Nanocrystallization and phase formation in $\text{Fe}_{73.5}\text{Nb}_3\text{Cu}_1\text{Si}_{15.5}\text{B}_7$ amorphous ribbon under laser heating

YULIA S. NYKYRUY^{1,*}, STEPAN I. MUDRY¹, YURIY O. KULYK¹, MARCIN LAPINSKI²

¹Ivan Franko Lviv National University, Physics of Metals Department, 8 Kyrylo and Mephodyj St., Lviv, 79005, Ukraine

²Gdańsk University of Technology, Department of Solid State Physics, 11/12 Narutowicza St., Gdansk, 80-233, Poland

Laser-induced local crystallization in Finemet-type alloy was studied using X-ray diffraction, SEM and EDX methods. For investigated conditions of irradiation (wavelength $\lambda = 1.06 \mu\text{m}$, laser power density 50 W/cm^2), it was found that primary crystallization starts with the formation of the nanocrystalline $\alpha\text{-Fe}(\text{Si})$ solid solution at shorter exposure time and the second step crystallization with the nanocrystalline hexagonal H-phase formation occurs in longer exposure time. Changes in the local element concentration were observed at the surface of the irradiated zone and at the ribbon fracture. It was shown that the nonlinear temperature field due to the laser irradiation resulted in changes of the local elements concentration and this feature changed crystallization mechanism of the Finemet-type alloy.

Keywords: *laser-induced crystallization; amorphous metallic alloy; nanostructure*

1. Introduction

Amorphous metallic alloys (AMA) have been the subject of thorough research for a long time because of their unique properties caused by disordered metastable structure. It is known, that heating of the amorphous structure results in its relaxation and then crystallization. Isothermal and low-rate heating crystallization processes in Finemet-type amorphous alloys was studied in the literature [1–3]. It was found that the crystallization process of the Finemet-type AMA has two stages. The isothermal annealing at the temperatures typically between 770 K and 800 K leads to the primary crystallization of the bcc Fe or $\alpha\text{-Fe}(\text{Si})$ solid solution, with DO_3 (Fm3m) ordering for the Fe_3Si phase, resulting in excellent soft magnetic properties, whereas the annealing at more elevated temperatures (above 900 K), leads to crystallization of boride compounds, such as Fe_2B or Fe_3B and can be referred to the second crystallization stage.

Laser heating of AMA also leads to crystallization process [4–6]. However, the laser-induced crystallization process has such a feature that both

stages of crystallization in most cases occur simultaneously at the irradiated zone which is due to the uneven temperature distribution [7–9]. The presence of boride phases significantly worsens the soft magnetic properties [10]. For efficient application of the laser heating of AMA, a complex study of the kinetics of the laser-induced crystallization is required. Besides, the laser irradiation of AMA is also interesting from the fundamental viewpoint, because in this case, we have an open thermodynamic system and occurring processes are under conditions far from equilibrium and, on that reason, the self-organization processes or other related phenomena should be taken into account. Therefore, the study of structural transformations in an amorphous alloy under different conditions of laser irradiation is of great importance.

2. Experimental

Amorphous $\text{Fe}_{73.5}\text{Nb}_3\text{Cu}_1\text{Si}_{15.5}\text{B}_7$ ribbon was produced by melt quenching. The ribbon thickness was about $24 \mu\text{m}$ and width about 1.5 cm. Fiber laser (wavelength $\lambda = 1.06 \mu\text{m}$ and power $P = 50 \text{ W}$) were used to irradiate the ribbon samples. During irradiation, the samples of the ribbon were

*E-mail: Yulia_nyk@ukr.net

fixed at a steel substrate and placed at a distance from the focal plane of the lens so that the size of the laser spot on the ribbon surface was about 1 cm (by level $1/e^2$). The exposure time τ changed within 0.25 s to 0.70 s with the interval of 0.05 s. The laser power density was 50 W/cm^2 and laser fluence F varied within 12.5 J/cm^2 to 35.0 J/cm^2 .

The changes in structure of the irradiated samples have been studied by means of the X-ray diffraction method (XRD) using X-ray transmission technique and DRON-3 diffractometer (CoK α radiation, $\lambda = 1.7902 \text{ \AA}$). The X-ray beam with a diameter of about 5 mm to 6 mm was directed to the irradiated zone of the ribbon. Phases, which crystallized under the laser irradiation, were determined by interpretation of diffraction peaks positions. The fraction of each phase X and the average grain size of the crystallites L_{cr} were determined using formulas [11, 12]:

$$X = \frac{I_{cr}}{I_{cr} + I_{am}} \quad (1)$$

where I_{cr} and I_{am} – the integral intensities for the crystalline and amorphous phases, respectively.

$$L_{cr} = \frac{\lambda}{\beta \cos(\theta)} \quad (2)$$

where $\beta = B - b$; B and b – the half-peak width for the investigated and reference samples respectively, 2θ – scattering angle.

The study of changes in the irradiated surface topology and the elements distribution in and out of the irradiated zone was performed using scanning electron microscopes (SEM) SELMI and FEI QUANTA FEG 250 with a secondary or backscattered electron detector. Energy dispersive X-ray analysis was performed, utilizing an EDAX TEAM EDS analysis system.

3. Results and discussions

3.1. X-ray analysis

We have detected structure changes in the irradiated zone of the amorphous ribbon using XRD method. X-ray scattering intensity curves obtained from the ribbon samples irradiated at the mentioned exposure time τ are shown in Fig. 1. It can

be seen that the curves obtained for the irradiated samples with the exposure time from 0.25 s to 0.30 s as well as for the non-irradiated one, reveal their amorphous structure. A low intensity peak is visible on the curve related with $\tau = 0.35$ s, which indicates a presence of some amount of crystalline phase. The number of peaks has increased at the longer exposure time, which indicates the increasing of the crystalline phase amount.

Fig. 1. Diffraction curves for amorphous $Fe_{73.5}Nb_3Cu_1Si_{15.5}B_7$ ribbon irradiated at various exposure times τ .

Experimental XRD-curves allowed determining the phases that crystallize under influence of laser irradiation. Positions of the intense peaks marked as 1 in the Fig. 1, correspond to the α -Fe(Si) – solution-based nanocrystalline phase of DO3 type structural ordering, which usually crystallizes in the amorphous alloys with $Fe_{73.5}Nb_3Cu_1Si_{15.5}B_7$ composition [1, 2]. Positions of the intense peaks marked with 2 in Fig. 1 correspond to the H-phase, which is hexagonal phase, notably the rhombohedral distortion of α -Mn structure [13].

To obtain the composition of the irradiated zone we performed the analysis by multi-peaks Lorentzian function fitting of XRD main maximum, as it is shown in the Fig. 2. The XRD-pattern obtained from the as-quenched ribbon has been correctly approximated by one Lorentzian function as well as the XRD-patterns, which are related to $\tau = 0.25$ s and $\tau = 0.30$ s. These patterns represent the amorphous structure. When the value of

Fig. 2. Fitting of the main maxima of intensity curves by Lorentzian functions.

exposure is 0.35 s and 0.40 s the two Lorentzian functions fit the patterns, one of them represents the amorphous structure while the other, smaller one, is related with crystalline phase of α -Fe(Si) solid solution. Second peak reveals the onset of the crystallization process. When the exposure is 0.45 s and 0.50 s the two Lorentzian functions do not correctly fit the patterns, so it is necessary to add a third Lorentzian function, which was found to be related with hexagonal H-phase. So, the structure of the ribbons irradiated at the exposure times of 0.45 s and 0.50 s is characterized by three phases: amorphous one, α -Fe(Si) solid solution and hexagonal H-phase. Eight Lorentzian functions were applied to correctly fit the experimental XRD patterns at higher values of the exposure, so the resulting multi-peak function fits the patterns. One of eight peaks corresponds to the α -Fe(Si) solid solution while the rest peaks correspond to the H-phase reflexes, and there is no peak corresponding to the amorphous phase. It allows assuming that there is complete devitrification of the irradiated zone.

Phase content, which has been formed under the laser irradiation, was obtained by means of formula 1 and is presented in the Table 1. As can be seen from the table, the laser fluence of about 17.5 J/cm² to 20.0 J/cm² results in formation of amorphous-nanocrystalline mixture of phases, which consists of amorphous and α -Fe(Si) phases. In other words, owing to such irradiation conditions, the formation of nanocomposite materials is possible. Moving the beam along or across the ribbon it is possible to control the formation of the ordered two-phase composite structure with amorphous and nanocrystalline α -Fe(Si) phases. Higher values of laser fluence of about 22.5 J/cm² to 25.0 J/cm² result in formation of two crystalline phases: α -Fe(Si) and H-phase, randomly distributed in residual amorphous matrix. And, finally, irradiation at laser fluence of about 27.5 J/cm² to 35.0 J/cm² results in complete devitrification of irradiated zone with formation of two-phase nanocrystalline composite structure with α -Fe(Si) and H-phases. Irradiation at laser fluence ≥ 40.0 J/cm² leads to material destruction. Difference in laser fluence values, which is needed for α -Fe(Si) and H-phase crystallization, is caused by different temperatures for the onset of crystallization in these phases (about 700 K for the α -Fe(Si) and about 970 K for the H-phase) and different values of activation energy (about 418 kJ/mol for the α -Fe(Si) and about 700 kJ/mol for H-phase formation) [14, 15].

Average size of crystallites was calculated using half-peak width of the highest peak from α -Fe(Si) and H-phases following formula 2. It was determined that the size of crystallites changes within 10 nm to 30 nm. Fig. 3 shows that the size dependencies on exposure correlate with the exponential decays of first order.

So, the mechanism of laser-induced crystallization of amorphous Fe_{73.5}Nb₃Cu₁Si_{15.5}B₇ alloy under 50 W/cm² power density is as follows: irradiation at exposure time about 0.35 s results in starting of crystallization process in a local zone with the formation of α -Fe(Si) nanophase with the average size of crystallites of about 35 nm. When the exposure time is about 0.45 s, the second crystallization process – the formation of H-nanophase with the

Table 1. Compositions of $\text{Fe}_{73.5}\text{Nb}_3\text{Cu}_1\text{Si}_{15.5}\text{B}_7$ alloy after irradiation at the specified exposure time τ .

τ [s]	F [J/cm ²]	Composition
0	0	A*
0.25	12.5	A
0.30	15.0	A
0.35	17.5	1.39 % α -Fe(Si) + 98.61 % A
0.40	20.0	7.51 % α -Fe(Si) + 92.69 % A
0.45	22.5	12.72 % H-phase + 15.65 % α -Fe(Si) + 71.63 % A
0.50	25.0	11.33 % H-phase + 12.57 % α -Fe(Si) + 76.10 % A
0.55	27.5	38.50 % H-phase + 61.52 % α -Fe(Si)
0.65	32.5	33.15 % H-phase + 66.85 % α -Fe(Si)
0.70	35.0	37.88 % H-phase + 62.12 % α -Fe(Si)

*A-amorphous phase

Fig. 3. Crystallites size dependences on exposure time.

average size of crystallites of about 22 nm, starts in the local zone. Irradiation with τ longer than 0.55 s results in complete devitrification of amorphous phase in the irradiated zone and formation of two-phase nanocomposite structure with α -Fe(Si) and H-phases, in which the average size of crystallites reduced from about 10 nm to 17 nm.

When the first crystallization stage is finished and the α -Fe(Si) phase is formed, the residual amorphous matrix consists of Fe, B, Nb and Cu clusters (fcc). Since Nb and B do not dissolve in α -Fe(Si), on the base of the elemental composition of the alloy we can assume that the residual matrix contains 3 % Nb, 7 % B and about 20 % Fe. Such a composition is close to $\text{Fe}_{67}\text{Nb}_{10}\text{B}_{23}$ alloy. Crystallization of amorphous alloys $\text{Fe}_{90-x}\text{Nb}_{10}\text{B}_x$

($x = 10$ and 30) occurs as shown in Table 2 and the crystallization mechanism changes from 1-type to 2-type when boron concentration is from 18 % to 20 % [16]. In our case, boron concentration seems to be higher than 20 % and Fe_{23}B_6 type phase is expected, furthermore this phase was detected in laser-induced crystallization of this alloy in our previous studies [8, 17]. However, laser irradiation of the alloy with mentioned time-energy parameters results in hexagonal H-phase crystallization. Therefore, we conclude that it is possible to change the crystallization mechanism in Finemet-type alloy by changing the parameters of laser irradiation.

SEM analysis

Laser-induced crystallization is the result of heating due to absorption of laser radiation. Because of nonlinear intensity distribution in the laser beam the temperature field in the irradiated zone is nonlinear too: the temperature is higher at the center and lower at the border. Since the irradiation is local, the crystallization of the amorphous ribbon is local too. The changes in the irradiated surface topology are shown in Fig. 4. In the general view (Fig. 4a), the round shape of irradiated zone, which has a light tone, is shown. The diameter of this zone is about 5.7 mm, and is less than the one of laser spot by $1/e^2$. This indicates that temperature has not changed uniformly on the irradiated surface and increased significantly in this part of the irradiated zone. The lighter tone in the SEM image

Table 2. Crystallization behavior of amorphous alloys $\text{Fe}_{90-x}\text{Nb}_{10}\text{B}_x$ ($x = 10$ and 30).

Type	B content	Crystallization mechanism
1	10	Amorphous – α -Mn type – α -Fe type – α -Fe, Fe_3B (orthorhombic), Fe_2B
2	30	Amorphous – supercooled liquid – Fe_{23}B_6 – α -Fe, Fe_3B (orthorhombic), Fe_2B

can be caused by somewhat higher concentration of light elements. Therefore, we may assume that the lighter shade in the irradiated zone is caused by structure transformation process and elements redistribution.

Hemispherical formations of about $100\ \mu\text{m}$ to $200\ \mu\text{m}$ diameter are randomly distributed in the central part of the irradiated zone (Fig. 4b). The detailed structure of such formation is shown in Fig. 4d and SEM studies of the ribbon surface, which was irradiated at τ from $0.55\ \text{s}$ to $0.70\ \text{s}$, also revealed such structures.

Fig. 5 presents the surface structure in the central part of the zones, which were irradiated at exposure times $0.55\ \text{s}$ and $0.65\ \text{s}$. It can be seen that the surface irradiated at $0.65\ \text{s}$ differs significantly from the others by the needle-like structure. However, both samples are characterized by the same phase composition and grain size (Table 1 and Fig. 3). Laser surface melting can explain this change. Directional growth of crystals occurs at crystallization from the melt, therefore we assume that irradiation at exposure time $\geq 0.65\ \text{s}$ initiates surface melting.

Energy dispersive X-ray (EDX) analysis of irradiated and non-irradiated surfaces shows differences in elemental distribution. Results of EDX analysis of non-irradiated ribbon coincide with elemental composition of the alloy under investigation, while the EDX for irradiated surface shows the presence of O element. EDX of the formations shows that their elemental distribution considerably differs from irradiated surface by significant increase in O content and decrease in Fe content (Table 3). Therefore, we assume that these formations consist from oxides, mostly FeO and some amount of SiO_2 , Cu_2O , Nb_2O_5 .

The sample of investigated ribbon was split out across the irradiated zone and the fractures were studied by SEM-method (Fig. 6a).

Table 3. Energy dispersive X-ray analysis.

Irradiated zone		Formation	
Element	Conc. [%]	Element	Conc. [%]
O	6.08	O	0
Si	8.5	SiO_2	2.36
Fe	75.83	FeO	94.38
Cu	1.57	Cu_2O	0.18
Nb	8.01	Nb_2O_5	2.41

The as-quenched ribbon fracture (Fig. 6b) is very smooth, uniform, no fluctuation of elements concentration or grain structure is observed. The ribbon fractures of the border and central parts of the irradiated zone are shown in Fig. 7 and Fig. 8, respectively, and the difference in their structures can be observed. The fracture of the irradiated zone border is not as smooth as the as-quenched ribbon fracture and it is characterized by a layered structure. The fracture of irradiated zone center differs significantly by the grain structure. The size of grains, which can be measured from SEM-images, is about $0.5\ \mu\text{m}$ to $1.0\ \mu\text{m}$. The layered structure of the border part results only from surface heating under laser irradiation, while the center part was heated equally at the top and bottom.

The concentrations of elements were measured at the points, which are marked in Fig. 6 to Fig. 8 by number 1 to number 9 (Table 4). Number 1, number 4 and number 7 denote the bottom of the ribbon, while number 3, number 6 and number 9 denote the ribbon's top. It should be noted that the bottom surface is the contact surface upon quenching. In the measurements B element has not been detected because of its low atomic weight. As can be seen in the Table 4, the concentration of elements close to the top, in the middle and near the bottom is almost the same for the as-quenched non-irradiated ribbon. The difference between

Fig. 4. SEM-images of the central part of zone, irradiated at $\tau = 0.65$ s: (a) – general view, (b), (c), (d) – detailed SEM images of the formations.

Table 4. The elements concentration (wt. %) in the different part of the ribbon.

Element	Position	Non irradiated ribbon	Irradiated zone border	Irradiated zone center
Fe	Next to the bottom	83.89	84.47	78.21
	In the middle	82.47	85.15	78.45
	Next to the top	82.35	83.25	77.44
Si	Next to the bottom	11.43	10.86	15.59
	In the middle	12.37	10.58	15.90
	Next to the top	12.67	11.89	16.10
Nb	Next to the bottom	3.50	3.68	4.89
	In the middle	4.17	3.49	4.73
	Next to the top	3.83	3.71	5.04
Cu	Next to the bottom	1.18	0.99	1.32
	In the middle	0.99	0.77	0.92
	Next to the top	1.15	1.14	1.42

the values is about 1 % and is close to the measurement error (1 %). However, the difference between the irradiated one and as-quenched ribbons is significant. The local content of Si element is higher in the center and lower in the border, while

the local content of Fe-element is higher in the border and lower in the center of the irradiated zone. The local content of Nb also increased in the central part, especially next to the top. By analyzing the changes of local content of elements we

(a)

(a)

(b)

(b)

Fig. 5. Surface structure at the center of the irradiated zone for (a) $\tau = 0.55$ s and (b) $\tau = 0.65$ s.

assume that the crystallization process in the border of the irradiated zone occurs with the formation of the crystalline structure of α -Fe(Si) solid solution with somewhat lower than 25 % Si content. Some amount of Si element during irradiation diffuses to the central part because of high temperature gradient. Nb atoms usually displace along the crystallization front and, whereas the front of crystallization moves from the border to the center, the local content of Nb elements increases. As it is known, small amount of Nb in the Fe-Si-B-Cu system prevents crystalline growth, resulting in the fine crystalline structure [18]. Therefore, the increasing of Nb leads to the decreasing of crystallite size and is the most likely the cause of crystallites size reducing, shown on Fig. 3. The local laser irradiation of the amorphous alloy results in changing the local element concentration. As for boron atoms, due to their high diffusion coefficient, we assume that

Fig. 6. (a) Ribbon fracture in the irradiated zone (general view); (b) fracture of cross-section of the non-irradiated ribbon (secondary electrons mode).

the local concentration of B increases in the central part of the irradiated zone. It is reasonable to conclude that such diffusion is the reason of the change in crystallization mechanism, which has been considered above.

SEM studies of ribbon fracture allow us to observe a change in thickness of irradiated part of the ribbon (Table 5). Thickness of the irradiated zone has decreased especially in the center of irradiated zone (thickness reduction is about ~ 4 μm).

It is considered [19] that metals and alloys after amorphization at the rates higher than 10^3 K/s are in phase G_F , which is characterized by high glass transition temperature and large volume. Under heating, the G_F phase transforms into the G_S phase, i.e. there is a relaxation of the structure. In the exposure time, unstable atomic configurations

Table 5. Change in ribbon thickness.

Parameter	Non-irradiated ribbon	Irradiated zone border	Irradiated zone center
Ribbon thickness [μm]	23.84	21.35	19.35

(a)

(a)

(b)

(b)

Fig. 7. SEM-images of cross-section of the irradiated zone border in modes: (a) scattered electrons; (b) secondary electrons.

Fig. 8. SEM images of cross-section of the irradiated zone center in modes: (a) scattered electrons; (b) secondary electrons.

that arise during the quenching convert into stable configurations by small atomic displacements, resulting in decreasing the free volume, and consequently the total volume. At sufficiently high temperature heating, there is an opportunity for the atoms displacement at relatively long distances (diffusion) and the process of crystallization begins with the significant volume reduction. Therefore, reduced thickness of the irradiated zone is the evidence of the local crystallization.

4. Conclusions

Laser-induced crystallization kinetics in a Finemet-type alloy has been studied. The kinetics of laser-induced crystallization of amorphous $Fe_{73.5}Nb_3Cu_1Si_{15.5}B_7$ alloy under 50 W/cm^2 power density has the following stages: the primary crystallization with the formation of nanocrystalline $\alpha\text{-Fe}(\text{Si})$ solid solution; the second stage crystallization with the formation of nanocrystalline hexagonal H-phase of rhombohedral

distortion of α -Mn structure; and the third stage, where complete devitrification of the amorphous phase takes place.

It was shown that the nonlinear temperature field under the laser irradiation results in changes of the local elements concentration and this feature changes the crystallization mechanism of the Finemet-type alloy.

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