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# The difference between the crystallization processes induced by mechanical milling and annealing under normal and high pressure in amorphous Fe–N alloy

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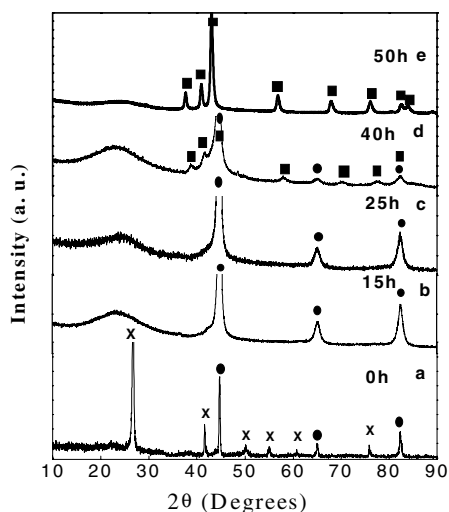
## Abstract

An amorphous Fe–N alloy was prepared by ball milling a mixture of Fe and h-BN. Its crystallization processes induced by mechanical milling (MM) and annealing under normal and high pressure were studied. The crystallization product of the amorphous Fe–N alloy induced by MM and annealing at temperatures between 690 and 800 K under pressures of 3–4 GPa is  $\epsilon$ -Fe<sub>x</sub>N, while the thermal crystallization product under normal pressure is  $\gamma'$ -Fe<sub>4</sub>N. The difference between the crystallization products produced by mechanical and thermal crystallization is attributed to the effects of local pressure and local temperature produced by ball collisions.

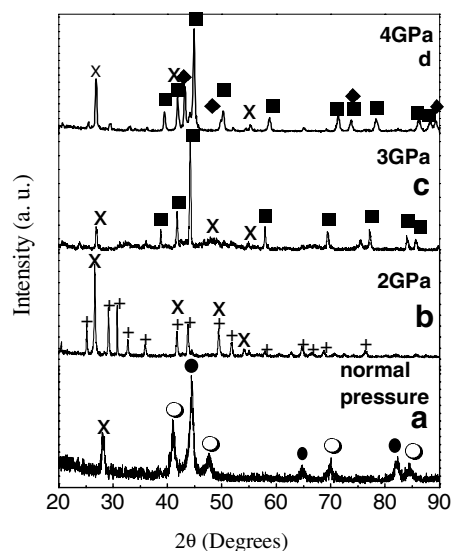
## 1. Introduction

It is well known that amorphous alloys can be prepared by mechanical milling (MM) of pure elemental powders or intermetallic compounds [1–4]. Recently, a process of crystallization of amorphous alloys driven by MM has also been reported and studied widely in experiments [5–10] and is referred to as mechanical crystallization. Much of the previous research work has shown that mechanical crystallization is different from thermal crystallization, however, its crystallization mechanism is still argued.

It is well known that crystallization of amorphous alloys are mainly influenced by pressure, temperature and composition. However, only the effects of temperature and composition on mechanical crystallization were considered in previously reported works [5–7, 10]. In fact, local pressure generated upon impact by steel balls during MM has been evaluated to be as high as 6 GPa [11, 12], and in this range pressure has an important influence on crystallization of amorphous alloys [13–15]. However, there is no report about effect of local pressure on the mechanical crystallization so far.



**Figure 1.** XRD patterns of the mixture of  $\alpha$ -Fe and h-BN powders milled for 0–50 h. ●:  $\alpha$ -Fe; ■:  $\epsilon$ -Fe<sub>x</sub>N; ×: h-BN.



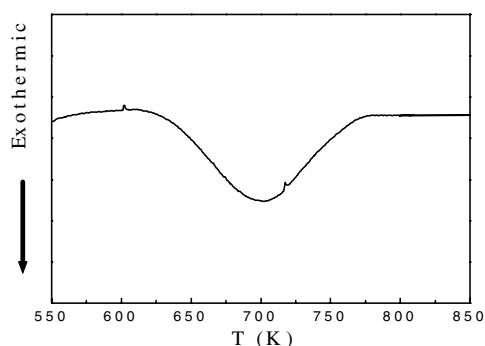
**Figure 2.** XRD patterns of the 25 h milled mixture annealed at a heating rate of 20 K min<sup>-1</sup> to 900 K under normal pressure and annealed for 1 h at 800 K under 2–4 GPa. ●:  $\alpha$ -Fe; ○:  $\gamma'$ -Fe<sub>4</sub>N; ■:  $\epsilon$ -Fe<sub>x</sub>N; +: new Fe–N phase; ◆:  $\gamma$ -Fe(N); ×: h-BN.

## 2. Experimental procedures

A mixture of Fe (99% purity) and hexagonal BN (h-BN) (99.99% purity) with the Fe:h-BN atomic ratio of 22:78 was placed into a stainless steel vial with milling balls under an argon atmosphere. The mixture-to-ball weight ratio is 1:15. MM was performed in a vibrating ball mill and was interrupted every 5 h to take a small number of samples for various analyses. High-pressure crystallization of the amorphous alloys was performed in a Bridgman anvil high-pressure apparatus [16]. The microstructures and thermal stability of the sample were characterized by x-ray diffractometry (XRD) with Cu K $\alpha$  radiation, differential scanning calorimetry (DSC) and Mössbauer spectroscopy (MS).

## 3. Experimental results and discussion

Figures 1(a)–(e) are XRD patterns for the mixture of Fe/BN powders milled for 0, 15, 25, 40 and 50 h, respectively. Figure 1(b) shows that all diffraction peaks of the h-BN disappeared after 15 h milling and a diffuse diffraction maximum appears for the diffraction angles  $2\theta$  ranging from about 10° to 35°, showing that the h-BN transforms into amorphous BN (a-BN). However there is no change in the diffraction pattern for  $\alpha$ -Fe in figure 1(b). After milling for 25 h, it is found from figure 1(c) that there is a small diffuse diffraction maximum, overlapping partly with the (110) diffraction peak of  $\alpha$ -Fe, for diffraction angle  $2\theta$  between 35° and 55°, besides diffraction peaks of  $\alpha$ -Fe and a-BN. The former is the (110) diffraction peak, it is a typical XRD pattern of an amorphous alloy. Hence the sample obtained by milling for 25 h is composed of  $\alpha$ -Fe, a-BN and an amorphous phase. In order to further identify the composition of this amorphous alloy, the 25 h milled sample was heated to 900 K at a heating rate of 20 K min<sup>-1</sup> under a flowing argon atmosphere. An exothermic peak was observed at about 660 K in the DSC curve, and diffraction peaks of  $\gamma'$ -Fe<sub>4</sub>N were seen in the XRD pattern of



**Figure 3.** The DSC curve for the 25 h milled sample annealed at a rate of  $20 \text{ K min}^{-1}$  to 900 K.

figure 2(a). Annealing the 25 h milled sample isothermally at normal pressure for 1 and 10 h produces only  $\gamma'$ - $\text{Fe}_4\text{N}$  phase. The amounts of  $\gamma'$ - $\text{Fe}_4\text{N}$  obtained are the same for both annealing times. These results show that the formation of the  $\gamma'$ - $\text{Fe}_4\text{N}$  result from crystallization of the amorphous Fe–N alloy (a-Fe–N) rather than any diffusion reaction. However, on extending the milling time to 35 h, the  $\varepsilon$ - $\text{Fe}_x\text{N}$  phase with hexagonal structure [17] was found. Figure 1(d) and MS results reveal that the 40 h milled sample consists of  $\alpha$ -Fe, a-BN, a-Fe–N and  $\varepsilon$ - $\text{Fe}_x\text{N}$  alloy. Upon further milling to 50 h, the sample is found to be composed of  $\varepsilon$ - $\text{Fe}_x\text{N}$  and a-BN. No  $\alpha$ -Fe and a-Fe–N were observed, as shown in figure 1(e) and the MS results, meaning that all  $\alpha$ -Fe reacts with N from the a-BN to form the a-Fe–N and subsequently transforms into a single  $\varepsilon$ - $\text{Fe}_x\text{N}$  phase. It should be noted from the XRD results in figure 1 and MS results that formation of  $\varepsilon$ - $\text{Fe}_x\text{N}$  is always accompanied by that of a-Fe–N until all  $\alpha$ -Fe is consumed. Therefore, it is deduced that the mechanical crystallization product of the amorphous Fe–N is  $\varepsilon$ - $\text{Fe}_x\text{N}$ , which differs from the thermal crystallization product of  $\gamma'$ - $\text{Fe}_4\text{N}$  seen in figure 2(a).

By means of measuring the lattice constants of  $\varepsilon$ - $\text{Fe}_x\text{N}$  in the as-milled sample and the relationship between the lattice constants and N concentration [18]. The N content in the a-Fe–N formed by milling for 25 h was estimated to be near to but less than 20 at.%. According to the equilibrium Fe–N phase diagram, the a-Fe–N should transform to  $\gamma'$ - $\text{Fe}_4\text{N}$  with a small amount of  $\alpha$ -Fe(N) at normal pressure, in agreement with the thermal crystallization result in figure 2(a). However, no  $\gamma'$ - $\text{Fe}_4\text{N}$ —only  $\varepsilon$ - $\text{Fe}_x\text{N}$ —was observed in the crystallization product for the a-Fe–N phase during MM, indicating that the mechanical crystallization of the a-Fe–N may be related not only to temperature and composition but also to the high local pressure.

In order to confirm the effect of high local pressure on crystallization of a-Fe–N, the 25 h milled sample containing a-Fe–N was annealed for 1 h at pressures of 2–4 GPa and at temperatures ranging from 580 to 1170 K. Figures 2(b)–(d) reveal XRD patterns of the samples annealed for 1 h at a temperature of 800 K under 2, 3 and 4 GPa, respectively, and indicate that the products of crystallization of the a-Fe–N alloy and solid-state reaction between Fe and a-BN are two new paramagnetic Fe–N phases at 2 GPa [19],  $\varepsilon$ - $\text{Fe}_x\text{N}$  at 3 GPa and  $\varepsilon$ - $\text{Fe}_x\text{N}$  and a small amount of  $\gamma$ -Fe (N) at 4 GPa, respectively. Furthermore, the N content in the  $\varepsilon$ - $\text{Fe}_x\text{N}$  produced under high pressure is much less than 27 at.%. For example, the N content in the  $\varepsilon$ - $\text{Fe}_x\text{N}$  prepared at 4 GPa was estimated to be about 16 at.%, near the N concentration in the  $\varepsilon$ - $\text{Fe}_x\text{N}$  produced by milling of 35 h. The experimental results indicate that the  $\varepsilon$ - $\text{Fe}_x\text{N}$  with N content much less than its equilibrium content at normal pressure can be obtained under high pressure, and the pressure and temperature ranges of formation of  $\varepsilon$ - $\text{Fe}_x\text{N}$  in the present experiment are 3–4 GPa and 690–800 K, respectively. A similar result was also found for  $\varepsilon$ -Fe(Ru) solid solutions [20].

On the basis of the above results, a mechanism of mechanical crystallization of a-Fe-N is suggested. Firstly, the  $\alpha$ -Fe milled to a smaller size than the critical grain size reacts with the a-BN to form a-Fe-N [21]. Since high pressure can enhance polymorphic crystallization [16], such as that from a-Fe-N to  $\varepsilon$ -Fe<sub>x</sub>N, and the present experimental results under high pressure have shown that the  $\varepsilon$ -Fe<sub>x</sub>N containing N at a level much less than 27 at.% can be formed under 3–4 GPa and at 690–800 K, which are within the temperature and pressure ranges produced by ball collisions, the a-Fe-N can crystallize at lower temperature and transforms into  $\varepsilon$ -Fe<sub>x</sub>N rather than  $\gamma'$ -Fe<sub>4</sub>N during MM.

#### 4. Conclusions

An amorphous Fe-N alloy is prepared by ball milling of a mixture of Fe and h-BN. It crystallizes to  $\varepsilon$ -Fe<sub>x</sub>N with an N content much less than its lower composition limit of 27 at.% at normal pressure during MM and annealing under high pressure, while it transforms into  $\gamma'$ -Fe<sub>4</sub>N during annealing at normal pressure. It was demonstrated in the present experiment that  $\varepsilon$ -Fe<sub>x</sub>N with a lower N content is a thermodynamically stable state under pressures of 3–4 GPa and at temperatures from 690–800 K, though it is not at normal pressure. Therefore, the difference between the crystallization products of mechanical and thermal crystallization is attributed to the effects of local pressure and local temperature on a thermodynamically stable state of Fe-N alloy.

#### Acknowledgments

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