研 究

X-ray Study on the Formation of Nano-crystallite and Amorphous Phase of Mo-Fe by Ball Milling

Hisashi Kuwano^{☆1}, Hiroyuki Morita^{☆2} and Toru Ishigaki^{☆1}^{☆1} Muroran Institute of Technology, 27-1 Mizumoto-cho, Muroran 050. ^{☆2} Graduate School, Muroran Institute of Technology, [Present Address: Mitsumi Electric Co., Ltd., 1601 Sakai, Atsugi 243].

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SYNOPSIS

Pure Mo powders are mechanically attrited with a hardened steel vial and balls in an Ar atmosphere to produce nanostructural and amorphous Mo-Fe alloys. A time evolution of the solid state amorphization caused by the attrition is classified into three stages. In the initial stage the crystallite size of Mo decreases down to 10 nm together with the increase in the lattice strain up to 1.8%. Plastic deformation is a dominating cause of the crystallite size reduction. In the next stage, the crystallite size decreases down to a minimum dimension of 5nm. The reduction of the grain size is accompanied by a decrease in the lattice strain and the solid solutioning of the Fe impurities which are introduced from the vial and balls in the prior stage. The grain size reduction in this stage is interpreted in terms of recovery process of the stored strain. In the final stage where the Fe content in the Mo lattice saturates about 18at%, a transition from the nano-crystallites to an amorphous phase takes place.

KEY WORDS

nanocrystallite, amorphous phase, grain size, ball milling, Mo-Fe,

I Introduction

Ball milling is a distinguished technique to produce nanoscaled grains and amorphous phases in solid state^(1,2). The process usually accompanies an increase in the lattice strain⁽³⁾, reduction in the crystallite size^(1,3), and mixing of elemental powders in the atomic scale⁽⁴⁾. The lattice strain increased in the short time milling followed by a decrease in the longer milling times^(3,5). A correlation between the lattice strain and the reduction of the crystallite size has not been clearly understood.

Ball milling of Cr-18.5%Fe in an argon atmosphere yielded a nanocrystallite of 3nm grain size after 96 hours milling, but the formation of the amorphous phase has not been confirmed⁽⁶⁾. On the other hand, ball milling of Cr₇₀Fe₃₀ powders in a nitrogen atmosphere finally yielded amorphous phases containing 15.1at% nitrogen content⁽⁷⁾. These facts suggest that the solutioning of nitrogen atom plays an important role to yield amorphous phase since atomic size difference between Fe and Cr is quite small. In case of Mo-Fe, however, a mixture of Mo and Fe mixed in ratios of 4:6 to 6:4 yielded amorphous phases after the 500h ball milling in an argon atmosphere⁽⁸⁾. In this case, a large difference of the atomic size between Mo and Fe seems to be meaningful for the amorphous formation.

In the present study, Mo powders are mechanically attrited in an argon atmosphere to produce nanostructures and Mo-Fe amorphous phases. Fe is intended to be mixed from the vial and ball materials by abrasion. Processes of straining, mixing and alloying of Fe, reduction of the crystallite size, and formation of amorphous phase are investigated to clarify the solid state amorphization.

II Experimental procedure

Mo powders of 99.9% purity were mechanically milled by steel balls in a steel vial both of which are made of SUJ2 steel in an Ar atmosphere using a high energy type SPEX 8000 mixer/mill. Nominal chemical compositions of the SUJ2 steel are 1.0%C, 0.75%Mn, 0.25%Si, 1.5%Cr and the balanced Fe. A powder-to-ball weight ratio was 1 to 8. X-ray diffraction(XRD) patterns of Cu-K α radiation were decomposed into K α 1 and K α 2 component by using a profile-fitting program. The X-ray profiles were analysed as a superposition of the crystalline and the amorphous component for the long term milling. Broadening of the X-ray diffraction peaks was interpreted in terms of the reduction of the grain size D and the increase in the lattice strain ϵ . Mo and Fe contents in the milled powders were analyzed by a X-ray energy dispersive spectrometer (EDS).

III Results

3.1 Mixing and alloying of Fe

As shown in Fig.1, XRD peaks due to Mo become broader with increasing milling time. Their peak positions shift to higher angles with the milling time becomes longer than 10h. After the 470h milling, sharp diffraction peaks characteristic of the crystalline Mo are entirely replaced by halo peaks which are ascribed to an amorphous phase. Since a (110) diffraction peak of Fe appears about 45° for $t=5$ and 25h, Fe impurities which originate from the abrasion of the vial and balls are mixed with Mo powders. However, the (110)_{Fe} peak disappears when the milling time becomes longer than 80h, which means that the Fe impurities from the vial and balls dissolve to make solid solutions with Mo.

Fig.1 Change in the X-ray diffraction profiles of Mo after high energy ball-milling with the milling time labelled(CuK α radiation).

The lattice parameter a of Mo changes in three stages with milling time as shown in Fig.2. In the first stage for $t < 15$ h, there is no appreciable change in a although (110)Fe diffraction peak coexists with diffraction peaks of Mo. So the iron impurities introduced from the vial and balls exist as a mechanical mixture. In the second stage between $t = 15$ h and 100h, a gradual decrease in a occurs. The change is ascribed to the alloying of Fe impurities into Mo because the total iron content measured by EDS increases as mentioned below. In the third stage for $t > 100$ h, no appreciable change in a occurs.

Open circles in Fig.3 present the Fe content measured by EDS as a function of milling time. The Fe content increases with the milling time becomes longer. It is reasonable to consider that the decrease in a of Mo mentioned above is caused by the alloying of Fe into the Mo lattice. Hence the Fe content dissolved in the Mo lattice may be estimated from a on the basis of Vegard's law. As shown by solid circles in Fig.3, the Fe content determined by XRD increases with an increase of the milling time after an elapse of the duration time of about 10h, and saturates to a value of 18at% for $t > 100$ h. Since halo peaks characteristic of the amorphous phases appears about 80h, we may consider that the saturated iron content is a critical one where a transition from the nanostructure to the amorphous phase takes place.

Large discrepancies between the results of XRD and those of EDS may be explained as follows. Fe atoms may exist as the finely dispersed iron mixtures, solutes in the nanostructured Mo, those in the amorphous phase, and chemical segregations at grain boundaries. EDS measurements can detect a sum of these Fe atoms in different situations. However in case of XRD measurements, only Fe atoms substituted in the bcc Mo lattice are detected to result in the lower Fe content than EDS.

Fig.2 Lattice parameter of Mo as a function of milling time.

Fig.3 Iron content of Mo measured by energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD) as a function of milling time.

3.2 Formation of the nano-crystallite

The widths of the X-ray diffraction peaks due to Mo become broader with the milling time becomes longer. In general two contributions are responsible for the line broadening. One is a decrease in the crystallite size D , and the other is an increase in the lattice strain ϵ . These two contributions are separated using the following relation;

$$B \cos(\Theta/\lambda) = 1/D + 2\epsilon \sin(\Theta/\lambda) \quad (1)$$

where B , λ are the integrated line width and the wave length, respectively. A typical example of the plot for

Fig.4 $B\cos\theta/\lambda$ versus $\sin\theta/\lambda$ plot for Mo diffraction lines after ball milling for 10 hours.

eq.(1) is given for the 10 h milling in Fig.4. A good linear relationship is confirmed among five data as shown by a solid line. Deviations of the experimental points from the line are not strongly dependent on the diffraction plane. This result suggests that ϵ is nearly isotropic. D and ϵ are determined from the y intersection and the slope of the line obtained by a least-square-fitting according to eq.(1), respectively. Values of D obtained in such a way are plotted versus milling time in Fig.5. In the first ten hours, D decreases rapidly down to about 10nm, and then gradually approaches to a constant value of 5nm. The size is a little larger than 3nm for the Cr-Fe nanocrystallite⁶⁾. Further longer ball-milling causes no appreciable change in D .

Fig.5 Crystallite size of Mo measured from the X-ray diffraction line broadening as a function of milling time.

As shown in Fig.6, ϵ changes in three stages in a similar way with a . At first, ϵ increases to a maximum of 1.8% with increasing milling time, then decreases in the milling time periods of $20\text{h} < t < 100\text{h}$. Though the scattering of the experimental data is a little large, ϵ has a tendency to approach to a constant of ca. 1.4% in the final stage. In Fig.7, ϵ is plotted versus D . Since the reduction in D down to 10nm is

accompanied by the increase in ϵ in the first stage of the ball milling, a plastic deformation of Mo caused by the ball collisions may be a controlling process of this stage. But the following reduction in D occurs with the decrease of ϵ , indicating that a controlling mechanism is different from one mentioned above. It is well known that recovery during thermal annealing involves a reduction of ϵ introduced by cold work.

Fig.6 Strain of Mo induced by high-energy ball milling as a function of milling time.

Fig.7 Strain as a function of crystallite size of Mo ball milled for various times.

In order to confirm whether the reduction of ϵ and D are cooperative in the recovery process during thermal annealing of nano-structured phases, a ball-milled sample with $D=7\text{nm}$ has been annealed at 400°C for various times. The 400°C annealing causes a negligible small change in the lattice parameter as shown in Fig.8(a), which means no appreciable change in the Fe content. However the annealing is accompanied by a reduction in D from 7 to 5nm together with a decrease in ϵ . in a similar way of the second stage of the ball-milling. The process may be interpreted in terms of recovery which usually involves a rearrangement of dislocations and annihilation of point defects.

3.3 Formation of the amorphous phase

The bottom of the (110)_{Mo} diffraction peak swells gradually around $2\theta=41$ degree when the milling time becomes longer than 80h, as typically confirmed in the profile of the 250h milling in Fig.1. After the 470h milling, the swelling grows to a halo peak to replace the (110)_{Mo} peak. The XRD peaks due to the

Fig.8 Change in the lattice parameter(a), strain(b) and crystallite size(c) of the nano-sized Mo during annealing at 400°C.

crystalline Mo-Fe are replaced entirely by two broad peaks around 41 and 75 degree of two-theta angle. These XRD pattern changes are interpreted in terms of a phase transition from the nanocrystallite to an amorphous phase. The transition occurs when D and the Fe content become about 5nm and 18at%, respectively.

IV Discussion

According to Fecht⁽³⁾, three different stages were defined in the ball milling process of hcp Ru and CsCl-type AlRu. We can also confirm three stages in the ball milling process of bcc Mo. In the initial stage less than 15 hours of milling time, the crystallite size reduces down to 10nm. Since strain increases up to 1.8%, the reduction in the crystallite size is mainly caused by plastic deformation which introduces the fragmentation of crystalline grains due to tangled dislocation networks. The crystallite size of 10 nm may be a critical dimension to which the grain size reduction can be attained by the plastic deformation, because finer the crystallite size becomes higher the yield strength of Mo does.

An annealing experiment for ball-milled powders has revealed that the crystallite size of the nanophase reduces with a decrease in the stored strain. A similar phenomenon is expected to occur during ball milling. We anticipate that an instantaneous temperature rise due to the collision of

the high energy balls would give rise to recovery process in the second stage of ball milling, in which a further reduction in the crystallite size from 10 to 5nm occurs. The rearrangement of dislocations to form stable arrays such as low-angle boundaries or subboundaries may be responsible for the grain size reduction. According to an equilibrium phase diagram⁽⁹⁾, the solubility of Fe in Mo is expected to be negligibly small below 1000K. However nanosized Mo prepared by ball milling can dissolve Fe to a maximum amount of 18at%. A transition from the nanophase to the amorphous phase takes place when the Fe content in Mo exceeds the solubility limit. The distortion stored by the solute solution plays a role to induce the transition.

V Conclusion

Solid state amorphization of Mo caused by the high energy ball-milling is defined in three stages.

1 In the initial stage, the crystallite size reduces down to 10nm due to the plastic deformation, accompanied by the increase in the lattice strain. Fe impurities introduced from the vial and balls are mechanically mixed with Mo powders during the stage.

2 In the following stage, further reduction of the crystallite size down to a minimum value of 5nm occurs together with a decrease in the lattice strain. Spontaneous recovery is responsible for the process. Fe mixtures makes solid solutions with Mo to a saturation content of 18at%.
3 A transition from the nanocrystallite to the amorphous phase occurs finally when the Fe content in the nanocrystalline Mo lattice reaches to a critical value and the crystallite size becomes about 5nm.

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References

- 1) H.J.Fecht, E.Hellstern, Z.Fu and W.L.Johnson: *Advances in Powder Metallurgy*, 1-3, (1989),111.
- 2) Ricardo B. Schwarz: *Appl.Phys. Lett.* 49(3), (1986), 146.
- 3) H.J.Fecht: *Nanostructured Materials*, 1,(1992), 125.
- 4) B.Fultz, G.Le Caer and P.Matteazzi: *J.Mater. Res.*, 4,(1989), 1450.
- 5) H.Kuwano and Y.Hamaguchi: *JSPM*, 39,(1992), 211.
- 6) H.Kuwano, H.Ouyang and B.Fultz: *Nanostructured Materials*, 1,(1992), 143.
- 7) T.Fukunaga, E.Ishikawa, N.Kuroda, C.H.Lee and U.Mizutani: *Proc.4th Japan-Russia Sympo. on Mechanochemistry*(1992) 69.
- 8) Junji Kuyama, Keiichi N. Ishihara and P.H.Shingu: *JSPM*, 38,(1991),910.
- 9) O.Kubaschewski: *Iron-Binary Phase Diagrams*, Springer-Verlag Berlin Heidelberg New York, (1982),p65.