Phase transformations of the nanostructured iron-platinum system upon heating

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Abstract. Joint reduction with hydrazine from aqueous solutions of precursors produced nanostructured powders of the Fe – Pt system in three characteristic phase regions. The samples were subjected to heat treatment in the range up to 800 °C and characterized at all stages by X-ray diffraction and high-resolution electron microscopy; the elemental composition of the samples was refined by the method of optical emission spectroscopy with inductively coupled plasma. In the initially obtained samples, only a part of the substance is detected by diffraction - the largest, platinum-rich crystals with dimensions of about 10 nm (established from TEM images and broadening of diffraction lines). The fcc-type cubic lattice parameters and the composition of the observed crystals were estimated from the distances between the regular bands in TEM images, identified with atomic rows, based on the composition dependence of the bulk characteristics of mixed iron-platinum phases (according to ICDD databases). In the course of heating, the processes of phase transformation are traced in detail, the parameters of the resulting crystal structures of intermetallic compounds are fixed, and the mechanisms of these transformations are discussed. Based on the measured lattice parameters, the thermal expansion coefficients of some mixed phases are calculated and the phase compositions are estimated at different stages of heat treatment.

1. Introduction

Consideration of conditions and elucidation of schemes (models) for the formation of intermetallic (IM) phases, especially with the tetragonal structure L₁₀ in a highly ordered state, during the synthesis and subsequent processing of bimetallic nanostructured systems of the "iron group metal - noble metal (Pd, Pt)" type is relevant for a number of reasons. First, in the preparation of nanostructured polymeric systems (NPS) with the participation of metals of the iron group (Fe – Co, Fe – Ni, Co – Ni, Fe – Co – Ni, Ni – Cu, Ni – Cd) by joint reduction of metals from solutions of various precursors (MRPS) [1–7], the resulting product does not always correspond to the known phase diagrams (PD) in terms of phase composition and composition f phases. The main reasons for this are considered to be the features of the synthesis reactions and the high energy saturation of NPS due to their nanoscale [8–10].

One of the insufficiently studied in this area is the question of the possibility, conditions and schemes of formation in NPS of intermetallic compounds known from PDs. The results obtained on the structural and phase features of NPS show that in this case, several general circumstances should be taken into account. As is known, IM are stable only up to the temperatures Tₘ of each system. However, the observed state of each specific NPS (phase composition and composition of phases) obtained at relatively low temperatures (80–120 °C) corresponds to the region of
significantly higher temperatures on PD, which we called effective temperatures $T_{\text{eff}}$ [2–5]. As a result, if $T_{\text{eff}}$ is greater than $T_{\text{im}}$ or these temperatures are close, IM is not formed.

Thus, for the Fe – Co and Fe – Ni systems we obtained, the estimated $T_{\text{eff}}$ in the regions of existence of IM were 930–980 °C and 870–920 °C, respectively [1–3]. According to the PD of these systems, the $T_{\text{im}}$ for FeCo is about 1000 °C, and for FeNi 770 °C [11]. As a result, when trying to detect the predominant environment of atoms of one metal by atoms of another using the EXAFS and XANES methods on synchrotron radiation [3], which would be a confirmation of the formation of IM, this could not be established.

In addition, when NPS is obtained by the MRPS method, due to the difference in redox potentials (ROP) of precursors, which is often significant, at the first stages the product is inevitably enriched in a more noble metal, therefore, the conditions for the formation of phases richer in this metal than the system as a whole, respectively, are more favorable [7-10]. Thus, it is hardly possible to get a certain IM directly during the reduction, simply by taking the appropriate composition.

The Fe – Pt system considered in this work is convenient for studying the described problems and features of the process of IM formation in NPS, since IM in this system is thermally stable enough (Figure 1, a), and the difference in ROPs of the corresponding precursors is significant [12].

![Figure 1. Phase diagram of FePt (a) and the dependence of the molar fraction of platinum in cubic phases on the average volume per 1 metal atom according to ICDD base data (b).](image)

Along with these general issues, consideration of the formation and temperature transformations of phases in Fe – Pt seems interesting and important in connection with the fact that in the group of systems “iron group metal - noble metal (Pd, Pt)” the formation of IM with a tetragonal structure of the L10 type is possible characterized by extremely high values of coercivity in combination with a fairly significant magnetization, which are retained under moderate heating. For these reasons, the potential for their practical use in the nanocrystalline state in biomedicine, for the creation of ultraminiature permanent magnets, media for recording and storing information with a high density and structures with giant magnetoresistance is estimated very high [13-15].

The aforementioned impossibility of obtaining these IM directly by MRPS methods requires subsequent heat treatment in order to convert the formed phases of the A1 and L12 types into the target IM with the L10 structure. In this case, an undesirable general enlargement and an increase in polydispersity occur, and too high a temperature prevents the achievement of the required ordering of the L10 structure [18–20]. Therefore, the unresolved issues of lowering the formation temperatures of L10 while ensuring complete conversion to L10, the maximum degree of ordering of IM, and acceptable changes in the particle size distribution are relevant. The solution of these problems is impossible without clarifying the reasons for the unusual phase compositions of NPS obtained by MRPS methods, analyzing changes in the phase composition and structural-phase parameters during heat treatment, and understanding the models for the formation of nanophases, including IM L10; however, we have not found published works of such a complex content.

In this communication, we consider the preparation of a nanostructured Fe – Pt system by the MRPS method using $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ as a reducing agent, the oxidation products of which ($\text{N}_2$ and $\text{H}_2\text{O}$)
do not contaminate the target product. Using high-temperature X-ray diffraction and high-resolution electron microscopy (HRTEM), the sequence of phase transformations upon heating of systems of three compositions is considered, on the basis of which the foundations of the scheme (model) of these processes, including the formation of the L1\textsubscript{0} phase, are proposed, which is probably common for similar systems of the type MZG-BM. A study with a detailed elaboration of these issues requires an expansion of the scope of work, therefore, results have also been obtained and accumulated on small-angle scattering, derivative mass spectrometry, temperature-programmed oxidation, magnetic measurements, but due to the limited volume of the article, especially in the number of figures, these data will be presented in subsequent publications.

2. Experimental

2.1. Materials and sample synthesis

NPS Fe – Pt powders were obtained by joint reduction of metals with hydrazine (in the form of hydrazine hydrate) from aqueous solutions of HPtCl\textsubscript{6} • 6H\textsubscript{2}O and FeSO\textsubscript{4} • 7H\textsubscript{2}O (analytical grade). Hydrazine (six-fold excess) and alkali (NaOH) were added to acidified solutions of precursors heated to 90 °С with vigorous stirring to pH 13 – 14. The reduction lasted 10 minutes. The resulting finely dispersed black powders were washed with distilled water, dried at room temperature, and stored in a sealed glass container.

The calculation of the reagents was carried out on the basis of the condition for obtaining metal systems with platinum content in the samples designated 1 (Fe\textsubscript{0.21}Pt\textsubscript{0.79}), 2 (Fe\textsubscript{0.50}Pt\textsubscript{0.50}), and 3 (Fe\textsubscript{0.75}Pt\textsubscript{0.25}), 79, 50, and 25%, respectively (hereinafter, molar percentages) to cover the areas of possible formation of the main phases: A1 - disordered solid solution (SS), L1\textsubscript{0} - ordered layer-by-layer tetragonal IM FePt and L1\textsubscript{2} - IM of both types - FePt\textsubscript{3} and Fe\textsubscript{3}Pt (Figure 1, a).

2.2. Research methods

Elemental analysis of samples by optical emission spectrometry with inductively coupled plasma was performed on an iCAP 6500 DUO spectrometer (USA) in a radial plasma observation mode with a power of 1150 W. The content of the main components and impurities was determined at their characteristic wavelengths in the ranges free from spectral and other interference. The obtained values of the concentrations of the elements to be determined were averaged over different analytical wavelengths.

HRTEM images of particles were obtained with a JEOL JEM 2100 electron microscope in light-field mode. To prevent sputtering of (magnetic) nanoparticles in the microscope column and to obtain images of satisfactory quality, a suspension of nanoparticles in a solution of polymethyl methacrylate was placed in a bath of an ultrasonic disperser to disintegrate agglomerates and create an aerosol layer of microdroplets above the surface, containing nanocrystals (NC) of samples. Preparative grids (TEM-grids) with a thin layer of carbon deposited on their surface were introduced into an aerosol cloud, from which microdroplets were deposited onto a carbon surface with subsequent fixation of nanoparticles from microdroplets on it during polymethyl methacrylate polymerization.

X-ray diffractograms for phase analysis to measure unit cell parameters (UCP) and estimate the phase composition were recorded on a Bruker D8 ADVANCE A25 powder diffractometer (Germany) with an iron tube (Fe K\textalpha, wavelength 1.9373 Å) in the range of angles 20 – 140 ° with a scanning step 0.02 – 0.04 °. Phase transformations were studied at temperatures of 30 – 800 °C in a high vacuum (about 10 – 8 mbar) in situ in an Anton Paar HTK 1200N high temperature chamber (Austria). The measurements were carried out at fixed temperatures with a preliminary holding of 10 minutes. The effect of high temperatures in the isothermal regime was recorded by repeated measurements at intervals of 1 – 2 hours. Data collection and processing of diffraction patterns were performed using the Diffrac.Suite.Eva (V3.1) software package.

X-ray phase analysis was performed on the basis of the ICDD PDF-2 database. To assess the composition of the phases, based on the ICDD data, the volumes of the unit cells of the cubic phases (A1 and L12) and the average volumes per 1 metal atom (AAV) were calculated, the dependence was
plotted in the coordinates "mole fraction of platinum (X_{Pt}) - AAV (V_{at})" (Figure 1, b) and approximation by a polynomial of the second degree, the expression (1):

$$X_{Pt} = 2.4108 - 0.60677V_{at} + 0.033992V_{at}^2$$  \hspace{1cm} (1)

The acceptability of the composition estimate by this formula for cubic phases is based on a sufficiently high correlation coefficient (0.998) and on the fact that all the structures under consideration are different variations in the arrangement and mutual arrangement of atoms in a single three-layer closest packing. From this point of view, the tetragonal structure of the L1_0 type is also quite close to those considered; therefore, with some caution, its composition can also be estimated. In any case, the estimation of the compositions of a number of IMs using this formula, declared in the ICDD databases as 50%, gives values of 0.47–0.52, and it may be that the true compositions of the phases in these studies really differ from equiatomic ones.

The size estimation of crystallites - coherent scattering regions (CSR) - which are either independent particles in powders or their constituent parts, was carried out according to the well-known Scherrer formula, using the technology of detecting broadening directly in doublet X-ray radiation [21].

3. Results and discussion

3.1. Electron microscopy

Note that the elemental analysis of the samples confirmed the calculated composition used in the synthesis with an accuracy of 0.2–0.3%. In addition to iron and platinum, Co, Ni, Cu, Zn, Si were also found in a total amount within 0.5 wt. %.

The obtained HRTEM images (Figure 2) show that the samples consist of small crystallites with a size of about 10 nm, combined in agglomerates - loose polycrystalline particles - with a size of 50–120 nm. The distinct streaky structures (Figure 2a and b) confirm the ordered structure of the observed particles. A fairly common distance between the bands is 2.38 ± 0.01 Å and 2.70 ± 0.03 Å. The first of them can be interpreted as the distance between atomic rows in the 111 plane in a three-layer closest packing. For platinum, it is 2.402 Å (UCP according to the ICDD base data is 3.9231 Å), the inverse calculation of UCP from the distance between the bands gives a value of 2.89 ± 0.01 Å, which, according to formula 1, corresponds to an iron content of 16 ± 5%.

Another distance, probably, is the distance between the atomic rows in the coordinate planes 100 of the cubic lattice, simultaneously being the doubled interplanar distance d_{200} of the fcc lattice (structure type A1), although the UCP calculated from this distance is only 2.82 ± 0.04 Å. The underestimation is most likely due to the worse conditions for the arrangement of crystals with their planes parallel to the surface of the carbon film, in contrast to the more developed 111 planes in the first case. The
inclined arrangement of the crystals precisely reduces the distance between the stripes in the projection onto the observation plane of the HRTEM images.

In confirmation of the validity of this, we can cite our experience of observing and evaluating with high accuracy the UCP of gold over distances in the same 111 plane [22]. The distances of 2.495 ± 0.004 Å found from HRTEM images are not any interplanar distances, as is often interpreted in relation to the bands under consideration, and coincide with the calculated 2.498 Å according to the UCP of gold (4.0786 Å according to the ICDD base data).

Thus, in agreement with TEM data, no iron-rich crystals are found among sufficiently large crystals. However, in addition to the described single crystal particles and their agglomerates, in the images you can often find rather shapeless formations with sizes of 1–3 nm, for example, in Figure 2, c. There are especially many of them in sample 3, which is rich in iron. Based on the logic of the reduction process, it can be assumed that iron, being reduced later due to a less positive (than platinum) ROP, forms already on the finished surface of the primary, platinum-rich crystals, in the form of smaller particles, forming something like a spherical layer around the core, conditionally platinum part. The geometry of such a system requires significantly smaller dimensions (thickness) for the outer layer compared to the size of the core (diameter), even in the case when the volume of the layer is greater than the volume of the core. So, if the volume of the layer is twice the volume of the core, its thickness will be only 22% of the diameter of the core, and with equal volumes, it will be only 13%. This is often due to a significant difference in the size of "core" and surface "layer" particles during the sequential formation of particles of one substance on the surface of particles of another.

3.2. X-ray phase analysis during heating

The powders of the system under consideration obtained directly during the synthesis can be classified as X-ray amorphous, since initially, diffractograms show essentially only one very weak and diffuse maximum in the region of the 111 reflection of the cubic phase, which is quite close in position to platinum, regardless of the composition of the system. Fragments of diffraction patterns (Figure 3, a and 4, a) show these areas in the heating mode, starting from a temperature of 100 °C, at which significant changes in the diffraction pattern still do not occur. The weak and narrow reflections also present in all diffraction patterns, the position and intensity of which practically does not change upon heating, refer to corundum from which the cuvette is made.

![Figure 3](image-url)

**Figure 3.** Fragments of diffraction patterns during heating of the Fe$_{0.21}$Pt$_{0.79}$ system (a) and the fine structure of the 311 reflection after heat treatment (b)
The closeness of the broad maximum to platinum 111 in position and a significant increase in its intensity upon heating suggest that the diffraction visible part (DVP) of the samples is initially only a group of the largest and richest in platinum crystals. The UCP at 100 °C for samples 1, 2, and 3 is 3.904, 3.875, and 3.902 Å, which (so far without taking into account thermal expansion) corresponds to approximately 10% iron in samples 1 and 3 and about 20% in the sample 2 according to formula 1 above. Together with the data of elemental analysis and electron microscopy, this means that in the samples obtained by MRPS methods, along with DVP, there are diffractionally undetectable phases, which can be summarized by the term diffraction invisible part (DIP) and in which the main part of iron is concentrated. These phases can be either different IM or SS with the A1 structure.

The picture of the gradual change in the composition of DVP upon heating is illustrated by the diffractograms and graphs in Figures 3–5. It is obvious that this complex nature of the observed changes is due to the joint, but opposite effect of certain factors on the position of reflexes. On the one hand, heating and the associated thermal expansion (and an increase in UCP) leads to a shift in reflections towards smaller angles. On the other hand, the subsequent (after synthesis) heating of the samples is intended to transfer them to an equilibrium state with the formation of final phases, in particular, IM, and this, given that the initial state of DVP is a state with a low iron content, should inevitably lead to an increase in iron content, a decrease in UCP, and, as a consequence, to a shift of reflexes, on the contrary, to larger angles. Moreover, the expansion factor, which itself monotonically depends on temperature, still depends on the composition that changes with heating. The second factor (concentration) is more changeable, and the diffusion exchange of components between phases is slowed down both at the beginning of heating, when the temperature is still low, and at the end, due to the approach to equilibrium. As a result, the graphs of the dependence of UCP of cubic phases (A1 and L12) and iron content on temperature have a complicated s-shaped character.

Let us consider in more detail how and through what stages the process of bringing systems to the final equilibrium state proceeds. To evaluate the composition of the DVP phases during heat treatment, it is necessary each time to bring the UCP calculated from the diffractograms to the usual temperature conditions in which the measurements were carried out, which are then presented in the ICDD databases, and these are usually temperatures of about 25 °C, for which it is necessary to know the coefficients of thermal expansion (CTE). The eigenvalue 0.896 • 10⁻⁵ K⁻¹ was taken as the basis for the linear CTE, according to the results of measurements during cooling of the phase L12 obtained
in the experiment with sample 1. (Figure 5, b). The tabulated value for platinum averages $0.94 \cdot 10^{-5}$ K$^{-1}$, for iron $1.3 \cdot 10^{-5}$ K$^{-1}$ at temperatures of 300–400 °C. [23]. Apparently, CTE in this case is not additive, but it should be borne in mind that iron has a slightly different structure, namely A2 - of the bcc type. Platinum itself, SS based on it (with the same A1 structure) and all IMs (both L1$_2$ and L1$_0$) are arranged in the same way - according to the law of three-layer densest packing.

We applied the found CTE to samples with different but similar compositions; moreover, there is reason to believe that it changes insignificantly in the investigated compositional region, especially little influence of possible deviations is at low temperatures. Thus, the corrections for thermal expansion based on the experimentally measured CTE seem to be quite satisfactory, and careful consideration of thermal expansion makes it possible to obtain very nontrivial conclusions from the measurement results.

First, the shift of reflections at the initial stage of heating to smaller angles (Figure 3, a and 4, a) and an increase in UCP of cubic phases (Figure 5, a) in samples 1 and 2 only at first glance seem to be the result of ordinary thermal expansion. A close examination shows that the growth at the beginning of heating occurs faster than follows from the pattern of thermal expansion, clearly represented by the cooling line, this is especially noticeable for sample 1. Accordingly, at the very beginning of heating, some enrichment of DVP in samples 1 and 2 occurs not with iron but platinum. With an increase in the iron content in the samples, this growth decreases, which can be explained by the increasing participation of iron in the UCP change, whose content in samples 2 and 3 is 50 and 75%, respectively, in contrast to sample 1, where it is 21%.

![Diagram](a) ![Diagram](b)

**Figure 5.** Change in UCP of cubic phases upon heating and cooling of samples (a) and corresponding change in iron content in these phases (b); graphs 1–3 correspond to samples by numbers, 4 - cooling of sample 1; horizontal dashed lines (b) show the approximate boundaries of the two-phase region (A1 + L1$_2$).

However, it is difficult to draw serious conclusions with respect to sample 3, since, as it turned out, at high temperatures, a lot of weak reflections appear on the diffractograms, which we presumably attributed to oxide phases. Their presence, apparently, somehow interferes with the penetration of iron into DVP directly during the synthesis, although penetration is sharply activated already at 300 °C, however, the concentration of iron in the cubic phase does not exceed the level of sample 2 (Figure 5, b). Obviously, some of the iron is simply taken out of the game, being bound into oxide phases.

At temperatures above 200 °C, the iron enrichment of DVP is enhanced, and the effect of decreasing UCP for this reason exceeds the effect of thermal expansion. The iron content in DVP is monotonously increasing. The structural state of DVP in sample 1 is A1, but with sample 2 it is not
entirely clear. As is known, the localization of atoms of different types at certain positions in a three-layer cubic packing according to the L1\(_2\) type leads to the appearance of so-called superstructural reflections in addition to the fundamental reflections characteristic of the usual fcc structure - A1. However, the superstructural reflections are much weaker than the fundamental ones; therefore, it is difficult to detect them against a strong background scattering while the phase is insufficiently formed (degree of ordering, CSR size). Judging by the iron content (Figure 5), DVP should initially be in the L1\(_2\) state, but only above 400 °C one can speak with relative confidence about the appearance of superstructural reflexes, when fundamental ones become sufficiently bright (Figure 4). This also applies to sample 1 with the only difference that in this case the initial state is definitely A1. In sample 2, the initial structural state can also be the A1 state, since the supersaturation of DVP with iron is low, and the formation of the densest packing during the reduction of metals is fast enough and proceeds under highly nonequilibrium conditions.

Upon further heating, the UCP of cubic DVP reaches a limit corresponding to about 20% iron, which is in good agreement with its content in the synthesis. However, the indicated composition and UCP value on the graph correspond to the two-phase state. And, indeed, at large angles at the end of the heating process, the reflections can be confidently decomposed into two according to the technology [21], each of which is a diffraction response in doublet Kα\(_1\) – Kα\(_2\) radiation (Figure 4, b). Hence, the individual UCPs of the two phases are 3.8895 Å (A1) and 3.8773 Å (L1\(_2\)), and the iron content in them is 15.9 and 21.3%. The smaller value is somewhat spaced from the boundary of the two-phase region in the given diagram (Figure 1, a), but, firstly, it cannot be absolutely excluded that equilibrium has not yet been reached, and, secondly, we are forced to compare the compositions at different temperatures: diagram plotted from 600 °C, and measurements were taken at 30 °C. The decomposition of the reflex makes it possible to estimate the phase ratio by the ratio of the areas of the doublets - 21:79. If, in this respect, the found parameters of the two phases are averaged, we obtain 3.8798 Å, whence the iron content of 20.2% is exactly the same as when calculated from the averaged diffraction angles.

Decomposition of reflections, when possible, makes it possible to more adequately estimate the crystal sizes of the phases, which in both cases reach 50–55 nm. At earlier stages, the broadening estimates are underestimated, since the reflections at T> 400 °C are not only doublet due to biphasicity, but, most likely, broadened also due to the compositional variability of crystals due to complex processes of diffusion mass transfer and fusion of small particles with the formation of larger ones. However, an estimate of about 10 nm for directly synthesized powders seems plausible and coincides with the estimate from TEM images.

Upon heating of sample 2, the reflections of the cubic phase, as in sample 1, become more intense and gradually narrowed due to the enlargement of the crystals, but, unlike sample 1, after 500 °C the transformation of the L1\(_2\) structure into L1\(_0\) begins, which is observed as a gradual formation of reflections of the tetragonal phase near the reflections of the cubic phase (Figure 4), which, on the contrary, decrease in intensity and then disappear altogether, without reaching the position and composition of the limits corresponding to the boundary between the region of existence of the L1\(_2\) phase and the two-phase region (Figure 1, a and 5, b). In sample 3, the formation of the L1\(_0\) phase begins already after 400 °C.

The measurement of the UCP of the tetragonal phase becomes possible only from 700 °C for sample 2 and from 500 °C for sample 3. The results of measurements as the temperature increases and then decreases and the corresponding calculations are summarized in Table 1.
Analyzing the data obtained, one can note a high degree of similarity between the \( V_{at} \) values reduced to 25 °C and, accordingly, \( X_{Fe} \), which characterize the final composition of the tetragonal phase. A certain satisfaction is also caused by the fact that the composition of this phase established by X-ray diffraction for sample 2 (on average 49.9% Fe) coincides with the established and confirmed elemental analysis. All this, on the one hand, indicates the completeness of the process at 800 °C and the rather complete transformation of the sample into the tetragonal phase. A certain satisfaction is also caused by the fact that the composition of this phase established by X-ray diffraction for sample 2 (on average 49.9% Fe) coincides with the established and confirmed elemental analysis. All this, on the one hand, indicates the completeness of the process at 800 °C and the rather complete transformation of the sample into the tetragonal phase, on the other hand, the correctness of measuring CTE and introducing temperature corrections. The calculated value of the iron content in the tetragonal IM in the cooling mode for sample 3 is also highly stable, the average value being 53.7%.

Below are the equations for the dependence of UCP (Å) and AAV (Å3) on temperature (°C) for the tetragonal phase in samples 2 and 3 and the linear (\( \alpha \)) and bulk (\( \beta \)) CTE (K^{-1}) obtained from them, respectively.

\[
\begin{align*}
a_2 &= 3.856 + 6.524 \times 10^{-5} T; \\
c_2 &= 3.702 - 1.864 \times 10^{-6} T; \\
V_2 &= 13.760 + 3.984 \times 10^{-4} T; \\
\alpha_a &= 1.69 \times 10^{-2} T; \\
\alpha_c &= -0.50 \times 10^{-2} T; \\
\beta &= 2.90 \times 10^{-3}; \\
\end{align*}
\]

\[
\begin{align*}
a_1 &= 3.839 + 7.271 \times 10^{-7} T; \\
c_1 &= 3.704 - 3.593 \times 10^{-7} T; \\
V_1 &= 13.65 + 3.844 \times 10^{-4} T; \\
\alpha_a &= 1.89 \times 10^{-2} T; \\
\alpha_c &= -0.97 \times 10^{-2} T; \\
\end{align*}
\]

The known thermal expansion anomaly is confirmed [18]. It is also noteworthy that the bulk CTEs are quite close for both phases - “averaged” cubic (A1 and L12) and tetragonal (L10). For comparison, \( \beta_t = 3 \times a_t = 3 \times 0.896 \times 10^{-5} T = 2.69 \times 10^{-5} T \). The reason for this proximity, in part, lies in the same organization of these structures - they are essentially organized according to the principle of three-layer closest packing, and the coordinates of all structural positions are the same. Differences are in nuances - according to the degree of filling of certain positions with different atoms.

It is believed that an important indicator associated with the manifestation of the maximum values of coercivity, among others, is the degree of anisometry of the unit cell - the ratio a/c, which should also have the greatest value [18]. Indeed, this anisometry arises due to the fact that atoms of different metals form alternating planes, and this explains the high coercivity of the equiatomic tetragonal IM. With a deviation of the composition from 50%, the layers can no longer be mono-element, that is, they become less different, and with an increase in the deviation of the composition from 50%, the
differences decrease, and the values of parameters $a$ and $c$ become closer. Upon reaching a certain limit, it becomes more advantageous to have the same structure of the layers either with complete disordering or with a different organization of selectivity in the arrangement of atoms of different kinds. In both cases, structures with an isometric cubic cell are realized, and the ratio $a/c$ becomes equal to 1.

This ratio $a/c$ in samples 2 and 3 with different compositions (49.9 and 53.7%) illustrates this pattern. Thus, at 30 °C, this ratio for an almost equiatomic sample 2 is 1.042, and for sample 3, with a slight excess of iron in the tetragonal phase, this value is less than 1.038. However, it is important to note that with increasing temperature, the ratio in both cases increases. So, for 300, 500 and 800 °C, according to the data in Table 1, we obtain 1.048 and 1.044, 1.053 and 1.052, 1.060 and 1.060, respectively. But the growth of the ratio in this case does not at all mean that the orderliness is growing. Of course, the opposite is true, high temperature promotes disordering. The ratio increases for another reason - due to the anomalous thermal expansion caused not by the order-disorder parameters, but by the specificity of thermal vibrations in the given structure. One should pay attention to convergence of ratios for different samples. This means that the high-temperature disorder in both samples reached such a high level that a small concentration difference is leveled.

Obviously, simple elemental analysis to establish the IM composition is not enough, since some of the substance may be outside the IM structure, as was the case for sample 3. In [18], the sample with the highest ratio of 1.035 showed the highest coercivity, but the true composition of the IM under study was unknown, although the goal was to obtain exactly equiatomic IM. The X-ray method used in this work for determining the composition of IM, like any mixed phase, seems to be quite promising.

4. Conclusion

Summarizing the observations and calculations made, the following can be noted in conclusion.

First, a significant part of the substance immediately after the synthesis of the considered systems is diffraction invisible. This DIP contains particles with different composition and structural organization, including those rich in platinum, which causes a slight increase in the platinum content in DVP at the very beginning of heating, especially in samples rich in it. Preliminary estimates of the composition of DIP, apparently enriched in iron as opposed to DIP, show that the average composition can correspond not only to the region of existence of IM Fe$_3$Pt (L1$_2$), but also FePt (L1$_0$).

Secondly, the particles obtained during the synthesis are distributed in such a way that the richer platinum and initially partially diffractively visible form the core, and structurally less organized and smaller particles form a loose shell around the core. The iron content in this microstructure increases from the center of the core to the periphery.

Third, at each moment of heat treatment (for 1–2 hours of isothermal mode), the processes of equilibration do not take place in the entire system as a whole, but only in a certain zone, including the core of the microstructure and a limited peripheral region adjacent to it. Of course, these processes include the diffusion exchange of components between particles of different composition, but the result is the same - smaller peripheral particles-crystals with a higher concentration of iron attach to larger core crystals, respectively, the iron content in them increases, while the amount of DVP increases.

Fourthly, the observed significant increase in the size of the DVP crystals occurs mainly not due to the attachment of small DIP particles to them, but due to the "usual" high-temperature sintering - the connection with each other. Even a fivefold enlargement of a particle in the process of successive attachment of small peripheral particles to it leads to an increase in size by only 70%, in fact, the increase in size is a multiple (4–6 times).

Fifth, elemental analysis of the sample as a whole is not enough to control the composition of IM; an analysis of a specific phase is required. The most productive method seems to be the X-ray method used in the work, based on data on the composition and lattice parameters.
Thus, the samples obtained by the MRPS method using hydrazine as a reducing agent are promising for the creation of nanostructured systems: they contain particles of the optimal size (about 10 nm), mainly of a noble metal, capable of attaching from the environment an amorphous material rich in iron (or other transition metal), and form both monophase and equilibrium two-phase systems. As measures to prevent massive co-crystallization of the initially formed nuclei, various methods of dispersion can be proposed for testing: ultrasonic dispersion, synthesis in the presence of indifferent salts, and others. Hydrazine is convenient as a reducing agent due to the fact that the products of its oxidation - gaseous nitrogen and water - are easily separated from the finished product.

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