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The effect of nitrogen on the glass-forming ability and micro-hardness of Fe–Cr–Mn–N amorphous alloys prepared by mechanical alloying

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Abstract

In this research, the effect of nitrogen on the thermal behavior and micro-hardness of Fe–Cr–Mn–N amorphous alloys synthesized by mechanical alloying under a nitrogen atmosphere has been considered. The characterization of the as-milled powders by X-ray diffraction, scanning and transmission electron microscopy showed that a fully amorphous structure has been developed by the mechanical alloying process. Differential scanning calorimetry results revealed that the glass transition temperatures and onset crystallization temperatures are in the ranges of 764 to 766 and 855 to 861 K, respectively, for the alloys containing 3.45 to 3.95 wt.% nitrogen, giving considerable supercooled liquid regions of 91 to 95 K. The amorphous alloys exhibited an increase in the glass-forming ability by increasing the nitrogen amount. Furthermore, the as-milled amorphous powders showed high micro-hardness values of nearly

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1015 to 1070 HV with an elastic-plastic deformation feature during the indentations. A decrease in the micro-hardness values was found by increasing the nitrogen content.

Keywords: Amorphous materials; Mechanical alloying; Glass-forming ability; Micro-hardness

1. Introduction

In the recent years, Fe-based bulk metallic glasses (BMGs) have developed into promising alloys for research and application due to their combinations of high strength and hardness, superior wear and corrosion resistance, good magnetic properties, relatively low cost, and higher thermal stability compared with most other bulk amorphous alloy systems [1-4]. It is well-established that mechanical alloying (MA) is a possible solid-state method to synthesize amorphous alloys in a wider range of composition than casting methods. The amorphous phase formation via MA is significantly dependent on the milling conditions. There are several reports on the synthesis of an amorphous phase by MA under a reactive nitrogen gas atmosphere. It is recognized that nitrogen has a significant contribution towards amorphization, in addition to the influence of the severe plastic deformation subjected to the powders during the milling process [5-13].

It is found [14-16] that the modification of the chemical composition of Fe-based BMGs can increase their glass-forming ability; thereby reducing the manufacture cost of these alloys coupled with an increase in their critical diameter and thickness. On the other hand, it is known that metal-metalloid interactions in Fe-based alloys are strong and capable of affecting the mechanical properties and thermal stability of Fe-based amorphous alloys. There are some reports in the literature on the effect of carbon, boron, and phosphorus on the properties of Fe-based amorphous alloys [17-20]. Concerning nitrogen-containing Fe-based amorphous alloys, the same authors studied the microstructural evolutions during MA of Fe–18Cr–8Mn–*x*N alloys under a nitrogen atmosphere [5]. It was found that an amorphization reaction occurs during the process; and by increasing the nitrogen content, the quantity and stability of the amorphous phase increase. Moreover, the synthesis and characterization of Fe–18Cr–4Mn–*x*N amorphous powders developed by MA were recently considered [6]. Nitrogen was found to be the main cause for amorphization and the significant glass-forming ability of the alloys. The other work conducted by the authors reported on the thermal and magnetic properties of Fe–18Cr–12Mn–*x*N amorphous-nanocrystalline alloys synthesized by MA and subsequent heat treatment [7]. The results showed that the amorphous phase exhibits a wide supercooled liquid region up to 93 K for the sample containing 4.31 wt.% nitrogen. Nevertheless, it seems that it is required to be conducted more systematic work on the influence of nitrogen on the thermal and mechanical behaviors of Fe-based amorphous alloys. This paper reports an experimental study on the effect of nitrogen content on the glass-forming ability and indentation response of Fe–18Cr–4Mn–*x*N amorphous powders synthesized by MA under a nitrogen gas atmosphere.

2. Experimental procedure

MA of pure elemental Fe (>99.5%, $D_{av.}$=50 μm), Cr (>99.9%, $D_{av.}$=150 μm) ,and Mn (>99.9%, $D_{av.}$=50 μm) powders supplied by Merck with a composition of 78Fe–18Cr–4Mn (wt.%) was performed in a planetary ball mill (Fritsch, Pulverisette 5) with a capacity of 250 mL. Tempered steel balls with 8 mm diameter were employed as grinding media. The powders were milled in a sealed container which had been filled with nitrogen gas. A constant rotation speed of 250 rpm and a ball-to-powder weight ratio of 30:1 were used during the process. Powder sampling was performed at 9-h intervals, ranging from 126 to 162 h, inside a nitrogen glove box.

The nitrogen, oxygen, and carbon amounts of the powder samples were determined by a LECO gas analyzer (Corp., St. Joseph, MI). The Fe, Cr, and Mn contents were measured by an X-ray fluorescence analyzer (Philips PW2400). In this test, the quantitative values were extracted by the PAN analytical software. The phase analysis of the as-milled powders was carried out by X-ray diffraction (XRD) (Shimadzu Lab X-6000 with Cu Kα radiation). An angular range of 20 to 100º, a step size of 0.02, and a step time of 3 s were used for the XRD experiments. Scanning electron microscope (SEM, JEOL-JSM 5310) and transmission electron microscope (TEM, JEOL-JEM 2010) were utilized to study the morphology and microstructure of the powder particles. The TEM samples preparation were done by dispersing the powder particles in ethanol and dropping down them in a copper rigid. To prepare the samples for thermal and indentation experiments, the as-milled powders were uniaxially cold-pressed to a cylindrical shape about 5 mm high and 5 mm in diameter at a compressive pressure of 500 MPa. The relative density of the compacts was measured as 70 %. The thermal stability of the powders was investigated in a differential scanning calorimeter (DTA/DSC, NETZSCH, STA 449C Jupiter) with an alumina container under a flowing purified argon gas atmosphere at a heating rate of 20 K min^{-1}.

For the indentations, the surfaces of the compacts prepared from the as-milled powders were polished with a paste containing diamond particles with a mean diameter of 1 μm. The micro-hardness measurements of the powder particles at pore-free zones were performed under a 25 g load and a 15 s dwell time at room temperature. In order to have accurate results, at least 5 indents were conducted for each sample and subsequently averaged. In addition, the upper surfaces of the indents after the hardness test were observed by SEM.

Lastly, in order that the behaviors are investigated in the absence of nitrogen, MA was performed under a non-reactive argon atmosphere. However, in this case, a single phase amorphous structure was not achieved after milling for the same milling periods applied in the reactive nitrogen atmosphere case, implying N atoms infused during MA play a major role in the complete amorphization reaction [5,6].

3. Results and discussion

3.1. Characterization of the as-milled powders

Table 1 lists the chemical composition of the powders obtained at the various milling times. It can be seen that the expected nominal composition of 18 wt.% Cr + 4 wt.% Mn was achieved and the only detectable contamination in the as-milled powders was oxygen, which can be due to the natural oxidation of the powders in the atmosphere [6]. It is visible that the amount of infused nitrogen increases with milling time due to a solid-gas reaction, approaching 3.95 wt.% after 162 h. This indicates that during MA under the nitrogen gas atmosphere, nitrogen is adsorbed on the newly created surfaces of the powder particles and penetrated into the structure by progression of the milling process [5,6,7,21]. For longer milling times, the content of infused nitrogen also increased by milling time. However, this was accompanied by the formation of nitride phases. Since this paper aims to study the properties of the amorphous single-phase alloys, the samples containing nitride were not considered.

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Figure 1 indicates the XRD patterns of the initial powder mixture and five representative as-milled powders. The XRD traces reveal that no peaks corresponding to crystalline phases are noticeable, indicating that these powders consist of a single amorphous phase (the diffuse and broad halo pattern is the characteristic of an amorphous material). Phase evolutions for the Fe–18Cr–4Mn powder mixtures during MA under the nitrogen gas atmosphere have been earlier investigated in more detail [6]. The results have portrayed that milling (with the same process variables) for the durations less than 126 h causes the development of nanocrystalline-amorphous Fe–18Cr–4Mn–xN powders; and by increasing the milling time, the amorphous phase content increases and after 126 h the amorphization process becomes complete.

Figure 2 is a scanning electron micrograph of the powder milled for 144 h. The powder particles are near-spherical, and have very smooth surfaces without any layered-structure morphology. This morphology is the characteristic of a typical amorphous powder synthesized by MA [22]. The powder particles depict a relatively narrow size distribution and their size is almost in the range of 10 to 30 μm. As shown in Figure 3, the high-resolution transmission electron microscopy (HRTEM) image of the powders milled for 144 h reveals a uniform contrast and no crystalline phase has been observed. The corresponding selected area diffraction (SAD) pattern represents a homogenous featureless pattern attributed to the amorphous structure. No diffraction spots or sharp diffraction rings related to crystalline phases can be detectable and merely diffraction halos associated with the amorphous phase can be observed.

The microscopic analyses of the other powder samples showed features similar to the sample milled for 144 h. These manifestations obtained from the powders characterization results suggest that the milling process for these selected durations has resulted in complete amorphization. On the other hand, the crystallization of the amorphous phase produced does not occur during the milling process, showing the stability of the amorphous phase.

3.2. Thermal properties of the Fe–Cr–Mn–N amorphous alloys

The thermal behavior studies of the samples were conducted in order to identify the influence of the nitrogen content on the supercooled liquid region of the alloys. The DSC curves present a glass transition, followed by a supercooled liquid region before crystallization (Figure 4). In the previous work by the same authors [6], it was realized that in the DSC scans, the endothermic event reflects the glass transition and the exothermic peak is related to a transformation from a supercooled liquid state to a crystalline phase. The glass transition temperatures (T_g) and onset crystallization temperatures (T_x) of the alloys obtained from the DSC results are tabulated in Table 2. It is seen that for all the alloys studied, T_g and T_x are in the ranges of 764 to 766 and 855 to 861 K, respectively, giving significant supercooled liquid regions (ΔT_x) of 91 to 95 K. Both T_g and T_x increase by increasing the nitrogen content; nonetheless, the increase in T_x is more considerable compared to that in T_g. This is consistent with the fact that T_g is relatively composition-independent. It demonstrates that by increasing the nitrogen concentration of the amorphous alloys, the supercooled liquid regions increase, as tabulated in Table 2. In addition, it is recognizable that the sharpness and intensity of the crystallization peak more or less increase by progression of the MA process. This is attributed to an increase in the homogeneity of the amorphous phase by progression of the MA process.

These amorphous alloys with the wide supercooled liquid regions are capable of being formed into bulk materials with large dimensions, by considerable viscous flow inherent to the supercooled liquid. In addition, mechanically alloyed amorphous powders are appropriate for subsequent compaction and densification in many shapes. It is possible to produce bulk amorphous materials from these mechanically alloyed amorphous powders by hot consolidation methods (such as hot isostatic pressing, hot extrusion) in the temperature ranges of their supercooled liquid regions. The origin of these considerable glass-forming abilities and their increase by increasing the nitrogen content is discussed as follows.

According to the Inoue's empirical rules [23,24], the glass-forming ability and supercooled liquid stability of amorphous alloys depend on (1) the number of the constituent elements, (2) the atomic size mismatch, and (3) the heat of mixing among the constituent elements. For the improvement of glass-forming ability, it is necessary for multi-component alloys to be composed of more than two elements. This aims to disturb the formation of crystal by imposing a chemical disorder. It is clear that this condition is satisfied for the Fe–Cr–Mn–N (even for the Fe–Cr–Mn) system. Referring to the atomic size consideration, it was found that a large atomic size mismatch prevents a solid solution to form, increasing the glass-forming ability. This is consistent with the Hume-Rothery rule which implies that an atomic size difference greater than 15% drastically restricts the solubility of two elements in a single crystal structure. Moreover, having a large negative heat of mixing among the constituent elements increases the viscosity of the supercooled liquid, thereby suppressing the atomic diffusion required for crystallization. Since Fe, Cr, and Mn elements are close to each other in the periodic table, their atomic size differences and mixing enthalpies are not considerable. As a result, it is anticipated that Fe–Cr–Mn amorphous alloys do not have significant glass-forming ability. However, since N is far from Fe, Cr, and Mn elements in the periodic table, the addition of nitrogen to the Fe–Cr–Mn alloys gives rise to a considerable increase in the atomic size differences. In addition, the creation of the strong bonding pairs of Fe–N, Cr–N, and Mn–N with negative heats of mixing is another consequence of the nitrogen introduced to the alloy.

On the other hand, the kinetics of redistribution of the constituent elements for crystallization is a critical factor affecting the glass-forming ability. It can be shown that the nitrogen addition to the Fe–Cr–Mn alloy makes the atomic redistribution difficult. First, the introduced N atoms occupy the interstitial sites of the atomic polyhedra or clusters of the structure, contributing to an increase in the dense random packing of the structure. This leads to a decrease in the atomic diffusion coefficients, increasing the viscosity of the supercooled liquid. Second, the addition of N atoms to the alloys disrupts the short-range order of the amorphous structure, retarding the formation of crystal nuclei. Finally, due to the high affinity of these transition metals for nitrogen and also the strong attractive bonds made up between the metal-nitrogen pairs, the N atoms are reluctant to be neighbors to each other. Subsequently, the N atoms are surrounded by the metallic atoms. The presence of these metal-nitrogen atomic pairs suppresses the atomic rearrangement required for the precipitation of the crystalline phases. Note that the increase in the homogeneity of the amorphous phase by progression of MA, as found from the DSC results, can be another reason for the increase of T_x. This increased homogeneity demands larger chemical fluctuations to form the critical nuclei of crystalline phases. The contribution of these factors is responsible for increasing the glass-forming ability of the Fe–Cr–Mn–N alloys by increasing the nitrogen content.

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3.3. Micro-indentation hardness studies on the Fe–Cr–Mn–N amorphous alloys

Currently, the evaluation of the indentation response of amorphous materials is converted into a valuable approach to identify their hardness values and micro-mechanisms of plastic deformation on micro and nano-scale. Figure 5 indicates the variations of micro-hardness (*HV*) at pore-free zones as a function of the nitrogen concentration. Since the indentations were performed on pore-free zones of the compacts and since the ratio of the indent-to-powder particle size was sufficiently small, the effect of pores on the hardness results is negligible. The substantial hardness values of these materials are attributed to the strong bonding between the constituent elements, as are expected from the large negative values of the mixing enthalpies. In contrast to the powerful strengthening effect of interstitial nitrogen in crystalline Fe-based alloys, the *HV* of these amorphous alloys decreases monotonically by increasing the nitrogen content from 1070 to 1015 for the alloys containing 3.45 to 3.95 wt.% nitrogen, as demonstrated by the plot of Figure 5. The maximum standard deviations of the *HV* measurements were as small as 5, implying the high homogeneity of the amorphous structure. The decrease in the *HV* shows that the bonding nature among the constituent elements becomes weak by the addition of nitrogen.

To clarify the origin of the observed mechanical behavior, the bonding configuration and electronic structure of the alloys are considered. Because of the strong interatomic interactions between these transition metals and nitrogen, notably the Cr–N and Mn–N pairs, a number of electrons in the metallic bonds are transferred to the metal-nitrogen bonding regions, forming the stiff metal-nitrogen bonds. As a result of the fact that N atoms possess a higher electronegativity than Fe, Cr, and Mn atoms, a strong accumulation of electrons forms towards N atoms, resulting in a depletion of electrons near Fe, Cr, and Mn atoms. Because of this decrease in the number of electrons in the metallic bonding regions, these bonds are weakened and a local electronic inhomogeneity is created. This means that some strong metal-nitrogen bonds form; a weakening in the metal-metal bonds connecting the atomic polyhedral clusters in the amorphous structure is resulted in turn. As a result, shear bands are able to initiate from the weakened intercluster regions, leading to a decrease in the yield stress and the hardness of the materials by increasing the nitrogen content. This suggests that within this range of nitrogen concentration, the weakening effect of the metal-metal bonds over-weighs the effect of the formation of some stiff metal-nitrogen bonds on the hardness behavior. In conclusion, the decrease of the hardness by increasing the nitrogen content is due to the weakening of the intercluster coupling.

It is assumed that the considerable decrease of the hardness with only a small addition of nitrogen concentration is due to the considerable difference of the electronegativity of N and the present metallic atoms. It would be worth mentioning that Fe, Cr, Mn, and N atoms have an electronegativity of 1.83, 1.66, 1.55, and 3.04, respectively.

With regard to the effect of nitrogen on the electronic structure of Fe-based alloys, Gavriljuk [25] has shown that nitrogen increases the conduction electrons concentration in austenitic steels, *i.e.*, nitrogen enhances the metallic component of interatomic bonds. On the contrary, a decrease in the conduction electrons concentration was found at nitrogen contents higher than 0.4 wt.%. That is, nitrogen increases the covalent contribution of the interatomic bond at the high concentrations, inducing clustering [25]. More studies on the electronic structure of Fe-based amorphous alloys provide useful information on the chemical interactions affecting a number of properties of amorphous alloys, such as ductility and fracture toughness.

Because of a great similarity in the stress and strain states around a crack and a sharp indenter, the morphology of the indented surfaces was investigated by SEM to observe the generation of slip marking or crack produced via the indenter. Figure 6 depicts a typical SEM image obtained from the upper surface of the indented Fe–18Cr–4Mn–3.62N sample after the micro-hardness test. One semi-circular shear band marking is visible on the one side of the indentation impressions. The formation of the shear bands on the free surface in the vicinity of the indentation impression suggests an inhomogeneous deformation mechanism. The absence of any visible crack demonstrates the material has an elastic-plastic deformation mode. The incomplete semi-circular elastic-plastic boundary feature is a consequence of the radial displacement of the material away from the depth of the indent. Note that the material situated out of the shear bands is only elastically deformed. Furthermore, as a result of the incompressibility of plastic deformation, the penetration of the indenter during the indentation contributes a pile-up and overlapping layers of the upwardly displaced material in the vicinity of the indented area, as shown in Figure 6. The observation on the indented surfaces of the other samples essentially presented characteristics comparable to the surface of the Fe–18Cr–4Mn–3.62N alloy.

Meanwhile, it is found [26] that pre-existing shear bands interact with new shear bands formed by indentation and suppress the latter, causing less pile-up during indentation. Moreover, the Berkovich nano-indentation test on amorphous samples containing pre-indentation traces revealed that the material near the traces exhibits a lower hardness compared to that far from the trace. The smaller pile-up and less shear bands related to the regions near the trace were recognized to be the reason for the lower hardness values of these regions compared to that far form the trace [26]. Because of the fact that these Fe–Cr–Mn–N amorphous powder particles have been subjected to the severe impacts of the grinding media during MA, they have been deformed by the generation of numerous shear bands. Accordingly, it can be speculated that the studied materials essentially have higher hardness values than those represented in Figure 5. In addition, the studied materials exhibit larger pile-ups and more shear bands than those shown in Figure 6, in the absence of the pre-introduced shear bands.

4. Conclusions

In this work, the effect of the nitrogen content on the thermal properties and micro-hardness of the Fe–Cr–Mn–N amorphous alloys synthesized by MA under a nitrogen gas atmosphere was evaluated. The outcome of this study can be summarized as follows:

1. During MA, the infusion of nitrogen into the powders gave rise to nitrogen concentrations exceeding 3 wt.%.
2. The characterization of the as-milled powders revealed that the employed MA process with the milling durations of 126, 135, 144, 153, and 162 h has resulted in complete amorphization.
3. The Fe–Cr–Mn–N amorphous alloys exhibited considerable supercooled liquid regions up to 91 to 95 K and high micro-hardness values up to 1015 to 1070 HV.
4. The alloys were found to show an increase in glass-forming ability by increasing the nitrogen content, following from the increase in the atomic size differences, heats of

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mixing of the constituent elements, and the difficulty of the atomic redistribution for crystallization.

5. A decrease in the micro-hardness was found by increasing the amount of nitrogen. It was attributed to the weakening of the metal-metal bonds, as a result of the strong metal-nitrogen interatomic interactions.
6. In the course of the indentations, the alloys showed an elastic-plastic deformation behavior and a pile-up around the indented areas.

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References

[1] Z.P. Lu, C.T. Liu, J.R. Thompson, W.D. Porter, Phys. Rev. Lett. 92 (2004) 245503.
[2] A. Inoue, A. Makino, T. Mizushima, J. Magn. Magn. Mater. 215–216 (2000) 246.
[3] A. Inoue, B. Shen, C.T. Chang, Acta Mater. 52 (2004) 4093.
[4] S.J. Pang, T. Zhang, K. Asami, A. Inoue, Acta Mater. 50 (2002) 489.
[5] R. Amini, M.J. Hadianfard, E. Salahinejad, M. Marasi, T. Sritharan, J. Mater. Sci. 44 (2009) 136.
[6] R. Amini, M.J. Hadianfard, E. Salahinejad, M. Marasi, T. Sritharan, J. Non-Cryst. Solids. (Submitted for publication).
[7] R. Amini, H. Shokrollahi, M.J. Hadianfard, E. Salahinejad, M. Marasi, T. Sritharan, J. Alloy. Comp. (In press).
[8] Y. Ogino, S. Murayama, Y. Yamazaki, J. Less-Common Met. 168 (1991) 221.
[9] Y. Ogino, T. Yamasaki, S. Murayama, R. Sakai, J. Non-Cryst. Solids. 117-118 (1990) 737.

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[10] T. Fukunaga, E. Ishikawa, T. Koyano, U. Mizutani, Phys. B. 213-214 (1995) 526.

[11] T. Fukunaga, N. Kuroda, C.H. Lee, T. Koyano, U. Mizutani, J. Non-Cryst. Solids. 176 (1994) 98.

[12] K. Aoki, A. Memezawa, T. Masumoto, Mater. Sci. Eng. A. 181-182 (1994) 1263.

[13] M.S. El-Eskandarany, K. Aoki, K. Suzuki, Appl. Phys. Let. 60 (1992) 1562.

[14] J. Shen, Q.J. Chen, J.F. Sun, H.B. Fan, G.Wang, Appl. Phys. Lett. 86 (2005) 151907.

[15] C.Y. Luo, Y.H. Zhao, X.K. Xi, D.Q. Zhao, M.X. Pan, W.H. Wang, S.Z. Kou, J. Non-Cryst. Solids. 352 (2006) 185.

[16] C.Y. Luo, M.X. Pan, S.Z. Kou, D.Q. Zhao, W.H. Wang, Chin. Sci. Bull. 50 (2005) 205.

[17] X.J. Gu, S.J. Poon, G.J. Shiflet, Scr. Mater. 57 (2007) 289.

[18] X.J. Gu, S.J. Poon, G.J. Shiflet, M. Widom, Acta Mater. 56 (2008) 88.

[19] A. Inoue, X.M. Wang, Acta Mater. 48 (2000) 1383.

[20] S. Sharma, C. Suryanarayana, J. Appl. Phys. 103 (2008) 013504-1.

[21] M.S. El-Eskandarany, K. Sumiyama, K. Aoki, K. Suzuki, Mater. Sci. Forum 88–90 (1992) 801.

[22] M.S. El-Eskandarany, A.A. Bahgat, N.S. Gomaa, N.A. Eissa, J. Alloy. Comp. 290 (1999) 181.

[23] A. Inoue, T. Zhang, T. Masumoto, J. Non-Cryst. Solids 156–158 (1993) 473.

[24] A. Inoue, Mater. Trans. Japan Inst. Met. 36 (1995) 866.

[25] V.G. Gavriljuk, ISIJ Int. 36 (1996) 738.

[26] C. Tang, Y. Li, K. Zeng, Mater. Lett. 59 (2005) 3325.

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Figures:

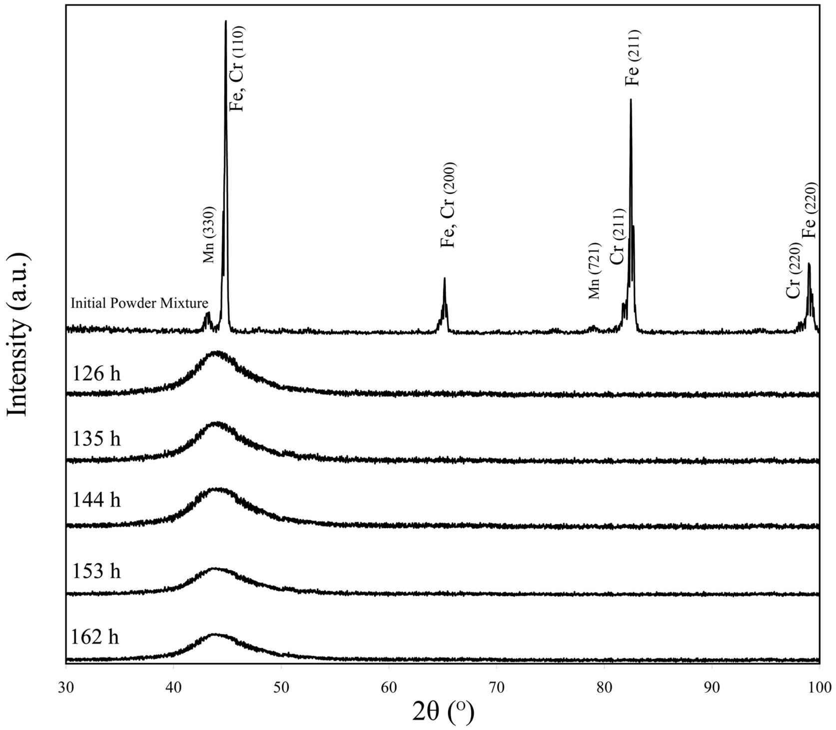

Figure 1. XRD patterns of the initial powder mixture and nitrogen-containing Fe–18Cr–4Mn powder mixtures milled for 126, 135, 144, 153, and 162 h.

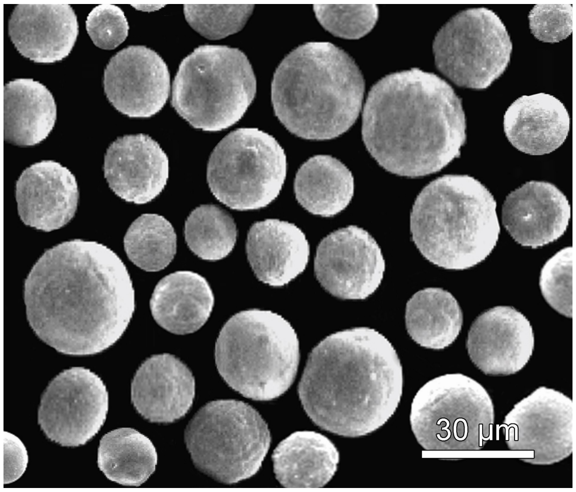

Figure 2. SEM image of the Fe–18Cr–4Mn–3.62N powder particles (milled for 144 h).

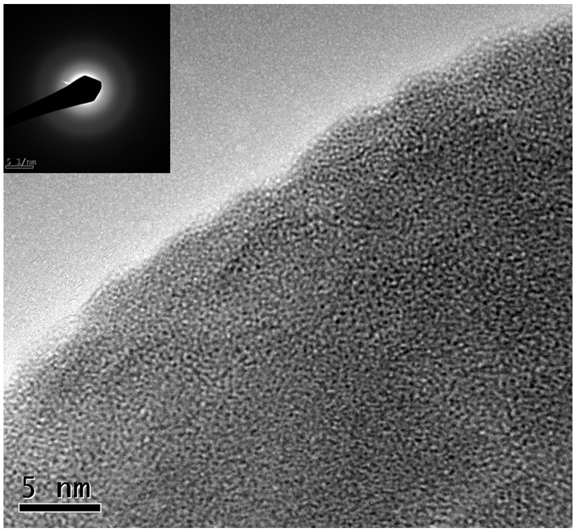

Figure 3. HRTEM image of the Fe–18Cr–4Mn–3.62N powder (milled for 144 h).

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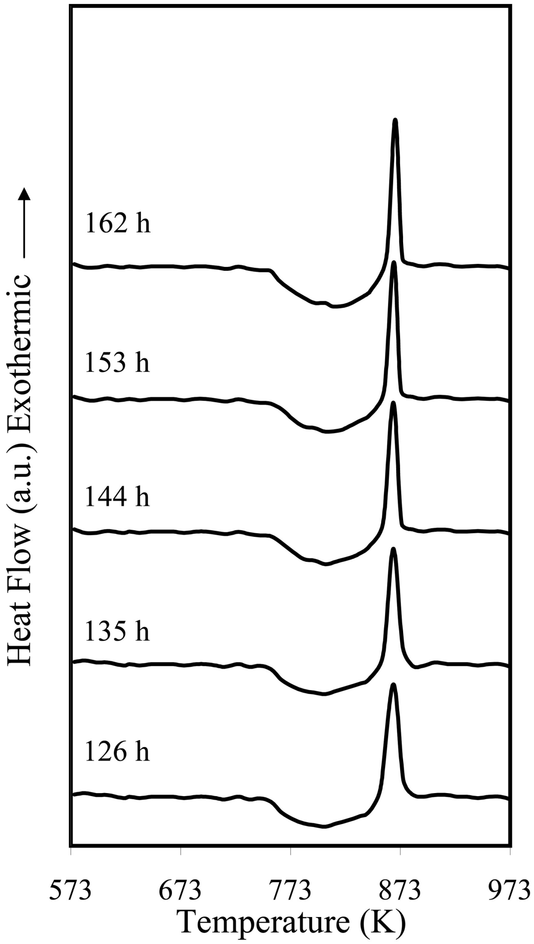

Figure 4. DSC scans of the Fe–18Cr–4Mn–*x*N amorphous alloys with different nitrogen concentrations.

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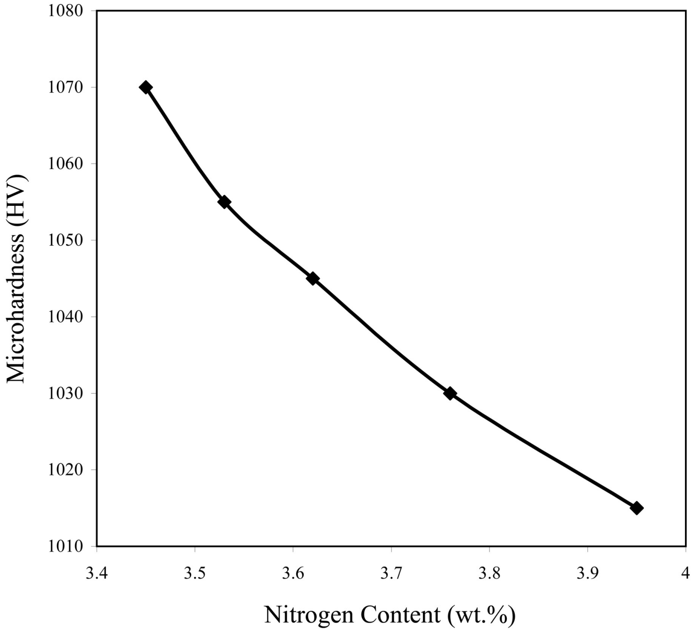

Figure 5. Variations in the micro-hardness values vs. the nitrogen concentrations of the Fe–18Cr–4Mn–*x*N amorphous alloys.

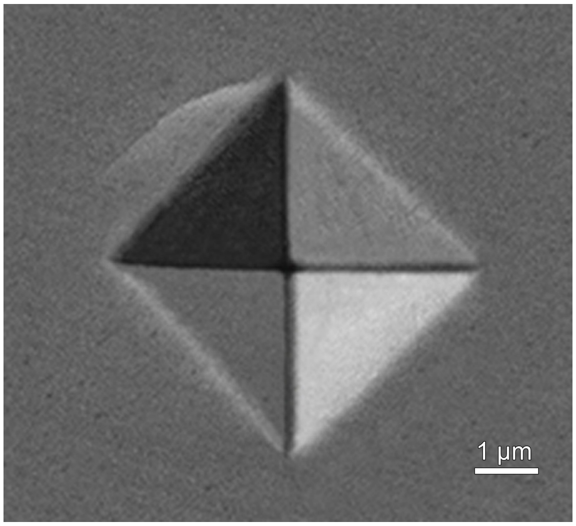

Figure 6. SEM image of the indentation related to the Fe–18Cr–4Mn–3.62N sample.

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Table 1. Chemical composition of the as-milled powders (wt.%)

Milling time (h)	Fe	Cr	Mn	N	O	C
126	74.706	17.666	3.821	3.451	0.324	0.032
135	74.732	17.558	3.825	3.534	0.321	0.030
144	74.568	17.546	3.905	3.618	0.332	0.031
153	74.437	17.597	3.848	3.764	0.325	0.029
162	74.172	17.759	3.759	3.949	0.332	0.029

This is the accepted manuscript (postprint) of the following article:
E. Salahinejad, R. Amini, M. Marasi, T. Sritharan, M. Hadianfard, *The effect of nitrogen on the glass-forming ability and micro-hardness of Fe–Cr–Mn–N amorphous alloys prepared by mechanical alloying*, Materials Chemistry and Physics, 118 (2009) 71-75.
https://doi.org/10.1016/j.matchemphys.2009.07.005

Table 2. Thermal properties of the Fe–18Cr–4Mn–*x*N amorphous alloys

Nitrogen concentration (wt.%)	T_g (K)	T_x (K)	ΔT_x (T_x - T_g) (K)
3.45	764	855	91
3.53	765	856	91
3.62	765	857	92
3.76	766	859	93
3.95	766	861	95