Moessbauer study of structure changes in Fe-Co-Cr alloys upon their alloying with W and Ga

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Abstract. Changes in the structure of the magnetically hard alloys Fe-Co-Cr alloyed with W and Ga to reach high mechanical properties were investigated. Moessbauer spectra processed in several steps present information on the influence of both different stages of treatment routine and concentration variations on the composition and fine peculiarities of the components that constitute the required structure states.

1. Introduction
Alloys on the basis of the Fe-Co-Cr system are magnetically hard materials which offer much promise as materials for manufacturing disc rotors of high-speed hysteresis engines. To realize this potentiality, different methods of improvement of their mechanical properties have been sought for, such as alloying elements and heat treatments. As a result of such trials, some advantageous combinations of strength, plasticity, and coercive force were gained [1]. Quite successful, in terms of enhancing strength and plasticity, alloys were found doped with W and Ga after quenching, rolling, and subsequent heat treatment. To understand the processes that are responsible for high mechanical properties, it is necessary to know the roles of alloying additions in the formation of structure of the corresponding states. X ray and electron microscopy diffraction methods failed to present sufficient information on the changes in the phase composition of the alloys. To this end, the objects were studied using Moessbauer spectroscopy.

2. Experimental details
The Moessbauer spectra were taken in the mode of constant acceleration with a $^{57}$Co source in a chromium matrix at 300K. The spectra were processed using an MSTOOLS program package [2] which allows, along with directly fitting spectra, multi-core distributions of the probability density of the hyperfine fields P(H) to be calculated if there are reasons to assume that different parts of a structure present different linearity in the relationships of at least two of the main Moessbauer parameters. We examined alloys which contained 20-24 wt.%Cr, 12-17 wt.%Co, 7-9 wt.%W, and 0-4 wt.% Ga after a treatment for the optimal state which includes quenching from 1300°C, cold deformation to 60% and heat treatment at 630°C. As a reference, spectra of the ternary composition Fe-22Cr-15Co were recorded, which served as the starting point for the series to be investigated first and then, to be compared to some other compositions.
3. Results and discussion

Figure 1 shows spectra and distribution functions for three compositions after quenching. It is seen that all the three distributions have the form featuring in the main a solid solution, though heterogeneous. In the case of the ternary alloy the effects of short-range order are pronounced to a greater extent, (even with the formation of nonmagnetic regions), whereas introduction of both W and Ga results in smoothing the distribution shifted towards lower fields. If an annealing for optimal properties is performed immediately after quenching, a common modulated structure is realized, which does not meet the requirements on strength and plasticity. An intermediate cold deformation is necessary, which might serve as a means of affecting the mechanism of phase transformations.

Changes in the alloy structure after rolling, common for the studied compositions, are exemplified by the spectra and distributions in Figure 2. The structure is seen to become more homogeneous. The most remarkable difference is displayed in the relative intensities of the outer and middle peaks in the spectra, which means reorientation of magnetic moments toward the normal to the sample plane. After annealing for the optimal state P(H) represents a continuous set of coordinations of Fe atoms, including those in low-to-zero field. To separate contributions from the structure regions with different compositions an attempt was made to construct two-core distributions.

Knowing that a common ternary alloy after annealing represents a modulated structure consisting of two Fe-Cr- and Fe-Co-based phases [3], we suggest two P(H) functions with different correlations of isomeric shift and hyperfine fields and trace the changes in these spectral contributions versus composition, see Figure 3. Already after addition of W the regions representing the next-to-zero field peak are formed, while the form of the high-field distribution becomes more distinct testifying to a more profound phase separation at least in chromium. Addition of Ga results in increasing intensities in the field range 200-300 kOe.

Based on the qualitative information about structure components taken from the P(H) shape for the sample without Ga, we performed fitting of the spectra with three sextets related to the high-field contribution, one sextet from the low-field contribution, and a nonmagnetic part, Figure 4. Then, we subtracted low-field and nonmagnetic subspectra and the remainder spectra were again analyzed using the P(H) apparatus. The results are shown in Figure 5. The changes in the structure of these regions are clearly seen. With increasing Ga content, the intensity of the highest-field peak related to the 0 -impurity - atoms configuration in the first coordination shell of iron atoms decreases, with its
position being shifted toward lower fields, Figure 5a. Judging by the changes in the width of distributions one can say that they become more inhomogeneous in concentration of impurity atoms. The similar changes in the samples of different compositions after optimal treatment are exemplified by the P(H) distributions in Figure 5b, which testifies that changes are common for these alloys.

Using the literature data on the H versus Cr concentration dependence and isomeric shifts for the binary compositions [4, 5] we managed to determine the phase compositions as follows: the paramagnetic phase is close to Fe₃W₂, with its volume fraction being insensitive to the presence of Ga; the low-field areas contain about 50%Cr (including possibly the rest of W) and, with increasing Ga, change in relative concentration of Fe from 20 to 15%, whereas the high-field areas take up from 75 to 81% Fe, varying in concentration of (Cr, Ga) from 8 to 15%. The changes in the parameters after introduction of W allow one to make a conclusion on a more pronounced phase separation with the formation of W-enriched regions of a new kind. After addition of Ga, the average parameters of spectral contributions change, though less remarkably than the position and intensities of partial lines which constitute the P(H) functions shown in Figure 5a,b. If to analyze these distributions by fitting them with a set of Gaussian lines of equal width, one can conclude that not only the very parameters of already existing coordinations are changed by introduction of Ga, but some new ones appear with increasing its concentration, which purports the formation of new configurations of impurity atoms around iron atoms and growth of inhomogeneity of elemental content over precipitates.
4. Conclusion
1. Intermediate plastic deformation affects the process of structure formation after optimal treatment independently of the initial alloy composition.
2. Introduction of W results in the appearance of a new type of paramagnetic regions enriched in W, whose amount is almost indifferent to the additional alloying with Ga.
3. Changes in the parameters of the P(H) distributions for the quaternary alloys in the optimal state allows one to conclude that Ga localizes itself in the magnetically hard part of the structure and affects the redistribution of Cr through a kind of interface between the chromium-rich and cobalt-rich structure constituents.

Acknowledgements
The work was supported by the Russian Foundation for Basic Research, grant № 08-02-99-077 and the Program of RAS №27.

References
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