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# On determination of volume fraction of crystalline phase in partially crystallized amorphous and nanocrystalline materials

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The method for determination of volume fraction of crystalline phase in amorphous-crystalline materials is proposed. The method is based on the analysis of X-ray patterns obtained under study of structure-phase changes in nanocrystalline Finemet- type alloys. Verification of the method was carried out with the use of X-ray diffraction data (including small-angle X-ray scattering) of specimens in as-quenched amorphous state as well as after annealing at various temperatures, which provided formation and growth of crystals in amorphous matrix with sizes in a range from 2 to 15 nm. The method is the most effective under nanocrystals' size exceeding 5–6 nm, when their further increase does not affect the height and width of diffraction reflexes.

## 1. Introduction

As it is known, the level of soft magnetic properties of amorphous metallic alloys can be substantially improved by their heat treatment, under which, in particular, in alloys of FeSiB base system there are formed up to 5 vol.% of crystalline phase – the primary crystals of $\alpha$-Fe based diluted solid solution [1]. This circumstance is especially important for iron based Finemet type nanocrystalline alloys, the high magnetic characteristics of which (comparable with cobalt alloys initial magnetic permeability, close to zero magnetostriction, etc.) are determined by structure - phase state, which is reached under their partial crystallization at the annealing temperatures $T_a \sim 550°C$ with formation in amorphous matrix of ∼70–80 vol. % of ordered by $DO_3$ type $\alpha$-Fe(Si) solid solution with the grain size of 9–12 nm [2–7]. The fast expansion of group of this type alloys and of areas of their practical application cause the large attention to these materials from the researchers and technologists. Besides, the nanocrystalline alloys represent interesting and perspective object from the point of view of an establishment of correlation between structures of liquid, amorphous and crystalline state, and also of clarifying the questions associated with processes of nucleation and growth of crystals in extreme nonequilibrum conditions, which were partially considered by us earlier in [8]). The reliable diagnostic methods are necessary for establishment of the appropriate laws and for directed influence on these processes, which would allow to receive the quantitative information on dynamics and kinetics of structure-phase changes occurring under heating, and thereby to optimize the heat treatment regimes for amorphous alloys towards achievement the higher level of their properties.

To the most important characteristics in this regard, the crystal size $d$ and part of crystallized volume $X_c$ should be attributed. Their definition is accompanied with serious difficulties, and less developed both in theoretical and in methodical respects is the definition of $X_c$. In essence, there are only single works, in which the attempt to determine this parameter is made, however information presented in them is not enough for estimation of advantages and a degree of correctness of used methods. Thus, in [9–12] the part of crystallized volume in nanocrystalline alloys is determined by the data of X-ray diffraction experiments. In [9, 10] this parameter is determined by the height of the first maximum of the structure factor which is linearly dependent on a volume part of crystalline phase, (i.e., actually by the one point of X-ray diffraction pattern). In [11, 12] the narrow fragment of X-ray diffraction patterns is used, namely, the range of diffraction vector values, in which the main maximum of diffuse X-ray pattern of amorphous object is located. The authors of [11] determine $X_c$ by comparison of integral intensities in this range calculated from X-ray diffraction patterns of amorphous, partially crystallized and completely crystalline objects. In [12] this region of X-ray diffraction pattern for partially crystallized sample is divided to parts corresponding to amorphous and crystalline phases (way of dividing is not indicated).

It should be noted that the definition of $X_c$ by the height of the first maximum [9, 10] might lead to significant errors, since during crystallization annealing not only the quantity of a crystalline phase is changing, but also its chemical composition is. It is accompanied with displacement of diffraction maximums and with changes of their heights, that can essentially affect the final result. Even less preferable is the method of definition $X_c$ by integral intensity [11]. Taking into account the energy conservation law, even in a narrow interval of the diffraction vector its essential changes during crystallization of amorphous materials hardly should be expected (there are no appropriate data in this work), and this also does not promote the high accuracy of $X_c$ definition.

The variant of $X_c$ definition in [12] (under presence of mathematically proved methods of dividing of the first maximum of X-ray diffraction patterns of amorphous-crystalline objects) seems to be more preferable in comparison with [9–11], but due to absence of error estimation in $X_c$ definition in the considered works, it is difficult to check up the received results. Besides, from the theory of the X-ray diffraction analysis [13] it follows that the change of nanocrystal sizes in the certain size interval affects the X-ray diffraction patterns (height and width of diffraction maximum are changed). This influence is supposed to be the most essential at $d$ values in an interval of 2–10 nm, but the theory does not determine the exact top border of this interval, and this fact should be taken into account in development of methods for determination of $X_c$ by the data of X-ray diffraction experiments.

The additional experimental researches of crystal samples with the same crystal sizes within the limits of the specified interval are necessary for this purpose (such samples are difficult to be produced), or introduction of the appropriate amendments into calculations is. At the same time, in equations for $X_c$ determination listed in [11] such amendments are absent, though the size of crystals is determined by width of diffraction reflexes.

In view of above stated, in the present work the task has been solved of development of the methods for determination of a volume part of crystalline phase in the amorphous-crystalline materials, wherever possible deprived of the specified lacks, as well as of the ways of their experimental verification.

## 2. Theoretical approach to a method for determination of the volume part of crystalline phase and the ways of its experimental verification

As amorphous and crystalline phases scatter X-ray radiation independently, the intensity of scattering by amorphous-crystalline objects can be written down as:

$$I(s) = X_c I_c(s) + (1 - X_c) I_a(s), \tag{1}$$

where $X_c$ is the volume part of a crystalline phase, $s = (4\pi \sin\vartheta)/\lambda$ is scalar value of diffraction vector, $I(s)$, $I_c(s)$, $I_a(s)$ are accordingly intensities of scattering from the investigated amorphous-crystalline, and also completely crystalline and amorphous samples. Equation 1 is valid under any value of diffraction vector. With known $I(s)$, $I_c(s)$ and $I_a(s)$, the $X_c$ value can be determined for any value of $s$, as

$$X_c = \frac{I(s) - I_a(s)}{I_c(s) - I_a(s)} \tag{2}$$

Owing to possible experimental errors in $I(s)$, $I_c(s)$ and $I_a(s)$ measurements, the values of $X_c$ calculated for different $s$ may essentially differ. The error of $X_c$ calculation by single point (for the given $s$ value) can be determined from

$$\mathrm{d}X_c = \frac{\mathrm{d}(I(s) - I_a(s))(I_c(s) - I_a(s)) - \mathrm{d}(I_c(s) - I_a(s))(I(s) - I_a(s))}{(I_c(s) - I_a(s))^2} \tag{3}$$

According to (3), the error in $X_c$ definition will be the less, the less is the numerator and, especially, the more is the difference in the denominator of this expression, which accepts the greatest value in the range of a maximum of the most intensive reflection of a crystalline phase. It means that in calculation of $X_c$ by the Equation 2 errors in its determination will be minimal for $s = s_{\max}$.

The part of transformed volume can be determined also by trial and error method, by changing of $X_c$ value in the right part of the Equation 1 with a fine step on $s$ up to the best correspondence of calculated $I(s)$ with experimental one; their comparison enables to estimate accuracy of $X_c$ determination.

For more detailed verification of accuracy of the method and of possible borders of its applicability, we shall rewrite the Equation 2 as

$$I_c(s) - I_a(s) = \frac{I_i(s) - I_a(s)}{X_c^{(i)}} \tag{4}$$

Where $I_i(s)$ is the intensity of X-ray radiation scattering expressed in electronic units, and $X_c^{(i)}$ is the volume parts of a crystalline phase in the $i$-sample. If the left part of the Equation 4 ($I_c(s) - I_a(s)$) is identical to the two amorphous-crystalline objects with a different part of a crystal phase $X_c(1)$ and $X_c(2)$, it is possible to write down the Equation 5

$$(I_1(s) - I_a(s)) X_C^{(2)} \cdot = (I_2(s) - I_a(s)) \cdot X_C^{(1)} \tag{5}$$

or Equation 6

$$\frac{(I_1(s) - I_a(s))}{X_C^{(1)}} \cdot = \frac{(I_2(s) - I_a(s))}{X_C^{(2)}} \tag{6}$$

where $I_1(s)$ and $I_2(s)$ are accordingly the intensity (in electronic units) of coherently scattered X-ray radiation from two amorphous-crystalline samples with different volume part of crystalline phase $X_c$. With using experimental X-ray diffraction patterns from amorphous sample and two such partially crystalline ones, it is possible to use expressions (5) and (6) for verification of results of determination of the content in such samples of the volume part of crystalline phase without X-ray diffraction pattern from completely crystallized sample with $X_c = 1$ (for convenience of realization of this procedure let's designate the left and the right parts of Equation 5 as $f_1(s)$ and $f_2(s)$).

At the large values of a difference $(I_i(s) - I_a(s))$ (annealing temperature $T_a \geq 540°C$) it is more preferable to use the Equation 5, and at small ones - the Equation 6.

Let's note, that it is possible to carry out an estimation of an error in $X_c$ determination, besides (3), as well by relative deviation of integrated intensities $\Delta I_{int}$, on experimental X-ray diffraction pattern and on the one calculated by Equation 1:

$$\Delta I_{\text{int.}} = \frac{\int_0^\infty 4\pi s^2 (I_{\text{exp}}(s) - I_{\text{cal}}(s))\,\mathrm{d}s}{\int_0^\infty 4\pi s^2 I_{\text{exp}}(s)\,\mathrm{d}s} \qquad (7)$$

## 3. Experimental procedure

The realization of calculations by Equation 1 imposes the high requirements to accuracy and carefulness of realization of X-ray diffraction experiments. Quality of the information received by their realization is essentially influenced by the degree of monochromatization of X-ray radiation, accuracy of diffractometer and sample adjustment, stability of the high-voltage power source for X-ray tube and single-channel pulse analyzer, and also by constancy of all experimental parameters during its realization.

In the present work monochromatization of X-ray radiation was carried out with the help of the perfect quartz single crystal made by special technology. Stability of the high-voltage power source for X-ray tube and single-channel pulse analyzer was controlled with the help of discrimination curve, which was taken before and after realization of experiment. The X-ray diffraction patterns from each sample were taken three times. At complete coincidence of discrimination curves and dispersion of X-ray diffraction patterns within the limits of statistical calculation error, they were averaged for use in the further calculations.

Taking of the X-ray diffraction patterns was carried out in monochromatic Mo $K_\alpha$ - radiation in a diffraction vector range from 1 up to 12.5 $A^{-1}$ with a scanning step of $6'$ in the field of the main maximum and $0.5°$ at other scattering angles. The time of one point taking was selected such that the statistical calculation error at the "tail" of X-ray diffraction pattern (at the large scattering angles) did not exceed 1%. The places of diffraction reflections of a crystal phase were determined with accuracy 0.001 $A^{-1}$ by X-ray diffraction patterns, interpolated with the appropriate step.

As-quenched amorphous ribbons of nanocrystalline alloys of more then 10 various compositions were obtained in air by melt spinning (planar flow casting). For structure researches after 30 min. isothermal annealings the ribbons were selected, for which in as-quenched state the small-angle X-scattering (SAXS) of X-ray beams was completely absent. Annealing was carried out in the vacuum furnace at temperature maintenance with accuracy $\pm 0.4°$ and at temperature gradient on sample length of no more than $5°$. The sizes of nanocrystals were determined by an inclination of dependence of the logarithm of intensity $\ln I$ on $s^2$ after the SAXS data, allowing to determine the sizes of inhomogeneities with an average effective diameter 2–12 nm [13]. The used technique was described by us in details in [7].

As the obtained results have appeared to be similar as a whole for alloys of all investigated compositions, they are illustrated on an example of $Fe_{73}Si_{15.8}B_{7.2}Cu_1Nb_3$ (FM-2, ribbon thickness is 24 $\mu$m) and $Fe_{73.6}Si_{15.8}B_{7.2}Cu_1Nb_{2.4}$ (FM-6, 26 $\mu$m) nanocrystalline alloys, which are close by composition to known $Fe_{73.5}Si_{13.5}B_9Cu_1Nb_3$ nanocrystalline alloy [2].

The special attention in the work was given to development of the programs allowing to increase the accuracy of processing of obtained experimental data.

## 4. Results and discussion

On Fig. 1 the data of small angle scattering for the as-quenched amorphous samples from FM-6, FM-2 alloys and for two samples annealed at different temperatures. Practically zero dispersion in the small angle region from as-quenched samples testifies to complete absence of a crystalline phase in them. Scattering in the small angle region becomes appreciable at the annealing temperatures $T_a \sim 420°C$, and at the further $T_a$ increase the intensity of small angle scattering grows. The most appreciable growth of intensity is observed near to a primary beam. It testifies to appearance of the crystalline phase, increase both of its volume part and of the sizes of the primary $\alpha$-Fe(Si) nanocrystals with increase of annealing temperature.

At Fig. 2 the X-ray diffraction patterns for as-quenched and annealed at $T_a = 420$–$480°C$ samples of FM-2 and FM-6 alloys are shown. In this interval of annealing temperatures the sizes of nanocrystals vary from ~2,2–2,3 up to 3,2–3,5 nm. The distinctions of X-ray diffraction patterns are insignificant, there are no any effects peculiar to X-ray diffraction patterns of a

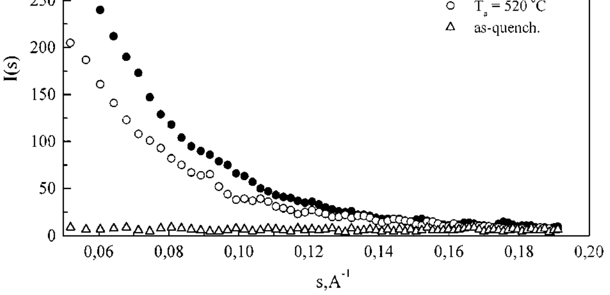

*Figure 1* SAXS intensity of as-quenched and annealed specimens of FM-6 alloy.

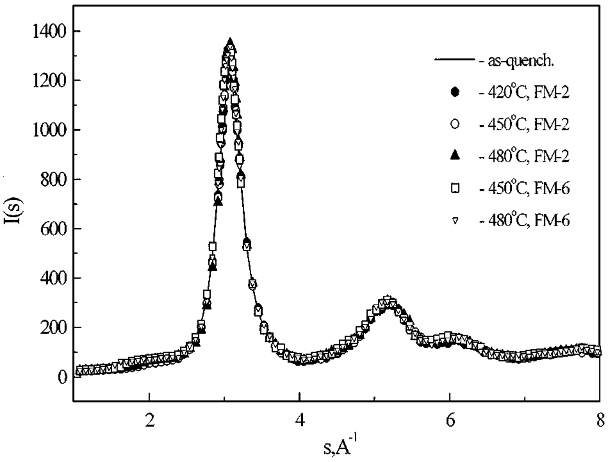

*Figure 2* X-ray patterns of as-quenched and annealed specimens of FM-alloys.

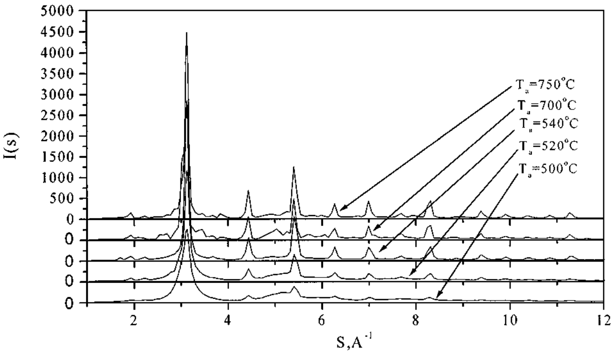

*Figure 3* Intensity of coherently scattered radiation (el. un.) of annealed specimens of FM-2-alloy.

crystalline phase (only the height of maximums and the depth of minimums a little bit change). At $T_a \sim 500°C$ the small narrow maximums appear on X-ray diffraction patterns, their height grows with the further increase of annealing temperature (Fig. 3) and at $T_a$ above 650°C X-ray diffraction patterns have already the form typical for crystalline objects.

In course of determination of the volume part of crystalline phase in all studied samples, the both described above approaches were used, i.e. by the single point of X-ray diffraction pattern $s_1 = s_{\max}$, as well as by method of $X_c$ fitting up to achievement of the best coincidence of experimental and calculated X-ray diffraction patterns. The rather well agreed results were obtained in most cases (in Table I the $X_c$ values determined by the second method are given). For calculations the $I_c(s)$ intensity values were taken from experimental X-ray diffraction patterns for samples annealed at $T_a = 700°C$.

In Fig. 4 there are shown X-ray diffraction patterns for several amorphous-crystalline objects obtained experimentally and calculated by the Equation 1 with use of the $X_c$ values from Table I. It is seen that for all samples the practically complete coincidence of the calculated functions with experimentally obtained is observed. In aggregate with calculated by Equation 7 relative deviations of integrated intensity $\Delta I_{\text{int}}$ these results testify, apparently, about high (<1 %) accuracy of $X_c$ determination for all samples, given in Table I.

TABLE I Structure parameters of FM-alloys after annealing at different temperatures for 30 min. ($T_a$ is annealing temperature, $h$ is thickness of ribbon, $s_1$ is position of the main maximum of the structure factor, $i(s_1)$ is height of the main maximum of the structure factor, $d$ is the most probable size of $\alpha$-(FeSi) nanocrystals, $\Delta I_{\text{int}}$ is relative deviation of integrated intensity, $\Delta I(s_1)$ is relative deviation of heights of the main maximum at calculated and experimental X-ray diffraction patterns

| No | $T_a$,°C | $s_1$, nm$^{-1}$ | $i(s_1)$ | $d$, nm | $X_c$ | $\Delta I(s_1)$ % | $\Delta I_{\text{int}}$ % |
|---|---|---|---|---|---|---|---|
| | | FM-2 ($Fe_{73}Si_{15.8}B_{7.2}Cu_1Nb_3$) | | | | | |
| 1 | As-quench. | 31.00 | 3.99 | - | - | - | - |
| 2 | 420 | 30.85 | 4.13 | 2.0 | 0.008 | 0,3 | 0.2 |
| 3 | 450 | 30.90 | 4.31 | 2.7 | 0.022 | 1,1 | 0.4 |
| 4 | 480 | 30.90 | 4.33 | 3.4 | 0.029 | 0,3 | 0.5 |
| 5 | 500 | 31.25 | 5.95 | 6.9 | 0.254 | 0,1 | 0.04 |
| 6 | 520 | 31.25 | 9.49 | 7.6 | 0.681 | 0,9 | 0.7 |
| 7 | 540 | 31.25 | 10.34 | 7.9 | 0.801 | 0,08 | 0.3 |
| 8 | 700 | 31.25 | 11.90 | 12.8 | 1.0 | - | - |
| 9 | 750 | 31.20 | 11.23 | 12.9 | 1.0 | - | - |
| 10 | 840 | 31.25 | 12.24 | 13.2 | 1.0 | - | - |
| | | FM-6 ($Fe_{73.6}Si_{15.8}B_{7.2}Cu_1Nb_{2.4}$) | | | | | |
| 1 | As-quench. | 30.9 | 4.12 | - | 0.020 | - | - |
| 2 | 420 | 30.9 | 4.20 | 2.2 | 0.030 | 0,3 | 0.1 |
| 3 | 450 | 30.85 | 4.27 | 2.9 | 0.030 | 0,7 | 0.6 |
| 4 | 480 | 30.9 | 4.41 | 3.2 | 0.050 | 0,09 | 0.4 |
| 5 | 500 | 31.25 | 9.09 | 7.3 | 0.470 | 0,1 | 0.06 |
| 6 | 520 | 31.25 | 11.39 | 8.08 | 0.700 | 4,3 | 0.05 |
| 7 | 540 | 31.25 | 13.02 | 8.3 | 0.850 | 3,8 | 0.07 |
| 8 | 700 | 31.25 | 15.18 | 12.8 | 1 | - | - |
| 9 | 750 | 31.25 | 14.60 | 12.9 | 1 | - | - |

Formally it would mean that the change of the sizes of nanocrystals in an interval from 2 up to 10 nm (part of transformed volume reaches thus ~80%) does not render influence on character of X-ray diffraction pattern obtained in experiments, that contradicts the known theoretical approaches.

This circumstance has formed the basis for fulfillment of additional verification of the obtained data on determination of a volume part of crystalline phase. Such verification can be carried out by comparison of the left $f_1(s)$ and the right $f_2(s)$ parts of the Equations 5 or 6, calculated by X-ray diffraction patterns for amorphous sample and two amorphous-crystalline ones. The results of such calculation by the Equation 5 for three pairs of samples, annealed at $T_a \geq 500°C$, are given in Fig. 5 (curve 1- 500 and 520°C, 2 - 500 and 540°C, 3-500 and 750°C).

In Fig. 6 the results of similar calculations by the Equation 6 for samples with $T_a \leq 500°C$ (1- 500 and 480°C, 2 - 480 and 450°C) are shown.

As it is seen from Fig. 5, at annealing temperatures $T_a > 500°C$ the left and the right parts of Equation 5 practically completely coincide for all pairs of samples, which cannot be said about the data shown in Fig. 6 for amorphous-crystalline samples, annealed at $T_a < 500°C$. Here it should be remind that in deduction of Equation 5 the equality of $(I_c(s) - I_a(s))$ for different pairs of samples was assumed, and this is possible only for those pairs, for which $I_c(s)$ does not depend on the size of nanocrystals. It follows herefrom that the good compliance of the data in Fig. 5 is the indication

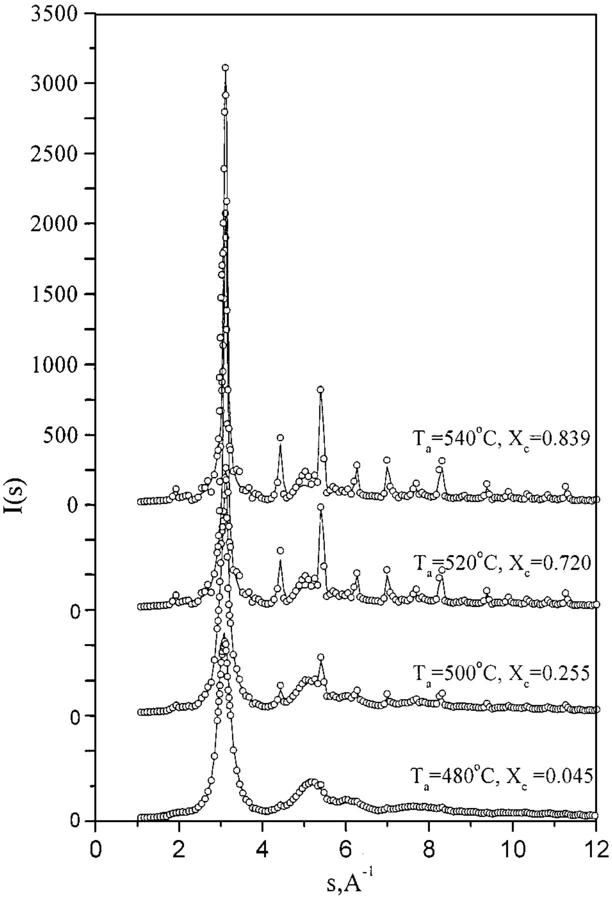

*Figure 4* X-ray patterns of annealed specimens: experimental – solid line, calculated by Equation 1 – open circles.

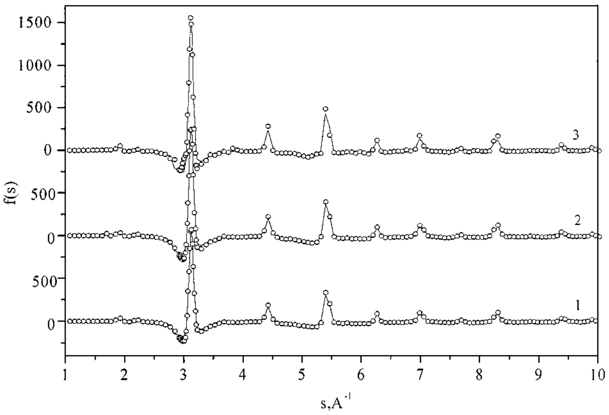

*Figure 5* Comparison of functions $f(s)$ calculated by left and right parts of Equation 5 for 3 pairs of specimens with different part of crystalline phase; $T_a \geq 500°\mathrm{C}$.

of that the increase of the sizes of nanocrystals in an interval with the bottom border ~6 nm at $T_a > 500°\mathrm{C}$ does not render influence on the character of X-ray diffraction patterns obtained experimentally from such objects. And, on the contrary, the divergence of the calculated data in Fig. 6 testifies that the reduction of the size of nanocrystals towards lower than 6 nm with decreasing of annealing temperature appreciably affects the appropriate X-ray diffraction patterns, resulting in reduction of $I_c(s)$ and in widening of diffraction reflexes. The specified distinctions are the more, the less is crystal size.

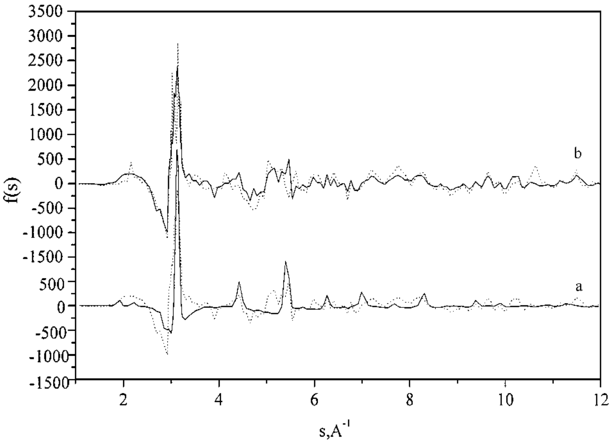

*Figure 6* Comparison of functions $f_i(s)$ calculated for pair of specimens which annealing temperature didn't exceed 500°C.

## 5. Conclusions

1. On the base of results of experimental researches of Finemet type nanocrystalline alloys, the method for determination of the volume part of crystalline phase $X_c$ in amorphous-crystalline alloys with using of X-ray diffraction patterns obtained in a wide range of a diffraction vector, is developed. The proposed method provides higher accuracy (~1%) in comparison with determination of $X_c$ by the single point, or by narrow fragment of X-ray diffraction pattern. The most adequate results with use of this method can be received for the crystal sizes more than 6 nm.

2. The analytical expressions and methods for processing the experimental X-ray diffraction data for verification of accuracy of definition of the volume part of crystalline phase are proposed.

3. Is shown, that increasing of the sizes of nanocrystals up to ~6 nm is accompanied only by change of the height and width of diffraction maximums with conservation of complete qualitative similarity of X-ray diffraction patterns from completely amorphous and amorphous-crystalline objects. The further increase of the sizes does not already affect the character of X-ray diffraction patterns from amorphous-crystalline or completely crystalline objects, that contradicts to existing theoretical conceptions.

4. It is supposed, that the proposed method of diagnostics of the structure state by the data of X-ray diffraction experiments is applicable not only for nanocrystalline alloys of Finemet type, but also for other types of ultradispersed metallic mediums.

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