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Laser-induced structure transformation in Fe-Cu-Nb-Si-B amorphous alloy

Introduction

In recent years, the interest in studying of amorphous metal alloys (AMA) has increased due to opportunities to create nanocrystalline materials by different processing of AMA. In this work, we used a laser to modify the structure of amorphous ribbon based on iron. Effect of laser irradiation on the structure of materials can be different and depends on the space-time and energy characteristics of laser radiation and the type of material that is irradiated. The number of papers devoted to this area of research has grown in recent years [1, 2, 3, 4]. However, structural changes and changing the properties of amorphous materials under the influence of laser treatment is much less studied than the mechanisms and kinetics of structural relaxation and crystallization of AMA after thermal annealing. The peculiarity that a laser technology available for use in a wide range of radiation power (from microwatts to gigawatts) as well as the spectral range (from 0.4 to 15 microns) and time range from continuous radiation mode to pulse mode with a pulse duration of 10^{-12} s significantly extends this problem. Notably that modulation of laser radiation enables to create various conditions of heat exposure within an arbitrary region of one material.

Experiment

For the studies mentioned, we have chosen amorphous metal ribbon of Fe-Nb-Cu-Si-B system, particularly $Fe_{73.5}Nb_3Cu_1Si_{15.5}B_7$, $Fe_{73.7}Nb_{2.4}Cu_{1.0}Si_{15.5}B_{7.4}$ and $Fe_{73.1}Nb_3Cu_{1.0}Si_{15.5}B_{7.4}$. Amorphous alloys obtained by melt spinning in the form of ribbons width of 1 – 2cm and a thickness of about 25 microns. Irradiation was carried out by pulsed laser radiation focused on the surface of the ribbon, at different modes of exposure, with parameters that are presented in Table 1. Irradiation parameters are combined in conventionally called modes, the main difference between them – the value of the laser pulse duration and for modes 1 and 2, the main difference is a step scan.

Tab. 1. Parameters of radiation: Pulse duration τ, pulse energy *E*, pulse frequency *f,* scan step *l*, effective diameter of the focal spot d_{ef}, wavelength λ

	Mode 1	**Mode 2**	**Mode 3**	**Mode 4**	**Mode 5**
τ, s	1.30×10^{-7}	1.30×10^{-7}	6×10^{-6}	2×10^{-5}	$10^{-4} – 10^{-3}$
P, W	up to 50	up to 50	up to 50	up to 50	up to 30
f, Hz	50×10^3	50×10^3	150×10^3	50×10^3	300
l, μm	23	45	20	20	100
d_{ef}, μm	30	30	10	10	35
λ, μm	1.06	1.06	1.06	1.06	10.6

Investigation of structural changes was performed by X-ray diffraction method before and after laser irradiation (DRON-3 diffractometer). If nanocrystalline phases were detected, we assessed the volume fraction of each of them using an additive approximation for the observed dependence of the scattering intensity on scattering angle. In other words, this dependence was represented as a sum of the intensities corresponding to the amorphous and crystalline phases. An observed diffraction peak was reproduced by fitting partial diffraction peaks with Lorentzians using the Origin 6.1 program. The fraction of nanocrystals was evaluated using the relation [5]:

$$X_{cr} = I_{cr} / (I_{cr} + I_{am}),$$

where I_{am} and I_{cr} are the integrated intensities of the peaks from the amorphous and nanocrystalline phases, respectively. The Debye-Scherrer formula was used for the calculation of mean size of nanocrystals [6]:

$$L_{cr} = \frac{\lambda}{\beta \cos(\theta)}.$$

Results and discussions

It is known that in the process of laser treatment there is the threshold power density (Q^{tr}), defining the heat of the material without destroying it. Basing on the radiation power at which we observed the destruction (caused by evaporation), the threshold power density Q^{tr} was experimentally determined for selected values of laser pulse durations [7]. Figure 1 shows that Q^{tr} decreases with increasing τ. These values Q^{tr} coincide with the data for crystalline iron at low pulse duration, while at increasing τ the value of Q^{tr} for AMA decreased relatively to the values for crystalline iron, which is likely due to the smaller value of thermal conductivity of amorphous metals.

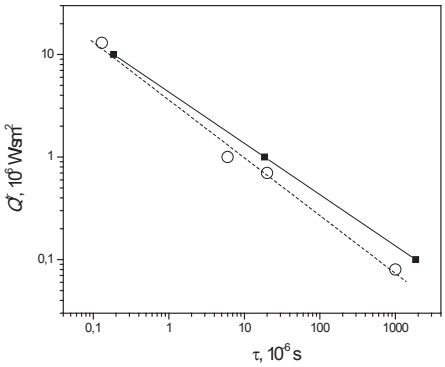
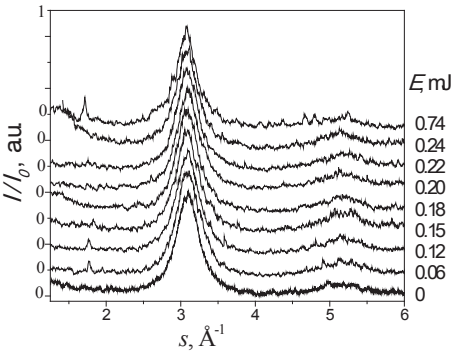
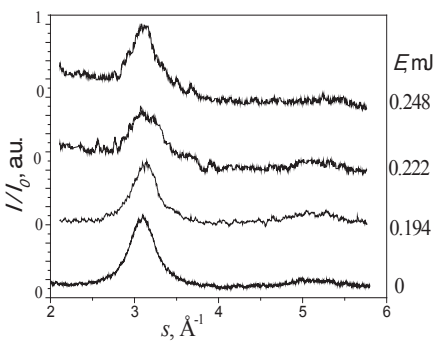


Fig. 1. The threshold power density Q^{tr} versus pulse duration τ (○ – for amorphous alloy, ■ – for crystalline iron [8])

The results of studies of laser-induced structural changes in amorphous alloys obtained by X-ray diffraction method are presented in Figure 2, which shows a series of intensity curves of diffracted X-rays obtained from samples that were irradiated at different pulse durations and different values of energy *E*, accordingly to modes 2–5 of Table 1 [9, 10]. As can be seen from this figure, for values of pulse duration (τ) 10^{-7} and 10^{-6}s, all of intensity curves are characterized by the amorphous structure. For values $\tau > 10^{-5}$s there are clear peaks, which indicate the formation of nanocrystalline phases in the amorphous matrix. Since the pulse energy in each case increased to a level that causes intense melting, it is clear that laser irradiation at this values of *E* entails heating the alloy to a temperature that is much higher than the temperature of onset of crystallization T_{kr}, which for this type of alloy is about 800 K [11], but crystalline phases detected only if $\tau > 10^{-5}$s. Thus, the pulse duration $\tau \leq 10^{-6}$s is not enough for the process of crystalline phase formation, whereas irradiation at $\tau \geq 10^{-5}$s and corresponding values of energy induce the crystallization process. Thus, it is shown that in the process of laser treatment of AMA there is a "threshold" value of the duration of exposure (τ^{tr}) below which the crystallization does not occur even at high values of radiation power. The most likely reason for this is a low diffusion activity of atoms at a short duration of exposure. For alloys of Fe-Nb-Cu-Si-B it equals $\tau^{tr} \approx 2 \times 10^{-5}$s.



a)



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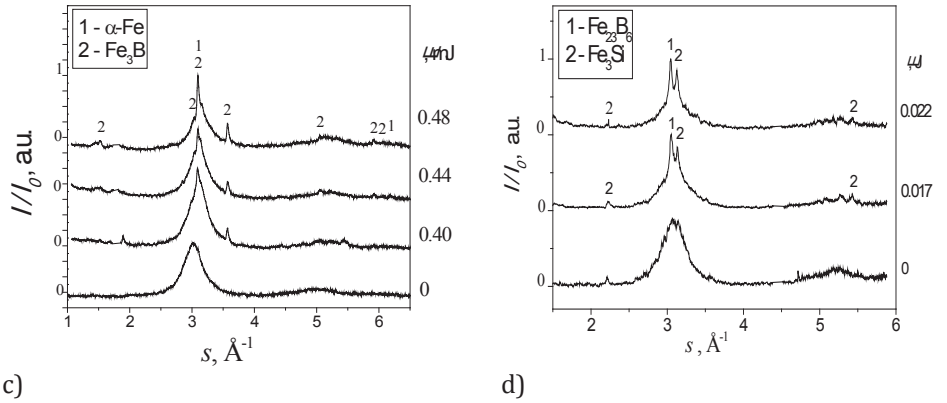

Fig. 2. Intensity curves of diffracted X-rays for alloys under irradiation modes 2–5: $\tau \sim 10^{-7}$ (a); 10^{-6} (b); 10^{-5} (c); 10^{-3}sec (d)

The analysis of the diffraction peaks of intensity curves that correspond to the samples irradiated at values of $\tau \sim 10^{-5}$ and 10^{-3}s, has been performed using additive approximation (Fig. 3). For values of 10^{-5}s there are clear peaks, which indicate the formation of nanocrystalline α-Fe phase in the amorphous matrix with an average grain size of 25–30 nm and Fe_3B phase (Fig. 3a). The total content of nanocrystalline phases in this case is less than 20%, but increasing pulse energy over 0.48 mJ leads to the destruction of the tape. For pulse duration of about 1ms, we have also observed clear diffraction peaks that indicate the formation of nanocrystalline Fe_3Si and $Fe_{23}B_6$ phases with an average grain size of 10–20 nm (Fig. 3b). Amorphous halo is caused by the presence of non-irradiated areas, due to the large step scanning.

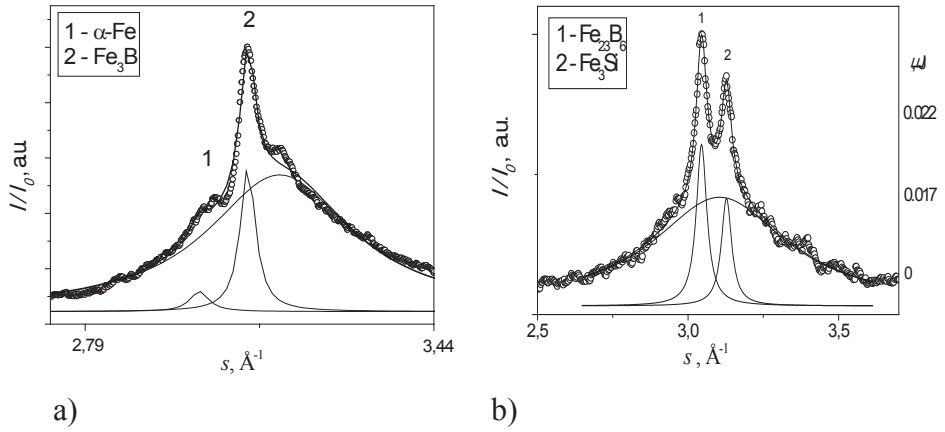

Fig. 3. Diffraction maxima corresponding to $\tau \sim 10^{-5}$s, E = 0.48mJ (a) and $\tau \sim 10^{-3}$s, E = 0.022J (b)

A common feature of the above described modes was that a large step scanning and focal spot is not imposed on one another. And in this case, the part of the surface was not irradiated. The following results were obtained for regime with a relatively small step scanning, which provided exposure surface completely. Intensity curves corresponding to samples irradiated in this way are presented in Figure 4 and the results of X-ray analysis – in Table 2.

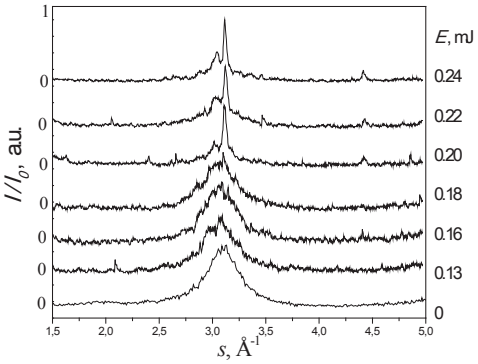

Fig. 4. Intensity curves for alloy of Fe-Nb-Cu-Si-B system irradiated under mode 1

Tab. 2. The results of X-ray analysis

E, mJ	Crystallization products
0.20	54% $Fe_{0.86}Si_{0.14}$ (60 nm) + 7% Fe_3B (40 nm) + 39% $Fe_{23}B_6$ (8 nm)
0.22	22% $Fe_{0.86}Si_{0.14}$ (120 nm) + 6% Fe_3B (26 nm) + 20% $Fe_{23}B_6$ (18 nm)
0.24	49% $Fe_{0.86}Si_{0.14}$ (130 nm) + 29% Fe_3B (11 nm) + 22% $Fe_{23}B_6$ (120 nm)

As can be seen from Figure 4, for values of E = 0.20 – 0.24 mJ the intensity curves are characterized by sharp peaks that indicate crystallization of irradiated samples, as opposed to those that were exposed for the same energy values according to mode 2. The result of laser-induced crystallization is the formation of Fe_3B, $Fe_{23}B_6$ and Fe–Si phases. We compared the peaks positions corresponding to s = 3.112505 Å (interplanar distance D = 2.018691 Å) and s= 4.412411 Å (D = 1.423980 Å), with the relevant parameters of other phases, that can crystallize in the alloy. This comparison shows more similarity to the $Fe_{0.86}Si_{0.14}$ phase (structure of b.c.c Fe–Si, 14 at.% Si; $d_{(101)}$=2.017 Å, $d_{(020)}$=1.426 Å [12]) than to α-Fe or Fe_3Si.

Comparing the results of laser-induced structural changes caused by irradiation under mode 1 and 2, it is clear that a single laser pulse duration with $\tau \sim 10^{-7}$, ($E \approx$ 0.1–0.7 mJ) does not initiate the formation of crystalline phases in the zone of action. Instead, repeated exposure by such short pulses at certain values of

E (0.18-0.25 mJ) increases the duration of the thermal field, and as a result, induces the crystallization process.

Tab. 3. Phase composition of laser-induced crystallization of amorphous alloys of Fe-Nb-Cu-Si-B system depending on the pulse duration

The pulse duration, s	Products of crystallization
$\tau < \tau^{tr}$	–
$\tau \sim \tau^{tr}$ (~10^{-5}s)	Fe_3B, α-Fe
$\tau > \tau^{tr}$	Fe_3B, $Fe_{23}B_6$, $Fe_{0.86}Si_{0.14}$
$\tau >> \tau^{tr}$ (~ 10^{-3}s)	$Fe_{23}B_6$, Fe_3Si

The obtained results make it possible to identify the kinetics of laser-induced crystallization. As can be seen from Table 3, for the values of the pulse duration close to the threshold value in alloys of Fe-Nb-Cu-Si-B system, phases Fe_3B and α-Fe crystallize, whereas at somewhat larger values of τ, phases Fe_3B, $Fe_{23}B_6$ and $Fe_{0.86}Si_{0.14}$ crystallize. If the pulse duration is much longer than threshold value, we detect crystallization of phases $Fe_{23}B_6$, Fe_3Si.

It is known that for amorphous alloys of Fe-Si-B-Nb-Cu system as a result of heating with low speed (~ 5 K/min) or isothermal heating, the two-stage crystallization occurs. During the first stage of crystallization from amorphous matrix the Fe(Si) phase is formed and its crystallization temperature is about 800 K, whereas at the second stage the borides are formed with crystallization temperature of above > 900 K [13, 14]. However, under the laser irradiation, due to uneven temperature distribution, both stages of crystallization process occur simultaneously.

Conclusion

It has been shown that laser radiation is an effective tool for the formation of nanoscale structure in Fe-based multicomponent amorphous alloy. Optimal parameters of radiation for the formation of nanoscale phases of different size and chemical composition have been determined.

It is shown that the change of pulse duration can affect the chemical composition of nanocrystalline phases. As it was shown, after exposure with pulse duration of 10^{-5} s in amorphous ribbon nanoscale phases α-Fe + Fe_3B crystallize, whereas at greater duration (~ 10^{-4}c) nanoscale phases Fe_3B + $Fe_{23}B_6$ + Fe(Si) crystallize. Further increase of pulse duration (~ 10^{-3}s) causes the formation of nanoscale Fe_3Si + $Fe_{23}B_6$ phases. All this indicate a crucial role of diffusion in non-equilibrium phase formation processes.

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Abstract

Changes of structure of Fe-Cu-Nb-Si-B amorphous alloy upon laser irradiation have been studied by means of X-ray diffraction method. It shown that nanocrystallization process occurs and this process significantly depends on energy of radiation and pulse duration. It is also shown that diffusion processes are most responsible for the formation of crystalline phases.

Key words: amorphous Fe-based alloys, nanocrystallization process, laser irradiation.

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