PECULIARITIES OF OBTAINING SINGLE CRYSTAL CASTINGS OF SOLID SOLUTION ALLOYS

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Abstract

In the work the results of the structural perfection of the cellular and dendrite single crystals with the diameter 24 mm of the Ticonal 9 alloy: 35 % Co - 14.5 % Ni - 7 % Al - 4 % Cu - 5 % Ti - Fe the rest (in wt.%) at the growing rates (R) from 0.1 to 9 mm/min with the constant temperature gradient 10 - 12 K/mm are presented. The block size decrease from 2.3 mm at R = 0.1 mm/min to 1 mm at R = 9 mm/min at the simultaneous disalignment increase from 1.8° to 7.8° accordingly was revealed. During the investigation the dependence of the working properties (magnetic parameters) of the single crystal casting samples obtained at different growing rates was determined. It is shown that the samples grown at high rates (5 ÷ 9 mm/min), i.e. the samples with the most imperfect structure have the highest magnetic properties (H_{cb}, B_r, BH_{max}). Theoretical and experimental investigations carried out in the present work allowed explain these contradictions and give recommendations regarding the manufacturing conditions of single crystal castings of the Ticonal 9 magnetic alloy.

Keywords: Single crystal, magnetic properties, growing rate, temperature gradient, structural perfection

1. INTRODUCTION

The demand for products with single crystal structure is constantly growing. At the present time the products with the single crystal structure include single crystal turbine blades based on the Fe-Ni, Ni-Ti alloys [1-3] and cast permanent magnets based on the Fe-Co-Ni-Al-Cu-Ti alloys (Ticonal 9 alloys) [4, 5]. Single crystal products have the highest working properties, and are the most stable to the external effects.

2. THEORY

The most simple and efficient manufacturing technique of the alloy single crystals is the directional controlled solidification method. However it is determined [4-7] that the formation of the plane crystallization front during the directional controlled solidification of the castings of the solid solution alloys with the crystallization range does not allow obtain chemically homogeneous along the length single crystals at any growing parameters. The only possible way to obtain single crystal ingots without zone segregation is to destroy the plane crystallization front and to form a transition liquid-solid cellular or dendrite structure. It allows change the zone macrosegregation for the dendrite microsegregation. This method ensures that after a short-term homogenizing one obtains homogeneous single crystals of multi-component alloys. At the same time the indispensable requirement is to obtain in the cast single crystal ingots the most perfect crystal structure with the minimum block disalignment which must ensure the best working properties.

The crystal structure perfection in the cast ingot besides the alloy characteristics (the liquidus temperature (t_L), the equilibrium ($t_{S.E}$) and the non-equilibrium ($t_{S.NE}$) solidus, the equilibrium (δt_E) and the non-equilibrium (δt_{NE}) crystallization ranges, the crystallization rate ($i = dm/dt$), the phase transitions in the solid state, etc.) depends to a great extent on the heat removal conditions, i.e. on the growing rate (R), the temperature gradients in the liquid (G_L) and solid (G_S) phases, the cooling rate (V_{Cool}), the size and the configuration of the dendrite single crystal being grown. It is considered that to grow top-quality single crystals high temperature gradients and low growing rates are required [1, 8-11]. However in manufacturing practice the growing rate is the main constituent of the production process efficiency and hence the cost of the final product.

3. EXPERIMENT

The structure perfection and the working properties of the single crystals of the Ticonal 9 alloy ingots of the composition 35 % Co - 14.5 % Ni - 7 % Al - 4 % Cu - 5 % Ti , Fe - the rest (in wt.%) were studied. Ticonal 9 alloy is a solid solution with the liquidus and solidus temperatures t_L = 1350 °C and t_C = 1290 °C accordingly. When the alloy is cooled from the solidus temperature to the room temperature polymorphy transitions take place in it. The alloy crystallizes as a one-phase α - solid solution and from the solidus temperature to 1200 °C it is in the one-phase state with the bcc lattice. In the temperature range 1200 - 900 °C the alloy is in the two-phase α + γ state. The γ - phase has the fcc lattice. Below 900 - 850 °C the mixture of the α + α/ - phases forms by the reactions α → α + α/ and γ → α + α/. The α and α/ - phases are retained till the room temperature. The α/ - phase is magnetic.

Single crystals with the diameter 24 mm and the height 120 ÷ 130 mm were grown in a one-position installation with a graphite resistance heater. The speed of the heater lifting was 0.1, 1, 3, 5 and 9 mm/min, the temperature gradient in the melt in front of the crystallization front was G_L = 10 ÷ 12 K/mm. Single crystal seeds in all experiments were placed on the butt end cooler in the thermal unit of the heater. Single crystals were cut along the {100} planes along and across the direction of the growth. The samples were cut at the equal height in the middle part of the single crystal.

X-ray structure analysis was used to certify the single crystals after growing. The Laue method was used to determine the crystallographic directions of growing, the rotating X-ray diffraction patterns were used to determine the phase lattice parameter (*a*). The block size (*l*) was determined by the topograms of the angular scanning of the longitudinal sections, the disalignment angle (Δ) of the single crystals was determined by the topograms of the angular scanning of the transversal sections.

4. RESULTS AND DISCUSSION

It was determined that the phase composition of the Ticonal 9 single crystals depends on the growing rate. In the single crystals grown at high rates the X-ray analysis revealed the ordered phases on the base of the bcc lattice. One of them has the FeAl type structure and *a* = 0.2866 nm. The other has the Fe_3Al type structure and *a* = 0.2897 x 2 = 0.5794 nm. The first is the strongly magnetic α/ - phase, the second is the weakly magnetic α - phase. Diffraction reflections from the α/ - phase are more intensive than from the α - phase, i.e. the volume fraction of the α/ - phase is higher.

In the single crystals grown at a lower rate (< 1 mm/min) the X-ray analysis showed the presence of the single crystal ordered α - phase having *a* = 0.2884 x 2 = 0.5768 nm, or both α/ - and α - phases at the same time with the parameters which do not differ from the mentioned.

Besides the reflections from these phases in the rotating X-ray diffraction patterns there are the lines of the polycrystalline phase with the bcc lattice the parameter of which in the first case is 0.2880 nm and in the second 0.2869 nm. According to [12] it is formed from the high temperature γ - phase and is named the α_γ - phase. The α_γ - phase is clearly revealed by the metallographic methods. Its content in the single crystals obtained at the rates 0.1 and 1 mm/min is considerable and decreases when the growing rate increases (which agrees well with the regularities determined earlier). In the single crystals grown at high rates, the α_γ - phase can be observed only by the metallographic methods. It is evident that in the course of the growing process the crystallized alloy bulk is in the region of the existence of the (α + γ) - phases as long as lower the heater lifting speed is. The formation of the γ - and then α_γ - phases leads to the fact that the ingots lose their single crystal characteristics. Therefore the term “single crystal” can be applied to the Ticonal 9 alloy ingots with some definite degree of conventionality.

The lowest growing rate (0.1 mm/min) results in the cell formation. The dendrite growth begins at the rates close to 1 mm/min, at 3 ÷ 5 mm/min the second order dendrite branches appear. When the transition from the cellular growth to the dendrite growth occurs, the duration of the electrolytic etching of the samples to reveal them increases. It is shown [13] with the YuNDK40T8 alloy having a similar composition that the increase of the etching time involves the decrease of the dendrite segregation.

The perfection characteristics of the Ticonal 9 alloy single crystals for different growing rates are given in **Table 1**.

Table 1 Perfection characteristics of the Ticonal 9 single crystals depending on the growing rate

Growing rate *R* (mm/min)	Cooling rate V_{Cool}, (K/min)	Block size *l* (mm)	Disalignment angle Δ (deg)
0.1	1.0 - 1.2	2.3	1.8
1	10 - 12	1.7	2.3
3	30 - 36	1.1	5.3
5	50 - 60	1.0	6.7
9	90 - 108	1.0	7.8

The largest block structure with the lowest disalignment angle of the crystal forms at the heater lifting speed 0.1 mm/min under conditions of the cellular growth (see **Table 1**). The increase of the growing rate leads to a higher disalignment of the single crystals, with this the constituent of the turn around the transversal directions <100> prevails. The transition from the cellular to the dendrite growth mode is accompanied by the block diminishing, which can be regarded to the reduction of the dendrite cell size. Single crystals obtained at the rates 0.1 ÷ 3 mm/min have a more stable perfection than the single crystals grown at the higher rates.

Single crystals show radial inhomogeneity of the structural perfection (**Fig. 1**). Their peripheral part is fragmented more than the central one. At the growing rates 3 mm/min and higher small size greatly disaligned blocks consisting of separate dendrites form at the periphery. The deterioration of the structure perfection in the periphery part may be the result of the abrupt change of the temperature gradient at the mould wall. It is known that the cooling rate has the greatest influence on the distance between the dendrite cells. Indeed, the distance between the dendrite cells at the periphery is less than in the central part.

The comparative analysis of the angular scanning topograms of the adjacent transversal samples revealed a curve of the single crystal lattice which increases with the rise of the growing rate. The area of the reflection from the lower sample, the normal to which surface and the growth direction coincide, is more and from the upper sample for which these directions are opposite is less than the area of the reflection from the perfect crystal. We believe that the lattice curving of the single crystals occurs during their cooling and is the result of the strains occurring owing to a much earlier solidification of the external layers and a later solidification of the inner layers of the single crystal.

The asymmetry of the thermal field of the heater influences significantly the process of the single crystal structure formation. The peculiarities of the diffraction topography patterns of the single crystals grown at the rates 0.1 ÷ 9 mm/min (**Fig. 1**) indicate this. They were grown with the seeds having similar alignment in the thermal unit of the installation.

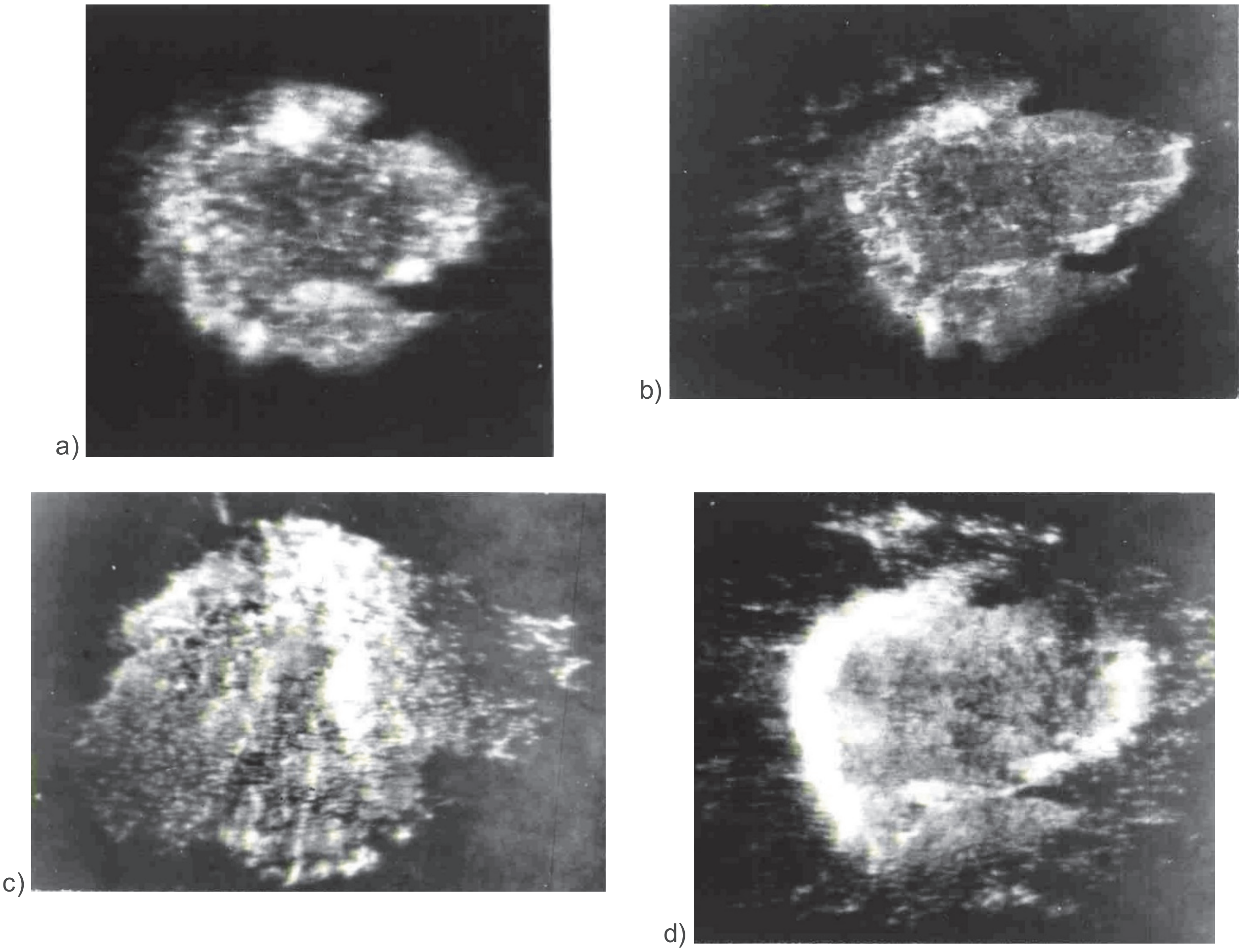

Fig. 1 X-ray topograms of the transversal sections of the YuNDK35T5 alloy single crystals obtained at the growing rates: a. 1 mm/min; b. 3 mm/min; c. 5 mm/min; d. 9 mm/min - reflection ($00\bar{2}$)

The following modes of the thermal magnetic treatment were applied to the single crystal samples grown at the mentioned rates: heating to 1250 °C, exposure 20 ÷ 25 min, cooling in the air in the magnetic field 2 ÷ 3 min, isothermal exposure at 800 °C, 12 min, step tempering at 650 °C, 5 hours and at 550 °C, 20 hours. The dependence of the magnetic properties on the growing rate is shown in **Fig. 2**. In the figure one can see that the magnetic parameters H_{cb} and BH_{max} increase while the growing rate increases, though the single crystal perfection deteriorates. The raise of the magnetic properties of the single crystal samples of the Ticonal 9 alloy at the growing rate increase was determined by the authors in the work [14]. Thus, it turns out that the formation of a more perfect structure in the single crystal ingots of the Ticonal 9 alloy leads to the decrease of the magnetic properties. In order to explain such contradiction it is necessary to consider other processes which are able to influence the final microstructure and the properties accordingly.

The final aim of the whole manufacturing process of the single crystal permanent magnets of the Ticonal 9 alloy is the decomposition into two finely dispersed isomorph phases α and $\alpha^/$ (**Fig. 3**). The maximum level of the magnetic properties will be only in that case when all particle of the highly magnetic phase ($\alpha^/$) are isolated by the paramagnetic phase (α) and their chemical compositions correspond to the final equilibrium at the room temperature for the given alloy composition. At the same time the disalignment of each particle must be minimal. In view of the fact that the single crystals are grown with the dendrite structure, in order to explain the working properties, it is necessary to take into account the parameters and the characteristics of that dendrite structure.

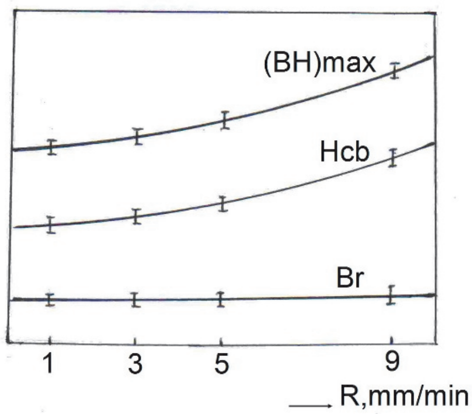

Fig. 2 Dependence of the magnetic properties on the growing rate of the Ticonal 9 alloy single crystals

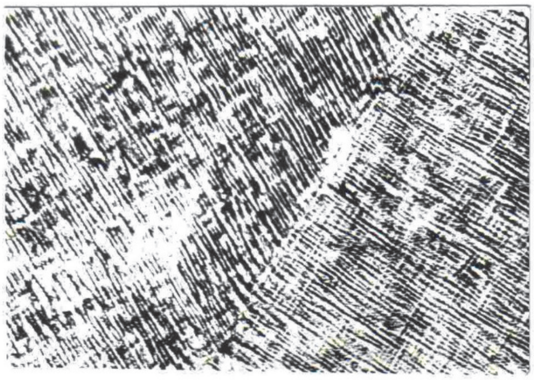

Fig. 3 High coercivity decomposition into the α and α' - phases in the Ticonal 9 alloy after the thermal magnetic treatment

The dependence of the dendrite cell size on the cooling rate (V_{Cool}) is shown in **Fig. 4**. Since the cooling rate is bound up with the growing rate (R) and the value of the temperature gradient (G_L) by the relation $V_{Cool} = G_L \cdot R$, the corresponding cooling rates are determined in this study for each growing rate at G_L = 10 ÷ 12 K/mm (see **Table 1**).

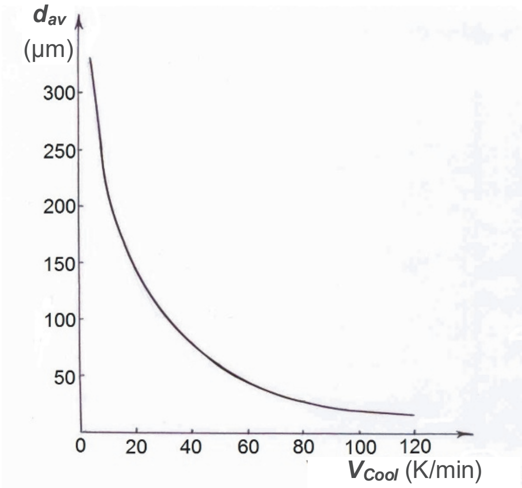

Fig. 4 Dependence of the average dendrite cell size (d_{av}) on the cooling rate ($V_{Cool} = G_L \cdot R$) of the Ticonal 9 alloy

In [4, 7] it was shown that the more the size of the dendrite cell and the more the segregation manifests itself, the longer the homogenizing annealing must be. Thus the annealing of the samples cooled at the rate 1 K/min at the temperatures 1240 ÷ 1250 °C, 120 min did not eliminate the dendrite inhomogeneity in the Ticonal 9 alloy. Homogenizing of the samples obtained at the cooling rates more than 20 K/min at the same temperature during 20 min eliminates completely the microsegregation. The low cooling rate of the Ticonal 9 alloy leads also to the formation of a greater amount of the γ - phase (up to 50 %) in the temperature range 1200 ÷ 900 °C and its further decomposition results in the formation of the randomly aligned structure of the α_γ - phase which in the end decreases the magnetic properties as well. Therefore the dendrite structure and the phase transitions in the solid state affect to a greater extent the magnetic parameters of samples with the dendrite single crystal structure.

5. CONCLUSION

To achieve the highest working properties in the products of the single crystal ingots of the solid solution alloys it is necessary not only to aim at the obtaining the most perfect single crystal structure but also take into account the influence of the dendrite structure and the phase transitions in the solid state on the generation of the micro-inhomogeneous zones and small size polycrystalline formations.

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REFERENCES

[1] ШАЛИН Р.С., СВЕТЛОВ И.Л., КАЧАНОВ Е.Б. Монокристаллы никелевых жаропрочных сплавов. Машиностроение: Москва, 1997.

[2] КАБЛОВ Е.Н. Литые лопатки газотурбинных двигателей. Сплавы, технологии, покрытия. МИСиС: Москва, 2001.

[3] LAPIN J. The effect of microstructure on mechanical properties of single crystal CMSX-4 superalloy. In Metal 2013: 22nd International Conference on Metallurgy and Materials. Ostrava: TANGER, 2013. CD-ROM.

[4] СИДОРОВ Е.В. Отливки магнитов с монокристаллической и столбчатой структурами. Теория и практика изготовления. Владим. гос. ун-т. Изд-во Транзит: Владимир, 2007.

[5] ПИКУНОВ М.В., БЕЛЯЕВ И.В., СИДОРОВ Е.В. Кристаллизация сплавов и направленное затвердевание отливок. Владим. гос. ун-т: Владимир, 2002.

[6] СИДОРОВ Е.В., ПИКУНОВ М.В. Выращивание монокристаллов из сплавов твердых растворов. Изв. ВУЗов Цветная металлургия, № 5, 2005, с. 26-30.

[7] SIDOROV E. Theoretical and experimental research of the single crystal growing of the Fe-Cr, Fe-Ni-Ti, Fe-Co-Cr-Mo, Fe-Ni-Al-Co-Cu-Ti based alloys. In Metal 2014: 23rd International Conference on Metallurgy and Materials. Ostrava: TANGER, 2014. CD-ROM.

[8] ВАЙГАРД У. Введение в физику кристаллизации металлов. Мир: Москва, 1967.

[9] ТИЛЛЕР У.А. Затвердевание. В сб. Физическое металловедение под ред. Кана Р. Мир: Москва, т. 2, 1968, с. 155-226.

[10] ЧАЛМЕРС Б. Теория затвердевания. Металлургия: Москва, 1968.

[11] ФЛЕМИНГС М. Процессы затвердевания. Мир: Москва, 1977.

[12] ЛИВШИЦ Б.Г., ИЗГОРОДИН А.К., НИКОЛАЕВА В.Н. Исследование кинетики образования γ-фазы в сплавах типа ЮНДК35Т5 при 830 - 900 °C. Металловедение и термическая обработка металлов, № 6, 1972, с. 65-67.

[13] ЛАРИЧКИНА Р.Я. Внутрикристаллическая ликвация в монокристаллах сплава ЮНДК40Т8. Тр. ВНИИЭМ, Москва, т. 35, 1971, с. 8.

[14] СЕРГЕЕВ В.В., ЛАРИЧКИНА Р.Я. Связь структуры монокристаллов из сплавов Тикональ с условиями роста и магнитными свойствами. Сб. Рост кристаллов, т. 12, 1977, с. 310-316.