

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

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Abstract

Single crystal products of metallic alloys allow secure extremely high operation properties of final products. Single crystal turbine blades of the Fe-Ni based alloys and cast Fe-Ni-Co-Al-Cu-Ti and Fe-Co-Cr-Mo(W) based permanent magnets belong to the main products. Single crystal ingots are also used to study physical properties of metals and alloys. The well-known theoretical knowledge of the processes of the single crystal structure formation is limited by general statements of the crystallization theory of metals and alloys. These statements predetermine perfectly enough the conditions of obtaining single crystals of pure metals and alloys with the zero crystallization range. In the present work theoretical and experimental study has been carried out to obtain single crystal ingots of alloys with the crystallization range by the directional controlled solidification. It is shown that at first dendrite single crystal structure must be formed of alloys with the crystallization range with the subsequent homogenizing. The dependence of the steady growth of the dendrite single crystal structure on the phase diagram configuration, the crystallization character indexes and the growing modes has been revealed.

Keywords: Single crystal, crystallization center, directional solidification, phase diagram, crystallization character index

1. INTRODUCTION

The application of the crystallographic anisotropy allows considerably improve the working properties of the metal and alloy products. At the present time the production of single crystal ingots of metals and alloys is based on the method of the directional controlled solidification from the melt. In commercial production single crystal turbine blades of refractory nickel based alloys are manufactured [1-3] and single crystal ingots of multi-component alloys based on Fe-Co-Ni and Fe-Co-Cr with Al, Cu, Ti, Mo additives for permanent magnets as well [4, 5]. Single crystal ingots are also applied to investigate physical properties of metals and alloys.

2. THEORY

When developing the fundamentals of the single crystal manufacturing technique of the alloys by the directional controlled solidification method as a rule the engineers base upon the diffusion (concentration) undercooling theory [6, 7] in which a specific process of the non-equilibrium crystallization of the C_0 alloy in the A-B binary system is considered (**Fig. 1**).

It is customary considered that the stable single crystal growth from the melt is ensured by the plane crystallization front formation and retaining during the whole growing process. Many authors [8-11] indicate that to grow high quality single crystals it is necessary that the interface between the liquid and solid phases is plane. The formation of the cells and dendrites must be eliminated by the increase of the temperature gradient in the liquid and the decrease of the growth rate to eliminate the concentration undercooling. The main condition of this is to observe the relationships

$$G_L / R > [a C_0 (1 - K) / K] D_L \quad (1)$$

$$\text{or } G_L / R > (t_L - t_S) / D_L \quad (2)$$

where G_L is the temperature gradient in the liquid in front of the crystallization boundary; R - the crystal linear

growth rate; α - the slope of the liquidus line in the A-B phase diagram; t_L , t_S - the liquidus and solidus temperatures of the C_0 alloy; $K = C_S/C_L$ - the equilibrium distribution coefficient of the B component at the alloy crystallization; D_L - the diffusion coefficient in the liquid phase.

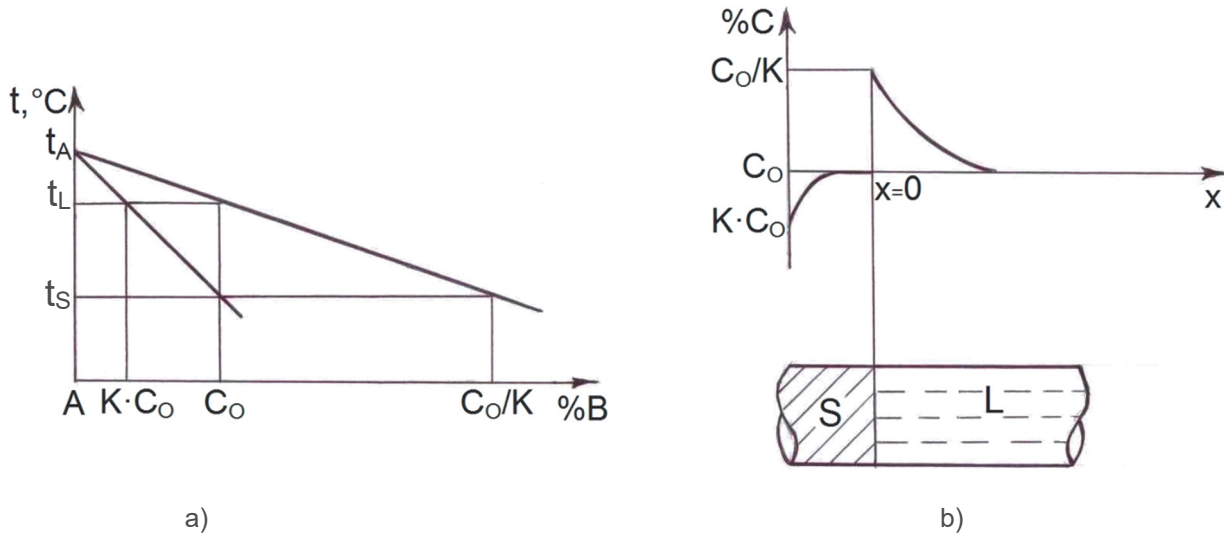


Fig. 1 Section of the phase diagram of the A-B system (a) and the distribution of the B component in the solid ($x < 0$) and liquid ($x > 0$) zones of the C_0 alloy (b)

Deducing the relationships (1) and (2) the authors [6, 8-11] proceeded from the following:

- the crystallization front (the interface between the solid and liquid phases) is a plane;
- the diffusion mass transfer in the solid phase is absent;
- in the melt the mass transfer is in one direction only;
- the heat removal is through the solid phase;
- the convection in the liquid is absent.

The observance of the conditions indicated above must ensure the stable growth of the single crystal with the homogeneous composition and the most perfect structure.

However laboratory experiments and manufacturing practice show that the single crystals grown from the alloys with a rather high crystallization range always have a cell or dendrite microstructure, even in the cases when the relationships (1) or (2) are observed completely [1-5]. It follows from these results that the conditions to retain the plane crystallization front set by the diffusion undercooling theory are not observed and the application of the criteria (1) and (2) to define the modes of the plane crystallization front formation becomes useless. The reasons why it is impossible to form a plane crystallization front in solid solution alloys with the crystallization range are the dimension characteristics of the resulting cast ingot and the presence of the convection stirring of the melt. The authors of the proposed criteria (1) and (2) always emphasized that these criteria would be observed only in case when the specified conditions of the non-equilibrium crystallization of the alloy are met. This is just the reason why it is impossible to obtain in practice perfect single crystals of the alloys with the crystallization range, even when we try to meet the relationships (1) or (2).

In case of the minimum content of the alloying components in the alloy and accordingly a very small crystallization range it is possible to form the plane front if the temperature gradients are really attained. However in this case the melt is enriched by the components with $K < 1$ and becomes poor regarding the components with $K > 1$. After the termination of the solidification process the resulting single crystal has inhomogeneous chemical composition along the length. It is practically impossible to eliminate this inhomogeneity (zone segregation) by the homogenizing.

It is possible to avoid the zone segregation in the casting only by the destruction of the plane crystallization front and the formation of the transition two-phase region, where there are the solid phase in the form of the dendrites and the remaining melt. Within the two-phase region the non-equilibrium crystallization is taking place and the micro-inhomogeneity occurs in the dendrites. At the same time in the melt in front of the two-phase zone the liquid composition within the whole solidification process will correspond to the C_o (Fig. 2). After the termination of the directional controlled solidification process the resulting single crystal will have the dendrite structure with the strongly pronounced dendrite segregation (Fig. 3) but without the zone segregation.

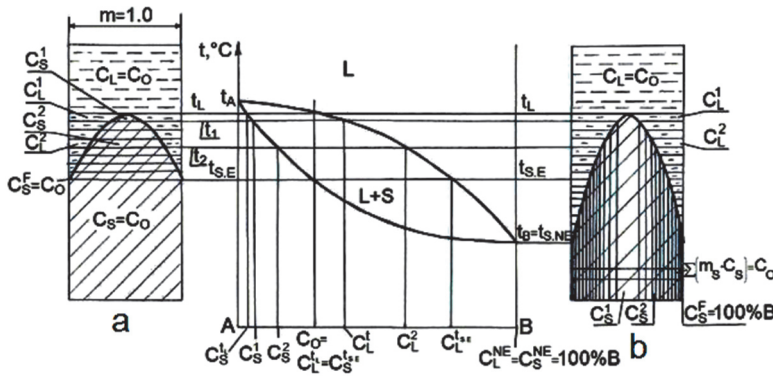


Fig. 2 Configuration of the transition region and the element distribution in the solidifying alloy ingot at the equilibrium ($D_S \rightarrow \infty$, $D_L \rightarrow \infty$) (a) and the non-equilibrium ($D_S \rightarrow 0$, $D_L \rightarrow \infty$) (b) crystallization

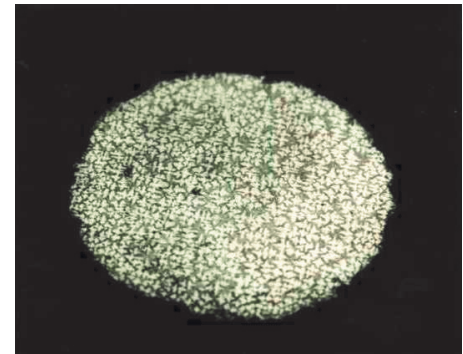


Fig. 3 Dendrite single crystal structure in the Ticonal 9 alloy casting with the 24 mm diameter

The dendrite segregation occurring inevitably in these conditions can be eliminated by the homogenizing annealing. The structure perfection is determined by the disalignment of the blocks in the range of 1-3° [12-14] and depends on the growth modes (solidification conditions) - G_L , G_S , R and on the crystallization character indexes - C_o , t_L , t_S , $t_{S,NE}$, $\delta t_{S,NE} = t_L - t_{S,NE}$, $\delta C = C_o(1 - K)$, M_{decom} , $M_{interact}$ [4, 5, 15, 16], where G_S is the temperature gradient in the solid phase, $M_{interact}$ and M_{decom} - the alloy fractions crystallizing by the diffusion interaction and the diffusion decomposition accordingly [5], δt_{NE} - the non-equilibrium crystallization range, δC - the range of the component content changing in the solid phase in the crystallization range.

There is an opinion in the literature that the size of the equilibrium crystallization range of the alloy predetermines the stability of the single crystal growth, at the same time it is considered that the smaller is the equilibrium crystallization range and accordingly the smaller the transition liquid-solid region it is easier to form the single crystal or columnar structure in the casting [10, 17, 18]. However a great number of experimental works contradict the existing opinion.

3. EXPERIMENTAL PROCEDURE

In **Table 1** literature and our own experimental results of the manufacturing process of single crystal ingots at the maximum possible growth rate (R) and the main alloy crystallization character indexes (δt_e , δt_{NE} , M_{decom}) are represented.

Table 1 The dependence of stable growth of the dendrite single crystals on the alloy crystallization character indexes and the heat removal conditions

#	Alloy (wt.%) Fe rest	Growing method	Crystal diameter (mm)	G_L (K/mm)	M_{decom}	$\delta t_e = t_L - t_{s.e}$ (K)	$\delta t_{NE} = t_L - t_{s.NE}$ (K)	R_{max} (mm/min)	Source
1	Fe-3.5 % Si	Bridgman	20-21	5-7	0.6	18-20	270-280	5-6	Own exper.
2	Fe-3 % Si	IZMWC*	12-13	-	0.6	16-18	275-285	2	[19]
3	Fe-20 % Cr	Bridgman	20-21	5-7	0.15	1-2	2-3	0.4-0.5	Own exper.
4	Fe-14 % Cr	IZMWC*	12-13	-	0.17	5-6	7-8	0.12	[20]
5	Fe-30 % Ni-20 % Co-7 % Ti	Bridgman	20	8-10	0.7	100-110	-	5	Own exper.
6	Fe-20 % Cr-11 % Co-3 % V	Bridgman	20	8-10	0.3	10-15	-	3	Own exper.
7	Fe-20 % Cr-11 % Co-3 % V	Bridgman	50	8-10	0.3	10-15	-	1	Own exper.
8	Fe-35 % Co-14 % Ni-5 % Ti-7 % Al-3 % Cu	Bridgman	24	5-7	0.68	70-80	-	4-5	Own exper.
9	Fe-18 % Co-22 % Cr-3 % Mo-1 % Ti	Bridgman	20	5-7	0.65	40-45	-	4-5	Own exper.
10	Fe-18 % Co-22 % Cr-3 % Mo-1 % Ti	Bridgman	50	5-7	0.65	40-45	-	1-1.5	Own exper.

*IZMWC - induction zone melting without crucible

Table 1 shows definitely that the stable growth of the dendrite single crystals depends on the alloy crystallization character indexes and the heat removal conditions. The castings of alloys with a greater equilibrium and especially non-equilibrium crystallization range (alloys 1, 2, 5, 8, 9) have the highest growth rate. Alloys with a smaller equilibrium crystallization range and particularly with the smallest non-equilibrium crystallization range make it possible to grow single crystals at very low growth rates (alloys 3, 4, 6, 7). The value of the temperature gradient (G_L) plays an important role in the growing process as well. When the Bridgman method is used and G_L is 5-7 K/mm, the alloy Fe-3.5 % Si has the maximum growth rate 5-6 mm/min, the alloy Fe - 20 % Cr - 0.4-0.5 mm/min. When the IZMWC method is used, the alloy Fe - 3 % Si has the growth rate 2 mm/min and the alloy Fe - 14 % Cr - 0.12 mm/min, i.e. 3-4 times lower.

Besides the effect of the crystallization character and the heat removal conditions non-metallic inclusions play a very important role in the process of the single crystal structure formation. When non-metallic inclusions with the crystallographic structure similar to the structure of the alloy solid solution are present in the melt and if the crystal lattice parameters differ not more than by 10-15 % such particle can be the crystallization center [21]. Therefore all laboratory and manufacturing techniques are based on the application of the particularly pure elements and the creation of the low residual pressure or inert atmosphere. However these methods often do not give the desirable result. So the formation of a large number of random crystals is observed when we grow single crystal ingots of the alloy Fe-35 % Co-14 % Ni-7 % Al-5 % Ti-3 % Cu (Ticonal 9) - see **Fig. 4**. In this case titanium nitrides (TiN), titanium carbides (TiC) and titanium carbonitrides (TiNC) are the crystallization centres.

However the authors do not observe the random crystal formation on such inclusions when they manufacture single crystal castings of the alloy Fe - 30 % Ni - 20 % Co - 7 % Ti [4, 22] and the turbine blade castings of the nickel based alloys [1, 23]. The explanation of this phenomenon is the following: The titanium nitrides (TiN) and titanium carbides (TiC) have the cubic structure of the NaCl type [24]. The titanium atoms on the planes

{100} of the lattice TiN and TiC are located in the corners of the square with the side 0.304 nm. Ticonal 9 alloy crystallizes also in the bcc-lattice with the period 0.294 nm. The difference is $(0.304-0.294)/0.294 = 3.04 \%$. Therefore the TiN and TiC particles can act as crystallization centers.

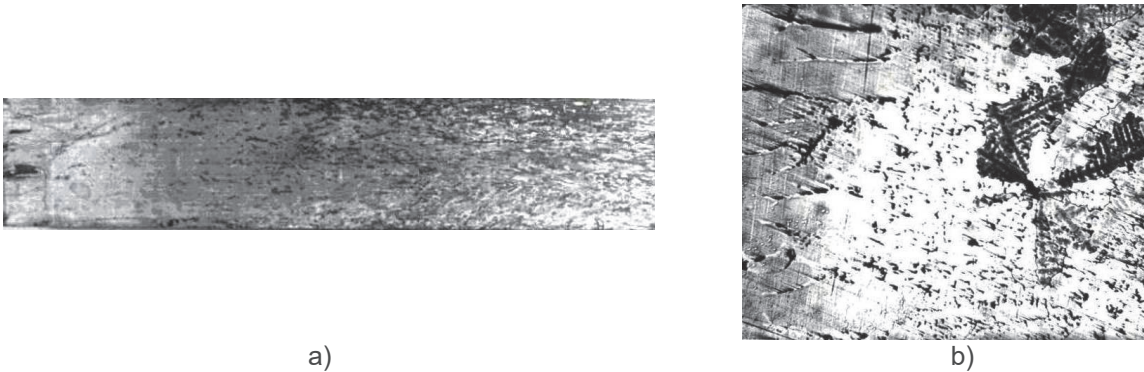


Fig. 4 “Random” crystal formation in the active crystallization centers in the Ticonal 9 alloy castings a) after the growing of the ingot with the diameter 24 mm; b) in front of the crystallization front, x120 (sample with the diameter 10 mm was quenched in the growing process)

The Fe - 30 % Ni - 20 % Co - 7 % Ti alloys and the nickel based alloys for the turbine blades crystallize in the fcc-structure which has no conformity with the TiN and TiC cubic structures. Therefore new crystals do not nucleate on the particles of these compounds as it is much easier to manufacture single crystal castings of such alloys.

In **Table 2** the results of the work [25] to determine the macro-grain dimensions in the castings of the NIMONIC alloys manufactured at the similar heat removal conditions are presented.

Table 2 The dependence of the considerable macro-grain size decrease on the increase of the total aluminum and titanium amount, i.e. bcc-stabilizing elements, and on the decrease of the nickel amount, i.e. fcc-stabilizing element

Alloy grade	Chemical composition (wt.%)						Grain size
	Ni	Co	Cu	Al	Ti	Fe	
NIM 95/11	14.1	28.2	3.18	-	4.0	rest	coarse
NIM 95/12	15.0	24.4	3.22	2.20	5.0	rest	mean
NIM 95/13	15.9	23.1	3.35	4.26	5.7	rest	mean
NIM 95/14	16.0	23.2	3.16	7.20	5.6	rest	fine (3550 pcs/cm ²)
NIM 95/15	25.0	23.0	3.02	-	4.25	rest	coarse
NIM 95/16	19.6	23.3	3.20	2.13	5.7	rest	mean

The authors of this work explain the change of the macrostructure by the diffusion undercooling and the absence of the plane crystallization front. However from **Table 2** the dependence of the considerable macro-grain size decrease on the increase of the total aluminum and titanium amount, i.e. bcc-stabilizing elements, and on the decrease of the nickel amount, i.e. fcc-stabilizing element is definitely seen. Thus the titanium presence in all NIMONIC alloys leads to the TiN and TiC inclusion formation, at the same time these inclusions “work” as crystallization centres only in alloys which crystallize in the bcc-structure (NIM 95/12, NIM 95/13, NIM 95/14, NIM 95/16) and do not “work” as crystallization centres in alloys which crystallize in the fcc-structure (NIM 95/11, NIM 95/15).

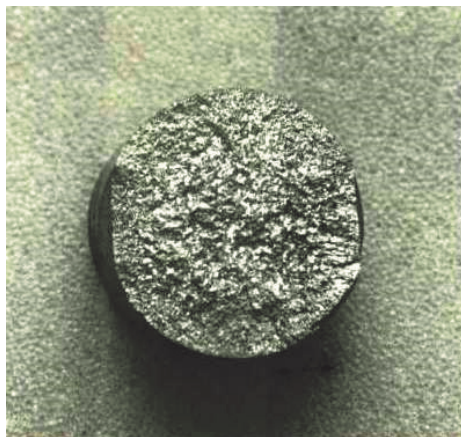
In **Fig. 5** the macrostructures of the castings of two alloys Fe - 1 % Ti - 0.05 % C and Fe - 1 % Ti - 2 % C poured in the cast iron moulds with the diameter 40 mm at equal undercooling above liquidus are shown. One can see that a fine crystal structure is formed in the casting of the alloy Fe - 1 % Ti - 0.05 % C crystallizing as

the α -solid solution with the bcc-structure (**Fig. 5a**) and a columnar structure through the whole depth is formed in the casting of the alloy Fe - 1 % Ti - 2 % C crystallizing as the γ -solid solution with the fcc-structure (**Fig. 5b**). In the microstructures of both alloys titanium nitrides, carbides and carbonitrides are also revealed. It should be noted also that the crystallization character indexes of the alloy Fe - 1 % Ti - 0.05 % C to a greater extent favour the diffusion undercooling elimination, the plane crystallization front ensuring and the columnar or single crystal structure formation.

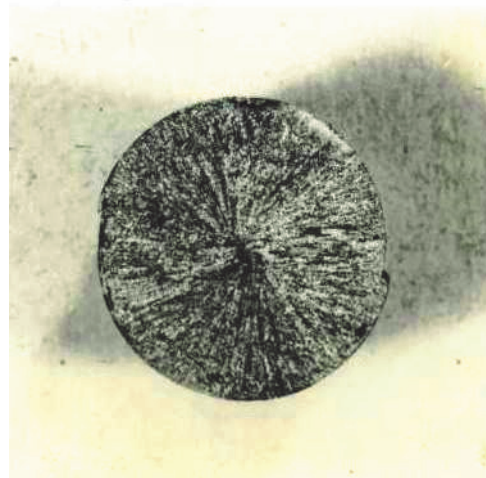
From the theoretical and experimental investigations it follows that to form the single crystal structure in the castings of the iron and nickel based solid solution alloys crystallizing with the bcc-lattice it is necessary to eliminate or neutralize the mentioned centres. In case of the alloys crystallizing with the fcc-lattice special measures to eliminate those inclusions are not needed.

When manufacturing castings with the single crystal or columnar structures of the Ticonal 9 magnetic alloy sulphur in the amount of 0.2-0.4 wt. % is added to the alloy. During the crystallization of this alloy with the sulphur additive instead of the titanium nitrides, carbides and carbonitrides titanium sulphides and carbosulphides are formed which are no longer crystallization centres [4, 5].

The other way to improve considerably the process of the single crystal structure formation in the Ticonal 9 alloy castings is to change slightly the chemical composition of the alloy basis so that initially the fcc-structure crystallizes instead of the bcc-structure. At the same time the additive elements must not decrease the main working properties. So the addition of the 0.8-1.2 wt.% hafnium to Ticonal 9 results in the fact that at first the γ -solid solution with the fcc-structure crystallizes and hence the formation of the single crystal and columnar structures is easier.



a)



b)

Fig. 5 Macrostructure of the castings of the alloys Fe - 1 % Ti - 0.05 % C (a) and Fe - 1 % Ti - 2 % C (b)

At the present time the scientifically valid quantitative conditions of the dendrite single crystal growing with the most perfect structure are obscure. To obtain these data is an urgent task. Naturally, the required working properties of different final products will define the necessary perfection of the dendrite single crystal structure.

The process efficiency - the growth rate (R) and the homogenizing time (τ) are very important in the dendrite single crystal product manufacturing. It is known [26] that the homogenizing time is proportionate to the square of the distance of the regions with the maximum and minimum concentrations, i.e. $\tau = d^2/\pi^2 D_S$, where d is the dendrite cell size. For the magnetic alloy Ticonal 9 the dependence of the dendrite cell size (d) on the cooling rate ($V_{cool} = G R$) was obtained (**Fig. 6**), and also the dependence of the maximum possible growth rate (R) on the diameter (\emptyset) of the growing crystal at the constant temperature gradient $G_L = 10$ K/mm (**Fig. 7**). One can

see in Fig. 6 that to decrease d_{av} it is expedient to increase V_{cool} , i.e. G and R , that is possible to do by means of the thermal scheme of the process (for example the application of the liquid metallic baths for the cooling, the thin wall moulds and so on). However it follows from Fig. 7 that at the same temperature gradient with the increasing of the growing crystal diameter the growth rate must decrease which leads to the decrease of the cooling rate and the increase of the dendrite cell size (d_{av}) accordingly and consequently to the increase of the homogenizing time. Therefore the dimension characteristics of the ingots must be taken into consideration as well when manufacturing dendrite single crystals.

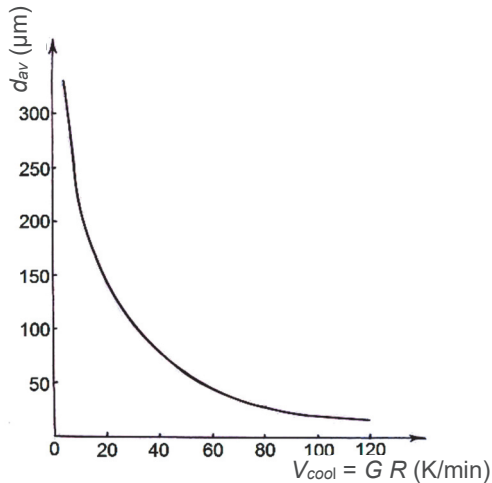


Fig. 6 Dependence of the average dendrite cell size (d_{av}) on the cooling rate ($V_{cool} = G R$) for Ticonal 9 alloy

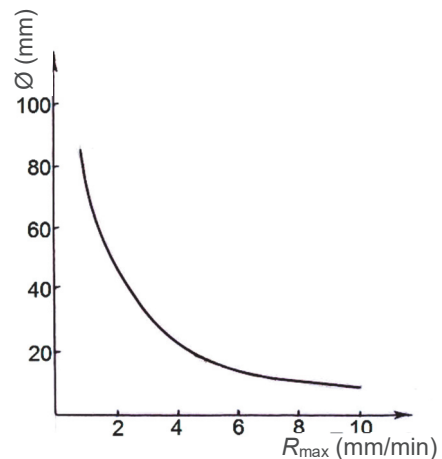


Fig. 7 Dependence of the maximum growth rate (R_{max}) on the diameter (\emptyset) of the growing crystal at the constant temperature gradient $G_L = 10$ K/mm

CONCLUSION

1. To obtain single crystal ingots of the alloys with the crystallization range by the directional controlled solidification method the processes are required ensuring the occurrence and the existence of the two-phase transition region. The arising at the same time the dendrite inhomogeneity must be eliminated by the homogenizing annealing.
2. The plane crystallization front is necessary undoubtedly and is really feasible when manufacturing single crystals of the maximum pure metals, when due to the practically zero crystallization range the two-phase region is absent and the arising macro-inhomogeneity reveals itself at large distances along the crystal length, which allows to choose the most pure regions regarding the impurities.
3. It is always necessary to pay attention to the affect of the non-metallic inclusions on the nucleation of extra crystals and to develop methods to eliminate or neutralize these inclusions when manufacturing castings with the single crystal or columnar structures.

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