Microstructural Characterization of Nb-Al Base ODS Alloys

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Abstract. Nb, Al and Y_2O_3 powders were mechanically alloyed together with 5 wt% stearic acid. The heavy plastic deformation of the powders by mechanical alloying led significant hardening to 970 Hv and the reduced grain size to 10 nm. Nb-Al base ODS alloys consolidated by HIP at 1500 ºC and 150 MPa for 0.5 h gave the dual phase of Nb solid solution and Nb_3Al compound. The oxide particles are of the hexagonal type $YAlO_3$ (YAH), with the size of 50 nm to 200 nm. The high-temperature ductility at 1200 ºC and capability of the grain growth at 2000 ºC were confirmed.

Introduction

Nb metal has a unique potential for applying to the advanced high-temperature materials because of its high melting-temperature and lower specific density among the high melting-temperature metals such as Mo, W and Ta. We have been developing the oxide dispersion strengthened (ODS) alloys for Fe-base [1], Ni-base [2] and Co-base [3] alloys. This technique is applied to develop the Nb-Al base ODS alloys, where high-temperature strengthening can be achieved by the dispersed Y_2O_3 particles and oxidation resistance can be led by an alumina scale formation on the alloy surface. In this study, Nb-Al base ODS alloys are produced by means of mechanical alloying (MA), and their microstructure of the consolidated alloys is characterized from a viewpoint of nano-meso scale structural control.

Experimental Procedures

Pure elemental powders of Nb and Al as well as Y_2O_3 powder were blended in appropriate amounts to give the target compositions. They were mechanically alloyed for up to 50 h in an argon gas atmosphere using a planetary-type ball mill (Fritsch P-6). At the same time, stearic acid, $C_{17}H_{35}COOH$, was added to prevent cohesion of powders on the surface of the balls and pot. A pot with a volume of 45 cm^3 was rotated at a speed of 420 rpm; the pot is filled with 7 g powders and 70 g balls; the weight ratio of balls to powders was set at 10:1. The chemical composition of the MAed powder produced is Nb–15Al–0.6Y_2O_3 (at%). Nb–15Al–3.3Y (at%) and Nb–15Al–30Re–1.7Y_2O_3 (at%) were also prepared in the same way. The MAed powders were consolidated by hot pressing at 1200 ºC and 42 MPa for 2 h and subsequently the consolidated alloys were treated by HIP (hot Isostatic Pressing) at 1500 ºC and 150 MPa for 0.5 h. The fully dense alloys were produced through these processing.

An appearance of the MAed powders was observed by means of the secondary electron microscopy (SEM) of JEOL JSM-6390. An X−ray diffraction (XRD) measurement was conducted using Philips X'Part Pro, which is equipped with an Mo X−ray source. The microstructure was analyzed by means of JEOL JET-2000EX-T transmission electron microscopy (TEM) with an energy dispersive spectrometer (EDS) allowed to identify the constituents. The thin foils for TEM analyses were prepared by precision ion polishing system (PIPS), because Nb-Al base ODS superalloys are too brittle to prepare by mechanical polishing. The compression test was conducted by using 3 mm×3

mm×6 mm specimens which were cut from the HIPed alloys. The test condition is at temperature of 1200 ºC and strain rate of 2×10^{-4} s^{-1} under argon gas atmosphere.

Results and Discussion

Characteristics of mechanical alloyed powders. Fig. 1 shows the SEM morphology of the Nb−15Al−0.6 Y$_2$O$_3$ powders, which were mechanically alloyed for 20 h without and with addition of 5 wt% stearic acid. MAed powders show typical featuer of severe plastic deformation, which is ascribed to the repeated fracture and cold-welding of powder mixture. The diameter of MAed powders without stearic acid seems to be around 80 μm, whilst the addition of stearic acid in MAed powders leads to bimodal distribution with the particle size of less than 10 μm and about 30 μm.

The XRD was conducted for Nb−15Al−0.6 Y$_2$O$_3$ powder mechanically alloyed for 1−50 h. The diffraction peaks of Y$_2$O$_3$ and Al can be slightly identified as−mixtured state. However, MA for only 1 h induces almost disappearance of their peaks, implying that Y$_2$O$_3$ decomposed and Al dissolved into Nb matrix during MA. Similar behavior in Y$_2$O$_3$ decomposition is reported in Fe-base, Ni-base and Co-base ODS alloys [1-3].

The diffraction peaks corresponding to Nb are broadened and shifted to higher diffraction angle, which are resulted from introducing the high density of dislocation and severe lattice distortion. The changes of grain size during MA can be derived from XRD broadening of Nb peaks on the basis of Hall-Williamson equation. Fig.2 shows the change of grain size and hardness in Nb−15Al−0.6 Y$_2$O$_3$ powders with respect to the MA time. Heavy plastic deformation gives rise to the hardening of the powders, which shows obviously two regions. In the first 10 h, the hardness increases rapidly and reaches 970 Hv; the longer MA time cannot further increase the hardness. The grain size is reduced to about 10 nm at the same time. Both hardness and grain size maintain almost same level up to the end of MA for 50 h. The hardening of MAed powder could mainly arise from strain hardening and nanometer-scale grain refining.

Fig. 1 Morphology of Nb-15Al-0.6Y$_2$O$_3$ powders mechanically alloyed (a) without and (b) with 5 wt% stearic acid.

Fig. 2 Changes of Vickers hardness and grain size during mechanical alloying of Nb-15Al-0.6Y$_2$O$_3$ powders.

Structure of consolidated alloys. As a representative of the produced alloys, Fig. 3 shows the results of SEM and TEM analyses of the consolidated Nb−15Al−0.6Y$_2$O$_3$ alloy. An area (a) turns out to be Nb solid solution and an area (b) corresponds to Nb$_3$Al intermetallic compound with the cubic A15 crystalline structure from the TEM-EDS analyses and the selected area diffraction patterns. These results are consistent with the Nb-Al binary phase diagram, composing of Nb solid solution and Nb$_3$Al intermetallic compound at Nb-15Al alloy. From the TEM-EDS analyses, it was
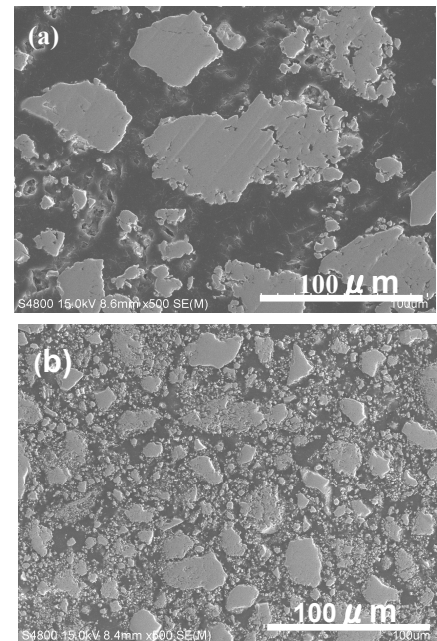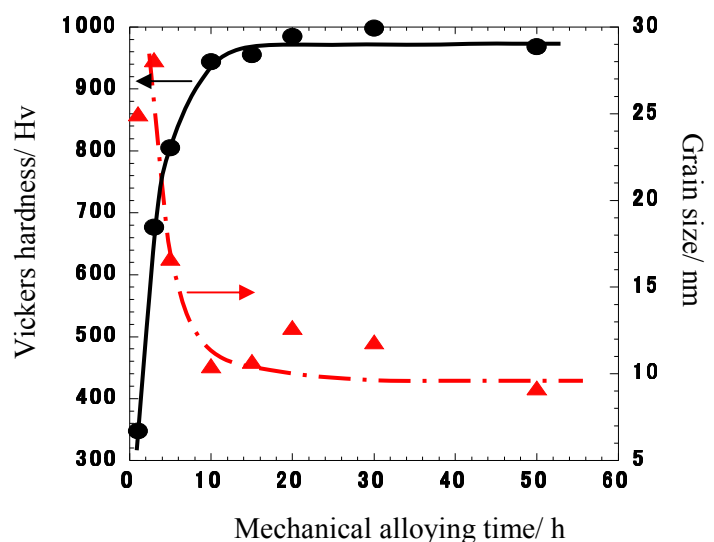
turned out that both phases contain a few atomic percent of oxygen. A small size of many dots observed in area (a) was formed during ion polishing by PIPS. These dots don't belong to the oxide particles. The same results were obtained in the specimens of Nb−15Al−3.3Y and Nb−15Al−30Re −1.7Y$_2$O$_3$.

Fig. 4 shows the oxide particles observed in Nb−15Al−30Re−1.7Y$_2$O$_3$. From the selected area diffraction patterns and the TEM-EDS analyses, it was revealed that major oxide particle is YAlO$_3$ (Yttrium Aluminum Hexagonal: YAH), and Y$_4$Al$_2$O$_9$ (Yttrium Aluminum Monoclinic: YAM) is minor one. The Y$_2$O$_3$−Al$_2$O$_3$ binary phase diagram is shown in Fig.5, indicating that Y$_4$Al$_2$O$_9$ (YAM) and Garnet type of Y$_3$Al$_5$O$_{12}$ (YAG) are stable and coexist at the HIP temperature of 1500 ºC. The hexagonal type of YAH is not indicated in Fig.5. However, Nishi and Shaffer [4] reported that YAH is the dominant oxide particles observed in Ni-Al base ODS alloys; this compound could be meta-stable state. The results of present study in Nb-Al base ODS alloys are consistent with the previous studies in Ni-Al ODS alloys. A formation mechanism of meta-stable YAlO$_3$ (YAH) in Nb-Al ODS alloys is to be further studied.

A size of YAH particles ranges from 50 nm to 200 nm, which are almost ten times larger than those of the oxide particles formed in Fe-base and Ni-base ODS alloys. Such coarsening of the oxide particles could be taken place during HIP consolidation at 1500 ºC. This temperature is only 300 ºC below a eutectic temperature of Al$_2$O$_3$−Y$_2$O$_3$ binary system (around 1800 ºC) shown in Fig.5. The oxide particle coarsening should be inevitable in Nb-Al base ODS alloys from two reasons; YAH type oxide particles, Y$_2$O$_3$:Al$_2$O$_3$=1:1, are formed with the reduced eutectic melting-temperature, and higher sintering temperature is necessary for Nb alloy with high melting-temperature. One of the solutions to prevent oxide particle coarsening is an addition of a specific element to replace Y$_2$O$_3$−Al$_2$O$_3$ oxide particles with another type with high melting temperature, such as Y$_2$O$_3$−HfO$_2$.
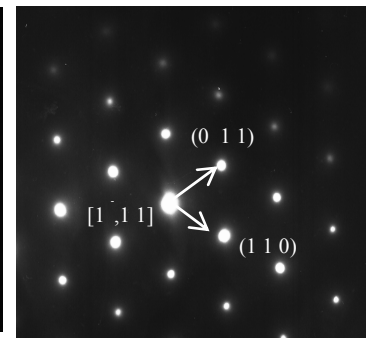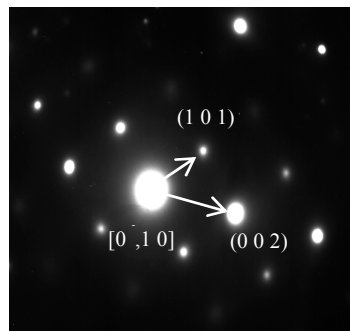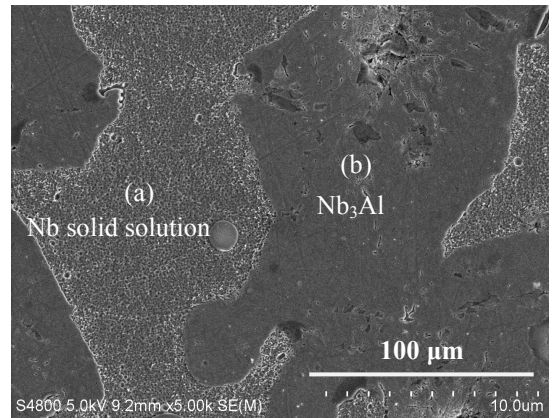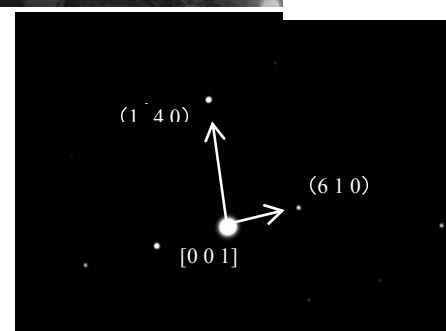

(a) Nb solid solustion   (b) Nb$_3$Al

Fig. 3 SEM and TEM analyses including the selected area diffraction patterns of the Nb solid solution and Nb$_3$Al in the consolidated Nb-15Al-0.6Y$_2$O$_3$.
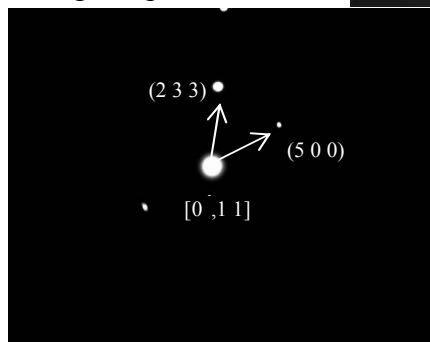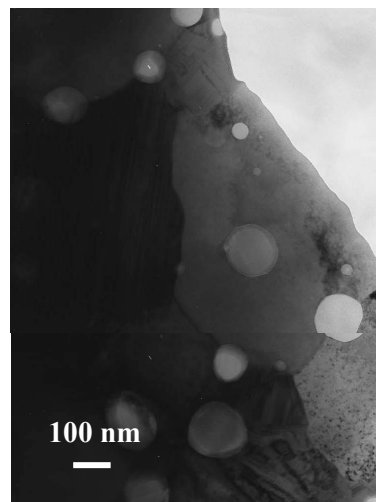
YAlO$_3$(YAH)   Y$_4$Al$_2$O$_9$ (YAM)

Fig. 4 TEM micrograph and selected area diffraction patterns of the oxide particles.

High-temperature ductility and grain coarsening.
High-temperature compression test was conducted at 1200 °C under the vacuum condition for evaluating ductility of $Nb-15Al-0.6Y_2O_3$ alloy. This alloy is very brittle at room temperature, however, it was revealed that the compressive ductility is adequately maintained more than 20 % at 1200 °C. Their microstructure is represented in Fig. 6 (a). The grain size fabricated by HIP at 1500 °C for 0.5 h is about 20 μm. The high-temperature heat treatment at 2000 °C for 1 h under vacuum induces grain coarsening to more than 100 μm as shown in Fig. 6 (b). Such grain coarsening should be substantial for high-temperature strengthening materials to minimize grain boundary sliding. In Fig. 6 (b), the bubbles pressurized by argon gases can be seen at grain boundaries, which were introduced during the process of mechanical alloying, and were grown at the high-temperature of 2000 °C. Another gas such as hydrogen instead of argon could be required as an atmosphere inside MA pot.

Fig. 5 Al_2O_3–Y_2O_3 phase diagram

Summary

The Nb-Al base ODS alloys were produced by MA with addition of 5 wt% stearic acid. The heavy plastic deformation introduced by MA gives adequate hardening of the powders and the reduced grain size to 10 nm within MA period of 10 h. Nb solid solution and Nb_3Al coexist in the matrix of the consolidated alloys, and the oxide particles are coarsened in size of 50 nm to 200 nm by the formation of hexagonal type of $YAlO_3$ (YAH). The compression ductility is maintained more than 20 % at 1200 °C. The grains can be grown to more than 100 μm in size by heat treatment at the elevated temperature of 2000 °C for 1 h, to minimize grain boundary sliding and thus to improve high-temperature strengthening.

Fig. 6 Optical micrographs of $Nb-15Al-0.6Y_2O_3$ alloy; (a) consolidated by 1500 °C HIP, (b) heat treated at 2000 °C for 1 h.

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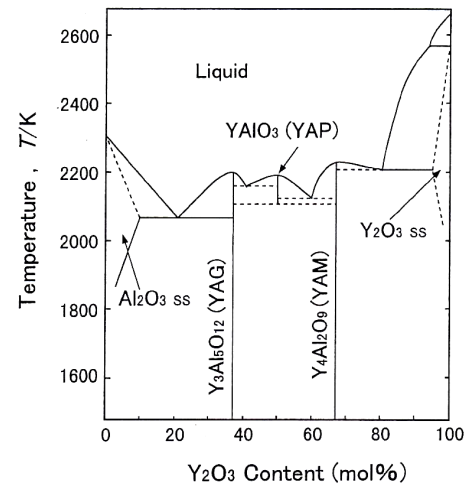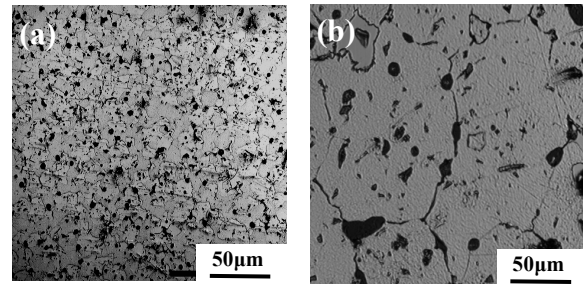[4]   G. B. Schaffer, M.H. Loretto, R.E. Smallman and J. W. Brooks: Acta Metall., 37 (1989), p. 2251.