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Synthesis of aluminum oxide dispersed α-Fe with nano sized grains by simple milling

Seung J. Hwang *

Department of Materials Science and Engineering, Daejin University, Hokook 1007, Pocheon, Kyung-gi 487-711, Republic of Korea

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ABSTRACT

Aluminum oxide (with 4 volume% of Al_2O_3) dispersed α-Fe (BCC) with nano-sized grain was synthesized by reactive-cryogenic milling with a mixture of the elemental Fe, Al and Fe_3O_4 (Magnetite) powders as a reactant. Prior to the Hot Isostatic Press (HIP) for further densification of the materials, the milled powders were hot pressed (HPed) at the elevated temperature. The microstructure of the consolidated materials was characterized by standard metallographic techniques such as TEM (Transmission Electron Microscopy), STEM–EDS (Energy Dispersive Spectroscopy), and XRD (X-ray Diffractometer). Mechanical properties of the materials were determined by compressive yield test and micro Vickers hardness test at room temperature. The grain size estimation was attempted for the materials by XRD, using the Scherrer formula and TEM pictures. The microstructure of the materials was comprised with a mixture of a homogeneous distribution of Fe and Al_2O_3 nano grains. The 0.2% off-set yield strength and micro Vickers hardness of the materials were as high as 824 ± 39 MPa and 3.70 ± 0.1 GPa, respectively.

1. Introduction

The mechanical alloying (MA) was developed to produce the oxide dispersion strengthened (ODS) alloys for high temperature applications in early 1970s by Benjamin [1]. An increasing attraction to MA as non-equilibrium processing has been made after the reports [2–5] since many unique phases could be synthesized by the processing such as extended solid solutions, metastable crystalline phases, quasi-crystals, and many other nanocrystalline materials.

While MA is independently developed as a route to produce ODS alloys, mechanochemistry or self-propagating (or sustaining) high temperature synthesis (SHS) has been studied as a simple, energy-efficient approach to the synthesis of monotonic or composite materials including solid solutions, nano-composites, and metastable phases [6,7]. Recently, the mechanically induced self-propagating reaction (MSR) has been significantly attracted as a combination technique of SHS and MA. The features of self-propagating reactions can be categorized in two groups: MSR and SHS depending on whether initiated by ball milling or local heating. Schaffer and McCormick performed first investigation on the MSR of ball milling in 1989 [8]. They have attempted to control the combustion manner of the reaction; some portions of inert material were added to the mixture of reactant powders in the MSR to lower the reaction temperature, resulting in smaller particles size of the product [9]. To synthesize a nanocomposite consisting of Fe and Al_2O_3 phases in a previous report, oxide displacement reaction using MSR with Fe_3O_4 and Al has been achieved by adding inert materials (Al_2O_3) to the powder charge [10]. However, the size of the dispersoid seemed to be still large to give rise to the dispersion strengthening effect where the increase of the strength is caused by the direct reaction of dispersoids to dislocation but not by load-bearing reinforcement elements.

In this study, it has been attempted to synthesize a type of the nanocrystalline Fe with a minimum size of Al_2O_3 dispersoid by reactive milling at the cryogenic temperature to attain the oxide dispersion strengthening effect. A purpose of the preliminary study here is to produce and to consolidate the Al_2O_3 dispersed α-Fe, and to characterize the microstructure and the mechanical properties for further understanding of strengthening mechanisms of the nano-sized grain materials in future.

2. Experimental

For the reactive milling of powder, mixture of elemental Fe, Al and Fe_3O_4 powder was prepared to derive the following displacement reaction:

$$341\,Fe + 3\,Fe_3O_4 + 8\,Al \rightarrow 350\,Fe + 4\,Al_2O_3 \quad (1)$$

* Tel.: +82 315391984; fax: +82 315391980.
E-mail address: sjhwang@daejin.ac.kr

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This reaction would end up with the formation of Fe matrix with 4 volume% Al_2O_3 at the completion of the milling. The volume percent of the Al_2O_3 in the powder was estimated by calculation, assuming that the reaction (1) has been completed so all of aluminum and oxygen reacts to Al_2O_3 while milling. The starting powders (Fe, −325 mesh, 99.7%; Al, −40 +325 mesh, 99.8%; Fe_3O_4, <1 μm, >99%) were premixed before milling and charged in the mill chamber filled with 1 bar of pure argon. The powder mixture of 100 g was milled in a high-energy attritor for 16 h with ball to powder ratio 18:1 at 210 K using liquid nitrogen (LN_2) for the first 2 h to prevent cold welding. After 2 h, LN_2 supply was switched to tap water to cool the mill chamber to the completion of milling. Evolution of milling was monitored by XRD to the end of milling at intervals. The result of XRD patterns of the milled powder was obtained from milling time of up to 16 h using Mo Kα radiation. The XRD patterns are plotted in Fig. 1 as a function of the milling time. A batch of pure Fe power was milled and consolidated to compare with the milled powder under same process conditions.

In order to minimize the contamination from the grinding ball and chamber wall, the pre-milling with pure Fe powder was performed to coat the possible contaminant such as chamber wall and balls. Button type (16 mm, Φ × 12 mm) samples were prepared by hot press (HP) at 1323 K and 80 MPa in vacuum for 2 h from the milled powder. The HPed samples were then HIPed at 1323 K and 100 MPa for further densification of the samples in the argon atmosphere. The grain size of Fe was calculated by Scherrer's formula [11] using the full width at half maximum (FWHM) of Fe (110):

$$D = 0.9\lambda/B\cos\theta \quad (2)$$

where

D: Grain size(nm).
λ: Wave length of Mo Kα radiation (0.7093 nm).
B: FWHM of Fe (110) plane in radian.
θ: Diffracted angle of Fe (110) in radian.

TEM specimens were prepared by Electro Discharge Machining (EDM) wire cutting to 3 mm diameter cylinders and slicing about 0.5 mm thick disks from the consolidated samples using a low stress diamond cutting saw. The disks were polished mechanically to 100 μm using SiC paper. Final specimen thinning was done using an electro-polisher to perforation with a 15% perchloric acid/methanol solution at 243 K. The perforated specimen was ion-milled for 5 min. to eliminate the ferro-oxide at the surface which have been formed while electro-polishing.

The micro Vickers hardness tests and compressive tests were performed on the HPed and on the HIPed samples to determine the mechanical properties of the samples. The compressive tests were run in a floor model Instron™ with 5 ton load cell at room temperature. The test specimens were machined by Electro Discharge Machine (EDM) and ground with a centerless grinder in order to achieve smooth, flat and parallel cylinders with 11 mm long by 5 mm diameter. The specimens were then deformed between hardened tool steel plates using Teflon™ tapes to reduce barreling effect. Load–elongation data were converted to true stress–true strain by digitizing chart recording with assumption of conservation of volume during deformation. The nominal strain rate for the tests was typically 1×10^{-3}/s. The Vickers hardness test was performed with a load of 500 g. The arithmetic averages of 0.2% off-set yield strength and Vickers hardness of the consolidated materials exclusive of the highest and the lowest from 10 measurements were reported along with the standard deviation in Pascal (N/m^2: Pa). The details of the processing and characterizing techniques are in elsewhere [12,13].

3. Results and discussion

Fig. 1 shows XRD patterns of the milled powder collected from milling times of from 0 h up to 16 h to observe the evolution of the displacement reaction (1). The result illustrates that Fe_3O_4 and Al peaks proportionally disappeared with increasing milling time; the counts of these peaks were well below the resolution limit of XRD after 12 h milling, which is indicative evidence of the milling completed. None of Al_2O_3 XRD spectra can be identified in the milled powder even after the completion of the milling. Fig. 2 illustrates the typical XRD pattern of the consolidated samples where only Fe and Al_2O_3 peaks are present. This XRD result is in agreement with STEM–EDS mapping (Fig. 3) which shows the size and distribution of Al_2O_3 dispersoid in the Fe matrix.

The grain size of the milled powder and the consolidated samples was estimated by using Scherrer's formula (2), measuring FWHM of Fe (110) XRD peaks. The results of the grain size measurement are shown in Table 1. The grain sizes of Fe in the consolidated samples are typically 15.8 nm while the milled powder 9.3 nm, which indicates that the presence of the dispersoids leads to the withholding the grains from the coarsening by grain boundary pinning effect even after HP and HIP processing. As shown in Table 1, the hardness of the HIPed samples was as much as 3.70 ± 0.1 GPa while the HPed sample was 3.17 ± 0.08 GPa. The difference of the hardness may be attributed to the existing pores even after HP.

The typical bright and dark field TEM images of the HPed sample are illustrated in Fig. 4. The bright field image, Fig. 4(a), shows overall microstructure of the consolidated materials with the grain size of matrix and the distribution of the dispersoids. An attempt was made to identify the phases in the samples by indexing electron diffraction pattern taken in the representative area. The diffraction analysis (Fig. 5) reveals that all of the diffracted beams (spotty rings) are attributed to the mixture of nano-sized Fe and Al_2O_3 dispersoids. Separation of Al_2O_3 phase from the Fe matrix was performed on the dark field image of the sample by taking only electron diffraction beams of Al_2O_3 (104) and (110). A set of TEM images of the HIPed sample was also given in Fig. 6 for the microstructural comparison with HPed sample. One dark field image, Fig. 6(c), shows the homogeneous distribution of the dispersoids with the uniform size; another dark field image, Fig. 6(b), reveals the grain size of Fe matrix. No significant microstructural difference (grain size, and size distribution of dispersoids) was found in between the HPed and the HIPed. A HRTEM (High Resolution Transmission Electron Microscopy) and a

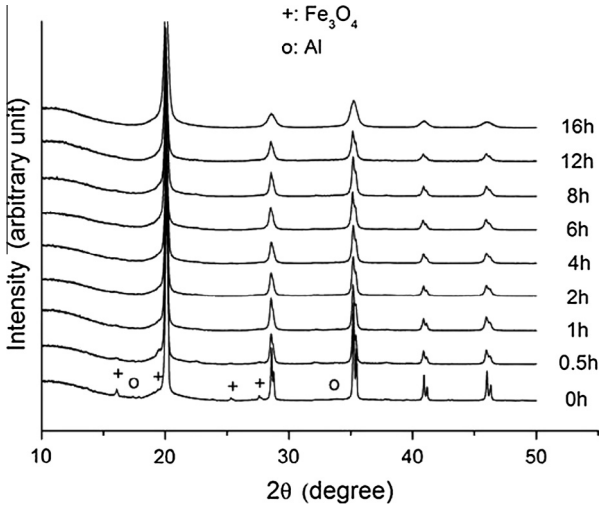

Fig. 1. XRD patterns as a function of milling time up to 16 h.

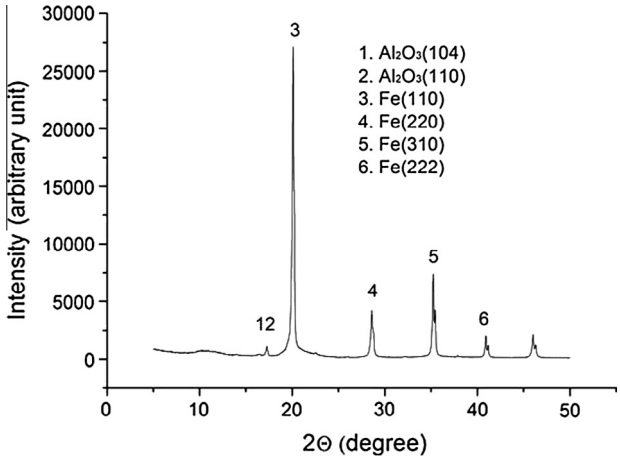

Fig. 2. XRD pattern of the HIPed Fe with Al_2O_3 (sample D, Table 1) after consolidation under the load of 100 MPa at 1323 K.