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Nitrogen-Induced Amorphization of BCC Type Solid Solution Alloys by Mechanical Alloying*

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Mixtures of elemental metal powders consisting of the group 5A and 6A metals, which form the bcc type solid solution alloys, have been mechanically alloyed using the planetary ball mill in an argon and nitrogen atmosphere. The products were characterized by X-ray diffractometry, transmission electron microscopy, differential scanning calorimetry and chemical analysis. The bcc type solid solution alloys were produced by mechanical alloying (MA) in an argon atmosphere. On the contrary, amorphization by the additive effects obtained by combining MA with nitrogenation was demonstrated in the alloys consisting of the group 5A and 5A metals, the group 6A and 6A metals, and $Ta_{50}Mo_{50}$. The factors controlling nitrogen-induced amorphization during MA and the formation conditions of the amorphous alloys were discussed.

KEY WORDS: amorphous, nitrogen, mechanical alloying, transition metals, solid solution

1.Introduction

The conditions and processes of solid state amorphization by mechanical alloying (MA) of the binary alloys with a large negative heat of mixing have been extensively investigated and its mechanism is now well understood [1-3]. On the other hand, the phase formation during MA in the systems with a small negative or positive heat of mixing is still less clarified. As well known, amorphization of pure metals and mixtures of elemental metal powders forming a complete solid solution, which show the zero heat of mixing, is generally difficult by MA in an inert gas atmosphere. The present authors have recently demonstrated nitrogen-induced amorphization by MA of mixtures of the group 4A metals, i.e. $Ti_{50}Zr_{50}$, which form the hcp type complete solid solution [4]. However, no amorphization was observed by MA of the Ni-Cu and Pd-Ni solid solution alloys under the same conditions. On the basis of these experimental results they have proposed that the existence of the stable nitride such as TiN_2 and ZrN_2 is essential to nitrogen-induced amorphization. The group 5A and 6A metals form the complete solid solution and the stable nitrides, so that MA of mixtures of metal powders consisting of them are expected to give rise to nitrogen-induced amorphization. In the present work, mixtures of metal powders consisting of the group 5A and 6A metals are mechanically alloyed in a nitrogen atmosphere. Nitrogen-induced amorphization is demonstrated.

2. Experimental

The purity and the size of the group 5A and 6A metal powders used in the present work are tabulated in Table 1. The powders were mixed to give the equiatomic composition in the glove box and were put into a SUS 316 stainless steel container together with SUS 316 stainless steel balls (3/8 inch in diameter). The ball-to-powder weight ratio was 20/1. A vial and a lid were sealed with a viton O-ring. Before introducing Ar or Ar + 20 % N_2 gas, the container was evacuated for 18 ks by the diffusion pump ($1x10^{-4}$ torr). MA was performed using a high-energy planetary ball mill (Fritsch P5). Structural changes of the samples were examined by means of powder X-ray diffractometry (XRD) using CuKα radiation. Thermal stability was investigated by a differential scanning calorimeter (DSC) under flowing argon. The nitrogen content was determined by the gas carrier fusion thermal conductivity method. The iron contamination content from the balls and the container was determined by the induction coupled plasma (ICP) emission method.

Table 1. The purity and the size of the group 5A and 6A metal powders used in the present work

	Purity	Size
V	99.5%	<325
Nb	99.9%	<200
Ta	99.9%	<325
Cr	99.9%	<100
Mo	99.9%	<325
W	99.9%	<325

3. Results and Discussion

3.1 Mechanical alloying of metal powders consisting of the group 5A and 5A metals

Figure 1 shows X-ray diffraction (XRD) patterns of $V_{50}Nb_{50}$, $V_{50}Ta_{50}$ and $Nb_{50}Ta_{50}$ powders mechanically alloyed for 360 ks in an argon atmosphere. The XRD pattern of $V_{50}Nb_{50}$ indicates the Bragg peaks of the bcc alloy. However, the XRD patterns of $V_{50}Ta_{50}$ and $Nb_{50}Ta_{50}$ indicate the broad peaks characteristics of the amorphous phase in addition to the Bragg peaks of the bcc structure, which suggest partial amorphization of these alloys.

Figure 2 shows XRD patterns of $V_{50}Nb_{50}$, $V_{50}Ta_{50}$ and $Nb_{50}Ta_{50}$ powders mechanically alloyed for 360 ks at 0.02 MPa N_2. These XRD patterns show the broad peaks around 2θ= 40° and 70°. Both a bright-field image and a dark field image of the 360 ks MA $V_{50}Nb_{50}$ are featureless and the

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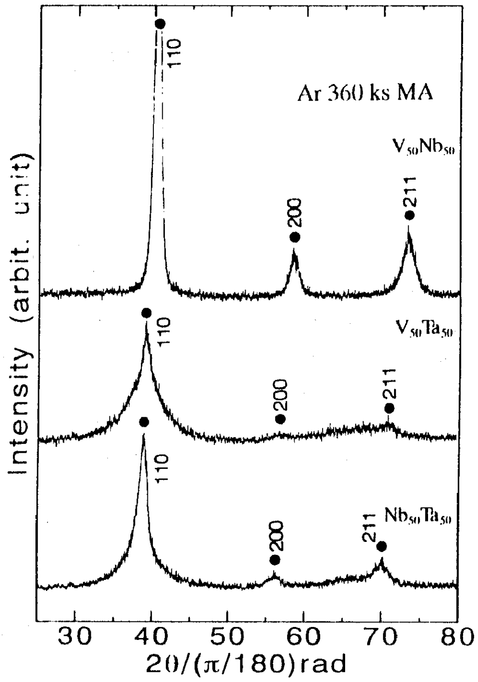

Figure 1 X-ray diffraction patterns of $V_{50}Nb_{50}$, $V_{50}Ta_{50}$ and $Nb_{50}Ta_{50}$ powders mechanically alloyed for 360 ks in an argon atmosphere.

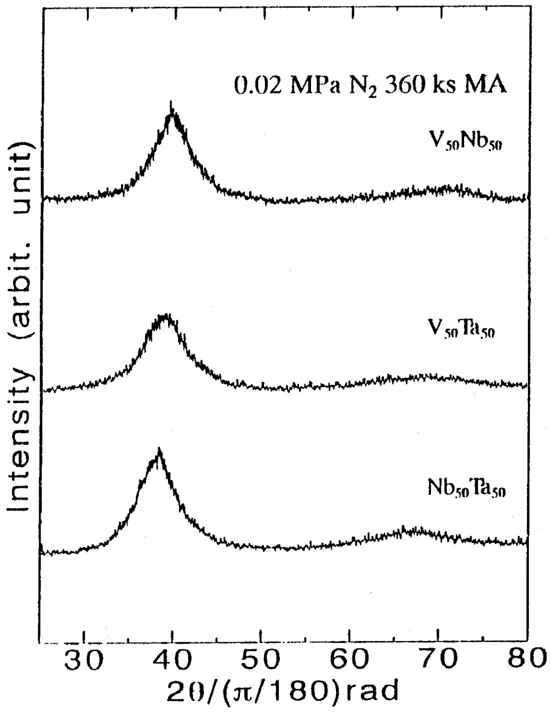

Figure 2 X-ray diffraction patterns of $V_{50}Nb_{50}$, $V_{50}Ta_{50}$ and $Nb_{50}Ta_{50}$ powders mechanically alloyed for 360 ks at 0.02 MPa N_2.

corresponding selected area diffraction pattern shows a halo characteristic of the amorphous phase [5]. The DSC curve of this sample shows exothermic peaks due to crystallization and the crystallization temperature T_x is 950 K as shown in Fig. 3. From the XRD, TEM and DSC experiments, $V_{50}Nb_{50}$ powders mechanically alloyed for 360 ks at 0.02 MPa N_2 is concluded to be amorphous. Similarly, the

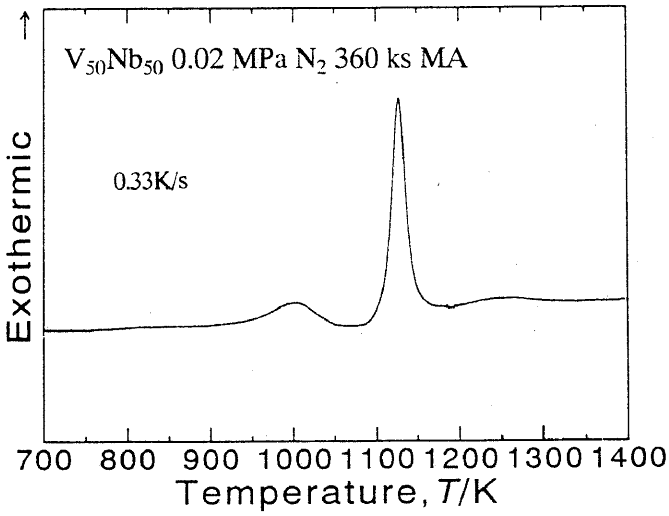

Figure 3 The differential scanning calorimetric curve of $V_{50}Nb_{50}$ powders mechanically alloyed for 360 ks at 0.02 MPa N_2.

$V_{50}Ta_{50}$ and $Nb_{50}Ta_{50}$ systems become amorphous by MA for 360 ks at 0.02 MPa N_2.

Table 2 shows the nitrogen content and the iron contamination content of the MA samples. The nitrogen content of the MA samples in an argon and nitrogen atmosphere is less than 1 at % and 8 - 11 at %, respectively. On the other hand, the iron contamination contents of these samples are comparable. Consequently, amorphization is concluded to occur not by the iron contamination, but by the additive effects obtained by combining MA with nitrogenation.

Figures 4 and 5 show XRD patterns of $V_{50}Nb_{50}$ powders before and after MA for different periods at 0.02 and 0.2 MPa N_2, respectively. The nitrogen contents of these samples are plotted against the MA time in Fig.6. Before MA, all the expected Bragg peaks of elemental V and Nb are clearly observed in the XRD patterns. After MA of 47 ks at 0.02 MPa N_2, the width of the Bragg peaks increases and the nitrogen content increases to 9 at %. After MA of 65 ks, the Bragg peaks of Nb overlap with those of V and results in the broad peak. As the MA time increases further, the sharpness of this broad peak fades gradually, and only the broad peaks are observed. The nitrogen content and the iron contamination content of the 360 ks MA sample at 0.02 MPa N_2 is 8 and 6.2 at %, respectively. On the other hand, the

Table 2. The nitrogen content and the iron contamination content of the mechanically alloyed samples in different nitrogen partial pressures

Alloys	Atomosphere	Nitrogen	Iron
V50Nb50	0.1MPa Ar	0.23	9.75
	0.02MPa N2	8.13	8.64
V50Ta50	0.1MPa Ar	0.75	2.74
	0.02MPa N2	10.70	9.40
Nb50Ta50	0.1MPa Ar	0.49	11.50
	0.02MPa N2	10.80	13.60

(at%)

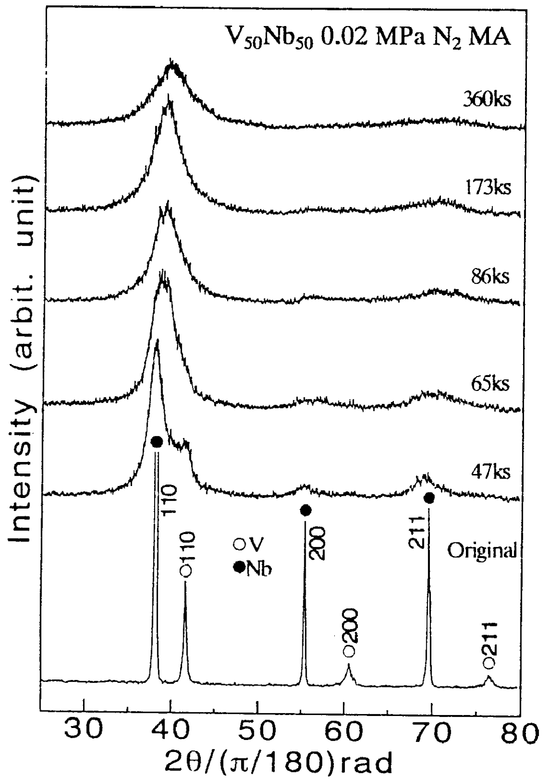

Figure 4 X-ray diffraction patterns of $V_{50}Nb_{50}$ powders mechanically alloyed for different periods at 0.02 MPa N_2.

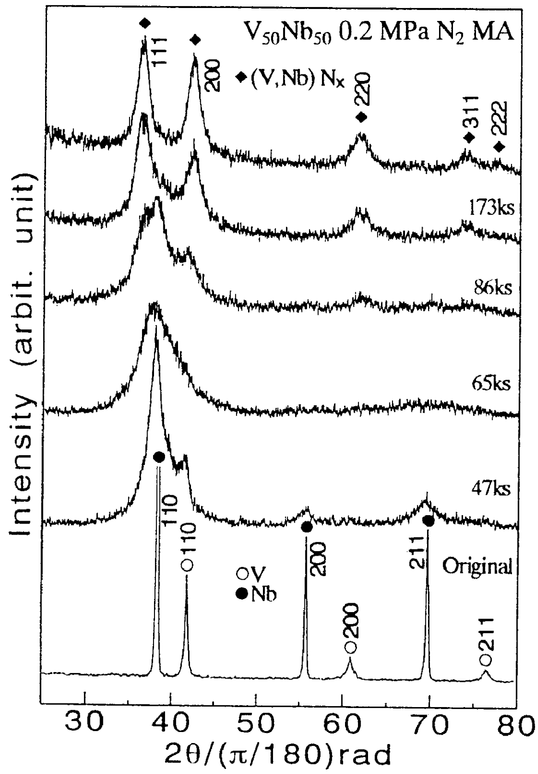

Figure 5 X-ray diffraction patterns of $V_{50}Nb_{50}$ powders mechanically alloyed for different periods at 0.2 MPa N_2.

nitrogen content increases sigmoidally by MA at 0.2 MPa N_2. An amorphous a-$V_{50}Nb_{50}N_{28}$ alloy forms at the intermediate stage, i.e., for 65 ks, subsequently the complex nitride (V,Nb)N_x appears overlapped with the broad amorphous halo. The complex nitride (V,Nb)$N_{1.77}$ is produced by MA for 360 ks. From Figs. 5 and 6, we can see that a-$V_{50}Nb_{50}N_x$ forms when x is smaller than 30. That is, the nitrogen content is the important factor controlling nitrogen induced-amorphization in the systems consisting of the group 5A metals.

Figure 7 shows scanning electron micrographs of (a) $V_{50}Nb_{50}$, (b)$V_{50}Ta_{50}$ and (c) $Nb_{50}Ta_{50}$ powders mechanically alloyed for 360 ks at 0.02 MPa N_2. These amorphous alloy particles have a globe shape with cabbage or orange skinlike morphology in the same way as the other amorphous alloys prepared by MA [6]. The average particle size of $V_{50}Nb_{50}$ powders is about 50 μm, while those of $V_{50}Ta_{50}$ and $Nb_{50}Ta_{50}$ are about 2–3 μm. Thus, the particle size of MA $V_{50}Nb_{50}$ powders is larger than one order of the others independent of the initial particle size.

3.2 Mechanical alloying of metal powders consisting of the group 6A and 6A metals

Figure 8 shows XRD patterns of $Mo_{50}W_{50}$ powders mechanically alloyed for 360 and 1080 ks in an argon and for 360 ks in nitrogen atmosphere. The MA sample at 0.02 MPa N_2 atmosphere shows a broad peak characteristic of the amorphous alloy, while the MA samples in an Ar atmosphere show the Bragg peaks of the bcc phase. The nitrogen content of $Mo_{50}W_{50}$ mechanically alloyed for 1080 ks in an Ar and N_2 atmosphere is 0.28 and 15.2 at %, respectively. On the other hand, the iron contamination content of them is 20.8 and 21.5 at %, respectively. Since the iron contamination level of both samples is comparable, amorphization is concluded to occur by the additive effect obtained by combining MA with nitrogenation. The XRD patterns of $Cr_{50}Mo_{50}$, $Cr_{50}W_{50}$ and $Mo_{50}W_{50}$ powders mechanically alloyed for 360 ks at 0.2 MPa N_2 show the broad peaks of the amorphous phase as shown in Fig.9. That is, nitrogen-induced amorphization occurs in the systems consisting of the group 6A and 6A metals, although the bcc solid solution alloys are produced in an argon atmosphere.

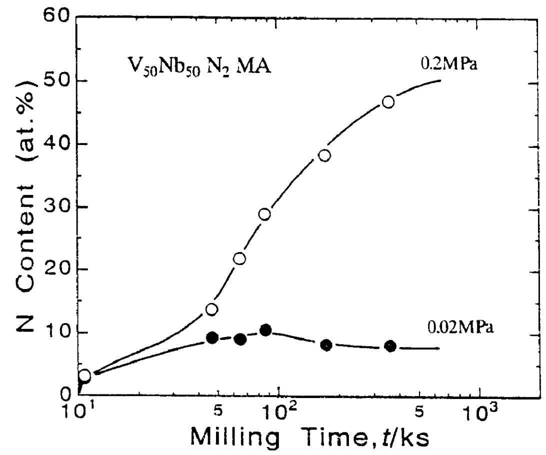

Figure 6 The nitrogen contents of $V_{50}Nb_{50}$ powders mechanically alloyed for different periods.

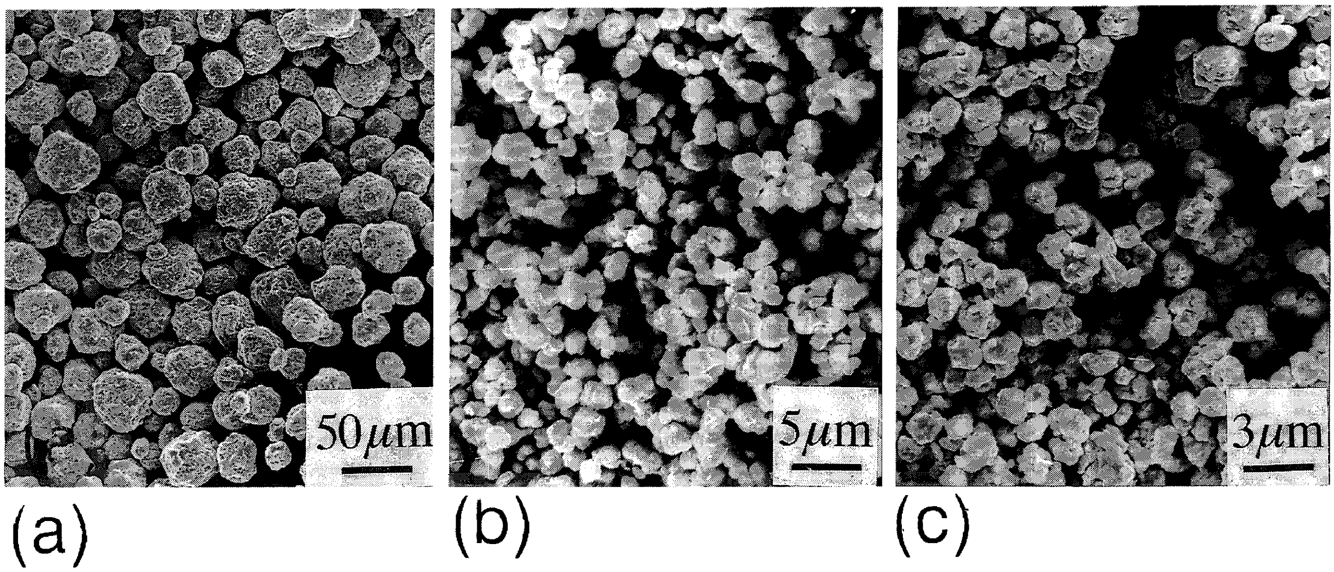

Figure 7 Morphology of (a) $V_{50}Nb_{50}$,(b) $V_{50}Ta_{50}$ and (c)$Nb_{50}Ta_{50}$ powders mechanically alloyed for 360 ks at 0.02 MPa N_2.

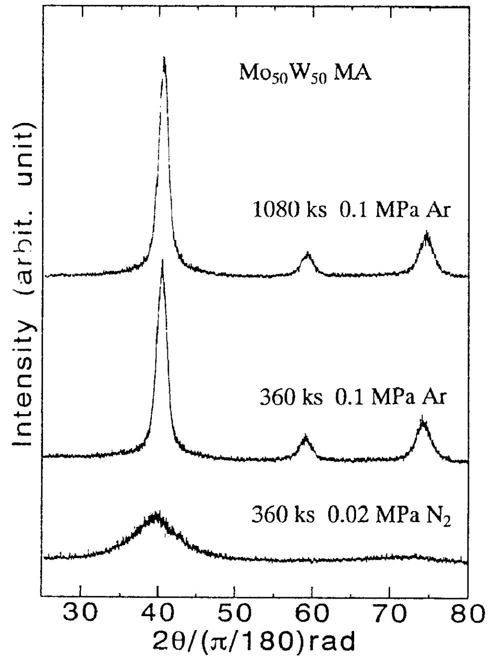

Figure 8 X-ray diffraction patterns of $Mo_{50}W_{50}$ powders mechanically alloyed in an argon and nitrogen atmosphere.

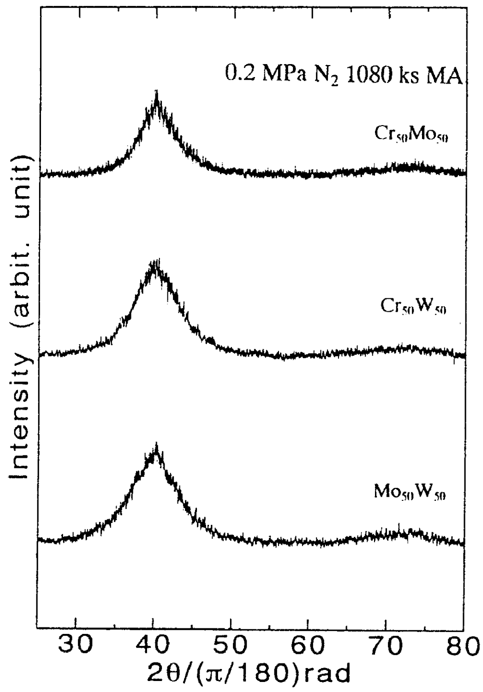

Figure 9 X-ray diffraction patterns of $Cr_{50}Mo_{50}$, $Cr_{50}W_{50}$ and $Mo_{50}W_{50}$ powders mechanically alloyed for 360 ks at 0.2 MPa N_2.

3.3 Mechanical alloying of metal powders consisting of the group 5A and 6A metals

Figures 10 and 11 show the XRD patterns of the MA samples consisting of the group 5A and 6A metals in a nitrogen atmosphere. The XRD pattern of 360 ks MA $Ta_{50}Mo_{50}$ shows the broad peak of the amorphous alloy. The DSC curve of this sample shows an exothermic crystallization peak. From the XRD and DSC experiments, we can see that the single phase amorphous alloy is produced by MA of $Ta_{50}Mo_{50}$ for 360 ks at 0.02 MPa N_2. On the other hand, the XRD patterns of the other samples show the broad peaks of the amorphous alloys overlapped with the Bragg peaks of the bcc solid solution alloy, suggesting partial amorphization of these samples.

3.4 The formation range of nitrogen-induced amorphous alloys

The present authors have recently proposed on the basis of the experimental results of $Ti_{50}Zr_{50}$ that nitrogen-induced amorphization occurs in the systems consisting of metals forming the complete solid solution and the stable nitrides. The group 5A and 6A metals satisfy such conditions. Structural changes of the metal powders consisting of the group 5A and 6A metals during MA in a nitrogen atmosphere have been investigated by XRD in the present work. The present work demonstrates nitrogen-induced amorphization in these alloys. That is, the present work supports their proposition. We discuss the formation conditions of the amorphous phases during MA in a nitrogen atmosphere.

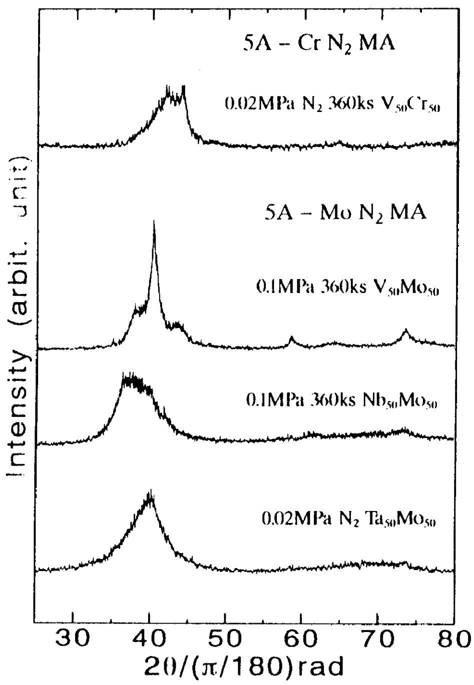

Figure 10 X-ray diffraction patterns of the MA samples consisting of the group 5A and 6A metals.

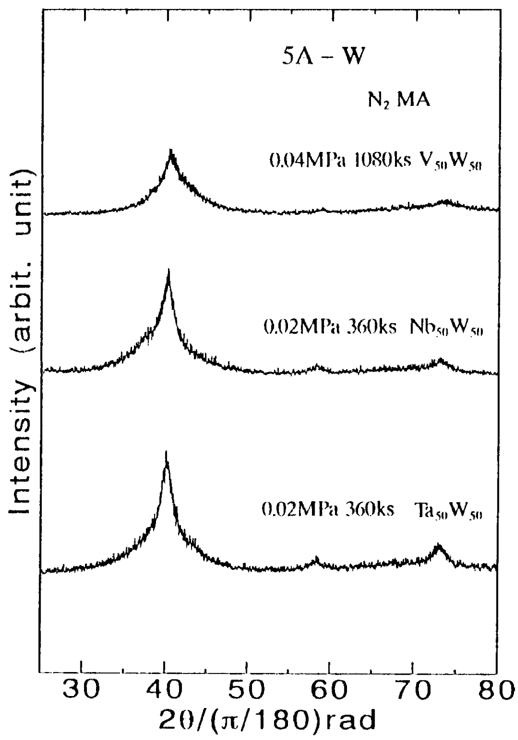

Figure 11 X-ray diffraction patterns of the MA samples consisting of the group 5A and 6A metals.

Figure 12 shows the formation range of the amorphous alloys prepared by MA in a nitrogen atmosphere against the enthalpy of mixing and the ratio of the atomic radius of constituting metals. The closed circles represent the single phase amorphous alloys and the closed square represent the mixed phases of amorphous and crystalline. The data on the Cr–Nb and Cr–Ta systems are not included, because they form the intermetallic compounds. The amorphous alloys are easily produced by MA of the systems consisting of the same group metals, i.e. V–Nb, V–Ta, Nb–Ta, Cr–Mo, Cr–Ta and Mo–Ta. On the contrary, partial amorphization occur in the systems consisting of the different groups, i.e. the group 5A and 6A metals. Generally, no amorphization occurs in the binary alloys in which the R_1/R_2 ratio and the enthalpy of the

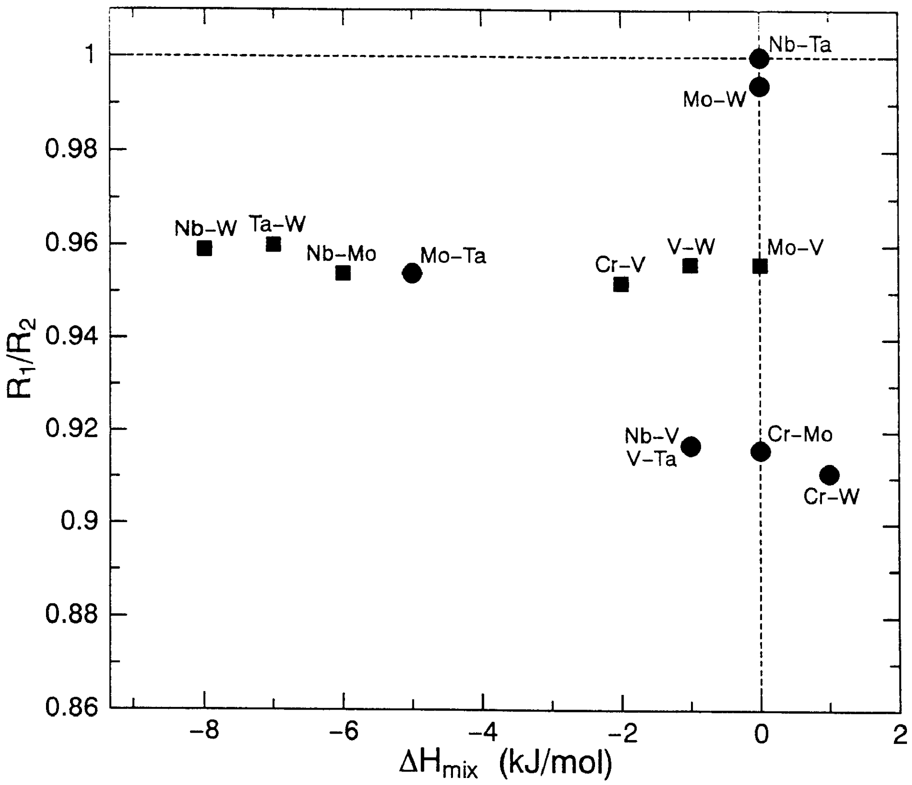

Figure 12 The formation range of the amorphous alloys prepared by MA in a nitrogen atmosphere.The closed circles and the closed square represent the single phase amorphous alloys and the mixed phases of amorphous and crystalline, respectively.

mixing is near to 1 and 0 kJ/mol, respectively. The bcc type solid solution alloys are produced by MA of the metal powders consisting of the 5A and 6A metals in an argon atmosphere. However, nitrogen–induced amorphization occurs even though the R_1/R_2 ratio is near to 1 and the enthalpy of the mixing is near to 0. Especially, it is worth noticing that $Nb_{50}Ta_{50}$ and $Mo_{50}W_{50}$ amorphize by MA in a nitrogen atmosphere in spite of 0 kJ/mol of the enthalpy of mixing and 1 of the atomic radius ratio. The binary alloys consisting of the same group metals show about 0 kJ/mol of the enthalpy of mixing, while the alloys consisting of the different group metals show the atomic radius ratio of about 0.96 as seen in Fig.12. Then, we can not say that nitrogen–induced amorphization is determined by these factors alone. The factors which determine nitrogen–induced amorphization of the alloys system consisting of the group 5A and 6A metals may be correlated to the formation enthalpy of the nitrides and the diffusion rates of nitrogen in the metals. The elucidation of the mechanism of nitrogen–induced amorphization is the subject for a near future study.

4.Summary

The single phase amorphous alloys containing nitrogen were prepared by MA of the metal powders consisting of the group 5A and 5A metals, the group 6A and 6A metals and $Ta_{50}Mo_{50}$ in a nitrogen atmosphere. However, the bcc type solid solution alloys were formed by MA in an argon atmosphere. The amount of the nitrogen in the samples determines the formation of the amorphous phase or the nitride. The formation range of the amorphous alloys were discussed on the basis of the enthalpy of mixing and the atomic radius ratio.

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