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Letter to the Editor

Addition of Fe_2O_3 as oxygen carrier for preparation of nanometer-sized oxide strengthened steels

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ABSTRACT

Nano-structured ferritic alloys, which are prepared almost exclusively via the mechanical alloying of Y_2O_3, have recently attracted much attention. Our preliminary results show that the usage of Fe_2O_3 as oxygen source leads to better control of powder properties than Y_2O_3 and a high density of nanometer-sized oxide particles can be formed by atomic mixing of Y, Ti and O. This may provide a new route with reduced costs and improved reproducibility for industrial production of nanometer-sized oxide strengthened steels.

1. Introduction

Nano-structured ferritic alloys (NFAs), which can sustain extremely hostile environment in fusion power plants, have drawn much attention since 1990s [1,2]. The fabrication route of NFAs consists of complex procedures: mechanical milling of matrix alloy powder and Y_2O_3 particles, canning, thermo-mechanical treatment and final heat treatment [3]. The precipitated nano-clusters (2–5 nm) [4] can serve as not only the sinks for irradiation-induced transmutation byproducts but also the obstacles for dislocation motion, and thus lead to excellent irradiation resistance and high temperature strength. Nevertheless, NFAs are still facing many challenges; particularly, the high cost and poor reproducibility [2] due to the intrinsically complex processing route.

Y_2O_3 has been widely used as both Y and oxygen sources, and the homogeneous dissolution of the Y_2O_3 particles during mechanical milling has been recognized as the key of success in the fabrication of NFAs. However, it usually takes a long time for Y_2O_3 decomposition during milling [5] because of its high binding energy. This apparently increases the fabrication costs and may also be one of the possible reasons for the poor reproducibility. Recently, Ukai and co-workers [6] found that the density of nanometer-sized oxides can be optimized by adjusting Ti and the excess oxygen content using Fe oxides. Inspired by the finding, in this work we use more soluble Fe_2O_3 and Y hydride as the sources of oxygen and Y to completely replace Y_2O_3 in order to reduce the milling time for atomic homogenization.

2. Experimental

The raw materials used in this study were Fe–14Cr–3W (wt.%, same as below) powders, Ti and Y hydrides, Y_2O_3 (40 nm) and Fe_2O_3 (100 nm) particles. Two types of powder mixtures with a nominal composition of Fe–14Cr–3.0W–0.3Ti–ω'Y_2O_3', one with Y_2O_3 and the other with Fe_2O_3 and Y hydrides, were pre-mixed with Fe–14Cr–3W powder and Ti hydride. To achieve reproducibility, 'ω'-the amount of oxide addition (for Fe_2O_3-added powder, YH_2 and Fe_2O_3 were weighed at the same Y and O content) was changed from 0.3 to 0.6, 1.2, respectively. Mechanical alloying was conducted in a Pulverisette-5 planetary ball mill (ball to powder weight ratio 8:1, rotation speed 350 rpm and 0.5 wt.% alcohol as process control agent was used); the milling intensity is low for economic purpose but enough to dissolve the hydride and oxide additions (XRD spectrums not exhibited here). After 48 h, the two as-milled powders (0.3 wt.% 'Y_2O_3') were hot can-forged and hot rolled into bulk sheet alloy with full density followed by 2 h annealing at 800 °C.

3. Results and discussion

Fig. 1 shows the differences in morphology and distribution between Y_2O_3- and Fe_2O_3-added powders after milling for 48 h. For comparison, the size distribution of pure Fe–14Cr–3W powder without the addition of any oxide is also plotted to show the effect of oxides on as-milled powder. It can be found that the addition of oxides results in more fine particles compared with pure Fe–14Cr–3W powder. With increasing the content of oxides, Fe_2O_3-added powder becomes fine gradually whereas Y_2O_3-added powder shows an inhomogeneous size distribution with large flakes mixed with fine particles (Fig. 1b). Thus, the morphology of the milled

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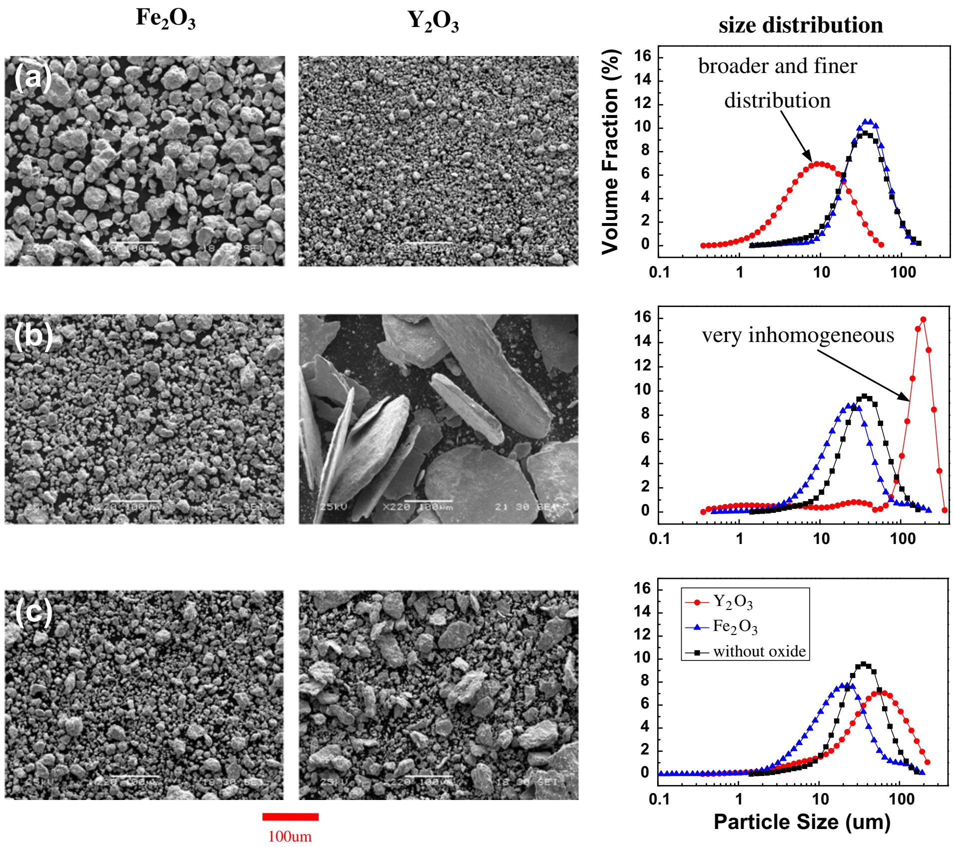

Fig. 1. Effect of oxide content: (a) 0.3, (b) 0.6 and (c) 1.2 wt.% 'Y_2O_3' on morphology and size distribution of Fe_2O_3- and Y_2O_3-added powders after milling for 48 h; the 48 h-milled Fe–14Cr–3W powder namely 'without oxide' in each 'size distribution' diagram is shown for comparison.

Table 1

ExO and S_{BET} of Y_2O_3- and Fe_2O_3-added powders at various contents of oxides and milling time. Extra oxygen content (ExO) = O content in as-milled powder – theoretical oxygen content; S_{BET} = specific surface area.

ExO (wt.%) /S_{BET} ($m^2\ g^{-1}$)	0.3 wt.% 'Y_2O_3'		0.6 wt.% 'Y_2O_3'		1.2 wt.% 'Y_2O_3'	
Milling time (h)	Y_2O_3	Fe_2O_3	Y_2O_3	Fe_2O_3	Y_2O_3	Fe_2O_3
12	2.24/–	0.13/–	0.48/1.52	0.18/0.06	0.24/–	0.29/–
24	2.20/–	0.19/–	1.51/3.22	0.25/–	0.56/–	0.74/–
36	2.13/–	0.23/–	2.28/4.83	0.42/0.10	0.75/–	0.41/–
48	2.29/0.53	0.30/0.12	3.43/4.13	0.61/0.18	0.85/0.47	0.76/0.33

'–': Unmeasured.

powder appears to be more controllable by using Fe_2O_3 instead of Y_2O_3.

Additionally, the two powders (0.3 wt.% 'Y_2O_3') at different milling time were compared in terms of the morphology and size distribution as shown in Fig. 2. During all stages, the milling with Fe_2O_3 results in relatively large powder particles but more uniform size distribution. In general, the large particles contain a less amount of extra oxygen contaminated from the atmosphere during milling [7]. Table 1 shows the extra oxygen content and the specific surface area (S_{BET}) of Y_2O_3- and Fe_2O_3-added powders at various amounts of added oxides and milling time. As usual, the specific area and the impurities increase with milling time. However, Fe_2O_3-added powders exhibit smaller specific surface area and a much lower content of extra oxygen in comparison with the Y_2O_3-added powder.

After milling for 48 h, the two powders (0.3 wt.% 'Y_2O_3') show the microstructure of single-phase bcc-Fe with a grain size of about 100 nm. After hot consolidation, the microstructure of the Fe_2O_3-added bulk alloy is shown in Fig. 3. Ultra-fine grains with an average size of ~200 nm (Fig. 3a) and nanometer-sized precipitates with a size of 5–10 nm (Fig. 3b) can be observed throughout the matrix. The energy dispersive X-ray mapping shows the particles mainly contain in Ti, Y and O. These observations demonstrate that the similar NFAs microstructure as reported in the literatures [6,8] can be achieved by using Fe_2O_3 and Y hydride as the precursor powders.

Compared with Y_2O_3 as the oxygen carrier, Fe_2O_3 can easily be decomposed and dissolved into bcc-Fe matrix during mechanical milling because of low binding energy as well as high inter-diffusion rate [9]. Moreover, the soft Fe_2O_3 particles may cover the surface of the matrix powder and prevent the cold-welding that generally leads to heterogeneous particle size distribution. Thus, the morphology, size distribution and extra oxygen content of the milled powder can be easily controlled by using Fe_2O_3. The

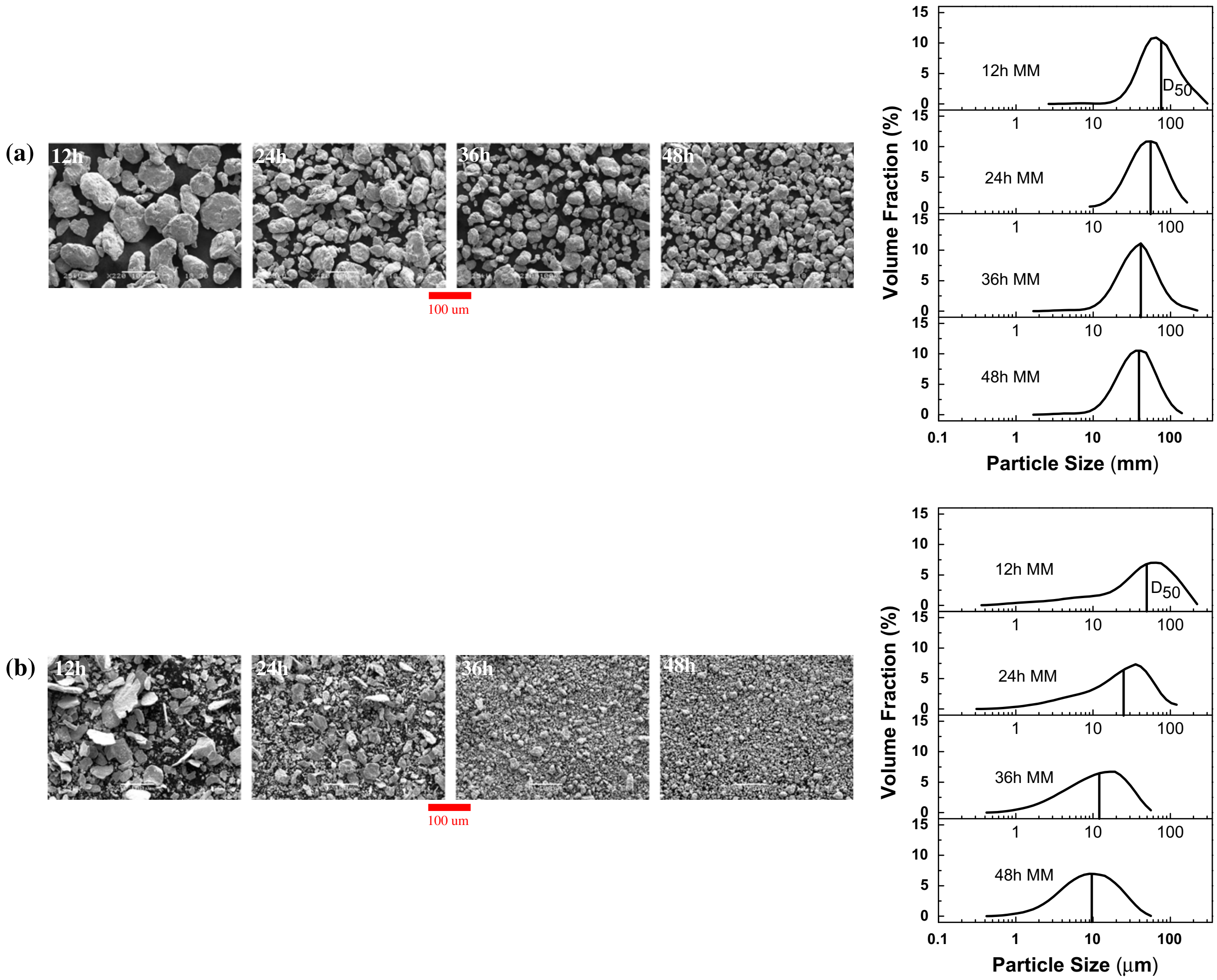

Fig. 2. Effect of mechanical milling (MM) time on (a) Fe_2O_3- and (b) Y_2O_3-added powder (0.3 wt.% 'Y_2O_3' addition) morphology and size distribution; D_{50} refers to the mean diameter at 50% cumulative volume percentage.

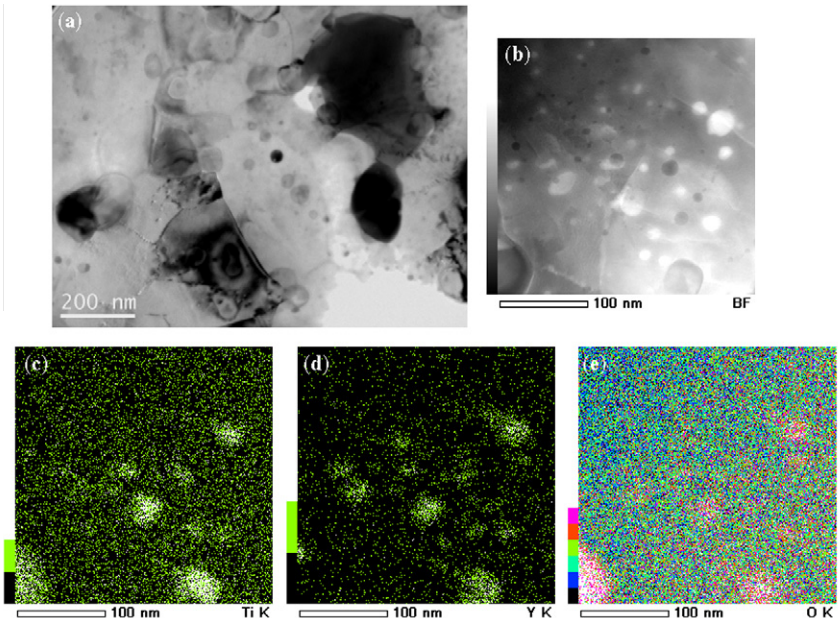

Fig. 3. TEM images of Fe_2O_3-added (0.3 wt.% 'Y_2O_3', 48 h milling) and hot consolidated alloy; (a) BF-TEM image, (b) BF-STEM image and EDS mapping of element (c) Ti, (d) Y and (e) O.

use of brittle hydrides as the Ti, Y source may also benefit the chemical homogenization because of the fragmentation of hydrides at the early stage of milling. Therefore, this study may provide a promising new route for industrial production of nanometer-sized oxide strengthened steels.

4. Conclusions

1. By using Fe_2O_3 powder in mechanical milling of NFAs, coarse powder mixtures with a uniform size distribution and low extra oxygen content can be obtained. The replacement of Y_2O_3 by Fe_2O_3 shows a better control of powder morphology and size distribution during milling.
2. Nanometer-sized oxide particles can be formed in the milled and consolidated Fe_2O_3-added alloy, demonstrating that the similar NFAs microstructure as reported in the literatures can be achieved by using Fe_2O_3 and Y hydride as the precursor powders. This study may provide a new route with reduced fabrication costs and improved reproducibility for industrial production of nanometer-sized oxide-strengthened steels.

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