***In-situ* Observation of C14 Type Laves Phase Nucleation from Mechanically Milled Amorphous Zr-Ni-V-Mn-Fe Alloy**

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Nanoscale polycrystalline powders which consist mainly of the C14 type Laves phase were obtained from the amorphous phase produced by mechanically alloyed (MA) metallic powders (pure Zr, pure Ni, and atomized Ni-V-Mn-Fe alloy) after annealing under vacuum atmosphere. The average diameter of nanoscale grains was of the order of 10 nm. Nucleation of the C14 type Laves phase from the amorphous phase was confirmed by the exothermic reaction in a differential scanning calorimeter (DSC), X-ray diffraction (XRD) and transmission electron microscopy (TEM). Onset of the exothermic reaction was observed at 473 and 889 K, respectively. *In-situ* observation of TEM with a heating stage determined the nucleation of the C14 type Laves phase at 473 K and the secondary recrystallization at 889 K with lattice images.

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I. Introduction

The MA process which enables homogeneous dispersion of foreign particles in matrix materials⁽¹⁾⁽²⁾, nanocrystalline materials⁽³⁾⁽⁴⁾, amorphous phase formation⁽⁵⁾⁽⁶⁾, and non-equilibrium phase formation⁽⁷⁾⁽⁸⁾ is introduced in various purposes which aims to solve the difficulties in materials manufacturing. The amorphous phase formation is a basic object for this study because the purpose of the present research is the evaluation of nanoscale polycrystalline of Laves phase in Zr-Ni-V-Mn-Fe alloy system. Lee *et al.*⁽⁹⁾ pointed out the composition range of amorphous phase formation in Ni-Nb system for MA is wider than any other processes such as splat quenching, r.f. sputtering, LASER quenching, and ion-beam mixing. Shultz⁽¹⁰⁾ also reported the excellence of MA process to obtain wide range composition of amorphous phase in Fe-Zr. The MA process can be applied for amorphous phase formation in wide range of alloy composition.

Sawa *et al.*⁽¹¹⁾ reported that coexistence of C14 and C15 type Laves phase is detected from the conventional ingot casting of Zr-Ni-Ti alloy. The grain refining of these Laves phases is the most concern for commercial application of this alloy system. If the MA process is introduced in amorphous phase formation, infinitesimally small grains can be obtained for each powder.

The manufacture of an infinitesimally fine grain size Laves phase is the primary goal of the present study. The evaluation of the structural change from MA metal powders to the recrystallized Laves phase via amorphous formation is investigated by *in-situ* TEM observation and EDS. The *in-situ* TEM observation at high temperatures is previously reported by Kamino *et al.*⁽¹²⁾ for ceramic

materials. The same method is utilized for observation of the nucleation from the amorphous phase at high temperatures.

II. Experimental

The mechanical alloying technique is utilized for mixing of metal powders (Zr, Ni, and atomized Ni-V-Mn-Fe). The fraction of metal elements is given in Table 1. The preparation of powders for MA is carried out in globe box under Ar atmosphere. The vessels (500 ml) and balls (10 mm dia.) for MA are made of stainless steel (SUS304). The contamination on specimen and equipment inner surfaces is removed by baking under vacuum (1.3×10^{-3} Pa) before MA. The vessels are wound by a heating wire which is heated at 393 K. High purity Ar gas is introduced into the vessels after baking. The mass of mixed powders is varied from 100 to 300 g for each vessel. The condition of the MA process is given as the rate of vessel rotation, 250 rpm, and the operation time 260, 500, and 680 ks, respectively.

Characterization of the amorphous phase and nanocrystalline is carried out by DSC, XRD and TEM. The condition of DSC is given as the temperature ascending rate, 0.33 K/s, under Ar gas atmosphere. The copper target of XRD is used at 40 kV and 150 mA. The conventional electron microscopy is used for MA particles by Hitachi H-800 at 200 kV.

The *in-situ* observation at elevated temperatures is car-

Table 1 Compositions of metal powders (mass%).

Zr	Ni	V	Mn	Fe
44.84	31.74	12.52	5.40	5.59

Fig. 1 Appearance of heating stage. (a) an example of the heating element, (b) Sample stage.

ried out with W filament where MA particles are sprinkled (Fig. 1). Four conventional dry batteries (1.5 V) are a directly connected to voltage controller as an external power unit for the TEM heating stage. The lattice image of nanocrystalline at elevated temperatures is observed by Hitachi H-9000NAR operated at 300 kV. The accommodation curve of temperature against applied voltage

has in advance been measured in a vacuum chamber. It is considered that the specimen temperature is same as W filament temperature because the size of MA particles is small compared to that of W filament.

III. Results and Discussion

Morphology of MA particles is shown in Fig. 2. The number of fold of particles is increased as a function of MA operation time. The size of particles is decreased also as a function of MA operation time. Homogeneity of each particle can be realized in the smaller particles. Some large particles contain a relatively large single element in folded grain. The shape of the single element is irregular but similar to a rectangle.

Broadening of Bragg peaks in XRD as a function of MA operation time is shown in Fig. 3. All spike peaks are smoothed after the MA operation time of 500 ks. No significant difference in X-ray peak profile is detected between 500 and 680 ks. It is another concern whether MA process for the present alloy system can form the amorphous phase.

The dark field image and diffraction pattern of MA particle is shown in Fig. 4. A halo ring and sharp spots are obtained in the diffraction pattern. The dark field image is obtained from the lower spot which brightens

Fig. 2 SEM image of (a) morphology of particles as a function of MA operation time, (b) cross section of kneaded particles corresponding to that of (a).

Fig. 3 X-ray peak broadening as a function of MA operation time.

Fig. 4 Nanocrystals in an amorphous MA particle.

Fig. 5 Beginning of exothermic peaks at 473 K and 889 K in DSC profile.

infinitesimal crystals in the amorphous particle. It can be concluded that the MA process for this alloy system causes not only grain refinement but also the amorphous phase.

Nanostructure powders can be obtained if nanocrystalline simultaneously nucleate in an amorphous particle.

Fig. 6 Nucleation of the C14 type Laves phase at elevated temperatures in XRD.

Fig. 7 Bright field image of the C14 type Laves phase.

The nucleation temperature can be detected by DSC. The DSC profile of powders MA for 680 ks is shown in Fig. 5. Exothermic peaks are observed 473 and 889 K.

It is necessary to determine why two exothermic peaks occur. The amorphous MA powders are annealed at various temperatures such as 855, 903, and 1033 K for 1.8 ks. The XRD profiles are shown in Fig. 6. The C14 type Laves phase has already appeared in the XRD profile taken from a specimen annealed at 855 K. This temperature is 34 K lower than the exothermic DSC profile in Fig. 5. The nucleation temperature of C14 Laves phase must be lower than 855 K. It can be concluded that the nucleation of the C14 Laves phase should correspond to the exothermic peak at 473 K.

Moreover, the peaks in the XRD profile of the C14 type Laves phase become higher as a function of temperature. No other peaks appear either at 903 or 1033 K. This may imply that secondary recrystallization of the C14 type Laves phase takes place at 889 K.

The bright field image and diffraction pattern of the

Fig. 8 Lattice image of a nanocrystal in amorphous phase before heating.

Fig. 9 Lattice image corresponding to nucleation of the C14 type Laves phase.

C14 type Laves phase of the MA specimen annealed for 1.8 ks at 1033 K is shown in Fig. 7. The crystal structure of the C14 type Laves phase is close packed hexagonal as shown in the figure. Morphology of the particle is similar to the previous shape of folded MA powder.

The MA particle is observed by *in-situ* observation as shown in Fig. 8. The most area of this image becomes blurred because of the amorphous phase. However, an elliptical nanocrystal is observed as the lattice image. The size of the ellipse is 10 nm long in dia. and 8 nm in short dia. which implies the shape of ellipse is similar to a circle. The lattice spacing of the ellipse is 0.16 nm which corresponds to Ni (200) but not to any Laves phase. This nanocrystal is used as the reference of the area during *in-situ* observation.

Nucleation of the C14 type Laves phase is observed as a diamond shape lattice image at 533 K (Fig. 9). The size of this nanocrystal is about 10 nm long. The lattice image of the nucleated area oscillates at the beginning of nucleation for a moment. The lattice image becomes gradually clear. The nucleated nanocrystals show a different crystallographic orientation from the reference crystal. The lattice images along specimen edge are caused by adhesion of contamination due to emission of electrons during the TEM observation.

The elevation of temperature above the nucleation of the C14 type Laves phase causes acceleration of the nucleation rate as shown in Fig. 10. The formation of grain

boundaries among nanocrystals is observed.

The size of nanocrystals indicates fast grain growth as shown in Fig. 11. The temperature of W filament reaches about 823 K at this stage. Moiré fringes are observed in a superposition of two nanocrystals. The whole area of this image consists of nanocrystals at constant temperature, 823 K. If the growth rate of the reference crystal is compared with other nanocrystals, the growth rate is remarkably small.

It is necessary to identify the structure of nanocrystals and its constituent elements. The diffraction pattern and the energy dispersed spectroscopy (EDS) are examined from the same particle after *in-situ* observation as shown in Fig. 12. The diffraction pattern indicates the C14 type Laves phase. The result of EDS from small area, 20 nm dia., shows that all constituents for the C14 type Laves phase exist in the selected area of electron diffraction. It can be concluded that the nucleation and recrystallization of the C14 type Laves phase is identified by *in-situ* observation with a heating stage combined with electron diffraction and X-ray energy dispersion spectroscopy.

IV. Conclusions

- (1) The amorphous phase is obtained from mechanically alloyed metallic powders, Zr, Ni, and atomized Ni-V-Mn-Fe alloy.
- (2) A new phase (C14 type Laves phase) was nucle-

Fig. 10 Lattice image corresponding to grain boundary formation of nanocrystals.

Fig. 11 Lattice image corresponding to secondary recrystallization.

(a)

(b)

Fig. 12 Identification of C14 type Laves phase with SAD and EDS. The beam size of EDS is about 20 nm dia. in the SAD area. (a) Profile of EDS at local area of recrystallized nanoscale grain in Fig. 11, (b) SAD pattern of the same area but aperture size is much longer than size of EDS.

ated from amorphous phase to form nanocrystals at 499 K.

(3) Secondary recrystallization occurred in the nanocrystals at 864 K.

(4) *In-situ* observation in TEM enables determination of nucleation and secondary recrystallization of the C14 type Laves phase with lattice images.

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