In-situ XRD studies of nanocrystallization of Fe-based metallic glass: Comparative study by reciprocal and direct space methods

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Structural changes occurring in an $\text{Fe}_{72.5}\text{Cu}_1\text{Nb}_2\text{Mo}_2\text{Si}_{15.5}\text{B}_7$ alloy during a combination of constant rate heating (20 K/min) and isothermal holding at 500 and 520 °C were investigated using in-situ high-energy X-ray diffraction. We found that the ferromagnetic-to-paramagnetic transition of an amorphous phase is revealed as a change of the slope of the thermal expansion curve when heating a sample with a constant rate up to 520 °C. Real space analysis by means of atomic pair distribution function (PDF) demonstrated that the rate and extent of the thermal expansion strongly depends on the interatomic separation. PDF proved to be a reliable method for the description of crystallization kinetics. Further it allows determination of sizes of ultrafine nanocrystals with grain sizes well below 8 nm and thus makes observation of early stages of nanocrystallization possible. Following grain growth kinetics during isothermal annealing at 500 and 520 °C we found that the activation energy of the process is 357 ± 12 kJ/mol.

1 Introduction

Nanocrystalline Fe-based alloys exhibit outstanding soft magnetic properties characterized by a very low coercivity and a very high saturation magnetization¹. Soft magnetic nanostructured materials can be obtained from many conventional metallic glasses (usually prepared by melt spinning method) by a controlled crystallization at temperatures slightly below primary crystallization². Optimized alloy compositions like $\text{Fe}_{73}\text{Cu}_1\text{Nb}_3\text{Si}_{16}\text{B}_7$ moreover reveal near-zero saturation magnetostriction and meanwhile have successfully entered into application under the trademarks FINEMET³ or VITROPERM 800⁴. These materials exhibit a microstructure in which ultrafine grains of BCC FeSi (typical grain size 10-15 nm) are randomly distributed within a residual amorphous matrix. The ferromagnetic character of the amorphous matrix enables exchange coupling between ferromagnetic nanocrystals, which yield a severe reduction of the average magnetocrystalline anisotropy^{5,6}. Since magnetic properties of Fe-based nanocrystalline materials are strongly related to their microstructure (mostly grain size distribution) many authors studied kinetics of their crystallization^{2,7,8}. Recently, significant advances have been made using the atomic pair distribu-

tion function (PDF) analysis of powder diffraction data coupled with the use of advanced X-ray and neutron sources and fast computers⁹⁻¹².

The aim of the present work is the investigation of structural changes occurring in $\text{Fe}_{72.5}\text{Cu}_1\text{Nb}_2\text{Mo}_2\text{Si}_{15.5}\text{B}_7$ alloy during combination of constant heating rate (20 K/min) and an isothermal holding at 500 and 520 °C by means of in-situ high-energy X-ray diffraction. Evaluation of X-ray diffraction data is done by two approaches, in reciprocal space by analysis of diffraction profiles and in real space by pair distribution function. One of the main goals is to demonstrate the benefits of using in-situ PDF techniques for the investigation of crystallization kinetics of nanocrystalline materials.

2 Experiment

The amorphous alloy with nominal composition $\text{Fe}_{72.5}\text{Cu}_1\text{Nb}_2\text{Mo}_2\text{Si}_{15.5}\text{B}_7$ (at. %) was prepared in the form of thin ribbons using single-roller melt-spinning technique. The width and thickness of the ribbons were 9 mm and 30 μm , respectively. A differential scanning calorimeter (NETZSCH DSC 404C) was used to detect the crystallization behavior of as-prepared ribbons under a continuous argon flow at a heating rate of 20 K/min. The thermomagnetic curve was traced at a heating rate of 10 K/min using a Faraday magnetic balance. In-situ annealing experiments using a high-energy photon beam (80.09 keV) were performed at the undulator beamline P07 (Physics Hutch) of the electron storage ring PETRA III (Hamburg, Germany). Few pieces of ribbon were stuck together and put inside a quartz capillary

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(wall thickness 20 μm) with a diameter of 1.2 mm and placed inside a Linkam THMS600 hot stage. The samples were heated in an argon atmosphere. Each in-situ experiment started with i) heating at a constant rate of 20 K/min up to the selected temperature and followed by ii) isothermal annealing at that temperature for at least 100 min. Two different annealing temperatures were chosen, namely 500 °C and 520 °C (we refer to as Vit500 and Vit520). X-ray diffraction patterns were continuously recorded in transmission mode using a two-dimensional detector (Perkin Elmer 1621, 2048×2048 pixels, pixel size 200×200 μm^2). The temporal resolution between two consecutive diffraction patterns was 12 seconds. The wavelength and beam size of monochromatic photon beam were set to 0.1548 Å (80.09 keV) and 0.5×0.5 mm², respectively. The sample-to-detector distance and the orthogonality of the detector with respect to the incident photon beam were calibrated using the reference material LaB₆ (NIST 660a). Two-dimensional X-ray diffraction patterns were radially integrated using the programme FIT2D¹³.

3 Background on data evaluation

In case of an angle-dispersive X-ray diffraction experiment the incident monochromatic photon beam with wavelength λ is diffracted under an angle $2\theta_{hkl}$ by the set of lattice planes having an interplanar spacing d_{hkl} . This is well known as Bragg's law

$$2d_{hkl} \sin(\theta_{hkl}) = \lambda. \quad (1)$$

Bragg's law, as stated above, can be used to obtain the lattice parameter of for example a particular cubic system through the following relation

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (2)$$

where a is the lattice parameter of the cubic crystal and h , k and l are the Miller indices of the Bragg plane. The simple relationship between diffraction angle θ , reciprocal q and real d -space is then

$$q = \frac{2\pi}{d} = \frac{4\pi \sin(\theta)}{\lambda}. \quad (3)$$

The angular distribution of scattered intensities around a Bragg peak can be satisfactorily described by the pseudo-Voigt function $I_{pV}(2\theta)$ having the analytical form

$$I_{pV}(2\theta) = A [\eta G(2\theta) + (1 - \eta)L(2\theta)], \quad (4)$$

where A is the amplitude, $G(2\theta) = \exp[-(\ln 2)k^2]$ represents the Gaussian and $L(2\theta) = (1 + k^2)^{-1}$ the Lorentzian part, with $k = 2(2\theta - 2\theta_{hkl})/\beta$, in which β is the full-width at half-maximum (FWHM), η the Gaussian content and $2\theta_{hkl}$ the position of the Bragg peak. The mixing factor η may have any value in the interval $\langle 0, 1 \rangle$.

3.1 Diffraction profile analysis

Diffraction profile parameters such as Bragg peak intensity, position and width carry important information about the sample's microstructure. The peak position θ_{hkl} is closely related with the lattice parameter a . Combining equations (1) and (2) and plotting $\lambda / (2 \sin \theta_{hkl})$ as a function of $1/\sqrt{h^2 + k^2 + l^2}$ one gets from the slope of such dependence the value of lattice parameter a . The width of the Bragg reflection β_{hkl} contains useful information about the mean size of coherently scattering domains. In 1918 Scherrer¹⁴ derived an equation which relates the mean (volume average) crystallite size D of a powder to the broadening β_{hkl}^D of its powder diffraction peaks

$$\beta_{hkl}^D = \frac{K\lambda}{D \cos \theta_{hkl}} \quad (5)$$

where K is the Scherrer constant (in our calculation of grain sizes, K was equal to unity). It should be noted that the Scherrer equation as stated above ignores effects of strain on diffraction line broadening.

The Williams-Hall method¹⁵ relies on the principle that the approximate formulae for size broadening β_{hkl}^D and strain broadening β_{hkl}^ϵ show different dependence on Bragg angle θ_{hkl} and thus the total line broadening β_{hkl} can be expressed in the form

$$\beta_{hkl} = \beta_{hkl}^\epsilon + \beta_{hkl}^D = C\epsilon \tan \theta_{hkl} + \frac{K\lambda}{D \cos \theta_{hkl}} \quad (6)$$

where ϵ is the mean strain and C represents the constant which depends on the assumptions made concerning the nature of the inhomogeneous strain, but is typically equal to 4¹⁶.

In order to get the correct information about the mean grain size determined from the peak broadening, it is necessary to correct the measured line widths β_{exp} for the instrumental contribution β_{ins} . The so called Instrumental Resolution Function (IRF) is usually determined by measuring standard materials such as LaB₆ at the same experimental and geometrical conditions as the studied material. The IRF expresses the evolution of the line broadening as a function of the diffraction angle 2θ and is usually fitted to the Caglioti formula¹⁷

$$\beta_{ins}^2 = U \tan^2 \theta + V \tan \theta + W \quad (7)$$

where U , V and W are fitting parameters characterizing the instrument. When describing diffraction profiles by a Lorentzian profile function (putting $\eta = 0$ in equation (4)) correction of the line widths is performed in the following way $\beta = \beta_{exp} - \beta_{ins}$, whereas using Gaussian profiles (putting $\eta = 1$ in equation (4)) yields the correction $\beta^2 = \beta_{exp}^2 - \beta_{ins}^2$. It should be noted here that the Williams-Hall plot defined by equation (6) is appropriate for situations when pure Lorentzian profiles are considered. If pure Gaussians profiles are considered then all terms in equation (4) should be squared¹⁶.

The integral intensity of the Bragg peak is proportional to the amount of the corresponding crystalline phase and can be used to evaluate its relative fraction within a multi-phase alloy system. According to work of Riello *et al.*¹⁸ the amount of crystalline phase X_{cryst} can be calculated as

$$X_{cryst} = \frac{M_{cryst}}{M_{total}} \frac{\sum_{i=1}^{n_{cryst}} m_i}{\sum_{i=1}^{n_{sample}} m_i} \quad (8)$$

where M_{cryst} and M_{total} are defined in the following way

$$M_{cryst} = \frac{\int_{q_{min}}^{q_{max}} I_{cryst}(q) q^2 dq}{\sum_{i=1}^{n_{cryst}} \int_{q_{min}}^{q_{max}} [f_i(q)]^2 + I_i^{inc}(q) q^2 dq} \quad (9)$$

$$M_{total} = \frac{\int_{q_{min}}^{q_{max}} I_{total}(q) q^2 dq}{\sum_{i=1}^{n_{sample}} \int_{q_{min}}^{q_{max}} [f_i(q)]^2 + I_i^{inc}(q) q^2 dq} \quad (10)$$

in which I_{cryst} is the intensity contribution of the crystalline phase to the global intensity I_{total} of the XRD pattern, $I_i^{inc}(q)$ is the incoherent scattering of i -th atom calculated using the Balyuzi formula¹⁹, $f_i(q)$ is the tabulated atomic scattering factor²⁰ of the i -th atom, n_{cryst} and n_{sample} represent the number of atoms in the unit cell of the crystalline phase and the number of atoms in the composition unit of the sample, respectively and m_i is the atomic weight of the i -th atom.

3.2 Structure factor and pair distribution function

The total structure factor, $S(q)$, was obtained using standard procedures described in^{21,22}. Considering background scattering, $bg(q)$, and sample absorption, A , the observed intensity $I^{obs}(q)$ was corrected in the following way $I^{cor}(q) = [I^{obs}(q) - bg(q)]/A$. The absorption of the sample at a given energy was determined by measuring the incoming and transmitted beam intensity using a beam monitor. To suppress fluorescence background we put a 1 mm thick aluminium sheet on the front face of the 2D detector. The corrected intensity $I^{cor}(q)$ can be expressed by the relation

$$\alpha I^{cor}(q) = I_{eu}^{coh}(q) + I_{eu}^{inc}(q) + I_{eu}^{mul}(q) \quad (11)$$

where $I_{eu}^{coh}(q)$, $I_{eu}^{inc}(q)$ and $I_{eu}^{mul}(q)$ are the coherent, incoherent (Compton)²³ and multiple scattering intensities, respectively, in electron units, and α is a conversion factor which is often called the normalization constant. To place data on an absolute scale, we employed the high-angle region method²² in which the normalization constant is calculated as

$$\alpha = \frac{\int_{q_{mid}}^{q_{max}} [\langle f^2 \rangle + I_{eu}^{inc}(q) + I_{eu}^{mul}(q)] dq}{\int_{q_{mid}}^{q_{max}} [I^{cor}(q)] dq} \quad (12)$$

where q_{max} and q_{mid} are the upper limit and an appropriate high value in the measured range of q respectively. Generally,

the adopted value of q_{mid} is $8-10 \text{ \AA}^{-1}$. Further we assumed isotropic fluorescence intensity which was adjusted to a constant value based on the behavior of the resulting structure factor $S(q)$. Once selected, the same fluorescence intensity was used for all data sets.

The total structure factor $S(q)$ was obtained from the normalized elastically scattered intensity, $I_{eu}^{coh}(q)$ using the Faber-Ziman formalism²⁴

$$S(q) = 1 + \frac{I_{eu}^{coh}(q) - \langle f^2 \rangle}{\langle f \rangle^2} \quad (13)$$

where $\langle f^2 \rangle = \sum_{i=1}^N c_i f_i^2(q)$, $\langle f \rangle^2 = [\sum_{i=1}^N c_i f_i(q)]^2$ in which c_i are the atomic concentration of the atomic species of type i ($i = \text{Fe, Si, Cu, Mo, Nb, B}$). The corresponding reduced pair distribution function, $G(r)$, can be obtained through a sine Fourier transformation

$$G(r) = 4\pi r [\rho(r) - \rho_0] = \frac{2}{\pi} \int_0^\infty q [S(q) - 1] \sin(rq) dq \quad (14)$$

where $\rho(r)$ and ρ_0 are the local and average atomic number densities, respectively, and r is the radial distance. Since $\rho(r)$ becomes zero below a certain r_{min} , the average atomic number density ρ_0 can be easily obtained by linear fit of $G(r)$'s low r part (where $r \leq r_{min}$) to $-4\pi\rho_0 r$. From $G(r)$ the radial distribution function, $RDF(r)$, can be calculated by

$$RDF(r) = 4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + rG(r). \quad (15)$$

The average coordination number, N , around any given atom in a spherical shell between radii r_1 and r_2 can be calculated as

$$N = \int_{r_1}^{r_2} RDF(r) dr = \frac{4\pi\rho_0}{3} (r_2^3 - r_1^3) + \int_{r_1}^{r_2} rG(r) dr. \quad (16)$$

4 Results and discussion

The room temperature X-ray diffraction measurements confirmed the fully amorphous character of the $\text{Fe}_{72.5}\text{Cu}_1\text{Nb}_2\text{Mo}_2\text{Si}_{15.5}\text{B}_7$ ribbons in the as-quenched state. X-ray diffraction patterns can be characterized by the first sharp diffraction peak (FSDP) located at $Q_1 = 3.08 \text{ \AA}^{-1}$ ($2\theta = 4.33 \text{ deg.}$) and relatively fast decaying oscillations visible up to $17 \text{ \AA}^{-1}$. Differential calorimetry measurements showed that the investigated alloy crystallizes in two steps. The primary and secondary crystallization occur at $T_{x1} = 516^\circ\text{C}$ and $T_{x2} = 688^\circ\text{C}$, respectively. The initial decrease of the magnetization with increasing temperature (see Fig.1) is related to the transition of the amorphous phase from the ferromagnetic to the paramagnetic state. The first derivative yields the Curie temperature of the amorphous phase $T_C = 325^\circ\text{C}$.

Fig. 1 (Color online) Temperature behavior of volume changes as derived from the relative change of the FSDP during constant rate heating at 20 K/min up to 520 °C. Blue and red dashed lines emphasize linear trends of thermal expansion curve. The solid black line shows the temperature dependence of the magnetization.

4.1 Reciprocal space analysis

4.1.1 Thermal expansion behavior In the first part we focus on structural changes occurring in the amorphous alloy $\text{Fe}_{72.5}\text{Cu}_1\text{Nb}_2\text{Mo}_2\text{Si}_{15.5}\text{B}_7$ during constant rate heating. To obtain quantitative results about the thermal expansion of the amorphous phase from X-ray diffraction data the profile of the FSDP was modelled assuming a linear background and a pseudo-Voigt function described by equation (4). As proposed by Yavari and co-workers²⁵ the third power of the principal peak position Q_1 scales with the coefficient of the volume thermal expansion α_{th} of an isotropic amorphous solid as

$$\left\{ \frac{Q_1(T_0)}{Q_1(T)} \right\}^3 = \frac{V(T)}{V(T_0)} = 1 + \alpha_{th}(T - T_0), \quad (17)$$

where $V(T)/V(T_0)$ is the reduced mean atomic volume at temperature T , with the reference temperature T_0 (in our study 100 °C). It should be noted here that for isotropic materials, the linear thermal expansion coefficient γ_{th} is one third of the volumetric coefficient α_{th} , i.e. $\alpha_{th} = 3\gamma_{th}$. Figure 1 shows the thermal expansion curve as determined from the relative change of the FSDP. It is interesting to note that the thermal expansion curve shows a distinct change of the slope at the Curie point T_C . The coefficient of volume thermal expansion in the ferromagnetic state is $\alpha_{ferro} = (2.41 \pm 0.05) \times 10^{-5} \text{ K}^{-1}$, whereas the paramagnetic state reveals a significantly larger value $\alpha_{para} = (3.46 \pm 0.05) \times 10^{-5} \text{ K}^{-1}$. This means that the magnetic interaction forces present below T_C compete with forces associated with thermal vibrations and effectively reduce the expansion of interatomic distances. On

Fig. 2 (Color online) Series of XRD patterns collected as a function of time t during isothermal annealing at 500 °C.

the other hand, at the moment when the temperature reaches T_C , ferromagnetic interactions are switched off and atoms can behave more freely. Michalik and co-workers²⁶ have recently shown that the change of the slope observed on thermal expansion curves of $\text{Fe}_{(73.5-x)}\text{Mn}_x\text{Si}_{13.5}\text{Cu}_1\text{Nb}_3\text{B}_9$ ($x = 1, 3, 5, 7$ and 9) metallic glasses is closely related to the ferromagnetic-to-paramagnetic transition of the amorphous phase.

4.1.2 Crystallization kinetics In the next part, the kinetics of crystallization at two different temperatures, namely at 500 and 520 °C, is described in detail. Figure 2 shows series of XRD patterns recorded as a function of time during in-situ isothermal annealing at 500 °C. One can readily see that after reaching the temperature of 500 °C the sample gradually devitrifies and Bragg reflections belonging to Fe_3Si become clearly visible. The times required for the initiation of crystallization are 12.5 min and 2.2 min for the Vit500 and Vit520 sample, respectively. The cubic Fe_3Si phase is the only phase formed during devitrification and it is typical for Fe-Si-Cu-Nb-B based amorphous alloys². Detailed information about the temporal evolution of the crystallized fraction, mean grain size and lattice parameter of the cubic Fe_3Si phase during isothermal annealing were evaluated from a series of XRD patterns. The crucial point in performing a quantitative analysis was to reasonably separate the amorphous and the crystalline contribution from the total scattering. The profile fitting was realized in the following way. The contribution from the crystalline Fe_3Si phase was expressed as a sum of seven Gaussian functions, describing the (200), (400), (422), (440), (620), (444) and (642) Bragg reflections. The XRD patterns of Vit500 and Vit520 samples detected after 11.6 min and 0.0 min (just before crystallization occurred), respectively, were multiplied with a scaling parameter and used for modelling of the amorphous contribution in the respective run. In

Fig. 3 (Color online) a) Comparison between the best-fit model and the experimental XRD pattern of the sample annealed at 500 °C for 100 min. b) The amount of crystalline phase calculated as a function of the upper limit of the 2θ range (the lower limit was fixed to 3 deg) using equation (8).

total 25 parameters were needed to refine the XRD profile in a 2θ interval ranging from 3 up to 12.5 degrees. Three profile parameters were needed for every Bragg peak (amplitude A , peak position θ_{hkl} and full-width at half-maximum β_{hkl}). Another three parameters were used to account for a quadratic polynomial describing background and one scaling parameter was used to adjust the contribution from the amorphous matrix. A similar approach was previously used by Michalik *et al.*²⁷ when studying the crystallization behavior of glassy microwires using in-situ XRD. As can be seen from Fig.3a, the proposed model satisfactorily describes the XRD profile.

The fitted profiles of crystalline and amorphous components, which contribute to the total scattering, were weighted following the work of Riello *et al.*¹⁸. The amount of crystallized fraction was calculated based on refined XRD profiles using equation (8). Figure 3b shows the crystalline amount as a function of the upper limit of 2θ used for its evaluation (the lower limit of 2θ was fixed at 3 degrees). It is seen that the relative fraction of the crystalline component calculated from the XRD profile strongly depends on the 2θ interval used. When studying devitrification of metallic glasses authors of many works tend to use a simple approach and refine only narrow part of the XRD profile, mostly in the vicinity of the first sharp diffraction peak^{28,29}. Then the intensity profile is fitted with two peak functions, one representing an amorphous

Fig. 4 (Color online) Temporal evolution of a) crystalline fraction X_{cryst} and b) lattice parameter a of the Fe_3Si phase during isothermal annealing at 500 and 520 °C.

component and a second one corresponding to a Bragg peak. Lorentz, Gaussian or Pseudo-Voigt function are usually used to describe intensity profiles. On the other hand some authors refine the XRD profiles on 2θ interval as large as possible^{18,30}. Actually this approach is followed in this work. Figure 4a shows the temporal evolution of the crystalline weight fraction X_{cryst} during isothermal annealing at 500 and 520 °C. In case of the Vit500 sample it takes about 12.5 min until tiny traces of Fe_3Si phase appear in the diffraction patterns. The sample Vit520 is crystallizing almost instantly with incubation time of only 2.2 min. Higher temperature of isothermal annealing implies faster crystallization kinetics. Nevertheless the crystalline fraction does not saturate even after 100 min of annealing at 520 °C. The time dependence of the lattice parameter a for samples Vit500 and Vit520 is shown in Figure 4b.

Figure 5 shows the time evolution of the mean grain size during isothermal annealing at 500 and 520 °C. The mean grain size was calculated either by the Scherrer equation¹⁴ (Fig.5a) or by the Williamson-Hall method¹⁵ (Fig.5b). In the case of the Scherrer approach, the mean grain size was calculated for every indexed Bragg peak shown in Fig.3 separately. Then the average value was calculated and is plotted in Fig.5. The error was estimated as standard deviation. It should be noted here that the Bragg reflection (444) was omitted from the calculations since it was small and imposed an error on the final values. Qualitatively speaking, both approaches, the Scherrer formula and the Williamson-Hall plot, brought very similar results. The main disparity between both methods is in the absolute values of the obtained sizes. It seems that values of the mean grain size obtained by the Williamson-Hall method are systematically larger by 20 Å than the ones calculated by the Scherrer formula. This is due to the fact that the Scherrer equation does not account for line broadening due to

Fig. 5 (Color online) Comparison of the mean grain size D calculated by a) Scherrer equation and b) Williams-Hall method. The uncertainty in determination of the mean grain size is ± 7 Å.

strain and therefore systematically underestimates grain size values. As can be seen from Fig. 5 the size of crystallites increases with the annealing time and higher temperature implies faster grain growth. Apparently, the growth of crystallites is much more pronounced in the first minutes of annealing. Longer annealing times mean gradual decrease of grain growth dynamics.

4.2 Real space analysis

Figure 6 shows the structure factor $S(q)$ and the corresponding reduced pair distribution function $G(r)$ for the Fe_{72.5}Cu₁Nb₂Mo₂Si_{15.5}B₇ alloy in the as-quenched state. Fitting $-4\pi\rho_0r$ to the $G(r)$ for $r \leq 1.9$ Å⁻¹ we determined the value of the mean atomic density $\rho_0 = 0.082$ Å⁻³. The average coordination number N in the first coordination shell (between radii 2.1 and 3.5 Å) was calculated according equation (16) and is 13.5. Due to the highest concentration and X-ray scattering power of Fe atoms, Fe-Fe atomic pairs are the ones which determine the shape of the first coordination shell appearing in $G(r)$. The mean atomic distance between two neighboring Fe atoms is $r_{Fe-Fe} = 2.64$ Å.

4.2.1 Thermal expansion behavior In the previous section 4.1.1 we presented thermal expansion behavior data evaluated by the relative shift of the FSDP in reciprocal space. In order to see what are corresponding distances in real space, we performed a Fourier transformation of the FSDP. As can be seen from Fig. 6, the Fourier transform of the FSDP is perfectly matching oscillations on $G(r)$ for distances r larger than 8 Å. This shows that the FSDP in reciprocal space is closely related to the medium range order (in the range 8-20 Å). Similar findings were recently reported in La-based metallic glass¹². Further we evaluated the relative shift of coordination shells as

Fig. 6 (Color online) Structure factor $S(q)$ and reduced pair distribution function $G(r)$ for the Fe_{72.5}Cu₁Nb₂Mo₂Si_{15.5}B₇ alloy in the as-quenched state. The red dashed line represents the result of the sine Fourier transformation of the FSDP appearing in $S(q)$ and covering a q -range $(2.78, 3.44)$ Å⁻¹. Roman numerals denote respective coordination shells.

a function of temperature. The center of mass for the respective coordination shell (denoted by roman numerals in Fig. 6) was calculated using numerical integration. As can be seen from Fig. 7, the extent of thermal expansion strongly depends on the radial distance r , i.e. different shells exhibit different expansion rates³¹ (see Table 1). Similar results were observed in case of temperature dependence of the short-range order of Cu₆₅Zr₃₅ metallic glass³². Previous study on various metallic glasses undergoing tensile deformation has also shown that the atomic strain calculated from different coordination shells shows dependence on the radial distance r ³³. Nevertheless all expansion curves presented in Fig. 7 show a change of the slope in the vicinity of the Curie temperature T_C . The observed r -dependence of the thermal expansion behavior is strongly correlated with the magnetic exchange interaction.

The ferromagnetism in amorphous materials is due to exchange interactions between the spins of neighboring unpaired electrons³⁴. The interactions are stronger when the magnetic atoms are at short distance, while their separation, for example by metalloid atoms, makes the interactions weaker and, as a consequence, the magnetic saturation decreases. The exchange stiffness constant, A , can be obtained from the mean field model and from the Curie temperature³⁵⁻³⁷. When assuming Hasegawa's model³⁵ one can derive the following re-

Fig. 7 (Color online) Relative change of the center of mass of the coordination shells I.-VII. during constant rate heating (20 K/min) up to 520 °C. Corresponding coordination shells are depicted in Fig.6. Vertical arrows indicate the Curie point T_C .

Table 1 Comparison of coefficients of volume thermal expansion in ferromagnetic (α_{ferro}) and paramagnetic (α_{para}) state calculated by means of reciprocal and real space methods. The values of α_{ferro} and α_{para} were determined from linear fits to expansion curves on temperature intervals $\langle 100, 320 \rangle$ °C and $\langle 340, 500 \rangle$ °C, respectively.

label	α_{ferro} [$10^{-5} K^{-1}$]	α_{para} [$10^{-5} K^{-1}$]	$\alpha_{para}/\alpha_{ferro}$
I.	1.27 ± 0.02	2.98 ± 0.04	2.35 ± 0.05
II.	0.66 ± 0.03	4.03 ± 0.10	6.11 ± 0.32
III.	3.05 ± 0.02	4.47 ± 0.05	1.47 ± 0.02
IV.	2.57 ± 0.01	5.10 ± 0.10	1.98 ± 0.04
V.	2.43 ± 0.01	4.54 ± 0.06	1.87 ± 0.03
VI.	2.76 ± 0.01	3.84 ± 0.03	1.39 ± 0.01
VII.	2.56 ± 0.01	4.55 ± 0.06	1.78 ± 0.02
FSDP	2.41 ± 0.05	3.46 ± 0.05	1.44 ± 0.04

lation for the exchange stiffness constant

$$A = \frac{c_{Fe} S_{Fe} k_B T_C}{4(S_{Fe} + 1) r_{Fe-Fe}} \quad (18)$$

where c_{Fe} is the concentration of Fe in atomic percent, S_{Fe} is the spin moment of Fe, T_C is the Curie temperature, k_B is the Boltzmann constant and r_{Fe-Fe} is the nearest-neighbor distance for Fe-Fe atomic pairs. One can readily see from the equation that the exchange stiffness constant A is inversely proportional to the interatomic distance r . From the relation $M = 2c_{Fe} S_{Fe} \mu_B$ in which M is the magnetic moment expressed in Bohr magnetons μ_B , one can calculate S_{Fe} . When we consider the following values of the nearest-neighbor distance for Fe-Fe atomic pairs, room temperature specific magnetization, density and Curie temperature 2.64 Å, 130 Am²/kg, 7.7 g/cm³ and 325 °C, respectively, we obtain the value of the exchange

Fig. 8 (Color online) Comparison of pair distribution functions $G(r)$ at different times of isothermal annealing performed at 500 °C. Dotted lines correspond to $\Delta G(r)$ calculated according equation (19).

stiffness constant $A = (2.9 \pm 0.2) \times 10^{-12}$ J/m.

4.2.2 Crystallization kinetics The following section describes the kinetics of crystallization in real space by means of the pair distribution function $G(r)$. Figure 8 shows selected PDFs at various times of isothermal annealing at 500 °C. With increasing annealing time t oscillations on $G(r)$ become stronger and sharper. Also the distance δ at which oscillations fade out increases with annealing time t . All profile changes observed on PDFs are closely related to the formation of crystalline Fe₃Si phase. To be more sensitive to temporal changes of the PDF during isothermal annealing we calculated the difference PDF, $\Delta G(r)_t$, in the following manner

$$\Delta G(r)_t = G(r)_t - G(r)_{t=0} \quad (19)$$

where $G(r)_t$ and $G(r)_{t=0}$ are corresponding to the PDF at a given time t and reference time $t = 0$, respectively. Kramer³⁸ recently proposed an efficient way for the calculation of the difference PDF directly from difference of diffracted intensities $\Delta I(q)$. As can be seen from Fig.8, $\Delta G(r)_t$ reveals rather subtle changes in the nearest-neighborhood whereas medium and long-range order correlations show pronounced changes. It is worth noting that the difference PDF, $\Delta G(r)$, is almost identical with the total PDF, $G(r)$, for $r \geq 20$ Å. Therefore in our further analysis we did the quantitative analysis of $\Delta G(r)_t$, which were calculated up to $r_{max} = 150$ Å. Sharp oscillations appearing on the difference PDF are due to interatomic correlations within Fe₃Si grains. Since grains are

Fig. 9 (Color online) Schematic sketch showing the two-dimensional atomic structure obtained by isothermal annealing at 500 °C for a) 0 min, b) 30 min and c) 120 min. The gray dots depict atoms within the amorphous phase while the blue and the red dots represent Fe and Si atoms within the crystalline Fe_3Si phase, respectively. The parameters ξ , δ and Δ represent correlation lengths characteristic for the amorphous phase, the interior of the individual Fe_3Si grain and among two neighboring Fe_3Si grains, respectively.

randomly distributed within the residual amorphous matrix, inter-grain atomic correlations effectively cancel out and thus the distance δ at which correlations fade out actually corresponds to the mean grain size D ³⁹. The situation can be illustratively described by a simplified two-dimensional atomic structure shown in Fig. 9. At the beginning of the isothermal annealing the sample shows completely amorphous structure (Fig. 8, $t=0$ min). Due to lack of long-range order within the amorphous matrix, the maximum correlation length ξ (*i.e.* the maximum distance up to which oscillations on PDF are detectable) is in the range between 20 and 30 Å (Fig. 9a). After a specific incubation time (dependent on the temperature) the crystallization sets in and crystalline Fe_3Si grains are formed. The early stages of crystallization are governed by the process of homogenous nucleation. The structural changes associated with the nucleation occur at length scales shorter than ξ and therefore can be observed by the PDF in the nearest neighborhood (r -range $\langle 2, 5 \text{ Å} \rangle$) and medium range order (r -range $\langle 5, 20 \text{ Å} \rangle$). As the grains increase their size the interatomic correlation length δ within Fe_3Si grains gets larger than ξ

Fig. 10 (Color online) Detailed view on difference pair distribution functions $\Delta G(r)$ corresponding to annealing times 30 and 120 min at 500 °C. Arrows indicate radial distance δ at which oscillations fade out. Solid lines correspond to respective cumulative distributions functions $CF(x)_r$ calculated according equation (20).

(Fig. 9b). Since Fe_3Si grains are randomly distributed within the amorphous matrix the interatomic correlations among two neighboring Fe_3Si grains over the distance Δ ($\gg \delta$) effectively cancel out due to broken inter-granular structural coherence. As a result the extent of oscillations in the PDF is related to the correlation length δ within Fe_3Si grains which can be used to determine the mean grain size D . Further grain growth and typical microstructure coarsening is the dominant process during the late stages of crystallization (Fig. 9c).

One should keep in mind that the IRF in q -space determines the resolution of the PDF, namely in the high- r region⁴⁰. The experimental PDF is given as the product of the Fourier transform of the IRF and the ideal PDF obtained with infinite instrument resolution. The simplest approximation is that the IRF is a single Gaussian of constant width σ_q . The result from this model is a multiplication of the PDF by a broad Gaussian envelope function in real space with a width of $1/\sigma_q$ ⁴¹. In our study diffraction data have only moderate q -space resolution ($\sigma_q = 0.06 \text{ Å}^{-1}$). This results in a loss of structural information in the high- r region, for example beyond $r = 120 \text{ Å}$ in the LaB_6 PDF. In other words, the present experimental settings do not allow determination of grain sizes larger than 120 Å from the PDF. Figure 10 shows a detailed view of the differ-

Fig. 11 (Color online) Temporal evolution of a) crystalline fraction and b) mean grain size as inferred from the difference PDFs by means of the cumulative function $CF(x)$. Solid lines represent fits to equation (21). The uncertainty in determination of the mean grain size is $\pm 5 \text{ \AA}$.

ence pair distribution functions $\Delta G(r)$ corresponding to annealing times 30 and 120 min at 500 °C. In order to determine the distance δ at which oscillations on $\Delta G(r)$ fade out we propose the following cumulative function

$$CF(x)_t = \sqrt{\frac{1}{(r_{\max} - x)} \int_x^{r_{\max}} [\Delta G(r)_t]^2 dr} \quad (20)$$

where x is any value from $\langle 0, 150 \text{ \AA} \rangle$, t is the time and $r_{\max} = 150 \text{ \AA}$. The $CF(x)$ function defined by the above equation actually calculates root mean square (RMS) value of the $\Delta G(r)$ on the interval $\langle x, 150 \rangle$. It is worth noting that the $CF(x)$ is monotonically decreasing and above δ significantly drops in value and flattens due to missing structural oscillations in the high- r region. To determine the mean grain size D from $\Delta G(r)$ one can simply find the value of radial distance at which $CF(x)$ drops below the noise level calculated from the high- r region. Since the fraction of crystalline phase is proportional to the amplitudes of oscillations on $\Delta G(r)$ we suggest it can be directly calculated from $CF(x)$ by putting $x = 0$. Figure 11 shows the temporal evolution of the crystalline fraction and mean grain size as inferred from the difference PDFs by means of the cumulative function $CF(x)$. The fractions X_{cryst} of crystalline Fe_3Si phase calculated from reciprocal space (Fig.4a) and real space (Fig.11a) are showing qualitatively almost identical time dependence. When comparing the average grains size D determined from PDF in real space (Fig.11b) and from XRD profiles in reciprocal space (Fig.5) one can readily see that the PDF method offers much more resolving power for determining grain sizes well below 80 $\text{\AA}$.

Following the work of Zuo *et al.*⁴² the kinetics of the grain growth can be expressed in the form

$$\frac{D^2(t) - D_{\max}^2}{D^2(0) - D_{\max}^2} = \exp \left[-\frac{2kt}{D_{\max}^2} \right] \quad (21)$$

where $D(t)$, $D(0)$ and $D_{\max}$ is the average grain size at any time t , $t = 0$ and $t \rightarrow \infty$, respectively, the rate constant k is expressed in the Arrhenius form

$$k = k_0 \exp\{-Q/RT\} \quad (22)$$

where R is the gas constant, T is absolute temperature, k_0 is a constant and Q the activation energy for grain growth. Fitting the data presented in Fig.11b to equation (21) we obtained the rate constant values 228 ± 8 and $928 \pm 13 \text{ \AA}^2 \text{ min}^{-1}$ for isothermal annealing at 500 and 520 °C, respectively. The activation energy for grain growth, Q , calculated using equation (22) is $357 \pm 12 \text{ kJ/mol}$ ($3.70 \pm 0.12 \text{ eV/atom}$).

5 Conclusions

Constant heating rate annealing provided information about the thermal expansion of an amorphous phase. We found that the change of the slope of the thermal expansion curve is directly related to the ferromagnetic-to-paramagnetic phase transition. Real space analysis by means of PDF revealed that the rate and extent of thermal expansion depend on the inter-atomic separation. The temporal behavior of microstructural parameters such as lattice parameter, mean grain size and relative fraction of crystalline phase provides insights into the kinetics of nanocrystallization during isothermal holding. Both approaches, reciprocal and real space methods, reveal similar qualitative results. Analyzing XRD profiles in reciprocal space is straight forward and relatively easy to perform. However, assuming a proper model for line broadening is essential in getting reliable estimate of the mean grain size. Also the relative fraction of crystalline phase is strongly affected by choosing an appropriate 2θ range. On the other hand, calculations of the structure factor and pair distribution function are more computationally demanding but there are no further assumptions needed for determination of the mean grain size. We propose that the root mean square of the difference PDF can be successfully used to extract information about the mean grain size and fraction of crystalline phase. When comparing with the Williams-Hall method in reciprocal space, the PDF method offers much more resolving power to determine size of ultra-fine particles which are having grain sizes well below 80 $\text{\AA}$. Following grain growth kinetics during isothermal annealing at 500 and 520 °C we found that the activation energy of the process is $357 \pm 12 \text{ kJ/mol}$.

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