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The influence of magnetic field on phase nucleation in Cu–Be alloy

V V Runov[1], A V Pokoev[2], M K Runova[1] and O P Smirnov[1]

[1] Petersburg Nuclear Physics Institute RAS, 188300, Gatchina, Russia
[2] Samara State University, 443011, Samara, Russia

E-mail: runov@pnpi.spb.ru

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Abstract
We discuss the results of small-angle polarized neutron scattering on the diamagnetic Cu–Be alloy on annealing in the temperature range 300 K $< T <$ 650 K from the quenched condition. The characteristic scale of phase nucleation depending on temperature and time was determined. The correlation in change of the integral cross-section of scattering neutrons on annealing with modulation ('on' or 'off') of a constant magnetic field in the range 0 Oe $< H <$ 5700 Oe was found. These experimental results may be interpreted as the magnetic field influence on the kinetics of nucleation during artificial aging of Cu–Be alloy.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The influence of weak magnetic fields ($\mu H \ll kT$, where μ, H, k and T are the magnetic moment, magnetic field, Boltzmann's constant and temperature, respectively) on the mechanical, thermodynamical, kinetic and other properties of nonmagnetic materials is one of the fundamental problems of condensed matter physics. The importance of this problem is discussed in many works; see, for example, [1–5]. It is realized that this influence can be revealed only in nonequilibrium processes in crystals with defects. The corresponding terminologies have appeared from analogy to spin-magnetic effects in chemical reactions: cf the 'magnetoplastic effect' or 'spin micromechanics'. The theoretical analysis of experiments has also been performed using the analogy to the theory of spin-dependent reactions between particles with unpaired electrons developed in chemical physics. However, no microscopic theory of this process for condensed matter physics has yet been developed. As for experiments, the most reliable data were obtained via investigations of the magnetoplastic effects in ionic crystals, revealing a change of the dislocation motion in the applied magnetic field [2]. Interpretations of experiments performed on metallic alloys are most complex and ambiguous.

It was shown in [6, 7] that the microhardness of the beryllium bronze (grade BrB-2) increases up to 30% under annealing (artificial aging) from the quenched condition within the temperature range 600 K $< T <$ 700 K in a magnetic field less than 1 T as compared to annealing in the absence of a field. No adequate interpretation of this experiment has yet been proposed. The technology of annealing is based on the process of the decomposition of the alloy, fixed by quenching under oversaturated conditions. It is well known that during annealing of an alloy there can be clustering, and so-called Guinier–Preston zones, areas enriched by one of the components of the alloy, are formed. This clustering influences the mobility of the dislocations and, thereby, defines in many respects the strength properties of the material. This change in mesoscopic structure of the alloy is registered by neutron small-angle scattering (SANS) directly. Our neutron experiments on Cu–Be alloy have shown that during annealing within the temperature range 300 K $< T <$ 650 K the nucleation of a phase with typical size of the order of hundreds of angstroms occurs in the system. Moreover, this separation at $T >$ 600 K resembles a phase transition. Thus, if changes in plasticity of Cu–Be alloy, depending on annealing with or without magnetic field, are connected with separations of the phases in the volume of the material, then the changes in scattering, depending on the conditions of annealing with or without the field, are expected to be seen in the neutron experiment. Based on this conclusion, we have performed a series of experiments on small-angle polarized neutron scattering to search for such changes. The experiments have shown that the correlation indeed appears in variations of the neutron integral cross-section with switching the magnetic field 'on' or 'off'. Therefore, the magnetic field influences

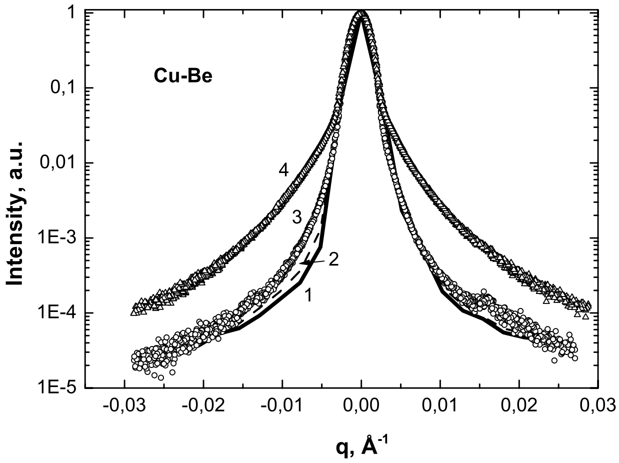

Figure 1. Intensity of SANS versus scattering vector on Cu–Be alloy: 1—measurement without the sample; 2—measurement on a quenched sample; 3—annealing at 600 K; 4—annealing at 630 K.

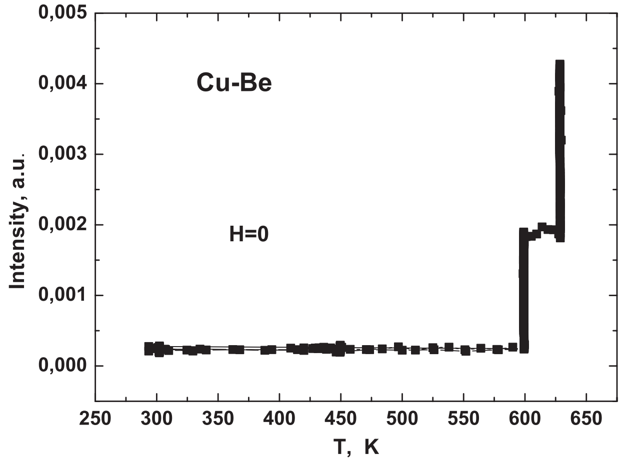

Figure 2. Temperature dependence of scattering intensity with scattering vector $q = 0.01$ Å^{-1} on annealing the Cu–Be alloy.

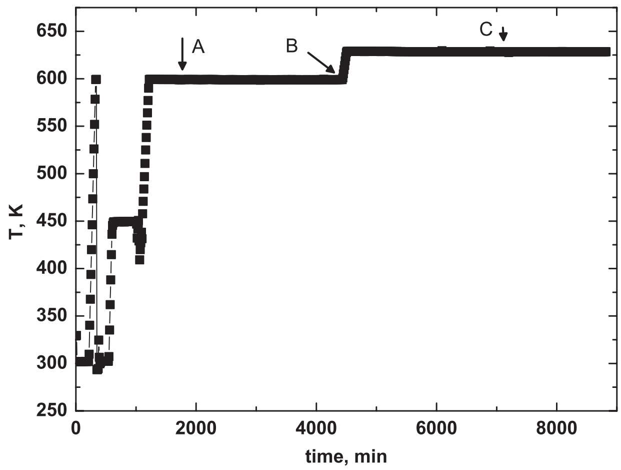

Figure 3. The temporary temperature diagram for annealing the Cu–Be alloy. The positions A, B and C on the graph correspond to changes in the mode of annealing (refer to the text).

the kinetics of the clustering in Cu–Be alloy. It is important to note that the SANS method enables us to examine this influence on the same sample, removing possible uncertainties connected with comparison data from different, though with similar annealing, samples.

2. Experimental details

The experiments on small-angle polarized neutron scattering in the course of the artificial aging of Cu–Be alloy were performed on the VECTOR setup (WWR-M reactor, Gatchina) at a wavelength $\lambda = 9.2$ Å ($\Delta\lambda/\lambda = 0.25$) [8]. This setup is equipped with a 20-counter (^{3}He) detector with a multichannel analyzer. It operates in a slit geometry in the scattering vector range $1.5 \times 10^{-3} < q < 3 \times 10^{-1}$ Å^{-1} ($\vec{q} = \vec{\kappa} - \vec{\kappa}'$, where $\vec{\kappa}, \vec{\kappa}'$ are the wavevectors of the incident and scattered neutrons, respectively). The samples of Cu–Be alloy that were studied had the chemical composition which corresponds to beryllium bronze of the grade BrB-2 by atomic-absorptiometric analysis: Be—1.8 (13); Ni—0.33 (0.04); Co—<0.01 (0.001); Fe—0.05 (0.006); Pb—0.004 (0.0001); Si—0.07 (0.02); Cu—remainder (the weight % and atomic %, respectively). Samples of size $2 \times 10 \times 30$ mm^3 were quenched by heating up to $T = 1100$ K with the following cooling in water. For annealing *in situ*, they were placed into a heater, which was pumped out, filled with helium as heat-exchange gas and placed in a uniform magnetic field between the poles of the magnet. The magnetic field was varied within the range 0 Oe $< H <$ 5700 Oe and was directed horizontally. The temperature in the heater was adjusted by a temperature controller with long-term stability better than 0.1 K. The time of the measurement of one spectrum of scattering in the solid range of the detector was 10 min.

Scattering vector scans of one of a number of samples of BrB-2 at a different stage of annealing are shown in figure 1. It is seen that the process of quenching homogenizes the sample (2); the scattering curve practically coincides with the instrumental curve (1). Such testing on homogenization was made on all quenched samples before the annealing procedure.

One of the problems to be addressed in the study of artificial aging is a temporary temperature dependence of clustering and, accordingly, small-angle scattering. The typical temperature dependence of SANS is shown in figure 2 with wavevector $q = 0.01$ Å^{-1}. The increase of intensity at $T \approx$ 600 K and 629 K reflects the temporary dependence of SANS at these temperature for times approximately 60 and 70 h, respectively. The temperature–time diagram of the annealing of this sample is shown in figure 3 (the short sharp ascent of the temperature at the beginning of the annealing and fluctuations of the temperature in the region of 400 K result from adjusting the temperature controller).

Now, we go into details of the temporary dependences of SANS at the annealing temperatures $T \approx 600$ K and 629 K in different magnetic field conditions (figure 4). To increase the statistics, the scattering intensity was summed over the entire solid angle of the detector, $\Omega_s \approx 2 \times 10^{-4}$ sr, within the q-range 0.005 Å^{-1} $< q <$ 0.03 Å^{-1} (upper curve in figure 4). The lower curve in figure 4 shows the transmission of neutrons

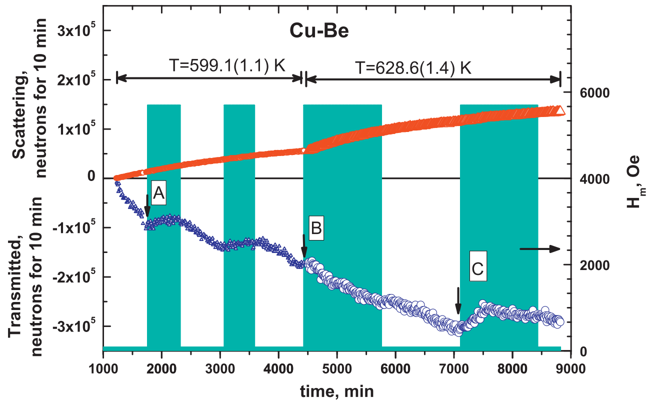

Figure 4. The left axis is the temporary dependences of SANS on the Cu–Be alloy in the solid angle of the detector $\Omega_s \approx 2 \times 10^{-4}$ sr within the q-range 0.005 $Å^{-1} < q <$ 0.03 $Å^{-1}$ (upper curve) and transmission to the central counter with the solid angle $\Omega_s \approx 7 \times 10^{-7}$ sr with the q-resolution $0 < q <$ 0.002 $Å^{-1}$ (lower curve) at temperatures $T \approx 600$ K and 629 K. The right axis is the temporary dependence of the magnetic field. The positions A, B and C on the graph correspond to changes in the mode of annealing (see text for details).

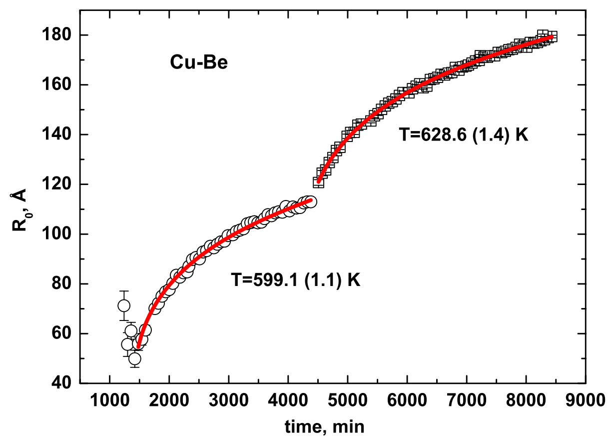

Figure 5. The temporary dependences of the typical radius of nucleation in the Cu–Be alloy for two annealing temperatures of the Cu–Be alloy: $T \approx 600$ and 629 K. The solid lines are results of fitting to the formula $R_0 = a(t - t_0)^{\alpha}$, where a, t_0, α are the parameters of fitting which for the two annealing temperatures are: $a = 17.6(3)$, $t_0 = 1350(30)$, $\alpha = 0.233(2)$ and $a = 47(1)$, $t_0 = 4134(26)$, $\alpha = 0.160(3)$, respectively.

to the central counter with solid angle $\Omega_s \approx 7 \times 10^{-7}$ sr within the q-range 0 $Å^{-1} < q <$ 0.002 $Å^{-1}$. The sample was heated at $T \approx 600$ K for $t \approx 20$ h and was annealed under this temperature in the remanent field of the magnet $H < 100$ Oe for $t \approx 10$ h, up to point 'A' in figures 3 and 4. Then magnetic field $H = 5700$ Oe was periodically switched 'on' or 'off' during a period of 58 h, up to point 'B'. Then the sample was heated up to $T \approx 629$ K for $t \approx 2$ h in a magnetic field $H \approx 5700$ Oe and it was held at this temperature with the periodically switched 'off' and 'on' magnetic field for 70 h, as shown in figures 3 and 4. As is seen in figure 4, the magnetic field does not influence the neutron scattering within the q-range 0.005 $Å^{-1} < q <$ 0.03 $Å^{-1}$. However, switching the magnetic field 'on' and 'off' influences the transmission of neutrons, i.e. influences the integral cross-section of neutrons defining all processes of the scattering within the solid angle range $0 < \Omega < 4\pi$. Switching the magnetic field 'on' in the interval 'AB' produces a reduction of the velocity of the neutron transmission. Switching the magnetic field 'off' within the interval 'BC' practically does not change the velocity of the transmission; however, the next switching 'on' of the field at point 'C' caused a rather sharp reduction of the transmission, like changes within the interval 'AB'.

Note that the observed correlations between variations of neutron transmission with those of the magnetic field are typical. More than ten series of measurements were performed. Although not all measurements were executed with such long annealing under sufficient temperature stabilization, the tendency of the transmission variation with the varied magnetic field was found to repeat, and, therefore, is well established. Also, multiple checking measurements, including those of the scattering neutrons from the heater without a sample with a similar program of temperature and magnetic field variations, were performed. The analysis of the entire collection of data brings us to the conclusion that the observed correlations are connected with a process occurring in Cu–Be samples under annealing.

It was found that the intensity of SANS within the q-range 0.005 $Å^{-1} < q <$ 0.03 $Å^{-1}$ is satisfactorily described by a Guinier function: $I \propto nV^2(\text{contrast})^2 \exp(-R_g{}^2 q^2/3)$, where R_g is the radius of gyration, V is the volume of scattering particles and n is their concentration. The neutron scattering at room temperature was subtracted from the scattering data as a background for these fits, and averaging of the temporary measurements over one hour was applied. The temporary dependence of the radius of the scattering nucleation obtained from these processes in spherical approximation is shown in figure 5 for two annealing temperatures: $T \approx 600$ and 629 K. It is seen in figure 5 that an increase of the radius occurs under these annealing conditions within the 50 Å $< R_0 <$ 180 Å range. Moreover, the temporary dependence is well described by the power law $R_0 \propto t_{an}^{\alpha}$, where t_{an} is the annealing time, and $\alpha = 0.233(2)$ and 0.160(3) according to the annealing temperatures.

3. Discussion

Below, we itemize the experimental facts being established due to the observations under the artificial aging of Cu–Be alloy and requiring explanations.

- Nuclei of the new phase with their sizes grow with time of annealing and temperature is formed under annealing. The neutron diffraction measurements confirm another unlike matrix crystal structure in the new arising phase.
- Annealing enlarges the microhardness of the alloy. Moreover, annealing in the magnetic field enlarges the microhardness by ~30% more than without the field [6, 7].
- Analysis of SANS data within the q-range 0.005 $Å^{-1} <$ $q <$ 0.03 $Å^{-1}$, which forms approximately one-third of

all scattered neutrons, gives an estimation of the scattering radius 50 Å $< R_0 <$ 180 Å. The magnetic field does not affect the temperature evolution of this nucleation.

- At the same time, the magnetic field influences the integral cross-section of the neutron scattering defining all processes of scattering within the solid angle range of $0 < \Omega < 4\pi$, i.e. including scattering on inhomogeneities of the scale comparable with the neutron wavelength λ. This is diffuse background with the intensity of the order of two-thirds of the all scattered neutrons (figure 4).

It is well known that the transmission of a neutron beam, T_s, can be written as

$$T_s = I(T,t)/I_0 = \exp\left(-\sum \sigma_i n_i d\right), \qquad (1)$$

where I_0 and $I(T,t)$ are intensities of neutrons, incident and passing through the sample, registered by the detector with high angular resolution Ω_0, respectively; $\sum \sigma_i n_i(T,t)$ is the integral cross-section of the scattering neutrons, i.e. the sum of the cross-sections σ_i of all scattering objects with the corresponding concentration n_i, removing neutrons from the direct beam; d is the thickness of the sample. In our case, it is possible to assume that the integral cross-section may be written as the sum of scattering on objects with three typical scales: $\sum \sigma_i n_i = \sigma_0 + \sigma_1 + \sigma_2$, where σ_0 is a virtual section of the scattering within the divergence of the incident neutron beam Ω_0, realized, with certainty, on micron-scale inhomogeneities; $\sigma_1(q,T,t)$ is the part of scattering on the 50 Å $< R_0 <$ 180 Å scale inhomogeneities, defining the scattering intensity depending on the temperature and time (figure 4); σ_2 is the part of the scattering within the range $0 < \Omega < 4\pi$ on the $R \approx \lambda$ scale inhomogeneities, which register only as changes of transmitted neutrons. It seems natural to expect a growth of the larger formation of inhomogeneities in the process of annealing due to the absorption of smaller ones. In such an event, to explain the itemized experimental observations in the process of annealing in the magnetic field, it is necessary to expect a steady decrease of the concentration of inhomogeneities of the $R \approx \lambda$ scale. One may expect the primary growth of the largest, micron-size formation, on annealing in a magnetic field enlarging the virtual cross-section σ_0 and, because of the reduction of the concentration of $R \approx \lambda$ scale nucleation, reducing σ_2. This suggestion is in agreement with the observed increasing microhardness on annealing in the magnetic field [6, 7]. These changes, probably, weakly influence the cross-section $\sigma_1(q,T,t)$, i.e. do not lead to increased scattering on the 50 Å $< R_0 <$ 180 Å scale inhomogeneities, since the surfaces of these formation, defining the probability of the process of growing, differ by several orders. Certainly, this suggestion is only an attempt to explain the experimental facts.

The purpose of this experiment was to observe the fact of correlation in the variations of the scattering with modulation of the magnetic field in the process of the artificial aging as a starting factor to study this phenomenon by neutron methods. The experiment has shown the presence of such correlation. This means that neutron methods can be efficient to study the diffusions and kinetics of phase separation in condensed matter with magnetic impurities, both d-elements and those created by dislocations [9], in a magnetic field.

In conclusion, there are several remarks. As was already noted, the influence of the weak magnetic field may occur in a nonequilibrium process only; this criterion is satisfied completely by artificially aging Cu–Be alloy. As was found in experiment, the temporary dependence of the radius of nucleation is described by a power law in a broad temporary range. From an analysis of the scattering data, we may expect a scattering scale of inhomogeneities, affected by the magnetic field, of the order of the wavelength of neutrons, i.e. $R \sim \lambda \sim 10$ Å. The typical interaction time of the neutron with the scattering area of such a scale is 10^{-10}–10^{-11} s. SANS experiments were performed with analysis of polarizations to try to select some magnetic part in intensities of scattering. It is well known that magnetic scattering must change the polarization of scattering neutrons, however it does not seem possible to identify this effect. The observed changes in the polarization of the transmitted neutrons are too small to attribute them to the magnetic scattering rather than, say, to variations of the analyzer efficiency in the range of the measuring wavelengths. Additional calibration measurements and polarization analysis of the diffuse scattering background of neutrons are planned to clarify this point. Further experimental and theoretical efforts are needed to explain a mechanism of the observed temperature–time evolution under artificial aging of the Cu–Be alloy in the magnetic field.

Acknowledgments

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