Simulation of heat transfer processes during the growth of crystals of the NiFeGaCo alloy

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Abstract. Long crystals of NiFeGaCo alloy with shape memory effect, including magnetically controlled ones, were obtained by the methods of Czochralski and Stepanov. A strong influence on the properties of crystals of dendritic formations, especially noticeable in the initial part of the crystal, has been revealed. In order to optimize the growth experiments, the heat transfer process in the thermal growth zone was simulated. It is shown that the formation of dendrites is due to a change in heat transfer during growth, which leads to an increase in the axial temperature gradient near the crystallization front as the crystal grows. This fits into the framework of the classical concepts of the transition from dendritic growth to normal growth.

1. Introduction
In recent decades, crystals of shape memory alloys and, in particular, NiFeGaCo have been intensively studied by many researchers [1-3]. In addition to the shape memory effect, these crystals are interesting for the possibility of obtaining large reversible magnetically induced strains, superelasticity, and the effect of high-speed memory strain recovery [4].

Currently, NiFeGaCo crystals are grown by the Bridgman method [5] for research purposes only. The implementation of the functional properties of these crystals in new apparatus and devices requires further development of the technology for obtaining highly perfect crystals, including large lengths, which is provided by the methods of crystallization of Czochralski and Stepanov.

The aim of this work was to grow Ni_{49}Fe_{18}Ga_{27}Co_{6} crystals, study their structure, and simulate heat transfer processes to optimize the crystallization regime

2. Experiment
Ni_{49}Fe_{18}Ga_{27}Co_{6} crystals were grown by the Czochralski method from the free surface of the melt and by the Stepanov method using a shaper floating on the melt surface. Crystals of the [001] orientation up to 250 mm in length and 5–8 mm in diameter were grown on a single-crystal seed. A diagram of the growth zone and a photo of a growing crystal are shown in Figure 1.

The crystal structure was revealed on transverse thin sections etched in a mixture of acids (3 parts nitric and 1 part hydrochloric). The details of the structure were studied using a Carl Zeiss Jena Amplival optical microscope and a Phenom PROX scanning electron microscope. The latter was also used to control the chemical composition by the EDS method. The measurements showed that the composition changes insignificantly along the length of the crystal and corresponds to the initial composition Ni_{49}Fe_{18}Ga_{27}Co_{6}.
Figure 1. Schematic of the thermal growth zone (a) and a photograph of the crystallization process during growth using a shaper (b). 1 - crystal, 2 - melt, 3 - crucible, 4 - thermal insulation, 5 - inductor, 6 – shaper.

The temperature of the onset of the phase transition ($M_s$) into martensite was determined when the sample was cooled at a rate of ≈ 0.04 deg/min. The polished end surface of the sample was visually observed and photographed. The time from the appearance of the first martensite needles to their spread over the entire section was 18 minutes. Under these conditions, the martensite structure in the crystal forms and develops in the temperature range of 9.5–9.0 °C. The reverse martensitic transition occurs in the temperature range 15-16 °C.

The samples cut from the crystal along the crystal elongation axis were deformed by uniaxial compression and subsequent heating above the temperature of the reverse martensitic transformation completely restored their original shape. At the same time, the magnitude of the shape memory strain depended on the part of the crystal from which the sample was cut.

It was also found that the maximum concentration of dendrites was observed in the initial part of the crystal, then gradually decreased and at a distance of about 160 mm from the seed, dendrites were completely absent (Figure 2).

Figure 2. Photographs of thin sections of the cross-section of a NiFeGaCo crystal with a characteristic dendritic structure at a distance of 15mm (a), 100mm (b) and 160mm (c) from the seeding site.
Such inhomogeneity of the structure along the length of the crystal can be associated either with a change in the chemical composition, or (and) with a change in thermal conditions during crystallization. Since measurements of the chemical composition along the length of the crystal showed insignificant changes, the formation of a dendritic structure in its initial part is most likely associated with a change in thermal conditions at the crystallization front.

3. Simulation

To study of structural inhomogeneity along the length of the crystal in order to optimize the thermal zone, the process of heat exchange during the cultivation of the crystal of this alloy was carried out. The temperature distributions in the melt and crystal were calculated, as well as the hydrodynamics of the melt flow in the crucible for successive stages of growth with crystal lengths of 50, 100, and 160 mm.

The simulation was carried out using the Basic CGSim software package for an induction heating zone. The calculations were made for the case of growing a crystal 5 mm in diameter by both the Czochralski method and the Stepanov method using a floating shaping plate with a hole.

The growth rate was 60 mm/h for the basic design version, the rotation rate for the Czochralski method was 30 r/min. The crystallization temperature was taken equal to 1600K [3].

Since the properties of the FeNiGa (Co) alloy at high temperatures are still unknown, the data for the Fe-Ni alloy [6] were used: the thermal conductivity of the crystal is 56.2 and the melt is 51.5 W/(m K), the specific resistivity is 1.4 $10^6$ Ω m. The latent heat of fusion was taken to be $2.8 10^5$ J/kg, the emissivity of the crystal was 0.3, and that of the melt was 0.4, the growth angle was 15 degrees, and the specific density of the crystal was 7.9 g/sm$^3$ and that of the melt was 9.57-1.24 $10^{-3}$ T g/sm$^3$ (T in K).

In figure 3 shows pictures of isotherms and lines of melt flow for two design options with a crystal length of 160 mm.

![Figure 3](image)

**Figure 3.** Picture of isotherms (on the right) and lines of hydrodynamics of melt flows (on the left) for the cases of crystal growth according to Czochralski(a) and Stepanov(b). The line isotherm is shown with a resolution of 5 K.

The temperature distribution along the growth axis of the ingot for the Czochralski method with crystal rotation and the Stepanov method with a shaper are given in figure 4. It can be seen that both the temperature distribution and the pattern of the melt flow differ little from each other. The temperature gradient near the crystallization front for the Stepanov method is slightly higher, which is associated with the screening effect of the shaper. It can be expected that when crystals in the form of thin ribbons are grown by the Stepanov method, the differences between the temperature fields and the hydrodynamics of the melt will be more significant.

Figure 5 shows a comparison of the temperature distribution near the crystallization front along the growth axis for crystal lengths of 50, 100, and 160 mm. Calculations show that as the crystal grows and its length increases, the temperature gradient in the melt near the crystallization front increases also from 8 K/mm to 9.7 K/mm for the Czochralski method and up to 11.7 K/mm for the Stepanov method (Figure 6).
The influence of some technological parameters and design features of the growth unit on heat transfer in the growing zone was also modeled. It is shown that the change in the growth rate in the range from 10 to 240 mm/h has little effect on the temperature distribution along the axis, while the change in the configuration of the heat shields is more significant. So, for example, the absence of an upper screen increases the temperature gradient at the crystallization front to 16.4 K/mm, but at the same time the total heating power consumption also increases by 20%.

Figure 4. Temperature distribution along the crystal axis, when grown by the Czochralski (1) and Stepanov (2) methods, FC - the position of the crystallization front.

Figure 5. Temperature distribution near the crystallization front in the melt along the Y axis of the crystal when grown by the Stepanov method at different stages of growth; 1, 2 and 3 - crystal lengths 50, 100 and 160 mm, respectively, 4-variant of calculation for a length of 100 mm, without the upper shielding cover.
4. Discussion

Thus, comparing the simulation results with experimental facts, it can be noted that there is a correlation between an increase in the temperature gradient in the melt at the front with an increase in the crystal length and the disappearance of dendrites. This corresponds to the classical concepts of the formation of a dendritic structure upon concentration supercooling of the melt.

According to [7], the criterion for the transition from cellular and dendritic growth to normal (planar) is an increase in the $G_l/V$ parameter, where $G_l$ is the temperature gradient in the melt at the crystallization front and $V$ is the growth rate. An increase in the temperature gradient leads to a decrease in the height of the liquid-solid zone at the crystallization front, in which the dendritic structure is directly formed. On the other hand, an increase in the growth rate leads to an increase in supercooling under the crystallization front, which increases the possibility of the formation of a dendritic structure.

The relationship between the $G_l/V$ parameter and the formation of a dendritic structure has been observed in many crystallization processes. For example, in [8], the formation of a dendritic structure during the crystallization of a ferromagnetic alloy Co$_{37}$Ni$_{34}$Al$_{29}$ at a high temperature gradient was studied.

It was found that a flat crystallization front and single crystal growth occurs at a large $G_l/V$ value, while a 10-fold decrease in the value of this parameter leads to a cellular (dendritic) crystallization front and the growth of a polycrystalline sample. To obtain a single-crystal structure of billets for turbine blades based on nickel alloys in the processes of directional solidification, it was also important to increase the temperature gradient [9, 10].

The results of these works and our data are shown in the table 1.

| $G_l$ (K/mm) | $V$ (mm/s) | $G_l/V$ (Ks/mm$^2$) | Dendrites | References |
|--------------|------------|---------------------|-----------|------------|
| 80           | 0,015      | 5333                | no        | [8]        |
| 80           | 0,15       | 533                 | yes       | [8]        |
| 10-12        | 0,0017     | 100-120             | no        | [9]        |
| 10-12        | 0,005      | 30-40               | yes       | [9]        |
| 10,3         | 0,017      | 606                 | no        | our data   |
| 9            | 0,017      | 529                 | yes       | our data   |
| 9            | 0,0083     | 1084                | no (?)    | our data   |
5. Conclusions
1. Based on the study of the dendritic structure along the length of the crystal and the results of modeling the crystallization process, it is shown that the formation of the dendritic structure at the beginning of growth is associated with a small temperature gradient in the melt near the crystallization front. An increase in the temperature gradient, as the growing crystal lengthens, leads to a decrease in the density of dendrites up to their complete disappearance.
2. Modeling the growth process showed that the temperature gradient changes little with changing technological parameters. In this case, a more effective way to increase the $G_L/V$ criterion and reduce the likelihood of dendrite formation is to reduce the pulling rate.

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