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Influence of magnetic field on the structure of glasses

STEPAN MUDRY, ANDREJ KOROLYSHYN, YURIJ KULYK, VOLODYMYR HALCHAK

Physics of Metals Department, Ivan Franko National University of Lviv, Kyrulo i Mephodyi Str. 8, 79005 Lviv, Ukraine.

The infleunce of magnetic field on the structure of amorphous alloys has been studied. It is shown that such infleunce occurs in both liquid state before glassing and in amorphous during thermal treatment. The structural changes investigated by X-ray diffraction method in liquid Co–B, Co–Cu, Ni–Pb and Mn–Bi eutectic alloys and $Ni_{0.64}Hf_{0.36}$ amorphous alloys are considered.

1. Introduction

There are few methods which are widely used to improve the properties of materials. Most of them such as thermal treatment, mechanical strengthening and other deal with the solid phase only. Although these methods still remain in practical use, their possibilities are restricted now. The new material production technologies begin to use the influence of external factors on liquid state still before solidification. For example, the mixing of liquid metals by applying the electromagnetic field allows us to improve the properties of alloys. Essentially the thermodynamical and structural state of liquid is important for structure formation in amorphous alloys. Having a similar structure as liquids the amorphous alloys can be modified by changing their structure before glass formation. One way of doing it is to apply magnetic field to liquid before solidification and to solid (amorphous or crystalline) during thermal treatment.

2. Experimental procedures

Amorphous ribbons of $Ni_{0.64}Hf_{0.36}$ with a typical thickness of 30 μm were prepared by melt spinning onto a copper wheel, rotating at a high velocity, which allowed the cooling velocity to reach the value of 10^6 K/s. The X-ray diffraction experiments with both amorphous and liquid alloys were performed in pure He-atmosphere using Mo K_α and Fe K_α radiation and the Bragg–Brentano reflection technique. The radiation was monochromatized by a single graphite crystal in the reflected beam. This crystal reflects about 35% of radiation and allows a high wavelength resolution. A schematic diagram of the experiment is shown in Fig. 1. The specimen was placed in the center of vacuum chamber and permanent magnet, installed in the chamber. The magnetic field strength was about

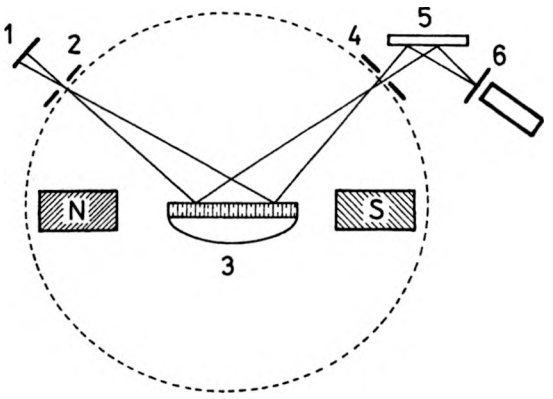

Fig. 1. Schematic diagram of X-ray diffraction geometry (1 — X-ray source, 2, 4 — slits, 3 — specimen, 5 — monochromator, 6 — X-ray counter).

200 kA/m and was cooled with water during experiment. The diffraction data were reduced to the mean atomic scattering factor taking into account background radiation, absorption, polarization, fluorescence and Compton scattering.

The structure factor $S(k)$, $k = \frac{4\pi \sin \Theta}{\lambda}$, can be calculated from coherently scattered intensity $I_{coh}(2\Theta)$

$$S(k) = [I_{coh} - (\langle f^2(k) \rangle - \langle f(k)^2 \rangle)]/\langle f^2(k) \rangle$$

where 2Θ is the scattering angle, λ — wavelength, $f(k)$ — atomic scattering factor.

The experimental structure factors were used to calculate the binary correlation $g(r)$ by Fourier transformation as follows:

$$g(r) = 1 + \frac{1}{2\pi^2 r \rho_0} \int_0^\infty [S(k) - 1] \sin(kr) \mathrm{d}r$$

where: ρ_0 — average atomic density, r — interatomic distance.

3. Fundamental framework

Studying the influence of magnetic field on the structure of amorphous alloys is closely related to investigation of their magnetic properties. In contrast to the glassy state the liquid state is suitable for investigation of alloys over the entire concentration range and pure metals. As shown in [1], [2], the magnetic susceptibility and the magnetic moment per Fe-atom for Fe–B alloys in the liquid state depend on the B-concentration in a way similar to that for corresponding amorphous alloys. A very similar behaviour has also been observed for other binary systems [3]. It is of fundamental importance to study the magnetic properties in liquid amorphous alloys.

First it should be established whether the ferrmagnetism can exist in liquid state or not. A wide discussion began upon the appearance of work [4], where the

ferromagnetism in liquid state was detected in $Au_{0.73}Co_{0.27}$ alloy. Ferromagnetic properties were found at 70 K above the melting point. Further investigations [5], [6] of that system showed the magnetic properties to significantly depend on the time and heating velocity. This fact was connected with the existence of small crystalline groups of Co-atoms, which can be dissolved in Au-based matrix during some definite period of time.

CHEN *et al.* [6] determined the Curie temperature T_c and glassing temperature T_g for amorphous alloys of different composition. It was shown that in the same cased T_c could be higher than T_g, which confirmed the principal possibility of the liquid ferromagnetic existence.

If the Curie temperature is higher than melting temperature, the magnetic field begins to exert influence on the amorphous alloys, still before glass formation, while the alloy exists in supercooled state. Although the treatment time is very short the application of magnetic field can change the structure and properties of alloy. In connection with this much attention was paid to studying structural changes in a liquid state when magnetic field was applied.

It is well known that binary systems whose phase diagrams show the deep eutectic point reveal easily their glass forming ability. In most cases the concentration interval of easy glass forming is located in the vicinity of eutectical point. On the other hand, the presence of the deep eutectical point in phase diagram allows to satisfy the condition $T_c > T_g$. Moreover, if the component of binary system is a ferromagnetic with the high Curie temperature it is possible that T_c be higher than crystallization temperature. In this case, liquid alloy will have the same temperature interval for ferromagnetic liquid to exist. Besides Au–Co, also Ni–Pb, MnBi–Bi, Co–S and several others belong to such binary systems. From this point of view systems with almost equal values T_c and T_m are of great interest, too.

Theoretical studies on magnetic properties of liquids are very scarce. In paper [6], the magnetic properties of model liquid, comprising magnetic hard spheres, interacting via exchange forces, are considered. The structure factor of liquid magnetic was calculated within a wide temperature range for different values of external magnetic field. It was found that height of the first maximum in structure factor increases with strength of magnetic field. The most significant increase is observed up to some value of magnetic field, and afterwards the dependence on magnetic field strength is slight. In other words, the degree of ordering stands for the saturation. It should be noted that the temperature under consideration is higher than Curie temperature. If the temperature becomes lower the height of the first maximum of $S(k)$ increases according to hyperbolic function. Such a behaviour of structure factor is caused by magnetic ordering due to the external magnetic field. In the absence of the field, no changes are observed in structure factor, when temperature varies down to T_c. In this case, there is a topological ordering only, but at temperatures lower than T_c, there exists the tendency to magnetic ordering due to effective internal field.

It is clear that these facts established theoretically should be proved by experimental results.

4. Experimental results and discussion

In order to study the influence of magnetic field on the structure of alloys in a liquid state the eutectic MnBi–Bi and Ni–Pb were chosen. Phase diagrams of these systems show that the Curie temperature for MnBi and Ni is higher than the corresponding eutectics melting temperatures. Similar behaviour can be seen in Co–B and Co–Cu alloys, whose structure we have studied earlier [7], [8]. For Co–Co_2B eutectic alloy the T_c of Co is only 12 K less than the melting temperature.

Analysing the structure factors and binary correlation functions it has been found that both Co-based clusters and chemically ordered associates Co_2B are the main structural units of molten eutectic alloy. A similar structural state can be found in $Cu_{0.95}Co_{0.05}$ liquid alloy. Therefore, it is clear that tendency to form the groups of similar kind atoms can be observed in other eutectic alloys with similar phase diagram. Taking into account these experimental facts we assume the existence of clusters of magnetic atoms with magnetic order. In order to bring into effect such clustered structure one does not need to have the external magnetic field of great strength, which is required in the case of hard sphere liquid.

The structure factor of liquid $Ni_{0.98}Pb_{0.02}$ alloy is shown in Fig. 2. As can be seen from this figure, application of magnetic field leads to the increasing of first maximum height in $S(k)$. This fact evidently shows that although the concentration of ferromagnetic component Ni is only 2 at.% the tendency towards ordering is obvious. Such a concentration of Ni-atoms allows us to consider this alloy as a paramagnetic one.

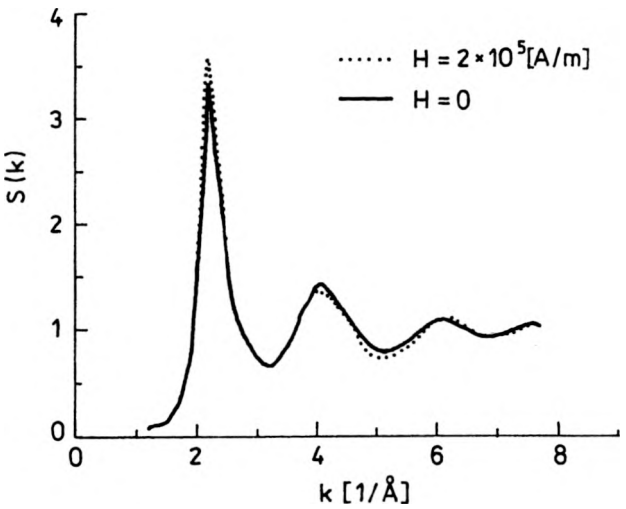

Fig. 2. Structure factor of $Ni_{0.02}Pb_{0.98}$ liquid alloy.

In MnBi–Bi eutectic alloy which consists of 97.5 at.% Bi, the ferromagnetic component is MnBi, whose Curie temperature is significantly higher than melting temperature. In the Table, the main structure parameters obtained from experimen-

tal $S(k)$ binary correlation functions are listed. Besides eutectic alloy the one with more enriched content of MnBi (90 at.% Bi) was investigated. As can be seen from this table there are some changes in structural parameters which were caused by ordering due to magnetic field application. It should be noted that in the case of liquid alloy containing 90 at.% Bi the splitting of the third maximum in $S(k)$ into two subpeaks if magnetic field is applied, is observed. These facts allow us to suggest that structural changes in magnetic field occur due to the existence of clusters whose atoms are ordered by means of exchange forces of interaction.

Table. Structure parameters of Mn–Bi liquid alloys.

at. % Bi	T	k_1	k_{min}	k_2	k_3	r_1	r_2	r_3	Z_{sym}
90 H = 0	645	2.10	3.00	4.15	6.25	3.29	4.20	6.75	8.0
90 H = $2.0 \cdot 10^5$ A/m	645	2.13	2.90	4.12	6.15 6.55	3.27	4.20	6.75	7.9
97.5 H = 0	545	2.11	2.90	4.10	6.20	3.31	4.30	6.50	7.8
97.5 H = $2.0 \cdot 10^5$ A/m	545	2.10	3.00	4.10	6.20	3.30	4.30	6.50	7.9
100	600	2.11	2.90	4.12	6.30	3.38	4.10	6.60	7.8

k_1, k_2, k_{min}, k_3 (in $Å^{-1}$) – position of corresponding maxima in $S(k)$,
r_1, r_2, r_3 (in $Å^{-1}$) – maxima in binary correlation functions,
Z_{sym} – the area under the first coordination peak in the radial distribution function, determined by symmetrical resolution of maximum.

Therefore, the atoms in liquid binary eutectic alloys, whose phase diagrams show the Curie temperature to be higher than melting temperature, tend to form ordered clusters but thermal motion promotes their decay.

The X-ray diffraction study of amorphous $Ni_{0.64}Hf_{0.36}$ alloy revealed that atomic distribution is characterized by the existence of chemical short range order. In order to study the influence of magnetic field on the structure we have annealed this alloy at different temperatures for two hours. Figure 3 presents the diffraction pattern obtained at different temperatures. The transition from amorphous state to crystalline one begins at $T = 423$ K. As can be seen the diffraction peak of crystalline phase does not fall in the first peak position of amorphous alloy. Hence, there are significant changes in atomic distribution topology upon crystallization.

In Figure 4, diffraction peaks for an alloy annealed in magnetic field and without it are compared. As is shown in this figure no significant changes are observed. The positions of maxima are almost the same, which indicates that the most probable

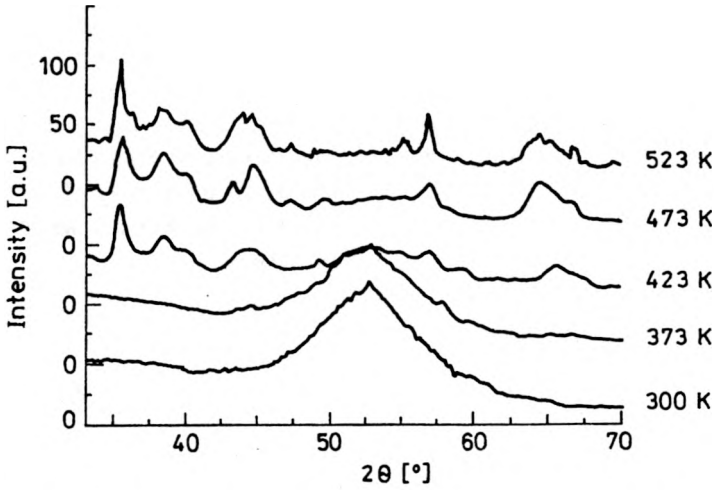

Fig. 3. X-ray diagrams of annealed $Ni_{0.64}Hf_{0.36}$ amorphous alloy.

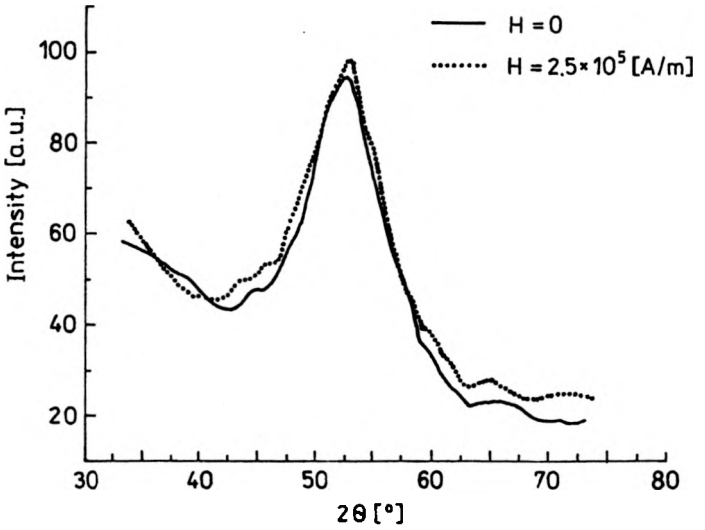

Fig. 4. X-ray diagrams of $Ni_{0.64}Hf_{0.36}$ amorphous alloy.

interatomic distances ramain unchanged. Asymmetry of the peak corresponding to the alloy annealed in magnetic field alloy is greater and some increase of peak wings is observed, particularly the left one. Taking into account the transformation of diffractograms when annealing temperature increases it is possible to conclude that magnetic field applied promotes the precrystallization process. At the same time the size of structural units is being unchanged. Thus, during annealing in magnetic field there is more intensive formation of ordered structure on the scale of clusters, which is also confirmed by increasing intensity at low values of scattering angles.

Such an increase does suggest the possibility of existence of small maximum, which in this range of scattering angles is precursor of intermediate range order.

5. Conclusions

Binary eutectic systems containing ferromagnetic component reveal the formation of lconsisting similar kind atoms which are stable within some temperature range. Studying the influence of magnetic field on the structure of glasses can be carried out in two stages: in liquid state before glassing and in amorphous state during annealing. It was found that application of magnetic field to liquid Mn–Bi and Ni–Pb eutectic alloy leads to formation of a more ordered structure on the clusters scale. Thermal treatment of $Ni_{0.64}Hf_{0.36}$ glass in magnetic field promotes both the ordering of clusters and formation of the crystalline structure.

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