time) is due to the influence of the two competitive processes viz.; strain hardening and dynamic recovery, which occur simultaneously. The steady state represents the balance between increase in dislocation density due to strain hardening and dynamic recovery due to cross slip.