On structural changes in the YuNDK35T5AA alloy during thermomagnetic treatment

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Abstract

Parameters of the weakly tetragonal lattices of the $\alpha'$- and $\alpha$-phases were determined in the YuNDK35T5AA (35\%Co-14\%Ni-7.5\%Al-4\%Cu-5\%Ti) alloy single crystals grown out of the melt. It is shown that the single crystal thermomagnetic treatment results in the increase of the tetragonality degree of the both phases and of the elementary cell volume in the $\alpha$-phase lattice, whereas the elementary cell volume of the $\alpha'$-phase decreases, the magnitude of the nonconformity of the $\alpha$ parameters of the $\alpha'$- and $\alpha$-phase lattices increases significantly. The X-ray dissipation patterns comparison was carried out on the modulated structure of the YuNDK35T5AA alloy after the single crystal growing, after their additional high temperature annealing with the air cooling and after the thermomagnetic treatment was applied; the modulation periods were determined.

The present work was carried out as the continuation of the structural state investigation of the Ticonal type YuNDK35T5 alloy permanent magnets [1]. Magnet manufacturing engages growing of single crystals with the given alignment [100] out of the melt and their thermomagnetic treatment (TMT) [2]. Selection of the TMT optimum parameters has led to the study of the isomorphal decomposition of the oversaturated solid solution in the Ticonal alloy by the X-ray structure analysis and the electron microscopy method [3-6]. The purpose of our work was to compare the structure of the as-grown single crystals with the one after the TMO of magnets to achieve a more complete understanding of the structural changes in the YuNDK35T5AA alloy during the TMT. This required to certify the phase structure in the grown single crystals, to specify the parameter values of the $\alpha'$- and $\alpha$-phase lattices in the single crystals subjected to TMT and also to compare the X-ray diffusion dissipation patterns of the single crystals in the as-grown state and after the TMT.

Investigation methods

The YuNDK35T5AA alloy single crystals were obtained by the directional crystallization out of the melt using the Bridgman method on the seeds with the orientation [100] in JSC “Magneton”. Growing was carried out in the one-position installation “Crystal EM” with the graphite resistance heater. The heater lifting rate was 3 mm/min at the temperature gradient in the melt before the
crystallization front 10 deg/mm. Single crystals were cooled to the room temperature in the furnace chamber. The diameter of the cylinder shape single crystals was 24 mm, their length – 120-130 mm. Samples for investigations were cut out of the middle part of the single crystals. Some of them were exposed to the homogenizing annealing\(^1\) at 1265\(^\circ\)C during 30 minutes with the subsequent air cooling.

Cylindrical magnets with the diameter 22 mm and height 10 mm, selected for the comparative study, were manufactured in JSC “Magneton”. Beforehand the YuNDK35T5AA alloy single crystals with the alignment [100] were grown in the commercial multi-position installation “Crystallizer 203” \(^1\). Single crystal ingots were exposed to the standard TMT. It included heating to the temperature 1250\(^\circ\)C and homogenization at this temperature during 20-25 min, cooling from 1250\(^\circ\)C to 800\(^\circ\)C at the rate not less than 150 deg/min. Then the ingots were kept 10 minutes in the isothermal bath at the temperature 795±5\(^\circ\)C with the magnetic field \(H\) with the strength not less than 240 kA/m applied along the crystallographic direction [001]. The TMT was completed with the two-stage tempering: 5 hours at 640\(^\circ\)C and 20 hours at 560\(^\circ\)C. Data on the perfection of the magnets crystal structure are given in [1].

The single crystal samples\(^2\) after growing, after their high temperature annealing with rapid cooling and after the TMT were cut parallel to the crystallographic planes \{100\}, (110) and (111) with the spark tool. The cut surfaces were ground and exposed to the electrolytic polishing. The sample structure was investigated by the X-ray diffractometry and the crystal rotation X-ray method. With the apparatus “DRON-1” structural and superstructural reflections with the small and large sum of the indexes squares \((\Sigma H_i^2)\) from the aggregation of planes \{100\} and also from the planes (110) and (111) were obtained. \(K_{\alpha}Cr\), \(K_{\beta}Cr\), \(K_{\alpha}Co\), \(K_{\beta}Co\), \(K_{\alpha}Mo\) and \(K_{\beta}Mo\) X-ray radiations of different hardness were applied. The distance from the source to the sample along the falling beam was 180 mm. Rotating crystal patterns were taken in the \(K_{\alpha}Cr\)-radiation. The distance from the sample to the film was 165 mm. The (100) and (200) reflections were obtained while rotating the crystal around the axis coinciding with the [100] direction, the (110) reflection was obtained when the crystal was rotated around the axis coinciding with the [1 \(\bar{1}\) 0] direction.

**Results of the investigation and their discussion**

Earlier it was shown \(^7\) that the YuNDK35T5AA alloy single crystals in the as-grown state mainly consist of the \(\alpha'\)- and \(\alpha\)-phases which are the decomposition products. Their structure was studied according to the X-ray patterns taken in the Cr-radiation with the RKU-114 camera. It was

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1. The annealing temperature falls on the one-phase region of the \(\alpha\)-solid solution existence \(^2\).
2. The term “single crystal” is used instead of the more exact “pseudo single crystal”.

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found that the \( \alpha' \)- and \( \alpha \)-phases have the bcc-lattice. The application of the X-ray diffractometry allows to make these data more correct.

During the analysis of the diffraction patterns of the grown single crystals some widening of the \( \alpha \)-phase (310) line was observed compared to the (222) line. It is well known that the transformation of the cubic structure of a substance into the tetragonal one leads to the widening or splitting of the diffraction lines. The exception are the lines from the planes with three identical indexes. Further, the splitting of the \( \alpha' \)-phase (400), (600), (800) lines plotted in the \( K_\beta \)Mo-radiation was observed (fig. 1). Their incomplete segregation into two lines can be attributed to the small degree of the \( \alpha' \)-phase lattice tetragonality in single crystals after growing.

Investigation of the phase composition of the YuNDK35T5AA alloy single crystals exposed to additional high temperature annealing and air cooling was carried out. It was found that they also consist of the \( \alpha' \)- and \( \alpha \)-phases although the solid solution decomposition time was not long. The \( \alpha' \)-phase diffraction lines configuration is indicative of the tetragonal distortion of its lattice. Line (600) or line (800) of the tetragonal duplicates and line (444), which were obtained in the \( K_\alpha \) and \( K_\beta \)Mo-radiations, were used to determine the \( \alpha' \)-phase lattice parameters in the single crystals in the as-grown state and after the homogenizing annealing.

In the process of the structural specification of the \( \alpha \)-phase in the single crystals as-grown and after the homogenizing annealing there occurred difficulties. The \( \alpha' \)-phase strong lines merge with the weak indistinct \( \alpha \)-phase lines thereby not allowing to determine the angular position of the latters. This is not relevant to the \( \alpha' \)- and \( \alpha \)-phase lines from the planes with three identical indexes, these lines are divided. According to the data by the authors \[4, 8\] the YuNDKT alloys exposed to the TMT contain two isomorph phases which have tetragonal lattices with different \( \alpha' \) periods and similar \( c \) period. Assume that the \( c \) parameter of the \( \alpha' \)- and \( \alpha \)-phase lattices in the case of the YuNDK35T5AA alloy single crystals under consideration is identical. Then using \( c \) obtained for the \( \alpha' \)-phase and the angle \( \theta \) corresponding to the line (444) from the \( \alpha \)-phase in the \( K_\alpha \)Mo radiation one can calculate the \( \alpha \) parameter of the \( \alpha \)-phase lattice. Parameters of the weakly tetragonal lattices of each phase in the single crystals in the as-grown state and after the high temperature annealing with the air cooling coincide (table 1).

In the work \[1\] the lattice parameters of the highly magnetic \( \alpha' \)- and the weakly magnetic \( \alpha \)-phases in the YuNDK35T5AA alloy after the TMT were determined. To make them more correct the lines (080), (008), (444) of the magnets in the \( K_\alpha \)Mo radiation were plotted. The parameters obtained with the help of these lines are presented in table 1. The diffraction investigation shows that the TMT of the YuNDK35T5AA alloy single crystals leads to the formation of the \( \alpha' \)- and \( \alpha \)-phases which have different lattice parameters compared to the synonymous phases in the single crystals as-grown and after the homogenizing annealing. The change of the lattice parameters of the
both phases together with the increase of the elementary cell volume in the α-phase lattice and some
decrease of it in the α'-phase lattice (table 1) indicates the change of the chemical composition of
each of the phases. The component exchange between them leads to the Fe and Co enrichment of
the α'-phase and to the Ni, Al, Ti enrichment of the α-phase [2,9]. This process was developed
during the two-stage tempering concluding the TMT. It should be noted that the single crystals
being cooled down after solidification in the furnace chamber are not exposed to a long term
 tempering.

The discrepancy value of the α parameters of the α' and α-phase lattices

\[ \frac{a_a - a_{a'}}{a} \]

is much greater in magnets than in single crystals as-grown and after the homogenizing annealing
(table 1). The tetragonality degree of the lattices of the both phases which had been formed during
the TMT was found to be increased (table 1). The tetragonality of the isomorph α'- and α-phases
with different lattice periods α are considered as the result of the effect of the anisotropic elastic
distortions which arise at their coherent conjugation [10, 11]. The authors [8] made the approximate
calculation of the stresses induced by the tetragonal distortion of the α' and α-phase particle lattices
in the Ticonal type alloys.

In view of the revealed tetragonality of the α'-phase lattice in the single crystals in the as-grown
state there arose the question about its axes orientation relative to the directions <100> set by the
seed crystal. Lines \{600\} from the three coordinate planes in the KβMo radiation were plotted.
Judging by the peculiarities of their configuration the axes α and the axis c of the α'-phase lattice are
located parallel to each cubic axis. The similarity of the shape of all lines allows to assume that the
amount of the α'-phase oriented by the axis c along any of the <100> directions does not differ
appreciably in the grown single crystals. For the single crystals exposed to the TMT the location of
the axis c of the α'- and α-phase particle lattices along the direction [001] coinciding with the H
field vector direction and the presence of the strong particle shape anisotropy in this direction were
confirmed [1].

The YuNDK35T5AA alloy single crystals as-grown, after the high temperature annealing and
after the TMT are characterized by different X-ray diffraction patterns depending on \( \Sigma H_i^2 \). Near
sharp main (Bragg) lines with small values of \( \Sigma H_i^2 \) diffusion satellites are located (fig. 2a-c, 3b).
The lattice parameter of the mean composition solid solution (\( a_{mean} \)) calculated according to the
main maximum positions is \( 2.878\pm0.001 \) Å for the single crystals as-grown and after the
homogenizing annealing, \( 2.883\pm0.001 \) Å for the single crystals after the TMT. The broad lines
corresponding to the higher \( \Sigma H_i^2 \) value do not have satellites. They belong to the α'- and α-phases,
solid solution reflections are absent (fig.1). There is no single crystal phase with the bcc-lattice and
the parameter \( a_{mean} \) in the alloy. The authors [6] came to the same conclusion.
According to the ideas \[10,12\] survey in the reflections with small \(\sum H_i^2\) values leads to the pattern of the coherent X-ray dissipation from some “mean” lattice of the YuNDK35T5AA alloy consisting of two type microregions. The microregions correspond to the \(\alpha'\)- and \(\alpha\)-phase particles. In the opposite space their site dimensions are much larger than the distance between the sites. For this, overlapping of the reflexes takes place and the particles of both phases dissipate coherently. When the survey is made at a higher \(\sum H_i^2\) value the independent of one another (incoherent) dissipation by the \(\alpha'\)- and \(\alpha\)-phase particles is observed.

The YuNDK35T5AA alloy single crystals possess the modulated structure which results in the satellite emergence in the X-ray patterns. Its period \((Q)\) was determined by the Daniel and Lipson formula:

\[
Q = \frac{(H_i)_{\text{max}} \cdot \tan\theta}{\sum H_i^2 \cdot \Delta \theta \cdot a_{\text{mean}}},
\]

where \(\theta\) is the Wolf-Bragg angle, \(\Delta \theta\) is the angular distancing of the satellite from the main line corresponding to the mean composition solid solution, \((H_i)_{\text{max}}\) is the index having the highest value in the given three indexes. The superstructural line (100) in the \(K_{\alpha}\)Cr radiation was used. \(Q\) is 184\(a_{\text{mean}}\) (530 Å) for the single crystal as-grown, 93\(a_{\text{mean}}\) (268 Å) after the high temperature annealing, 118\(a_{\text{mean}}\) (340 Å) after the TMT. Following the methods [13] the \(\alpha'\)-phase particle dimensions \((D)\) in the direction [010] for the magnet were estimated. The line (060) plotted in the \(K_{\alpha}\)Mo radiation was used. The D value turned out to be \(~150\) Å. This is in satisfactory agreement with the modulation period.

The obtained modulation period values in the YuNDK35T5AA alloy correspond to different solid solution temperature-time decomposition intervals and the modulated structure formation. When single crystals are grown at a small speed this process proceeds at temperatures close to the equilibrium temperature of the decomposition beginning \((T_s)\). According to the data [2] \(T_s=855^\circ\text{C}\). When the TMT of the single crystal ingots is carried out the solid solution decomposition temperature is \(795\pm5^\circ\text{C}\), that is a little lower than the Curie point of the \(\alpha'\)-phase precipitating at \(T_s\). On samples which were exposed to the high temperature annealing with the subsequent air cooling the decomposition must proceed at the lowest temperatures. According to the alloy cooling curves [2] the time of their cooling from 1250°C to 750°C is approximately 2 min. The YuNDK35T5AA alloy samples have not only different modulated structure periods but also different \(\sum H_i^2\) values at which the transition to the independent X-ray dissipation by the \(\alpha'\)- and \(\alpha\)-phase particles takes place. In the diffraction patterns of the single crystals exposed to the TMT satellites near the superstructural (100), (010) and structural (110) main reflections were observed (fig.2c, 4c). The lines (200) and (020) were obtained practically as the result of the independent dissipation by the \(\alpha'\)- and \(\alpha\)-phase particles (fig.3c). In the case of the single crystals in the as-grown state the satellites
are located near the reflections \{100\}, (110), \{200\} (fig.2a, 3a, 4a), the main maximum (300) is still noticeable. In the diffraction patterns of the single crystals after the high temperature annealing the satellites are present in many reflections: \{100\}, (110), (111), \{200\}, (300)(fig.2b, 3b, 4b), the main maximum (400) is visible.

A complex profile of the diffraction reflex (200) of the single crystal as-grown should be noted (fig.3a). Such profile can be obtained when superposing the X-ray dissipation on the modulated structure and at the independent dissipation by the weakly tetragonal α'- and α-phase particles. In the work [6] such superposition for the reflexes (110) and (220) of the Alnico 8 alloy is presented. Our observations allow to agree with the authors [6] regarding the gradual transition from one X-ray diffraction pattern to another at the increase of the $\Sigma H_i^2$ reflection.

According to the results of the electron microscopy investigations [5] Ticonal type alloy quenched at 1250°C into water and tempered at 700°C has an original three-dimension periodic structure. It represents the aggregation of colonies in each of which the rod shaped particles interchange along one of the three crystallographic directions of the matrix <100> with the minimum modulus of elasticity. The presence of the satellites near the reflections (100), (010), (001) points to the formation of such structure in the grown YuNDK35T5AA alloy single crystals and also in the single crystals exposed to additional homogenizing annealing with the subsequent air cooling. The difference in the X-ray diffusion dissipation patterns of the single crystals as-grown and after their homogenizing is related mainly to different modulation period. We suppose that the chemical composition of the precipitates in these objects differs little, because the synonymous phases have similar lattice parameters (table 1). A feature of the diffraction pattern of the single crystals exposed to the TMT is the absence of the satellites near the line (001) though they are located close to the reflections (100) and (010). The periodic concentration distribution manifests itself only in the directions [100] and [010], which together with the crystallographic orientation of the particles along [001] and their strong shape anisotropy in this direction correspond to the formation of the two-dimension modulated structure. Exactly such structure was observed in the electron microscopy photos of the (001) and (100) sections of the high coercivity Ticonal alloy [8, 10]. In addition to the change of the periodicity character, the TMT of the YuNDK35T5AA alloy leads to the increase of the component concentration fluctuation amplitude since in magnets the increase of the difference of the α'- and α-phase elementary cell volumes ($\Delta V_{\alpha', \alpha}$) was found. The $\Delta V_{\alpha', \alpha}$ values were estimated to be 0.91 Å$^3$ for single crystals exposed to the TMT, 0.73 Å$^3$ for single crystals as grown and after additional high temperature annealing with air cooling.
Conclusion

1. In the YuNDK35T5AA alloy single crystals grown out of the melt and consisting mainly of the α′- and α-phases a weak tetragonality of the α′-phase lattice with the parameters $\alpha = 2.863$ Å, $c = 2.873$ Å was revealed. Based on the literature data about the solid solution decomposition character in the YuNDKT alloys the conclusion was made that the α-phase also has a weakly tetragonal lattice. Its parameters were estimated to be $\alpha = 2.907$ Å, $c = 2.873$ Å.

2. The TMT of the YuNDK35T5AA alloy single crystals results in the increase of the α′- and α-phase tetragonality degree, in considerable raise of the nonconformity value of the α parameters of the both phase lattices. At the same time the elementary cell volume in the α-phase lattice increases, whereas in the α′-phase it decreases slightly. The determined alteration of the parameters as well as of the elementary cell volumes indicates the change of the α′- and α-phase chemical composition and the increase of the periodic fluctuation amplitude of the component concentration between the neighboring microregions in the alloy exposed to the TMT.

3. The YuNDK35T5AA alloy single crystal diffraction pattern is characterized by the presence of satellites close to the reflections with low indexes ($H_i$). The modulated structure period equals $184a_{\text{mean}}$ after growing, $93a_{\text{mean}}$ after the high temperature annealing with air cooling and $118a_{\text{mean}}$ after the TMT. The independent X-ray dissipation by the α′- and α-phase particles was obtained in the reflections with $\sum H_i^2 > 4$ on single crystals after the TMT, in the reflections with $\sum H_i^2 > 9$ and with $\sum H_i^2 > 16$ on single crystals as-grown and after their homogenizing annealing correspondingly. The TMT results in the alteration of the modulated structure periodicity character in the YuNDK35T5AA alloy.

Acknowledgment

The authors are grateful to Professor Ermolenko A.S. for his interest in the work and participation in the discussion of its results.
References

1. Agapova E.V., Gundyrev V.M., Sidorov E.V. Study of the crystal structure of the Ticonal type alloy magnets. FMM. 2003, v.96, no.4, pp.79-84.
Table 1. Lattice parameters of the $\alpha'$- and $\alpha$-phases in the YuNDK35T5AA alloy single crystals

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<tr>
<th>Objects of investigation</th>
<th>Lattice parameters</th>
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<td>$\alpha$, Å</td>
<td>$c$, Å</td>
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<td>2.873</td>
<td>1.003</td>
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<td>2.907</td>
<td>2.873</td>
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<tr>
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<td>After homogenization</td>
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<td>After TMT</td>
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The accuracy of the determination of the $\alpha'$ – and $\alpha$ – phase lattice parameters in the single crystal after the TMT is $\pm 0.0003$ Å, in the single crystals as-grown and after the homogenization - $\pm (0.001 – 0.002)$ Å.
Fig. 1. Lines \{600\} of the $\alpha'$- and $\alpha$-phases of the YuNDK35T5AA single crystal as-grown plotted in the $K\beta$Mo radiation. On the left is the tetragonal duplicate of the $\alpha$-phase in the rays with $\lambda K\beta_1$; on the right is the line consisting of two indivisible lines: very weak from the $\alpha$-phase in the rays with $\lambda K\beta_1$ and weak from the $\alpha'$-phase in the rays with $\lambda K\beta_2$. 
Fig. 2. Satellites of the first (↓) and second (↓) orders near the main (Bragg) reflection (100) of the YuNDK35T5AA single crystals as-grown (a), after the high temperature annealing (b), after the TMT (c) (the rotation axis [010], KαCr radiation). The following calculation speed measuring range was used: a - 2x10³, b - 5x10³, c – 1x10³ imp/sec.
Fig. 3. Diffraction pattern in the reflection (200) obtained on the YuNDK35T5AA single crystals as-grown (a), after the high temperature annealing (b), after the TMT (c) (the rotation axis [010], KβCr radiation). The main maximum position is shown. The calculation speed measuring range 5×10³ imp/sec is used.
Fig. 4. X-ray patterns (x4.0) of the YuNDK35T5AA single crystal rotation after growing (a), after the high temperature annealing (b), after the TMT (c) taken in the reflection (110) (the rotation axis [1 0 0], KαCr radiation). The first order satellites near the main maximum are shown.