Structural changes and mechanical properties of amorphous metallic ribbons Fe–(Ni, Co, Mn)–Mo–Si–B irradiated by powerful nanosecond laser pulses

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The influence of pulsed laser radiation on the structure and mechanical properties of amorphous Fe–(Ni, Co, Mn)–Mo–Si–B films has been investigated. The structural changes caused by the irradiation were studied by X-ray diffraction and the microhardness of the initial and irradiated samples was measured by the Vickers method. It was established that small additions of Ni, Co, or Mn have a significant influence on the crystallization process of the irradiated alloys. Irradiation leads to an increase of the microhardness for some values of pulse energy.

Amorphous alloys / Nanocrystalline materials / Laser irradiation

Introduction

The irradiation of amorphous materials by powerful short laser pulses makes it possible to achieve heating rates of the same order as, or even higher than the cooling rates used for the formation of amorphous structures. One can assume that the crystalline phase, or a different amorphous one, formed under such conditions will preserve structural features of the initial amorphous phase, transferring some of its most interesting physical properties, namely the mechanical ones, into the crystalline phase. In addition, local laser processing allows forming composites that are local crystalline bulk microregions or crystalline layers bordering an amorphous matrix. In order to understand the mechanism of structure formation in amorphous materials with desired properties, the influence of laser radiation on the structure of amorphous Fe-based ribbons has been studied in this work.

Experimental

Amorphous ribbons of $Fe_{75}Mo_5Si_6B_{14}$, $Fe_{75}Mo_{2.5}Co_{2.5}Si_6B_{14}$, $Fe_{75}Mo_{2.5}Mn_{2.5}Si_6B_{14}$, and $Fe_{75.5}Mo_{3.0}Ni_{3.5}Si_2B_{16}$, obtained by rapid cooling from the melt, were irradiated by a pulsed laser scanning the surface. The laser equipment emitted periodic pulses using a single pulse on each microzone. The number of irradiated microzones per unit area was $N \sim 2000$ mm^{-2}, wavelength $\lambda = 1.06$ μm, duration $\tau = 130$ ns, pulse generation frequency $f = 50$ Hz. The diameter of the irradiated microzone was $d \approx 30$ μm.

The irradiated samples were studied by X-ray diffraction (XRD) using a DRON-3 diffractometer (Fe Kα radiation, $\lambda = 1.9373$ Å). The experimental angular dependence was used to calculate the structure factors and pair correlation functions, which allow analyzing directly the atomic arrangement. The XRD-data were used to identify the phases created by the laser treatment, determine their volume fraction in the alloy and other parameters.

Results and discussion

Diffraction patterns of irradiated samples are shown in Fig. 1, where the energy of the laser beam increases from bottom to top for each sample. It can be seen that after irradiation at energies within the range $E = 0.134$-0.245 mJ formation of crystalline phases occurs in the amorphous matrix. At lower energies the crystallization process is very limited, and only at $E = 0.245$ mJ the ribbons exhibit complete crystallization. Analysis of the XRD-results allowed us to suppose that, at low energies, nucleation and formation of clusters take place in layers near the surface of the ribbons. These clusters have a structure close to that of the amorphous matrix, but they attempt
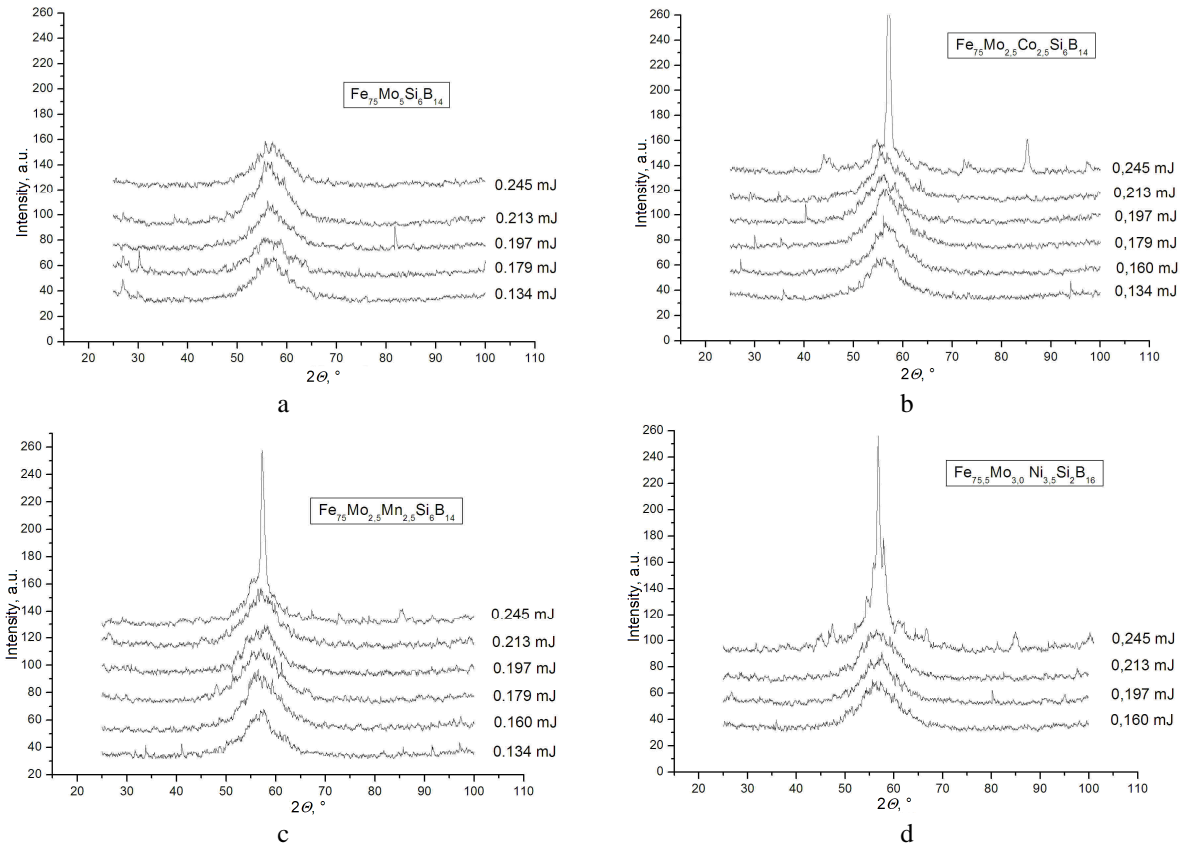
Fig. 1 X-ray diffraction patterns of amorphous alloys, recorded after laser irradiation with different pulse energy: a) $Fe_{75}Mo_5Si_6B_{14}$, b) $Fe_{75}Mo_{2.5}Co_{2.5}Si_6B_{14}$, c) $Fe_{75}Mo_{2.5}Mn_{2.5}Si_6B_{14}$, d) $Fe_{75.5}Mo_{3.0}Ni_{3.5}Si_2B_{16}$.

to transform this structure into crystal-like. However, because of the low energy and short duration of the impulse these clusters cannot aggregate into crystallites of larger size. As seen in Fig. 1, the alloy $Fe_{75}Mo_5Si_6B_{14}$ shows no complete crystallization, even not at the maximum value of laser beam energy. For this alloy significant dependence of the principal peak profile in the scattered intensity curve on the laser energy is observed, which reveals structural changes in the amorphous alloy. It can be seen that the width of the main peak, which is related to the size of clusters, changes with the energy of the laser radiation. It is probable that reamorphization of the alloy occurs due to the laser irradiation, but full crystallization would require more energy. A similar crystallization behavior has been observed for Co-based amorphous alloys exposed to radiation [1] and for laser irradiation of amorphous ribbons of $Fe_{73.7}Nb_{2.4}Cu_{1.0}Si_{15.5}B_{7.4}$ [2].

According to data obtained in [3], additions of Mo and Ni change the temperature of crystallization, the activation energy of primary crystallization, and the mechanism of crystallization. A comparison of the diffraction curves of samples irradiated at the same laser power levels (Table 1) allows asserting that the addition of Co, Mn, or Ni significantly affects the crystallization process and atoms of these elements are, most likely, the centers of nucleation of the crystal phase also at laser irradiation.

The specific energy that leads to crystallization can be evaluated applying the energy conservation law. The number of pulses per unit area during irradiation is $N \approx 2000$ mm^{-2} and the absorption coefficient of iron for the polished surface is $A = 0.35$. When the pulse energy $E = 0.245$ mJ, the total energy absorbed per unit area will be: $E_{total} = N \times E \times A = 171.5$ mJ/mm^2. Since the irradiated area is larger than the thickness of the ribbon, $d = 0.03$ mm, radial distribution of heat is negligible and the volume that absorbs energy is $V = 3 \times 10^{-11}$ m^3. Since the main mass portion of the alloy is iron, we can accept that the density of the alloy is $\rho = 7.6 \times 10^3$ kg/m^3, taking into account that the density of glass materials is lower than the density of their crystalline analogues by 1-2 %. Consequently, the absorbing volume has the mass $m = 22.8 \times 10^{-8}$ kg. The molar mass of the alloy $Fe_{78.5}Mo_{0.5}Ni_{1.0}Si_{6.0}B_{14.0}$ is $M = 48.1$ g/mol and the specific energy leading to crystallization, $E_{sp} \approx 37.2$ kJ/mol. For comparison, the activation energy of crystallization of the alloy $Fe_{78.5}Ni_{1.0}Mo_{0.5}Si_{6.0}B_{14.0}$ is 440 kJ/mol [3].

We have studied both sides of the samples: the irradiated side and the opposite side. Comparison of the diffraction curves shows significant differences between the structure of the irradiated side and the opposite one. Fig. 2 presents diffraction curves from both sides of the alloy $Fe_{75}Mo_{2.5}Mn_{2.5}Si_6B_{14}$, irradiated at $E = 0.245$ mJ. It can be seen that the irradiated side

Table 1 Phase analysis of amorphous alloys submitted to laser irradiation with different pulse energy; A – amorphous phase.

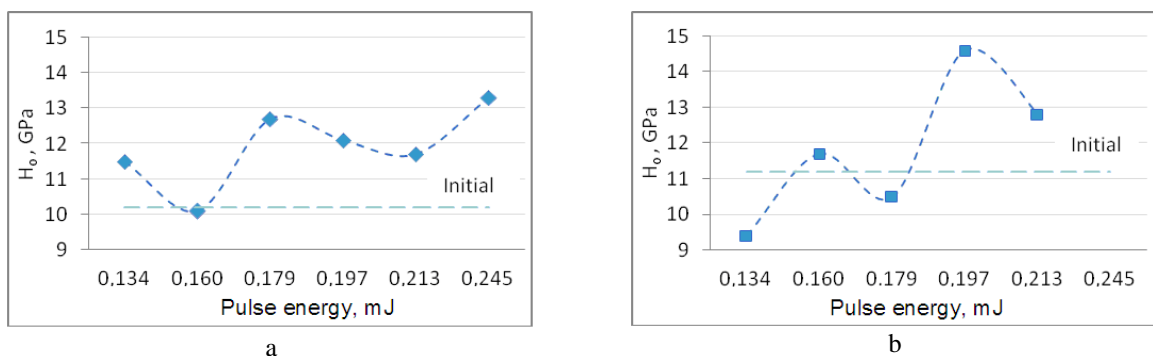| E, mJ \ Alloy	$Fe_{75}Mo_5Si_6B_{14}$	$Fe_{75}Mo_{2.5}Co_{2.5}Si_6B_{14}$	$Fe_{75}Mo_{2.5}Mn_{2.5}Si_6B_{14}$	$Fe_{75.5}Mo_{3.0}Ni_{3.5}Si_2B_{16}$
0.134	A	A	A	–
0.160	–	A	A + 13% Fe_3Si	A
0.179	A	A + 5% Fe_3Si	A	–
0.197	A	A + 2% Fe_3Si	A	A
0.213	A + 42% $Fe_{23}B_6$	A + 6% Fe_3Si + 10% $Fe_{23}B_6$	A	A
0.245	A + 1% $Fe_{23}B_6$+ 1% Fe_3Si	90% α-Fe + $Fe_{23}B_6$	20% $Fe_{23}B_6$ + 80% α-Fe	52% α-Fe + 34% Fe_3B + 14% $Fe_{23}B_6$
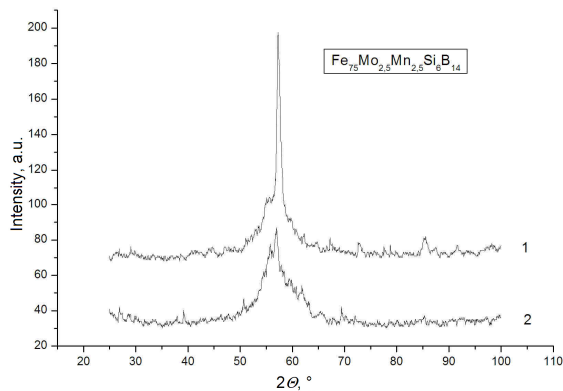
Fig. 2 Diffraction patterns of the alloy $Fe_{75}Mo_{2.5}Mn_{2.5}Si_6B_{14}$ irradiated at $E = 0.245$ mJ: curve 1) irradiated side, curve 2) opposite side.

is completely crystalline, while the opposite side is amorphous. There is a small peak only, which corresponds to crystalline phase Fe_3Si, the content of which was found to be about 5%. This difference between the structures of the two surface layers indicates that laser irradiation offers an opportunity to form composite materials, in which amorphous layers are contiguous with nanocrystalline ones.

The dependence of the microhardness of irradiated $Fe_{75}Mo_5Si_6B_{14}$ and $Fe_{75}Mo_{2.5}Co_{2.5}Si_6B_{14}$ ribbons on the pulse energy is shown in Fig. 3. The comparison of the microhardness and the diffraction curves shows that for slight differences in the diffraction curves more significant differences are observed in the microhardness. This feature is supposed to be caused by different structure of amorphous alloys after laser irradiation. From the XRD-results it follows that when part of the Mo atoms are replaced by Co atoms, the ability to change the atomic distribution, including crystallization, during laser irradiation increases. The substitution is probably accompanied by a significant change of the diffusion coefficient, which is an important characteristic for nucleation and crystallite growth. For this reason the fraction of nanocrystals in the Co-doped alloy is higher, which results in its higher microhardness. Another feature of the microhardness curve is that in both cases one can see nonlinear behaviour. Oscillating curves indicate that the microhardness depends not only on the short-range order, but also on other factors, such as the cluster-cluster structure, intercluster interactions, the size of the crystallites, stress and defects in structure. Each of them contributes differently to the total microhardness, which is one of the reasons why such behaviour is observed.

The increase of the microhardness occurring upon laser irradiation of the amorphous alloys may be attributed to the formation of nanocomposites, the matrix of which is an amorphous alloy while nanocrystals, created from the alloy, constitute the filler. The microhardness, like other mechanical properties, will depend on structure parameters of the matrix and the filler.

a

b

Fig. 3 Microhardness of irradiated alloys: a) $Fe_{75}Mo_5Si_6B_{14}$, b) $Fe_{75}Mo_{2.5}Co_{2.5}Si_6B_{14}$.

Conclusions

Laser irradiation of $Fe_{75}Mo_5Si_6B_{14}$, $Fe_{75}Mo_{2.5}Co_{2.5}Si_6B_{14}$, $Fe_{75}Mo_{2.5}Mn_{2.5}Si_6B_{14}$, and $Fe_{75.5}Mo_{3.0}Ni_{3.5}Si_2B_{16}$ amorphous alloys induces transformations of the short-range order structure that are accompanied by cluster size changes at lower energies, and complete crystallization at the energy $E = 0.245$ mJ. Due to the higher Mo content in the alloy $Fe_{75}Mo_5Si_6B_{14}$ the crystallization was not complete even for the highest pulse energy. The formation of nanocrystals in the amorphous matrix is responsible for the increase of the microhardness. A direct correlation between the short-range order structure and the energy dependence of the hardness was not observed because the hardness depends also on cluster-cluster interactions, strains and defects that are commonly created at non equilibrium conditions of heating and cooling.

References

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