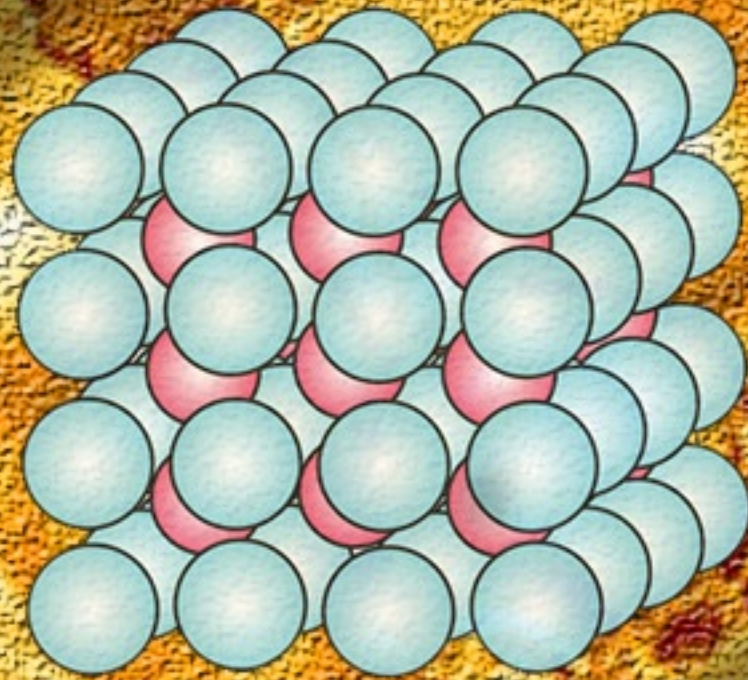


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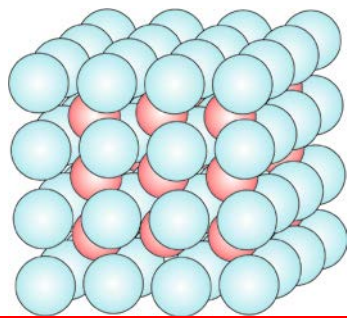
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IMPROVING THE CASTING PROCESS OF PERITECTIC STEEL GRADES

Prof. dr. E. Chickarev¹, Post grad. st. C. Y. Hu², Prof. dr. O. Isayev², Prof. dr. O. Hress², Prof. dr. K. M. Wu²

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Abstract: Longitudinal cracking when continuous casting of peritectic steels was studied in this work. Dependency of slab scarfing volume and surface cracking on the steel chemical composition was investigated. The optimum casting speed and taper parameter of the mold were determined based on analytical modeling and statistical analysis of surface cracks observed in industrial billets. It was shown that longitudinal cracks on peritectic slabs could be reduced when the Mn to S ratio was kept above ~150. Such surface defects were decreased to 30-35 % by optimizing the steel composition, melt temperature and casting speed. Also by using an optimum taper of the mold the scarfing volume was reduced to 32-36 %.

KEYWORDS: LONGITUDINAL CRACKS, PERITECTIC STEEL GRADES, MOULD TAPER

1. Introduction

One of the most important components that is essential for the smooth operation of the continuous casting machine (CCM) and optimal quality of continuously cast billets, is the water-cooled mold which absorbs 10 % to 30 % of total the heat. Continuous casting of peritectic steels with about 0.1% C is particularly difficult since these steels are prone to the formation of longitudinal cracks and surface defects. Despite recent advances in the continuous casting technology, the quality of cast billets and their surface condition in a number of cases remain problematic; especially casting rolled products for critical applications.

The problem of improving the surface quality of continuously cast slabs with a mass fraction of carbon is close to 0.1%, and there is at present.

The mechanism of heat transfer between the billet and the mold is an important issue because the conditions of heat exchange depends on the performance of the caster and the quality of surface and subsurface layers of the cast billet. Understanding the mechanisms of heat transfer between the billet and the mold is essential for designing an optimum mold [1, 2].

Peritectic medium-carbon steels exhibit an anomalous decrease of the heat flux on the mold surface due to the surface roughness of the solidifying shells, whereas ultra-low carbon steels exhibit large heat flux despite their large surface roughness. Such difference is caused by the fact that the surface roughness of ultra-low carbon steels arises from δ/γ transformation which occurs somewhat later than the completion of solidification [3].

The degree of peritectic solidification is a strong indicator of the cracking tendency of steel during continuous casting. To predict the crack susceptibility of regular carbon steel slabs, the characteristic index of solidification shrinkage (RV), which is determined by the volume shrinkage of the peritectic solidification and the remaining liquid phase after the peritectic solidification, is proposed as a means of evaluating the cracking tendency [4].

Slight variation of C or Mn, in the order of 0.04%, promoted significant changes in the evolution of phases during solidification. The variation in the C content has a larger influence than that of Mn on the evolution of phases, however, the Mn microsegregation generated at high cooling rate can promote a change in the solidification mode from hypo to hyper-peritectic. Cracking susceptibility observed in the hypo-peritectic steel is not only generated by differences in the mechanical behavior δ and γ phases, but also by the liquid inability to compensate the contraction associated to the peritectic transformation [5].

The possibility of cracking increased with increasing sulfur content and the carbon content at which longitudinal surface cracking frequency is maximized decreased because brittle temperature range extended to the lower temperatures. The effect of the steel composition on the formation of longitudinal cracks using the non-equilibrium phase diagram has not been reported yet, and a more quantitative and systematic study must be made to interpret the surface cracking phenomena [6].

The cracks are usually curved (wavy) and vary in length from a few centimeters up to several meters in some cases. Longitudinal cracks are usually formed in the central part of the mold. The defects usually appear at the beginning of the continuous casting. The low carbon (<0.08%) slabs with > 1.1 % manganese sometimes have relatively short longitudinal cracks of about 100 mm long.

It is difficult to detect longitudinal cracks on the slabs immediately after casting. These defects are often associated with small inhomogeneities located near the surface of the slab. Previous research showed [7], leads to the formation of cracks. The probability of longitudinal cracks formation in the peritectic steels billets depends on the variation in the withdrawing speed [3].

Previous work showed that the formation of longitudinal cracks in the continuously cast peritectic steels was due to the volumetric change during δ to γ transformations [8, 9]. It was also shown that the formation of cracks can be reduced by (1) stabilizing slag penetration into the gap between the mold and the billet, (2) controlling the casting nozzle, and (3) reducing the time required to establish a steady casting speed.

It is also of interest to improve the surface quality of continuously cast billets by addition of surface-active elements and/or reducing the concentration of harmful impurities.

The chemical composition of the steel, particularly carbon content has a significant effect on the formation probability of longitudinal cracks, e.g. carbon concentration between 0.10 to 0.14 wt.%. is reported to be undesirable.

The tendency of crack formation in steels depends of on the ferritic potential F_p as defined in Eq. (1) [10]:

$$F_p = 2.5 (0.5 - [C_{eq}]), \quad (1)$$

where

$$C_{eq} = [\%C] + 0.04[\%Mn] + 0.1[\%Ni] + 0.7[\%N] - 0.14[\%Si] - 0.04[\%Cr] - 0.1[\%Mo] - 0.24[\%Ti] - 0.7[\%S]. \quad (2)$$

For fully ferritic steels F_p is above 1 (e.g. $F_p = 1.25$ for pure δ - iron). If $F_p < 0$, the steel is fully austenitic.

In addition, the taper and heat transfer condition have a significant influence on the formation of crack.

This paper presents the results of statistical analysis carried out on the formation of surface cracks by taking in account the overheating of the melt in the tundish and the mold taper when casting various grades of steels.

2. Experimental method

All of the studied steel grades melted in oxygen converter with a capacity of 350 tons, finishing on the chemical composition and refining were carried out on the ladle furnace.

The casting was performed on double-stream curved continuous casting machine producing slabs with cross-sections from 220×1250 to 250×1850 mm².

Experiments and quality control of continuously cast slabs was carried out for a wide range of steel grades with carbon concentration in the range of 0.08 to 0.19 wt.% and manganese concentration of 0.60 to 1.75 wt.%. Three types of steel samples were investigated in this work; plain carbon steels, microalloyed-steels with 0.03 to 0.05 wt.% of Nb, and microalloyed-steels with 0.02 to 0.04 wt.% of Nb plus 0.050 to 0.120 wt.% of V.

The total volume of investigated heats for analysis was 1800 heats.

3. Results and discussion

3.1. Statistical analysis of industrial billets

It is established that ferritic potential is quite sensitive to variations in the steel composition and can be used to predict the occurrence of surface defects in rolled products Figure 1 shows the results of a statistical analysis of the relationship between fraction of slab with longitudinal cracks and ferritic potential of corresponding heats. It is clear that the variation in the concentration of alloying elements significantly affected the amount of surface scarfing (see Fig. 1).

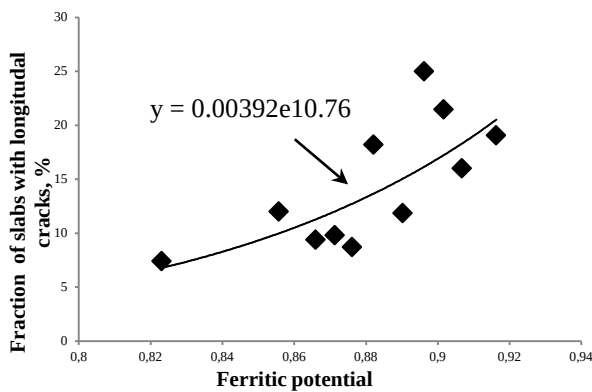


Fig. 1 - Influence of ferritic potential on longitudinal cracks in a peritectic steel grades, each point represents the average of 100 heats.

For example, an increase in the mass fraction of carbon from 0.11-0.12% to 0.13-0.14% decreased the volume of surface scarfing by third. For the steel with 0.14-0.16 wt.% carbon the optimal mass fraction of manganese was 1.35-1.50% (i.e. the largest value of Ferritic Potential). The decrease in the mass fraction of manganese to 1.23-1.35 % (at the same mass fraction of carbon) significantly affected the surface crack index.

In addition, the fraction of continuously cast billets with cracks increases with the sulfur content in the steel, because the formation of inclusions of manganese sulphide between dendrites depends on the ratio $[Mn]/[S]$ (a typical example of the formation of manganese sulphide on the surface in dendritic spaces is presented in Reference [10]).

Fig. 2 shows the steel with a mass fraction of carbon over 0.12% (i.e. high Ferrite Potential) the amount of scarfing was increased and for a group of heats with high ferritic potential impact of the mass fraction of sulfur affects more.

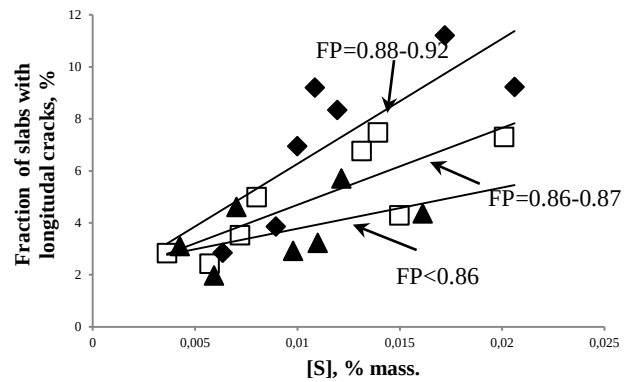


Fig. 2 - Effect of sulfur content on surface crack index in steels with various ferritic potentials.

On the basis of statistical analysis of industrial heats, shown in Fig.3, a manganese to sulfur ratio above 150 should be sufficient to substantially reduce longitudinal cracking in continuously-cast billets. A similar result, but less pronounced, was observed for correlation of the primary sorting slabs on longitudinal cracks and ratio $[Ca]/[S]$.

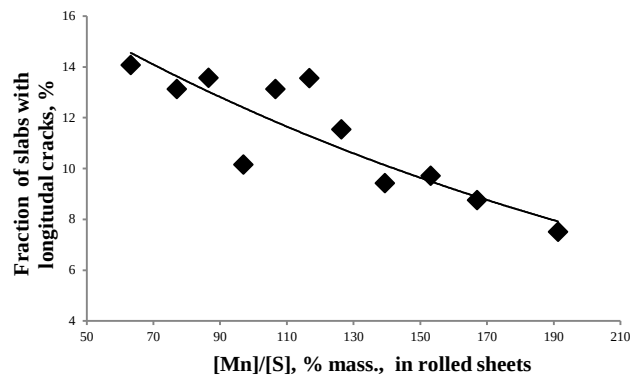


Fig. 3 - Influence of manganese to sulfur ratio on surface longitudinal crack index in peritectic steels, each point represents the average of 100 heats.

However, the possibility of varying the chemical composition of the metal is very limited; therefore, it is more practical to reduce the extent of cracking by optimizing the casting parameters such as the taper and heat transfer conditions in the mold.

Analysis of the continuous casting of peritectic steels using a curvilinear slab caster (220x1250mm to 300x1850 mm) showed that overheating of the metal in the tundish can increase the chance of longitudinal cracking (see Fig. 4). Thus, given the narrow range of chemical composition for this family of steels, it is advisable to reduce overheating in the tundish in order mitigate cracking problem. Additional benefit of reducing tundish temperate is having more uniform solidification of the shell.

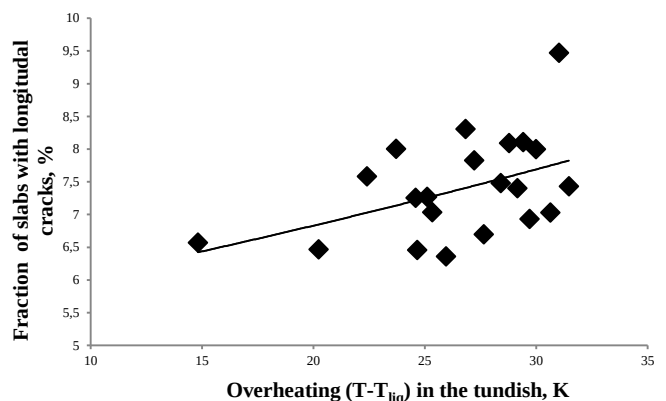


Fig. 4 - Effect of tundish superheating on surface crack index in a continuously cast peritectic steel billets, each point represents the average of 100 heats.

3.2. Calculation of optimal mould taper

However, changing overheating of the metal entails a change in the speed of casting. This is especially important for peritectic steel grades due to the strong dependence of the heat flux in the mold from the mass fraction of carbon with a sharp decline in it for peritectic steels [4].

Optimum casting speed, which depends on the heat flux and mass balance, can be estimated using the following equation (taking into account assumptions about the almost complete removal of overheating in the mold):

$$w = \bar{q} \cdot \frac{2h_a}{\rho(Rc\Delta T + 2xL)} \cdot \left(1 + \frac{R}{b}\right), \quad (3)$$

where $\bar{q}$ is the mean heat flow extracted from the slab surface in the mold; h_a is the height of the mold; b & R are the width and the thickness of the slab; c is specific heat of the metal; x is the thickness of the solid shell and L is the heat of crystallization.

The Calculation was carried out using a modified dependence [11], in which the coefficient A is assessed by monitoring the heat flux in the crystallizer:

$$\bar{q} = A \cdot \left(\frac{R}{2}\right)^{0.11} \cdot \left(\frac{2\mu}{1+\mu}\right)^{-0.75} \cdot \mu^{0.3} \cdot \left(\frac{h_a}{w}\right)^{0.43}, \quad (4)$$

where μ is the aspect ratio of the cross-section of continuously cast billets.

The statistical analysis showed that the volume of surface stripping depends on the casting condition, withdrawing speed corresponds as of Eq. (3). By proper selection of withdrawing speed and using an optimum tundish temperature the longitudinal cracks in the slabs could be reduced by 30-35%.

An important factor influencing the longitudinal cracking in the slabs is the mold taper. As shown by statistical analysis of industrial heats, with careful selection of a mold taper, depending on the coefficient of solidification kinetics and slab width, amount of stripping was reduced by 30-35%. Based on early work on the optimization of casting peritectic steel [3], the surface longitudinal crack index was reduced when using parabolic mold or a taper of 1.2-1.3 % compared with the conventional mold taper of 1.1%.

The taper of the mold must accurately reflect the change in the profile of the ingot caused by its shrinkage during solidification.

Assuming that the temperature of the metal in the cross-section solidified shell constant and equal to the average value between the liquidus temperature and the temperature on the shell surface, it is possible to calculate the optimal mold taper:

$$w = \frac{l_{up}}{h_{kr}} \cdot \left(1 - \frac{1}{1+k\sqrt{\frac{h_c}{v_{cast}} \left(\frac{\rho_{sol}}{\rho_{liq}} - 1\right)}}\right) \cdot 100, \quad (5)$$

where w is the taper of the narrow walls of the mold, %; l_{up} is the width of the upper section of the mold m ; h_c , h_{kr} are the real metal layer height for calculation and height of the mold, respectively, m ; ρ_{liq} , ρ_{sol} are density of liquid and solid steel, respectively, m^3/kg ; v_{cast} is the casting speed, m/min ; k is coefficient taking into account the kinetics of solidification of the shell (0.2-0.25), $min^{-0.5}$.

Hence, as of the statistical analysis of industrial heats, by correct selection of a cone mold, depending on the coefficient of solidification kinetics and slab width, the stripping volume reached 10-15%.

4. Conclusions

Based on analytical modeling and statistical analysis of the surface cracks observed in industrial billets, the optimum casting parameters for peritectic steels were determined. The proposed formulas were used to optimise withdrawing speed and mold taper. The outcomes were crosschecked against the industrial tests.

Almost complete prevention of longitudinal cracks on slabs of peritectic steels and significant reduction of surface scarfing was achieved when the Mn to S and Ca to S ratios were above about 150 and 0.3, respectively.

The optimal values of the ferritic potential when casting peritectic steels with various carbon contents were determined. For steel without niobium the ferritic potential should be less than 0.88, whereas the steel containing 0.12-0.16% C, 0.08-0.12 and 0.10-0.14% C and 1.35-1.50% Mn - in the range of 0.76 ... 0.80, 0.80 ... 0.84, 0.86 ... 0.90, respectively.

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NUMERICAL STUDY OF HEAT AND MASS TRANSFER AT INOCULATIONS FILING TO THE SLAB CC MOLD

ЧИСЛЕННЫЕ ИССЛЕДОВАНИЯ ТЕПЛО - И МАССООБМЕННЫХ ПРОЦЕССОВ ПРИ ВВОДЕ ИННОКУЛЯТОРОВ В КРИСТАЛЛИЗАТОР СЛЯБОВОЙ МНЛЗ

Prof. dr. Hress O., Prof. dr. K. Wu, Prof. dr. Isayev O., post grad. st. Chebotaryova O., post grad. st. Cong Zhang,
post grad. st. Chengyang Hu
Wuhan University of Science and Technology

Abstract: Mathematical and numerical models for calculating heat- and mass transfer of metal bath in the mold of a slab CCM, that equipment the submerged nozzle with inclined discharge openings are developed. The thermal and hydrodynamic regularities of melt's behavior, including, in the feed to the mould inoculant in the form of a metal strip with a chemical composition different from the base, with possible oscillation.

KEYWORDS: CONTINUOUS CASTING, SLAB, MOLD, MOLTEN METAL, MATHEMATICAL MODELING

1. Introduction

Today on the all over the world 2/3 continuous casting blanks are slabs. But in spite for that so big volume of output today we have many open problems connecting with slab quality simultaneously with increasing casting speed and decreasing the expenditure of energy and material cost.

One of advanced method of continuous casting is using different kinds of inoculators. For inoculators usually use the metallic materials with chemical composition similar to casting metal. Along with rare using methods inoculators input to the liquid pool in the mould that are pellets, water coolers, rods special attention deserve the using metallic band.

Most of continuous casting blank defects form in to the mould and connect with heat and mass transfer character and intensity. Because investigation the mould processes is very actual for continuous casting blank quality improving at the high casting speed.

This question is very urgent when we use additional materials inputting to the liquid pool in to the mould and only science-band recommendation can guarantee receiving products high quality.

Investigation objectives – development of mathematical and numerical models of heat and mass transfer of processes band's input in to slab CC mould.

This task can decide by methods of physical and mathematical modeling with following check and adaptation at the working environment. All decisions well be exclusive and can be use to special investigated type of CC and technological parameters. Mathematical modeling is most flexible method of investigation.

Most interesting investigation in this field are manuscripts [1, 2]. In manuscript [1] task decided for thin slabs casted at radial caster. Was used professional program packages for hydrodynamics and heat and mass transfer Fluent 5.5/Gambit 1.3 based on the RNG- $k-\epsilon$ turbulence model with accounting of liquid metal enthalpy changing. Model adequacy checked at physical model.

Joint two dimensional model of heat and mass transfer in the CC bloom mould with inert gas input to the metal stream decided in manuscript Joint two dimensional model of heat and mass transfer in to the CC bloom mould with inert gas input to the metal stream decided in manuscript [2].

The main disadvantage of that research works were impossibility to investigate speed and thermal fields in the mould with band feeding. But model from manuscript [2] that checked on the physical model and in the work environments can predict heat and mass transfer after inoculates feeding in to the liquid pool in the mould after model transformation from two dimensional to three dimensional.

2. Investigation methodic

1. The model created on the common approach basis to multiphase systems [3, 4]. The basic model assumptions:

2. Basic metal with specified chemical composition cast to slab mould through one SEN with two unloaded inclined side openings.
3. Steel band with different from basic metal chemical composition feeding in to the mould straight down parallel mould wide side at the specified distance from SEN.
4. Metal meniscus is quiet, without waves and covered by slag. Therefore the accounting of free surface dynamics isn't required.
5. Heat removal conditions to mould and band depend from metal streams speeds and describe the border between solid metal and mushy zone.
6. The band feed straight down on the vertical mould axis at the specified distance from SEN.

Well-known stationary Navier–Stokes equation, equations of liquid metal continuity and heat transmission in mold was the basis of moving and heat transfer mathematical model:

$$(\vec{v}\nabla)\vec{v} = -\nabla p + \nu\Delta\vec{v} + \vec{g}, \quad (1)$$

$$\nabla\vec{v} = 0, \quad (2)$$

$$\nabla(\vec{v}T) = \nabla(\lambda\nabla T) + Q, \quad (3)$$

where $\vec{v}$ – velocity vector; p – pressure; ν – coefficient of effective kinematic viscosity; $\vec{g}$ – vector, taking in account the action of mass volume forces (acceleration of gravity etc); T – temperature, λ – metal thermal conductivity; Q – thermal volume source, taking in account heat of phase transition at the steel solidification process.

Taking in account the task character mould geometry was approximated by orthogonal non uniform net and in equations (1–3) used Cartesian coordinate system. In equation (1) used Boussinesq approximation on the first stage calculations that taking in account lifting force because liquid metal has different density at different temperatures. Density at kinetic momentum equations is constant. Stationary equations system solved by assignment method.

Hence velocity vector $\vec{v}$ can divide to axis constituents OX, OY, OZ. Normalized presser for equation (1) introduced for convenience decision. Q in equation (3) changed to effective heat capacity C_{ef} . C_{ef} taking in account crystallization heat release at the time of steel solidification in the temperature range liquidus T_L – solidus T_S . Introducing additional assumption about metal fluidity absence at temperature lower than T_L .

The penetration absence and free sliding are conditions for velocity boundary conditions on the symmetry axis and near solid surface

$$v_{\perp}|_S = 0, \vec{n} \cdot \vec{\nabla}_{\parallel}|_S = 0, \quad (4)$$

and free moving stream condition on the free surface and on the down side of calculated field:

$$v_{\perp}|_S = v_S, \vec{n} \cdot \vec{\nabla}_{\parallel}|_S = 0, \quad (5)$$

where $\vec{n}$ – normal vector to surface.

v_s accept velocity stream finish value at the SEM exit and is equal 0 at the other surface.

Solidified skin freezing was calculated on the basis of well-known Fourier thermal conductivity equation with near-equilibrium mushy zone approximation

$$C_{ef}(T) \cdot \rho \frac{\partial T}{\partial \tau} = -C_L \cdot \rho \vec{\nabla}(T\vec{v}) + \vec{\nabla}(\lambda \vec{\nabla}T), \quad (6)$$

where

$$C_{ef}(T) = \begin{cases} C_s, & T < T_s \\ C + \frac{L}{T_L - T_s}, & T_s \leq T \leq T_L \\ C_L, & T > T_L \end{cases} \quad (7)$$

For equation (7) T , T_L , T_s – current temperature for calculated field, liquidus and solidus temperatures accordingly; C_{ef} – effective thermal capacity depended from thermal capacity in the solid phase (C_s), liquid phase (C_L) and in mushy zone (C). Thermal conductivity in mushy zone is equal:

$$C = (C_{liq} - C_{sol}) \frac{T}{T_L - T_s} + \frac{C_s T_L - C_L T_s}{T_L - T_s}. \quad (8)$$

This task can solve with natural variables by physical factor split method and can be realize in the form of three stage split schedule. This system is combination of physical factors split method to equation of hydrodynamics and recalculated difference scheme:

$$1. \quad \vec{v} = \vec{v} + \Delta\tau [-(\vec{v}^n \cdot \vec{\nabla})\vec{v}^n + \nu \Delta \vec{v}^n], \quad (9)$$

$$\tilde{T} = T^n - \Delta\tau c_{\rho_l} \vec{\nabla}(T^n \vec{v}^n). \quad (10)$$

$$2. \quad \Delta \vec{p}^{n+1} = \frac{\vec{\nabla} \cdot \vec{v}}{\Delta\tau}. \quad (11)$$

$$3. \quad \vec{v}^{n+1} = \vec{v} - \Delta\tau \vec{\nabla} \Delta \vec{p}^{n+1}, \quad (12)$$

$$T^{n+1} = T^n + \Delta\tau \vec{\nabla}(\lambda_l \vec{\nabla} \tilde{T}). \quad (13)$$

where n – number of times layer; τ – times pitch; λ_l, ρ_l – liquid metal thermal conductivity and density accordingly.

Stage 2 fulfill in the liquid phase only.

Boundary conditions for pressure on calculated field was received by project (12) to surface normal.

The heat exchange on the model symmetry axis set absent. Heat exchange on the slag surface set by means radiative and convection heat exchange. Specified superheat temperature set on the place of stream entrance to the mould.

First kind boundary conditions on the mould surface set by means power law (statistical literature data manipulation):

$$T_s = T_f + (T_i - T_f)^{1 - \frac{v_c}{l_{cr}}}, R=0,95, \quad (18)$$

where T_i, T_f – initial input metal temperature to the mould and slab surface temperature on the exit of the mould accordingly; v_c – casting speed; l_{cr} – mould length; R – multiple correlation coefficient.

Third kind boundary conditions was set on the slab surface after mould.

The net with variable pitch used for decrease the calculation time because the band width is low.

Presented model realized by Delphi 7.0 medium. The band feeding modeling fulfill after heat and hydrodynamics conditions were stabilize.

The model adequacy was check by comparison calculated data with physical modeling results and end-use measurements [5].

3. Discussion

Heat and mass transfer process on the mould with dimensions 2300*300mm and with 900mm length was investigated. Casting process of steel grade S355 with superheat 15°C at the mould entrance was modeling. The distance from SEN unloaded openings axis to metal meniscus was 150 mm. Unloaded openings inclination angle was 15° down. Casting speed set 0.9 m/min. The slab surface temperature on the mould exit was 1150°C.

Metal band has chemical composition correspond to steel grade 45. The band thickness was 1.5 mm and width was 400 mm. The distance from SEN axis to band end face was 200 mm. The inoculator feeding speed was 5 m/min to demonstrative calculations. Initial band temperature was equal 20°C. Heat and mass transfer investigated whet band feeding was in quiet mode and with transversal oscillation imposition to the band. The oscillation frequency was 150 Hz and amplitude was 2 mm.

Isosurfaces of metal stream absolute velocities without inoculators input you can see on fig.1. Here and after isosurfaces correspond 0.06; 0.15; 0.3; 0.55 m/s velocities. Obviously, two symmetric metal streams in this case arise in the metal volume around SEN with direction to mould narrow sides and down.

Flowing metal streams created enclosed extended along withdrawal axis vortexes in the longitudinal sections. That streams intensity decries from mould axis to mould wide walls and have the tendency to SEN unloaded openings approaching. More difficult conditions we can see on the transversal sections. On the upper side of the mould streams go to SEN with some down angles. On the deep side streams change them direction and create enclosed and extended with different angles to vertical axis vortexes. It process promote flow out of SEN unloaded openings metal stream energy dissipation.

Metal streams direct to mould narrow walls on the level below SEN unloaded openings except narrow walls neighboring fields. Short enclosed vortexes form near SEN body and promote solidification rate decrease in wide walls local zones. After some times that vortexes intensity and temperature decrease and solidification rate in that local zones increase and solidified shell thickness along mould perimeter become level. Metal motion become laminar and short enclosed vortexes remain in mould corners only.

Solid and liquid phases behavior in the case of band feeding without oscillation superposition you can see on the fig 2. The band thickness increased artificially for better visual clearness (here and after).

Liquid metal stream divide in two symmetric parts with vortexes between band and SEN similar previous case. High stream speeds and temperatures lead band near axis fields submelting with phase borders creation. Basic chemical composition solid shell on the band surfaces from steel meniscus deep down created due to band material cooling effect. The shell thickness increase from meniscus up to 0.3m depth and after that the band thickness decrease up to 0. Together with this process dual phase not mobile indelible layer of basic metal and inoculators material creates on the band surface The thickness of this layer increase along all mould length by exponential dependence. The band thickness initially increase and after decrease up to 0 in the direction normal to big mould axis. All this phenomena create liquid streams reorganization and change them direction to mould wide walls and more intensive streams influence to solidified layers. The solidified rate in that zones slightly decrease if compare with previous case. The solid shell thickness at the mould exit is high if use special coolers – inoculators.

Visualization of calculated data for band feeding process with oscillation give on fig.3.

The oscillation superposition to the band change heat and mass transfer in the mould. In particular steel streams arise on the surface steel layers directed to mould narrow sides. In this case cooling rate increase and solidified skin decrease from behind more high heat emission.

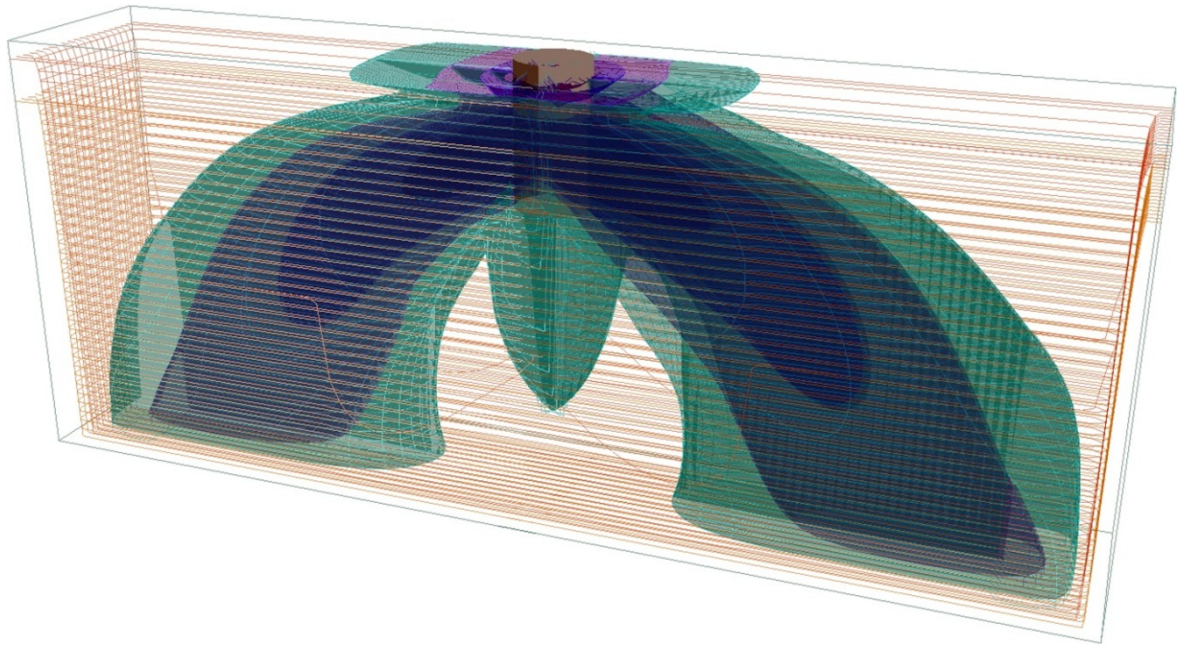
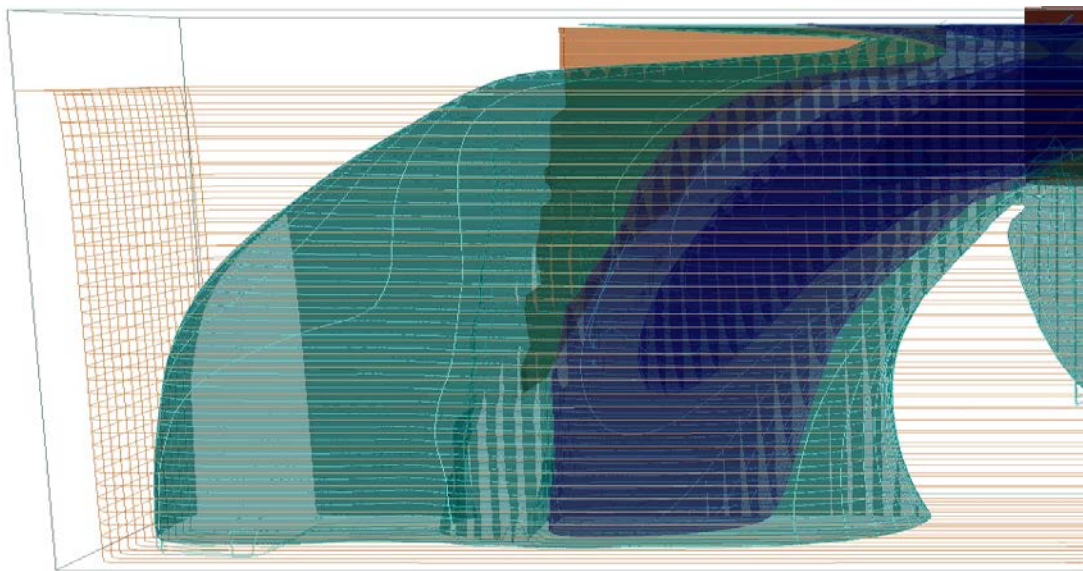
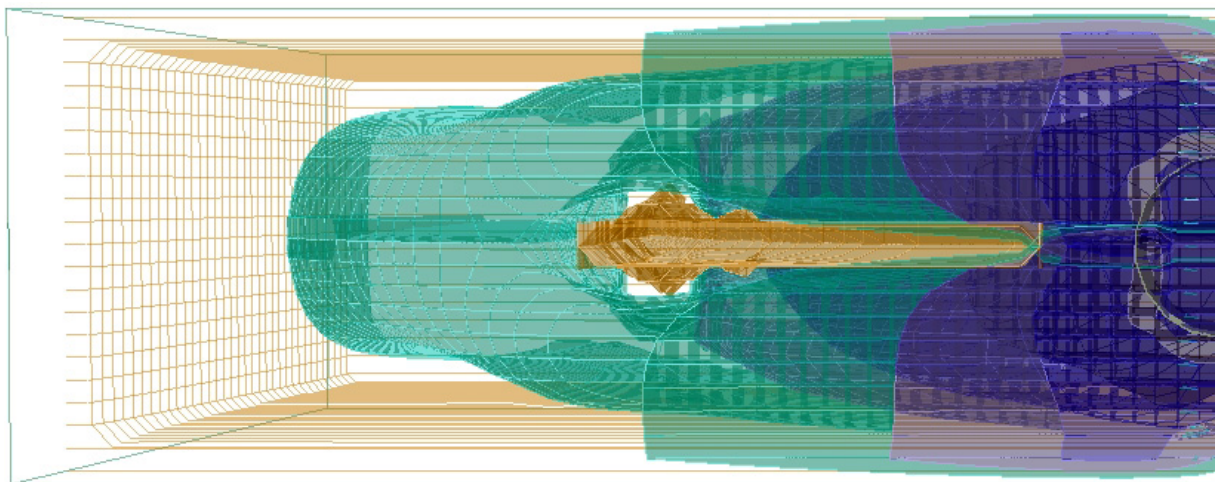


Fig. 1. The hydrodynamic of metal in the mould without band feeding



a



b

Fig. 2. The hydrodynamic of metal and solid phase location in the mould with band feeding and without band oscillation a – frontal view ; b – plan view

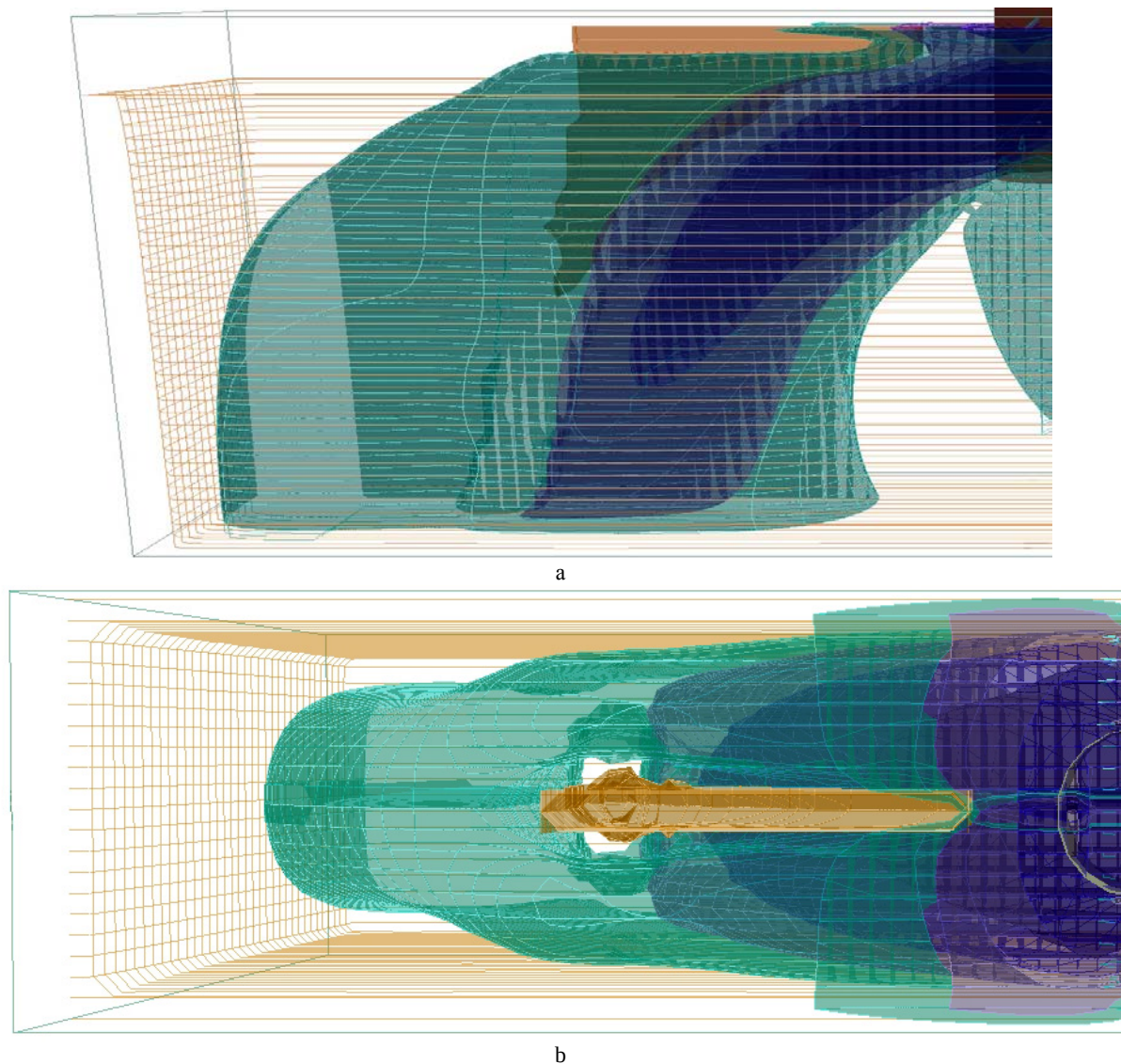


Fig. 3. The hydrodynamic of metal and solid phase location in the mould with oscillated band feeding (half of the mould) *a* – frontal view ; *b* – plan view

The decreasing of freezing skin thickness on the band surface after heat transfer increasing permit metal hot portion penetrate to the mould narrow sides and stabilize the mould heat conditions. Except that skin growth rate increase and even along perimeter. Feeding band melting rate increase up to 35% at the band oscillation superposition mode.

4. Conclusions

With assistance developed mathematical and numerical models of slab continuous casting was investigated heat and mass transfer processes in to the mould with submerging nozzle equipped inclined unloading openings and with inoculator (band) feeding device with band oscillation. Was defined that band with given thickness and chemical composition and oscillation mode improve liquid pool heat and hydrodynamics conditions with simultaneous thickness skin increasing on the mould exit. The model can use for any slab dimensions and steel grades.

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METALLOGRAPHIC ANALYZE OF PARTS FOR BREAKING SYSTEM MADE OF NODULAR CAST IRON EN-GJS-500-7

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Abstract: In this research work, metallographic investigation of two parts which are implemented to railway wagons breaking system was performed. Both parts are produced from EN-GJS-500-7 nodular iron. One of delivered parts leading nut (part 1) was broken during the exploitation and the second part working nut (part 2) was new. Metallographic investigation based on standard EN 945-1 was implemented in order to check the quality of the parts. The reason for breaking of part 1 one was analyzed too. After metallographic preparation, the polished specimens they were analyzed under optical microscope in order to determine form, size, density and distribution of graphite per unite area as first graphite nodules were analyzed after that microstructure of nodular iron. Figures from optical microscope were compared with reference images under the same magnification. After etching the specimens their microstructure was analyzed. It was concluded that quality of the part 2 is much better concerning the requirement of the EN 945 -1 standard.

Keywords: NODULAR IRON, GRAPHITE, VERMICULAR, MICROSTRUCTURE, METALLOGRAPHY

1. Introduction

EN-GJS-500-7 belongs to the middle class of nodular cast irons. Its characteristics are defined with EN 1563 standard [1], which is equivalent with DIN 1693, and has designation GGG50. Mechanical and chemical properties defined according EN-GJS 500-7 [2].

Table 1 Mechanical properties of nodular cast iron EN-GJS-500-7 standard and measured values for two parts

EN-GJS-500-7	% Stand.	Part 1	Part 2
UTS, MPa	min 500	532	542
Yield strength, MPa	min 320	366	374
Elongation, %	min 7	9	10
Hardness, HB	170-230	227	231

This type of nodular iron don't has defined requirement concerning impact toughness. Its mechanical properties are given in table 1 and concern to the castings with the wall thickness 30-60 mm. Basic parameters which have to be fulfilled are UTS, yield strength and elongation. Hardness is not treated as quality requirement except in special situations. Chemical composition of the nodular iron is given in table 2.

Table 2 Chemical composition of nodular iron according EN-GJS-500-7 and measured values

Elem..	% Stand	part 1	part 2
C:	2.7-3.7	3.2	3.4
Si:	0.8-2.9	2.4	2.3
Mn:	0.3-0.7	0.5	0.45
P:	≤0.1	0.06	0.05
S:	≤0.02	0.015	0.012

Chemical composition could be different for different standards. International standard gives broad freedom to the producers concerning to the chemical composition in accordance with their experience and production conditions until requirements for mechanical properties are fulfilled. Many foundries in the world can produce this type of nodular iron but always should to select good producer. Quality of this nodular iron is mainly determined by the present graphite nodules, their form size and distribution and their microstructure. Because of that that investigation in this research work was performed.

2. Material and experimental

Standard metallographic preparation of specimens was performed after grinding on different abrasive papers 100, 220, 280, 400, 600, 800 и 1200 polishing with diamond paste (1 and ¼ µm) was performed. Graphite nodules were analyzed at magnification of x100.

Part 1- Leading nut

Metallographic specimen from part 1 is given in figures 1 and 2, it is so called leading nut. This part was broken in the exploitation conditions. It has to be point out that this specimen was machined from cast bar φ55x400.

Before to start with metallographic analyses visual control of the part was performed. It was detected light areas on the fractured surface probably segregation of impurities which are the reason for fracture Figure 1. Besides, at the place of the fracture the wall of the leading nut is the thinnest. Metallographic prepared specimen from the broken part is given in the figure 2. Figure show longitudinally prepared specimen. Besides small surface near the broken specimens were prepared too in order to find some suspicious reasons for cracks appearing (Figure 2b). As can be seen from the fig fractured surface is not homogenous i.e. Light areas appear. Marked with arrows probably some segregation of impurities additionally has to be said that fracture location is on the thinnest part of the nut which is additional reason for the fracture.

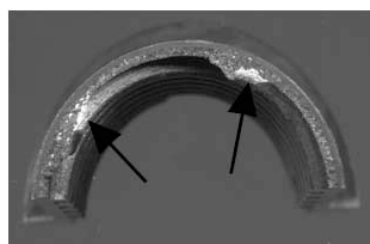


Figure 1 Broken surface of part 1

After visual control it was started with metallographic preparation. Cylindrical part was cut longitudinally to be obtained two equal parts. One of them was prepared for metallographic investigation (figure 2a). Besides lateral surfaces near the fractured surface were prepared too (figure 2 b), marked with rows.

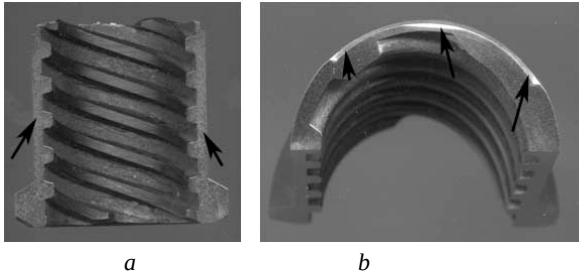


Figure 2 a longitudinally prepared specimen b laterally prepared surface

Presented nodules in the part 1 are given in the figure 3 (a and b), and its microstructure is given in figure 4.

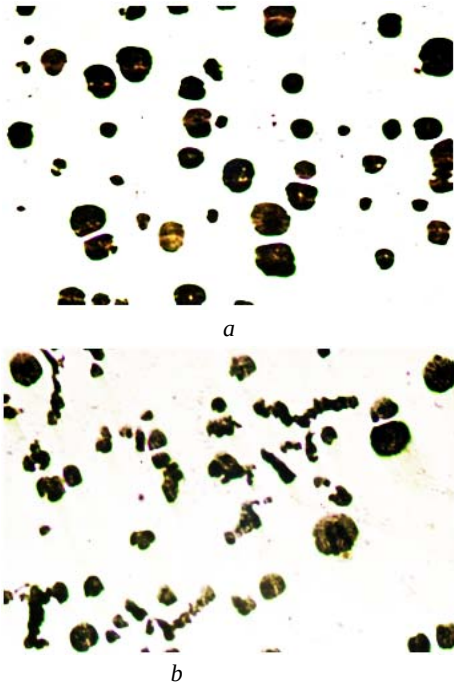


Figure 3 Polished specimen from part 1, x100

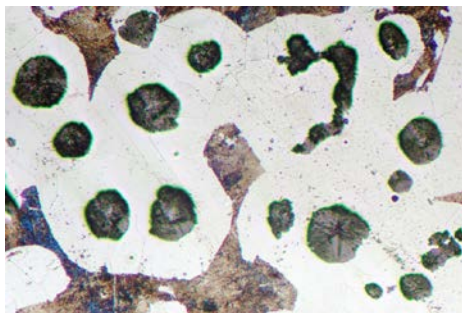


Figure 4 Microstructure of part 1, etching with Nital

Part 2 - working nut

The second investigated part i.e. Working nut is given at figure 5a, and the specimen prepared for metallographic investigation is given at figure 5b. As can be seen from the macro specimen, micro pores are noticed on the specimen (denoted with black arrow). Micro pores can appear in the cast specimen, in the case of very fast cooling when present gases are entrapped inside the specimen. But in this case they can't be serious problem for the quality of the part.

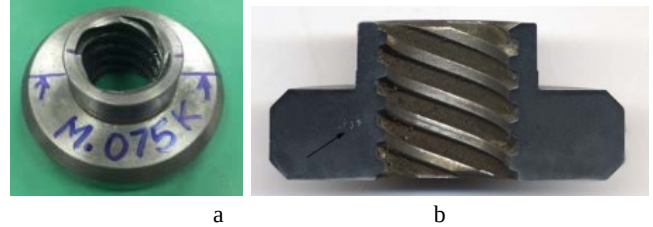


Figure 5 Investigated part 2 working nut a, prepared specimen b.

At the figure 6 are presented pores at higher magnification x200. It can be seen that they are with irregular shape. Figure 7 presents the nodules of free graphite in the part 2, Graphite nodules are much smaller compared with part 1. And Microstructure of part 2 is given at figure 8

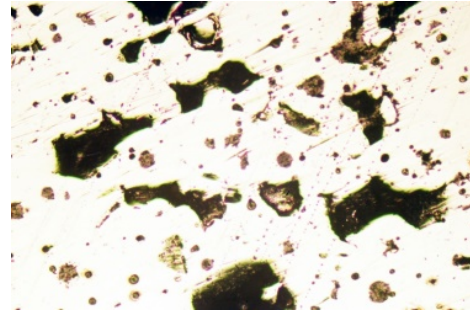


Figure 6 Micro photo of polished specimen with presented pores, x200

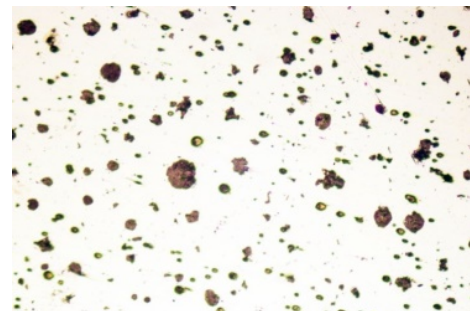


Figure 7 Micro photo of polished specimen with graphite nodules, x100

After analyze of graphite nodules, microstructural analyze was performed. Because of that, polished specimen was etched with Nital. Microstructure of part is given at figure 8. It consists of ferrite and perlite.

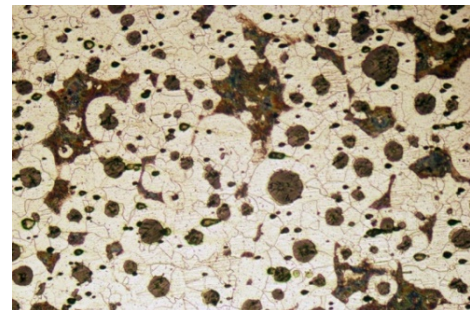


Figure 8 Microstructure of part 2

3. Discussion

Graphite nodules presented in both specimens were compared with reference pictures from EN 945-1 given in figure 9.

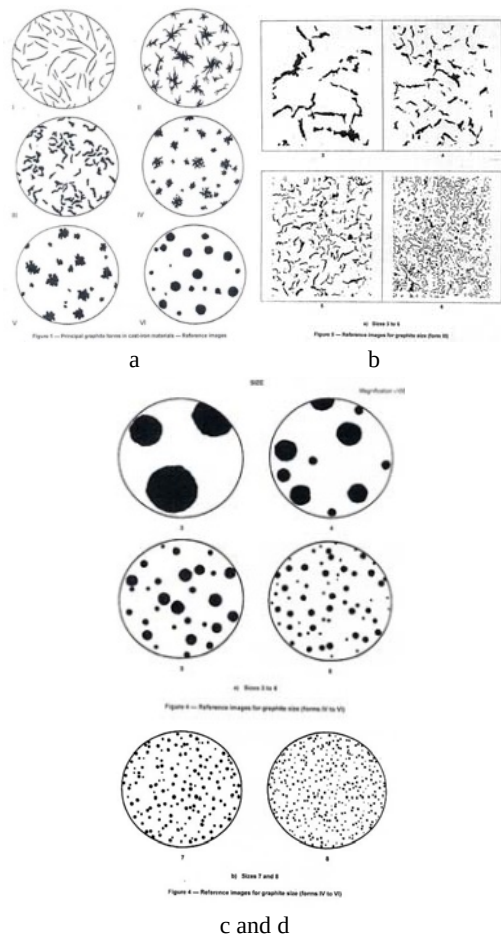


Figure 9 Reference figures from standard EN 945-1

Graphite forms are presented at figures 9a. They are denoted with Roman numbers I – VI. In both specimens graphite forms V and VI are dominated. Requirement from the purchaser is to be presented 90-95% and the rest form IV. In part 2 these requirement are completely fulfilled. But in the part 1 graphite form III so called Vermicular ferrite is presented too (figure 3b and figure 9b). This form of graphite according its mechanical properties is between form I i.e. laminar graphite and nodular graphite, form VI Concerning the properties of cast iron, the best solution is presence of form V and VI [3]. The worst situation is presence of the form I, because laminar graphite gives the highest stress concentration in the iron. Vermicular graphite is something thicker than laminar ferrite vermicular graphite i.e. forms III. The properties of vermicular graphite are between lamellar and nodular graphite [4]. This form could be required in some special cases but in this case it is not necessary.

Nodular ferrite is the best form compared to all other but finer nodules give the best results. Concentration of free graphite in the nodular iron should be 15-20 % from total investigated surface. Number of nodules per unite should be 200-250 nodules/cm². This requirement is fulfilled for part 2. And the number of nodules is lower than requirement for part 1 [5].

The size of nodules in part 1 is mainly 4 and 5. Nodules in part 2 are much finer and are in range 5-8 (Figure 9c). The size of presented vermicular graphite (figures 3b and 9b) is size 4.

4. Conclusion

Metallographically were investigated two specimens from nodular iron EN-GJS-500-7.

It was concluded that specimen 2 completely fulfilled standard requirement. On the contrary specimen 1 was broken in exploratory conditions and form, size and distribution on free graphite is not at appropriate level.

5. Literature

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STUDY THE INFLUENCE OF ALLOYING ELEMENTS ON THE STRUCTURE OF IRON-BASED ALLOYS WITH HIGH CONTENT OF CARBON, MANGANESE AND CHROMIUM IN MODES OF HEAT TREATMENT

ПРОУЧВАНЕ НА ВЛИЯНИЕТО НА ЛЕГИРАЩИТЕ ЕЛЕМЕНТИ ВЪРХУ СТРУКТУРАТА НА СПЛАВИ НА ЖЕЛЯЗНА ОСНОВА С ВИСОКО СЪДЪРЖАНИЕ НА ВЪГЛЕРОД, МАНГАН И ХРОМ ПРИ РЕЖИМИ НА ТЕРМИЧНО ОБРАБОТВАНЕ

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Abstract: Demand for alloys with high mechanical performance and optimum qualities in the service conditions require new studies regarding thermal stability, wear resistance and corrosion resistance to them. Of interest are materials in which the deficient and expensive Ni is partially or completely substituted with Mn, such as the alloys of the systems Fe-Cr-Mn-C or Fe-Cr-Mn-Ni. To build an accurate picture of the structural features, properties and their behavior in the operating conditions need to be carried out relevant studies. The objectives of the study are related to clarify the processes of structure formation in heating and cooling of this type of austenitic alloys. Object models are cast with an increased concentration of carbon and constant chromium and manganese in the starting composition, as well as those supplemented with vanadium and nickel.

KEYWORDS: ALLOYING, VANADIUM, NICKEL, HEAT TREATMENT, MICROSTRUCTURE

1. Introduction

The aim of this study are materials in which the deficient and expensive Ni is partially or completely substituted with Mn, such as the alloys of the systems Fe-Cr-Mn-C or Fe-Cr-Mn-Ni, [1-3]. To an accurate picture of the structural features, properties and their behavior in terms of their exploitation, we made the investigation plan and carried out the relevant studies. The objectives of these investigation are related to clarify the processes of structure formation at heating and cooling of this type austenitic alloys. A starting composition of the alloys include a high concentration of C, constant content of Cr and Mn, as well as supplemented with V and Ni.

Major contribution to the systematization of the results have previous studies of the team on the alloys of the system Fe-Cr-Mn with carbon content more than eutectic. Novelty is the further enriched with vanadium and nickel, the mechanisms of structure formation during the casting process and changes after heating and cooling of this type alloys that still contain unknown and should be fully investigated.

2. Preparation of starting materials

The starting materials are prepared in an induction autoclave with basic lining of crucible. The melting is effected in the closed position of the machine and under pressure of about $12 \cdot 10^{-5}$ Pa. Raw materials are St. 3, electrolytic manganese, chromium electrolyte, electrode graphite, technically pure aluminium and ferrosilicon. Melt is treated in the atmosphere with molecular nitrogen, ferroalloys are imported under pressure. The nitrogen is present in the composition of the alloys by the addition of ferromanganese and chromium as additives. The temperature of the casting is in the range of 1480-1500°C. Control over the temperature changes during the process is carried out by W-Re thermocouple and recording device "Servogor". Alloys are pouring into dry sand forms with a rectangular section. After crystallization of cast shapes are cut specimens on abrasive machine with special cooling, preventing strain hardening of the surface layer. Samples are shaped with an area of study $15 \div 20 \text{ mm}^2$, suitable for metallographic and X-Ray structural analysis.

3. Chemical composition

The percentage of chemical elements in resulting alloys is pre-determined by separation of filings according to standard technology and spectral analysis of Spectrolab, Germany. To specify the nitrogen content of the samples is made a gas analysis in Institute of Metal Science, equipment, and technologies "Acad. A. Balevski" with Center for Hydro- and Aerodynamics at the Bulgarian Academy of Sciences, (IMSETHAC-BAS). The exact chemical composition of materials is presented in Table 1.

Table 1. Chemical composition of the studied alloys

Alloys	C, %	Mn, %	Si, %	Cr, %	V, %	Ni, %	N, %
1 (300)	1,38	22,6	0,45	4,0	-	-	0,442
2 (310)	1,38	22,2	0,42	4,0	1,52	-	0,451
3 (320)	1,38	22,2	0,10	3,8	-	2,2	0,348

4. Heat treatment (HT) of the alloys

□ Homogenization

Thermal treatment of samples was conducted in two stages. The first stage of research is homogenization at 1150°C for 2 hours. The aim is dissolving of the compounds at high temperatures (carbides, nitrides, etc.) in the solid solution matrix which is homogeneous. Hardening after homogenization is in water for the purpose of fixing the high temperature state, i.e. in order to avoid disintegration of the solid solution and separation of the second phase from him. A greatest rate of absorption of carbon and nitrogen at high temperatures of homogenization is carried out at crumbling of carbide, nitride and carbo-nitride phases. This heat treatment is implemented in a furnace type Ks-400. The specimens are bombarded with corundum to be protected of the oxidation atmosphere of the furnace and reduce the surface diffusion processes. All samples are simultaneously placed in the furnace and after reaching the 1150°C the retention is two hours. After removing from furnace, the samples are immediately cooled in water.

□ Aging

At the next stage of heat treatment the samples are put on aging at temperatures 500°C, 700°C and 900°C and times of retention 1, 5,

10 and 20 hours followed by rapid cooling in water. The modes are presented in Table 2.

Table 2. Modes of heat treatment

Spesimens	Modes of HT	T [°C]	Time, [h]	Cooling
1 (300) 2 (310) 3 (320)	Homogenization	1150	2	H ₂ O
	Aging	500 700 900	1, 5, 10, 20; 1, 5, 10, 20; 1, 5, 10, 20;	H ₂ O

5. Measurement of hardness of samples

Device for measuring of hardness is combined device HP-250. A standard method of Rockwell with load 1471N is attached. Reporting is done on scale 1Rc=0,002mm depth of penetration. The results are summarized in Fig. 1÷3.

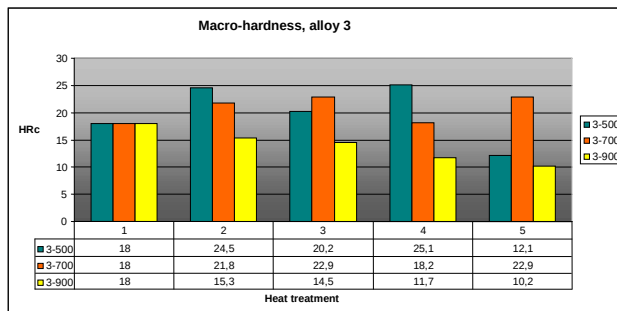
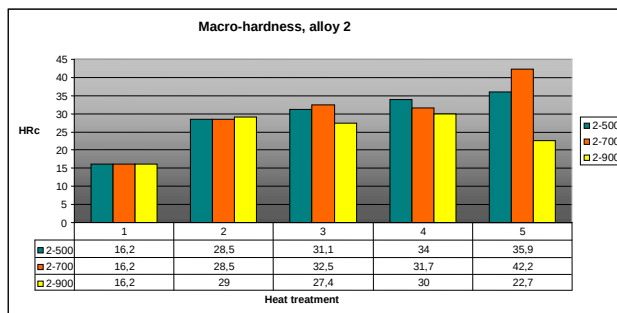
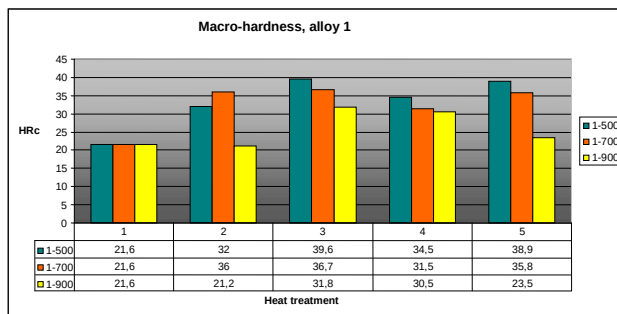


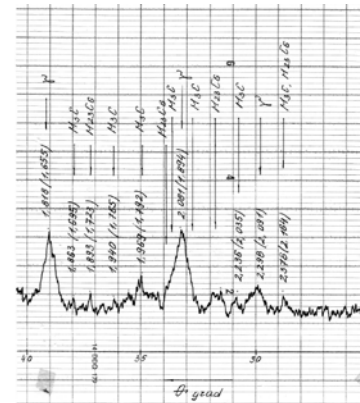
Figure 1÷3 Data for hardness of the alloys

6. X-Ray structural analyse

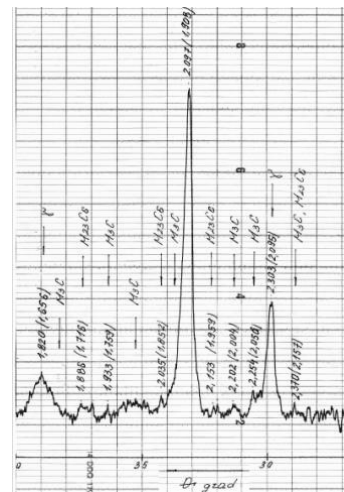
As a result of that analyse the facts are obtained for the distribution of elements at the alloys in the form of different phases and compounds. This is based on the fact that each phase has its own crystal lattice, and this affects the X-ray as a specific system of lines. The phase composition is determined by the data, calculated from formulas and compared with standards. The results are compared with existing datas for the lines of carbides and solid solution phases α and γ . According to the serial numbers of the elements from the research system in this analysis is used Cr-radiation because it has the greatest wavelength $\alpha = 2,29092 \text{ \AA}$, [4].

Roentgenograms are made of some specimens and are shown in Figure 4.

Alloy 1



Alloy 2



Alloy 3

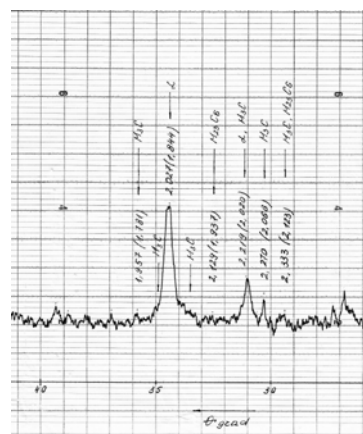


Figure 4. X-ray diffraction of the alloys after homogenization

7. Microstructure metallographic analysis

Samples are prepared for analysis by standard methods [5, 6]. The structure is developed with Nital (3% solution of HNO₃ in ethyl alcohol) and 10% solution of (NH₄)₂S₂O₈ in water. Metallographic images are made at 300x magnification. Fig. 5 shows only part of them.

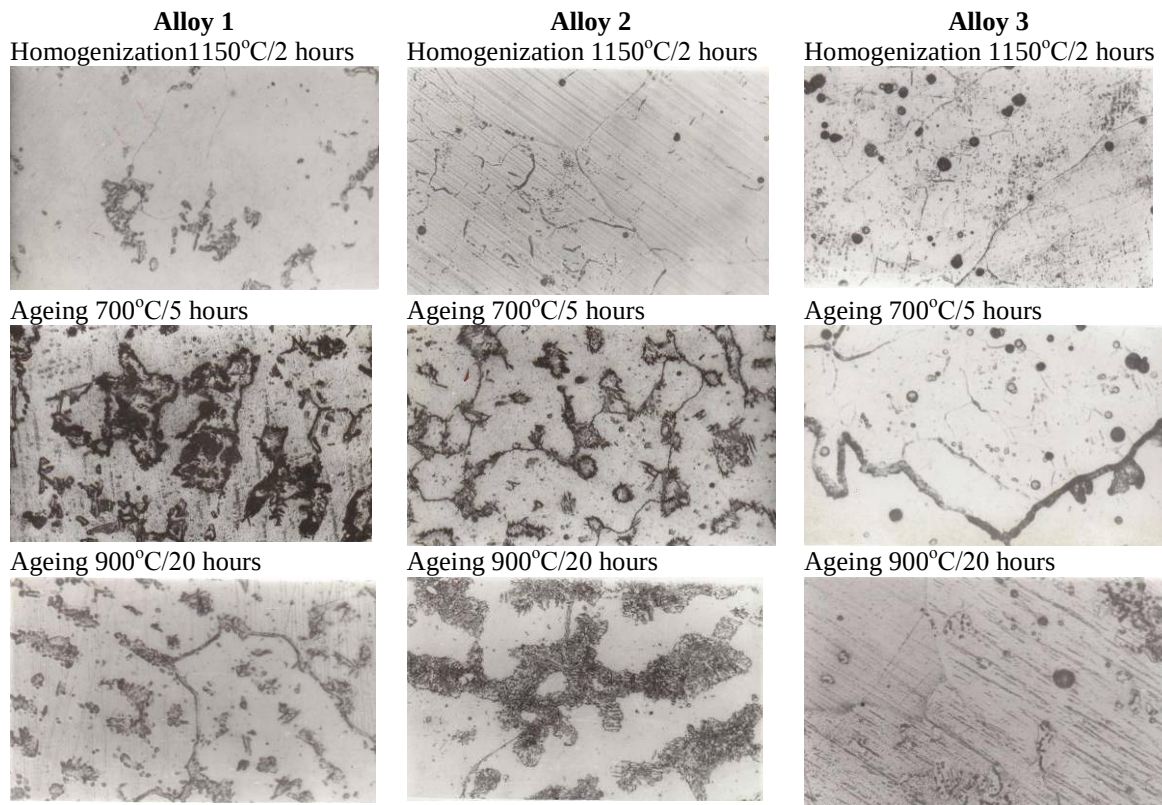


Fig. 5. Microstructures of the alloys after heat treatment (HT)

8. Conclusions

Alloy 1: In a homogenized state structure consists an austenitic phase and undissolved carbide of type Me_3C and Me_{23}C_6 - probably complex carbides $(\text{Cr}, \text{Mn}, \text{Fe})_{23}\text{C}_6$. The aging process starts separating the finely dispersed second phase of type Me_7CN_3 , as we conclude about this in accordance with variation of makrohardness. Upon aging $700^\circ\text{C}/5$ hours was observed maximum depositions and maximum in hardness. With longer retention disintegration takes place in the interrupted precipitation mechanism. Then are observed formation of sections of pseudo-eutectoid (γ +carbides), which quantity gradually decreases and is at least of prolonged retention of 20 hours. Upon aging $900^\circ\text{C}/20$ hours pass a dissolving the second phase (solid solution is saturated with the alloying elements and the amount of precipitates decrease).

Alloy 2: This composition has the greatest content of vanadium. According to X-ray structural analysis in homogenized condition are observed homogeneous austenitic grain and carbide phases type Me_3C and Me_{23}C_6 . Aging occurred with a change of microstructure. At low temperatures can be seen isolated grains, like teardrops, in austenite structure, around some non-metallic inclusions (HT at 500°C). With consolidation of the second phase at 700 and 900°C the hardness increase. The mechanism of precipitation under these temperatures is different from that at 500°C and with increasing of retention time leads to formation of colonies with analogy of eutectoid - γ + carbides.

Alloy 3: The composition has added Ni and missing V. Regularities, observed in aging are: absence of suspended eutectic carbides in a homogenized condition and correspondingly low values for HRC compared to the base alloy. At low temperature of aging there is not deposition from second phase in volume and over the grain boundaries. In 900°C and short retention are observed partial precipitates of the eutectoid type, and at 10 and 20 hours is observed the process of their dissolving in the austenite and consequently reducing in macro-hardness. The amount of second phase in any mode of aging is significantly less than the amount in the same mode, separated in the base alloy. This affects the absolute HRC, but the austenitic structure is more stable.

9. Literature

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MICROSTRUCTURAL CHARACTERISTICS OF AS CAST Ti-Zr ALLOYS

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Abstract: For many years casting alloys are widely used in dental applications. Among them, titanium and its alloys reveal the best properties for this purpose. However, the casting is difficult but it may be improved by alloying. This research deals with titanium-based alloys with zirconium additions. Investigated alloys were prepared by melting and casting in an electro-arc furnace under argon atmosphere. In order to identify the phases present in alloys, structural analysis was performed by X-ray diffraction method. It was showed two-phases microstructure of alloys. Further, zirconium addition in higher percentage contributes to formation of the beta phase of titanium which possesses more adequate properties than alpha titanium. Microstructural observations by scanning electron microscopy and energy-dispersive spectrometry showed that phases have similar chemical composition. Measured Vickers hardness values were lower than for pure titanium and are acceptable for dental applications.

Key words: Ti-Zr ALLOYS, DENTAL ALLOYS, MICROSTRUCTURE, CRYSTAL STRUCTURE, VICKERS HARDNESS

1. Introduction

Casting alloys are widely use for dental products making for many years. Among them, titanium and titanium-based alloys reveal the most adequate properties and continues to be the first choice for dental treatments [1]. Therefore are used for full-cast, metal-ceramic, and removable partial denture frameworks, dental crowns and bridges, endosseous dental implants and plates for oral maxillofacial surgery. However, the casting is difficult in these cases, because of titanium high melting point and its high reactivity with oxygen and impurities at elevated temperatures and because of need for special casting machines and investments [2,3]. To solve these problems as well as to improve mechanical properties, titanium is alloyed. Titanium alloys of interest to dentistry exist in three structural forms: alpha (α), beta (β) and alpha-beta. The alpha (α) alloys have a hexagonal closely packed (hcp) crystallographic structure stable at lower temperatures, while the beta alloys (β) have a body-centred cubic (bcc) form which is stable at high temperatures [4]. The phase α/β transformation takes place at 863 °C. Alloying elements affect this temperature, so α -stabilizing elements (Al, O) increase phase transformation temperature, while β -stabilizing elements (Mo, V) decrease it [5]. Zirconium is neutral element, which slightly lowers or decreases temperature of phase transition, depending on its content added to titanium [6]. Beta titanium is preferred against the alpha titanium since it has better properties acquired for dental use.

2. Materials and methods

In this investigation titanium alloys with 13 and 20 at. % of zirconium were prepared by casting and then examined. Zirconium was selected as alloying element since it improves mechanical properties of titanium and corrosion resistance as well as biocompatibility of titanium [7]. Preparation of alloys was performed by melting the pure elements (Ti 99.99% and Zr 99.9% in purity) in a laboratory arc furnace under argon protective atmosphere. Melting was realized by electro-arc established between the tungsten cathode and copper anode which was served as mould and it was rapidly water cooled. In order to achieve homogeneity, samples were remelted for five times. Obtained samples were in a form of "buttons" and then were casted in a cylindrical shape, 8 mm in diameter and 25 mm in a high. These cylinders were cut in pieces to acquire a several samples for examinations by different methods. Structural analysis, i.e. identification of present phases was performed by X-ray diffractometry (XRD) using a Philips PW3040/60 X'Pert PRO diffractometer with $\text{CuK}\alpha$ radiation generated at 40 mA and

45 kV. For microstructural characterization samples were metallographically prepared by grinding and polishing followed by etching in a Kroll's reagent. Microstructures of etched samples were observed by light microscope Olympus GX51 with digital camera. Detailed microstructural examinations were performed by scanning electron microscope (SEM) Tescan Vega TS 5136 MM and Bruker's energy dispersive spectrometer (EDS). Hardness of alloys was determined for polished samples by Vickers method at applied loads of 1.96 N (HV0.2) and 19.60 N (HV2) during 10 s. Diagonals of Vickers pyramids indented in samples were measured at 500 x magnification.

3. Results and discussion

According to the equilibrium phase diagram, zirconium and titanium form solid solutions in the entire range of concentrations. Precisely, low-temperature ($\alpha\text{Ti,Zr}$) and high-temperature ($\beta\text{Ti,Zr}$) solid solution [6]. Diffractograms of investigated alloys, obtained by XRD analysis, are displayed in Figure 1. Phase identification was performed by matching each peak with JCPDS-ICDD files [8]. As can be seen on identified XRD patterns shown in figures 1 both alloys consist of two phases. In alloy with lower Zr content (Fig.1a) alpha Ti and martensitic α' phase are present meaning that 13 at. % of zirconium is not enough to achieve β phase of titanium. Higher zirconium content (20 at. %) led to phase transformation $\alpha \rightarrow \beta$ and this β Ti was retained at room temperature (Fig.1b) due to fast water cooling of alloy through a copper mould. Since the alpha and alpha' phases of titanium as well as beta titanium show diffraction peaks at similar 2Theta values, it was necessary to observe micrographs of alloys for confirmation of present phases.

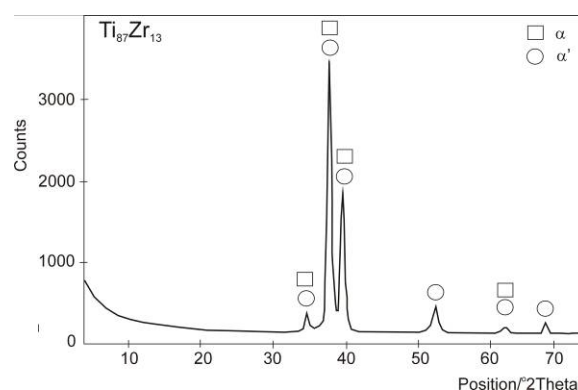


Fig.1a XRD analysis of alloy containing 13 at.% Zr

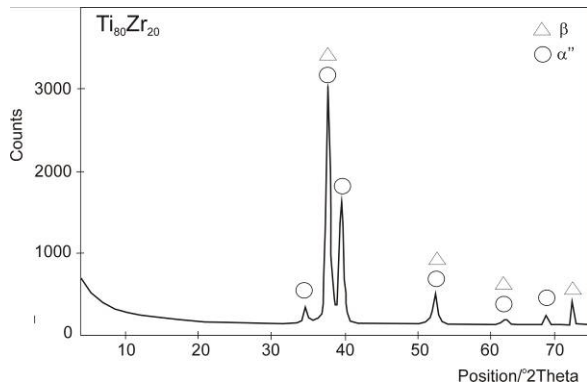


Fig. 1b XRD analysis of alloy containing 20 at.% Zr

Micrographs of investigated alloys are presented in Figure 2. It can be seen that microstructure of alloy with lower Zr content is two-phases indicating the martensitic α' phase (light area) within the matrix of α Ti grains (gray area). Dark area is not a phase, but presents the spots of stronger activity of etching agent. In figure 2b two phases are visible, but lighter one is in a much less extent.

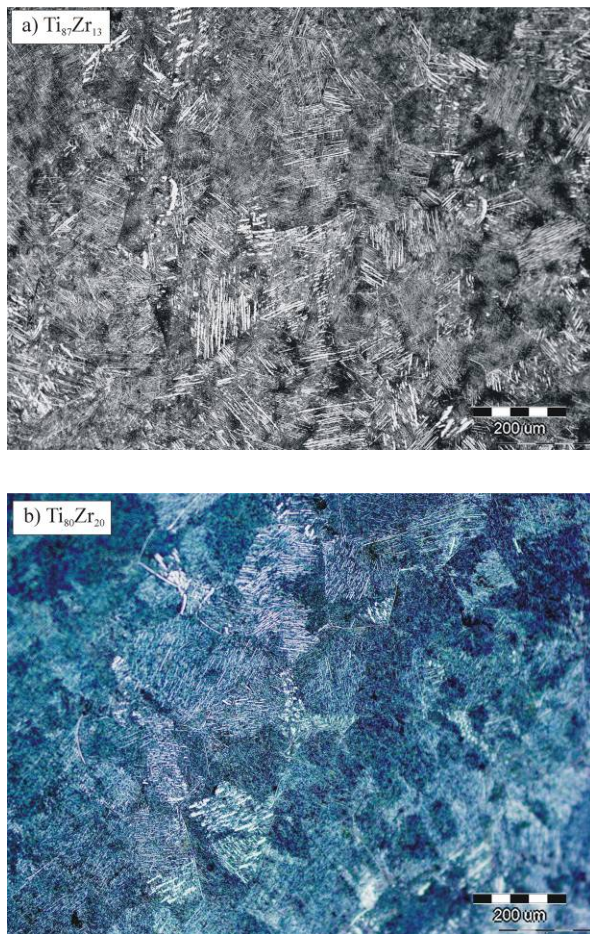


Fig. 2 Microstructures of alloys

It is known that alloy phases in titanium alloys depend on the chemical composition and cooling conditions during the casting. Therefore, if the cooling rate is a fast enough an acicular or lath-like martensite is formed. Martensitic transformation involves the movement of atoms in the groups using the shear process. This results in a microscopically homogeneous non-diffusional transformation of cubic volume centered crystal structure into the hexagonal close packed complex structure within the entire volume. This martensite with hexagonal structure is referred to as α' and occurs at high cooling rates and a small proportion of β -stabilizer. With the increasing content of alloying element distortion hexagonal structure of martensite takes place. From the

crystallographic point of view, it loses its hexagonal symmetry, so it is described as a rhombic and designated as α'' [5,9]. Detailed examination of microstructure was conducted using the SEM and EDS. It is obvious on SEM micrographs (Figure 3) that microstructure of alloy with lower Zr content consists of two phases which are differ from these in figure 3b. Namely, it is clear that alloy with higher Zr content contains coarse β Ti grains and needle-like phase. This phase is an evidence of beta phase transformation into martensitic α'' phase which occurs during the fast enough cooling of an alloy [10-12].

EDS analysis in point showed peaks characteristic for only Ti and Zr, indicating that alloys were not contaminated during the preparation. It means that only solid solutions (α Ti,Zr) and (β Ti,Zr) were formed. Further, similar intensity of peaks pointed in different phases means the similar chemical composition of phases (Table 1).

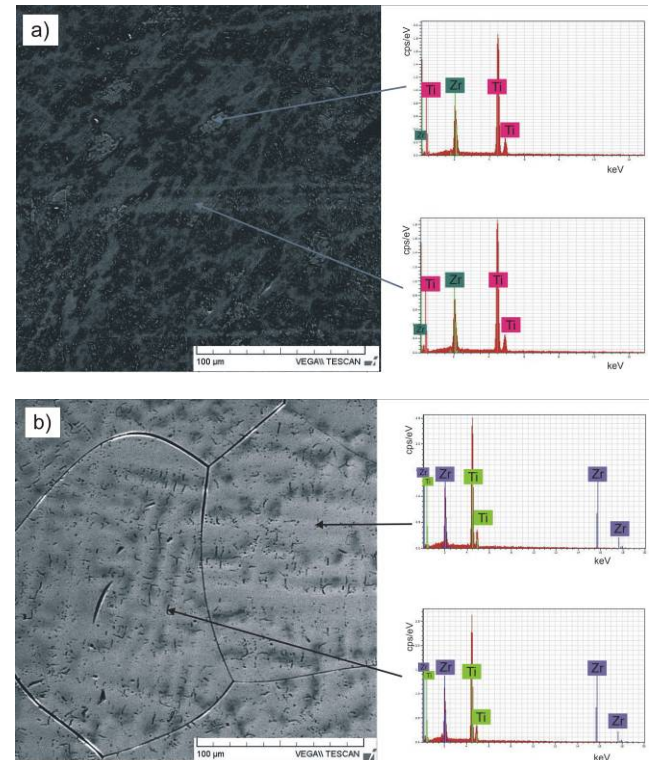


Fig. 3 SEM and EDS point analysis of a) $\text{Ti}_{87}\text{Zr}_{13}$ and b) $\text{Ti}_{80}\text{Zr}_{20}$

Table 1: EDS point analysis

Alloy, at. %	Element	Chemical composition of phases		
		α phase, at. %	α' phase, at. %	β phase, at. %
$\text{Ti}_{87}\text{Zr}_{13}$	Ti	86	87	-
	Zr	14	13	-
$\text{Ti}_{80}\text{Zr}_{20}$	Ti	-	81	79
	Zr	-	19	21

Chemical compositions of phases in both alloys are very similar and correspond to chemical compositions of alloys. This could be explained by the fact that only transformation of crystal lattice was take place without the change in chemical composition. Also, these results indicate that α and β phase are solid solution consist of α titanium and β titanium respectively and zirconium.

Above results were confirmed by EDS line analysis (Figure 4). Namely, by scanning the samples surface across the all different areas line profiles of Ti and Zr were obtained. It is obvious that there is no visible change in concentration of Ti or Zr during the scan transition through the different area, i.e. phases. This is

showed for both alloys indicating that all phases have the very similar composition. Accordingly, only crystal lattices are different.

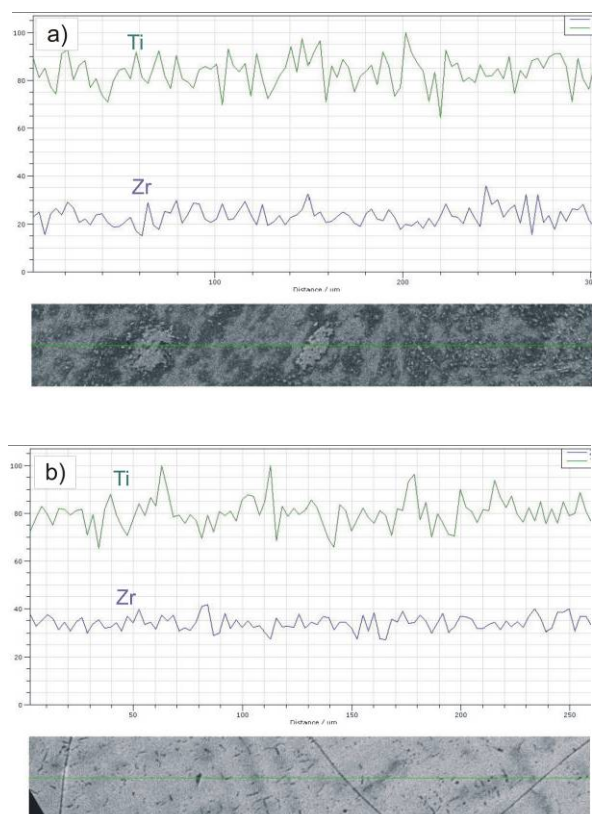


Fig. 4 EDS line analysis of a) $Ti_{87}Zr_{13}$ and b) $Ti_{80}Zr_{20}$

Hardness measurements were performed by Vickers method. For each alloy hardness was examined in five randomly chosen spots and mean values are given in Table 2. It can be seen that all values are lower than for pure titanium [5]. It is since the zirconium shows lower hardness than titanium [13].

Table 2: Vickers hardness

Alloy	HV0.2	HV2
$Ti_{87}Zr_{13}$	550	459
$Ti_{80}Zr_{20}$	387	379

Therefore, alloy with higher zirconium content shows lower hardness values HV0.2 (387 HVN) than alloy with lower zirconium content (550 HVN). That could be explained by the fact that revealed phases have primary effect on hardness along negligible solid solution hardening mechanism. Namely, it is known that beta phase of titanium shows lower hardness values than alpha phase [14]. Therefore, because of alpha phase precipitation, alloy with lower zirconium content showed higher hardness values. All resulted values are in the range of satisfactory hardness for dental applications [7,15].

4. Conclusions

In this paper, microstructural characterization of titanium alloys with 13 and 20 at.% addition of zirconium was presented. From the showed results it can be concluded that addition of 13 at.% of

Zr to pure Ti resulted in two-phase microstructure consisting of α and α' phases. Further, β Ti was achieved by applied casting conditions together with addition of 20 at.% of zirconium. Simultaneously a certain quantity of α'' phase are obtained. All phases have similar chemical composition corresponding to composition of alloy. Only differ is in their crystal lattice. Vickers hardness values of experimental alloys are lower than for pure titanium and acceptable for potential dental use. Finally, zirconium addition resulted in a fluent casting of titanium alloys.

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ELECTROCHEMICAL PROPERTIES AND CHARACTERISTICS OF BINARY AND TERNARY ALLOYS OF AL-ZN-MG SYSTEM

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Abstract: Sacrificial materials are widely used to protect metal structures from electrochemical corrosion. As a base of sacrificial alloys are used aluminum, zinc and magnesium. The article presents the main sacrificial, corrosion and casting properties of binary (Al-Zn, Zn-Mg, Mg-Al) and ternary alloys of Al-Zn-Mg system. The results allow reasonably choose alloy compositions with best electrochemical properties with regard to the operation conditions of cast protectors.

KEYWORDS: SACRIFICIAL MATERIALS, ELECTROCHEMICAL PROPERTIES, AL-ZN-MG SYSTEM

1. Introduction

One of the most promising means of combating with corrosion of metal constructions in sea water and soil is electrochemical protection using cast protectors. According to Russian and foreign experience, use of cathodic protection improves technical and economic indicators operated facilities by increasing their service life, reducing the thickness and weight of metal constructions, etc. [1-6].

The role of the sacrificial protection is further enhanced due to the increase in tonnage of ships and the duration of interdocking period of their operation, as well as due to the increase of the tank park of the country and network of main oil and gas pipelines. Sacrificial protection is used for corrosion control of ships and oilfield metallic structures, underground and underwater pipelines, heat exchangers, tanks, reservoirs and other objects. The simplicity and reliability of performance during operation provide to sacrificial protection a high competitive capacity in comparison with other methods of corrosion control.

The possibility of practical use of sacrificial materials for protection of metal constructions against sea and soil corrosion depends on specific properties and characteristics of alloys, existence and condition of paint and varnish coverings and insulating materials, temperature, structure and properties of the corrosion environment and is defined by the following criteria:

- stable on time and the negative potential of alloys low-changing at the wide modes of anode polarization;
- minimum possible and high activity of alloys in electrolytes with various conductivity at the changing external factors, providing set density of current and stable size of protective potential of metal;
- high and stable actual current capacity providing minimum possible unproductive losses of alloys and the greatest service life of protectors. Instead of the actual current capacity often use the coefficient of use efficiency (CUE);
- the minimum tendency of alloys to self-dissolution providing high CUE of protectors and a possibility of their effective application in combination with paint and varnish and insulating coverings;
- the rational form and the sizes of protectors providing the optimum size of current, a zone of protective action and the set service life of sacrificial protection;
- high activity of sacrificial alloys in electrolytes with various conductivity.

Proceeding from the above-noted criteria, specific requirements are imposed to sacrificial alloys, main of which are following: the actual current capacity (Q_n) and the coefficient of use efficiency (CUE) defining service life of protectors; stationary potential (φ_c) and corrosion rate (K) defining corrosion stability of alloys; working potential (φ_n) and the polarizability (P) defining anode activity of material of a protector in relation to the protected construction.

For improvement and stabilization of these properties sacrificial alloys must have the low maximum permissible concentrations of

harmful impurity elements, and the cast protectors made on their basis – chemical and structural uniformity.

2. Base metals and alloying components of sacrificial alloys

It agrees to the main criteria and the specific requirements imposed to alloys and cast protectors taking into account their cost, as a basis of sacrificial alloys have found application aluminum, magnesium and zinc [1-4]. These metals have a more negative potential values (Table. 1), than the average potential of the steel construction (-0,35...- 0,44 V).

Table 1. Electrochemical properties of base metals of sacrificial alloys

Metal	Anodic process	Negative potential, V		Current capacity, A·h/kg		CUE, %
		stand.	sea-water	theor.	fact.	
Al	$Al = Al^{3+} + 3e$	1.66	0.56	2980	2500	83
Mg	$Mg = Mg^{2+} + 2e$	2.36	1.40	2200	710	32
Zn	$Zn = Zn^{2+} + 2e$	0.76	0.82	820	800	97

Distinctive feature of sacrificial alloys is the presence at them of Al, Zn and Mg as the main alloying components. The famous grades of sacrificial alloys containing metals bases as the alloying elements have higher in comparison with not alloyed metals technological and operational properties. However these data belong to the areas of sacrificial alloys limited on structure. Lack of comparable data on mutual influence of metals bases of sacrificial alloys in all range of compositions in threefold system (Al-Zn-Mg) doesn't allow establishing nature of this interaction fully. The experience of production and operation of cast protectors which is saved up in recent years has allowed to estimate features of technological processes of their production and to plan ways of improvement of their quality. One of the directions providing improvement of technical and economic indicators of production and application of cast protectors serve not only search of new compositions of alloys, but also complex studying of properties and characteristics of alloys of binary and ternary systems. Complex electrochemical researches of alloys of the Al-Zn-Mg system are of special interest also because there is no information about them in literature.

3. Properties of sacrificial alloys of Al-Mg-Zn system

Below are the main sacrificial (standard and working potentials, CUE, current capacity), corrosive (corrosion rate) and casting (fluidity) properties of the alloys Al-Zn-Mg system. To study of the properties of the alloys were selected compounds belonging to

different phase and structural areas of the system. Controllable properties were determined according to the known technological methods and samples [6]. In accordance with the phase diagram of

Al-Zn-Mg system for research selected 25 alloy compositions belonging to different phase regions (Table. 2).

Table 2. Chemical compositions of alloys of ternary system, %

Number of alloy	Section	Al	Mg	Zn	Phase area
35	Zn - T-phase	0,2	0,2	99,6	γ
36		2,0	3,0	95,0	$\beta + \gamma + \nu$
37		4,5	6,0	89,5	$B + \gamma$
38		6,0	8,0	86,0	$B + \nu + \eta$
39		8,0	11,0	81,0	$\beta + \eta$
40		9,0	13,0	78,0	$\alpha + \eta$
41		11,0	16,0	73,0	$\alpha + \eta + T$
42		15,0	21,0	64,0	$T + \eta$
43		18,0	23,0	59,0	T
44	Mg - S-phase	0,9	97,0	2,1	ε
45		3,0	90,0	7,0	$\varepsilon + S$
46		6,0	80,0	14,0	$\varepsilon + S$
47		10,0	70,0	20,0	$\varepsilon + S$
48		13,0	27,0	60,0	$\varepsilon + S$
49		15,0	50,0	35,0	$\varepsilon + S$
50		20,0	40,0	40,0	S
51	T-phase - $Al_{12}Mg_{17}$	48,0	48,0	4,0	δ
52		40,0	40,0	20,0	$T + \delta$
53		32,0	35,0	33,0	$T + \delta$
54		27,0	28,0	45,0	T
55	Al - T-phase	24,0	26,0	50,0	T
56		32,0	23,50	44,5	$\alpha + T$
57		60,0	13,0	27,0	$\alpha + T$
58		80,0	7,0	13,0	$\alpha + T$
59		95,0	2,0	3,0	α

Phase diagram of system and alloys compositions shown at Fig. 1. The alloys of defined compositions were prepared using high-purity primary metals: zinc (99.99% Zn), aluminum (99.99% Al), magnesium (99.95% Mg). Preparation of alloys (electric resistance furnace) and cast specimens (metal form), as well as methods of corrosion and electrochemical tests are set out in works [1, 6].

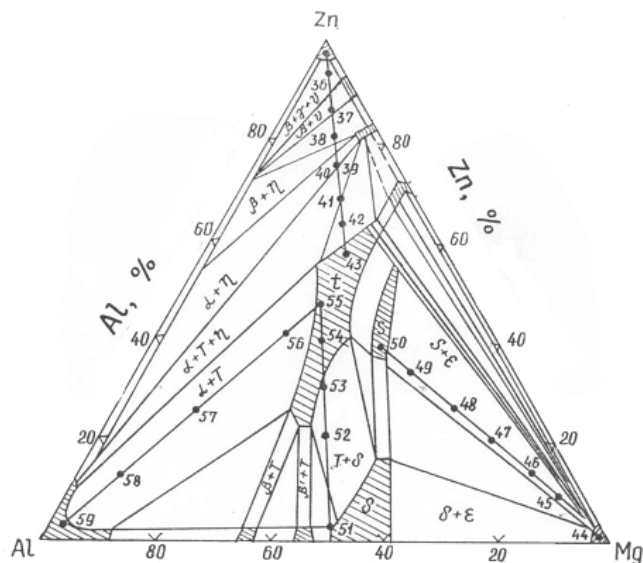


Fig. 1. Ternary system Al-Zn-Mg and alloys compositions (isothermic section at 330°C)

Nine alloy compositions (42,43,49,50,52-56) of the 25 (35-59) were excluded from the control of electrochemical and technological properties, due to their non-technological at the

smelting and manufacturing of samples. Alloys rich in magnesium have the highest corrosion rate (0.40 - 0.45 mm / year). Aluminum-zinc alloys with a high content of magnesium, as well as aluminum-rich alloys (58, 59) and zinc-rich alloys (35 - 39) are substantially the same and the minimum corrosion rate (≈ 0.1 mm / year). The negative potential of the stationary alloy ternary system varies from 540 - 600 mV (aluminum angle) 1350 - 1450 mV (magnesium angle). When aluminum doped with zinc and magnesium (58, 59) ϕ_c increases from -540...-620 to -680...-750 mV. Introduction of aluminum and zinc in magnesium (44 - 47) leads to a decrease ϕ_c from -1350...-1450 to -1100...-1200 mV. Alloying of zinc with magnesium and aluminum (35 - 37) practically does not change ϕ_c , which value is -800...-850 mV. Obviously, depending on the requirements for alloys according to the values of negative stationary potentials in seawater can choose these alloy compositions in a wide range of component concentrations.

Data on the change of the negative potential depending on the alloy composition and the polarization current sample ($I = 5$ A / m) in seawater. It can be seen that when adding magnesium and zinc in aluminum (58, 59) is an increase ϕ_n from -470 ... -550 to -700...-720 mV, and when adding of aluminum and zinc in magnesium (44 - 48) ϕ_n falls from -1100...-1240 to -900...-1000 mV. Zinc alloys (35 - 39) have similar values ϕ_n equal to -680 ... -710 mV.

Fig. 2 shows the change of CUE of alloys Al-Zn-Mg system depending on their composition. Analysis shows that for zinc alloys (9 - 11.35) CUE reaches maximum values (90-95%); the minimum values of the CUE have the following compositions of magnesium alloys (17-29, 44-48). For aluminum alloys (12; 31-33; 59) CUE reaches 70-75%. It is shown that at high contents of alloying elements in alloys of any basis of the system Al-Zn-Mg is more pronounced heterogeneity of the structure, leading to a decrease in current capacity and CUE.

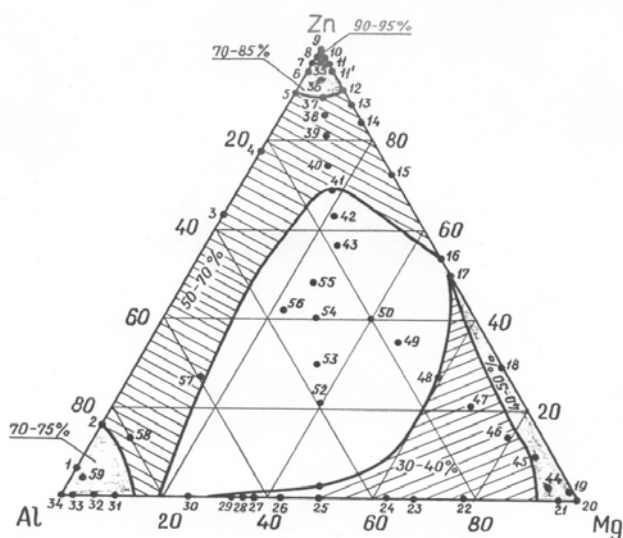


Fig. 2. CUE of Al-Zn-Mg system alloys

4. Conclusions

Analysis of the main electrochemical properties of alloys of Al-Zn-Mg system shows that on combination of corrosion and sacrificial properties low-alloyed alloys should be considered as the best that meet the conditions for the formation of single-phase structures. Depending on the requirements of the sacrificial alloys subject to the conditions of their operation given data allow reasonably choose the alloy compositions in the Al-Zn-Mg system, providing the best electrochemical properties.

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GENESIS OF ELEMENTS AT PRIMARY ALUMINUM PRODUCTION

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Abstract: The characteristic of the elements present in the primary aluminum at electrolytic method of production is given. Based on elemental analysis of aluminum on regulated and unregulated impurities, with accordance of their initial content and effect on operational characteristics of cast billets, in this paper we describe groups of useful elements, neutral and harmful impurities at production of materials for functional purposes (sacrificial, composite, electrotechnical, etc.).

KEYWORDS: PRIMARY ALUMINUM, IMPURITIES, SACRIFICIAL ALLOYS, ANTIFRICTION COMPOSITE ALLOYS

1. Introduction

Aluminum finds broad application as a base metal for functional and constructional alloys, such as sacrificial, antifriction, electrotechnical, etc. Functional alloys differ from other by design of properties at a stage of their creation, and achievement of set value of any special property which has crucial significance. For example, in sacrificial alloys used for protection of metal constructions from corrosion this property is stationary electrochemical potential [1]. For composite alloys depending on the purpose of material is possible to achieve various operational characteristics, such as wear resistance, heat resistance, thermal expansion coefficient, thermal conductivity, etc. [2]. For electrotechnical materials critical characteristics are electrical conductivity and specific electrical resistance. Regardless of the destination of manufactured products, at the achievement of predetermined characteristics of alloys for functional purpose on the aluminum base content of regulated and unregulated impurities plays an important role.

In grades of primary aluminum used for production of aluminum alloys the content of iron, silicon, copper, manganese, magnesium, zinc and other impurities is limited [3]. Raw aluminum produced by electrolysis of cryolite-alumina melts contains substantial amounts of metal impurities, non-metallic inclusions and gases. Sources of presence of various elements in primary aluminum are composition of raw materials and conditions of metal production. In bauxites, which are the main raw materials for production of alumina and then metallic aluminum, about 40 elements are revealed. Additional source of impurities is various constructive elements of electrolyzer. For example, the carbonaceous materials (anode paste, baked anodes, cathode products) applied at electrolysis are sources of such impurities as vanadium, titanium, manganese, zinc, etc.

2. Elements in primary aluminum: genesis and interaction

Based on the results of spectral analysis of aluminum produced by different factories in the Russia and abroad, in Fig. 1 in form of matrix of Mendeleev's Periodic Table are listed elements found in the aluminum ingots. Classification of the elements with their allocation to different groups carried out under consideration of the nature of interaction of aluminum with elements in accordance with their influence on the formation of various phases in aluminum alloys. At the same time we take into account the concentration of the impurity element in aluminum and its impact on the operational properties of the cast products.

Data on nature of interaction of elements of various groups of Periodic system with primary aluminum are given below.

Elements of group I. In the aggregate of considered criteria and properties for various types of functional materials the influence of these impurities can be shown differently. For instance, in sacrificial alloys copper will be most harmful impurity and its content reaches 0.01 - 0.02%. Sodium and lithium at concentrations

Elements in primary aluminum									
I	II	III	IV	V	VI	VII	VIII		
H	-	-	-	-	-	-			
Li	Be	B	C	-	O	F			
Na	Mg	Al	Si	P	S	Cl			
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
Cu	Zn	Ga	Ge	As	-	-			
-	Sr	Y	Zr	-	-	-			
-	Cd	-	-	Sb	-	-			
-	Ba	La	-	-	-	-			
-	-	-	Pb	-	-	-			

Fig. 1. Matrix of Mendeleev's Periodic Table indicating the elements found in aluminum ingots

of a few hundredths or thousandths of a percent have the property to activate the surface of alloy during its operation and can serve as activators of sacrificial alloys. At production of antifriction aluminum matrix composites sodium and lithium also play a positive role reducing the surface tension of matrix melt and facilitating wettability of exogenous reinforcing phase.

Hydrogen actively interacts with aluminum forming with it endothermic interstitial solid solution. Solubility of hydrogen at transition of aluminum from liquid to solid state is reduced from 0.69 to 0.039 cm³/100 g, whereby gas porosity in castings appears. The presence of pores in cast metal results in its macroinhomogeneity therefore hydrogen in aluminum must be considered as one of harmful elements at using of primary aluminum for production of sacrificial, tribotechnical and other alloys for functional and construction purposes. Moreover, in primary aluminum of various grades content of hydrogen can reach 2.85 cm³/100 g.

Due to the low concentration of potassium in the primary aluminum his influence on properties of castings from aluminum alloys can be neglected.

Elements of group II. From the elements of group II which are found in primary aluminum any can't be attributed to group of harmful elements. Conversely, such elements as Mg and Zn on combination of properties are the main alloying elements in sacrificial alloys. At producing of aluminum matrix composites magnesium acts as surface-active element improving the wettability of exogenous ceramic particles.

Beryllium which is present at concentrations to 0.001% has the refining effect and significantly reduces harmful impact of iron in aluminum, and also suppresses a possibility of oxidation of aluminum-magnesium alloys. Calcium, strontium, barium and cadmium practically not change properties of alloy due its low concentrations.

Elements of group III. Due to very low concentrations of Sc, Y, La, B and Ga in aluminum these elements should be regarded as neutral. Boron has a refining and modifying effect on aluminum alloys. In the electrotechnical alloys based on aluminum boron neutralizes the harmful effects of vanadium, chromium, zirconium

and titanium on the electrical conductivity. At production of antifriction metal matrix composites boron along with titanium, zirconium and some other elements which forms insoluble hard-melting compounds used as initial component-precursor for formation of new endogenous reinforcing phases (TiB_2 , ZrB_2 , MoB and others) in conditions of liquid-phase reactionary synthesis [4].

Elements of IV group. Titanium and zirconium forms with aluminum limited solid solutions and intermetallic compounds Me_mAl_n . Solid solution of titanium in aluminum ($\text{Al} + 0,1\% \text{ Ti}$) has stationary potential almost identical with aluminum. Taking into account that in A85 aluminum grade (Russian Standard 11069-2001) content of titanium and zirconium less than 0.04%, these metals will be completely in solid solution with aluminum without changing of its properties and without decreasing quality of sacrificial alloys. The carbon presented in aluminum at amounts $1 \dots 2 \cdot 10^{-4} \%$ is in type of thinnest carbide inclusions which won't make essential changes to electrochemical properties of alloy. Silicon at concentrations up to 0.19% does not change stationary potential of aluminum in positive direction. It can be assumed that silicon as impurity in aluminum in amounts up to 0.1-0.2% is not harmful. It should be noted that at production of aluminum matrix composites silicon promotes decrease the contact angle of wetting and improves assimilation of exogenous reinforcing particles by matrix melt [5]. Content of germanium in aluminum is negligible so its influence can be neglected. Solubility of lead in solid aluminum doesn't exceed 0.2% at monotectic temperature. As the content of lead in aluminum, as a rule, not more than $1 \cdot 10^{-3} \%$, this element can be considered as neutral for sacrificial alloys and antifriction composite alloys.

Elements of group V. Aluminum may contain thousandths of a percent of vanadium and phosphorus and up to 0.015% arsenic and antimony. Insignificant concentrations of elements of this group in primary aluminum and nature of their interaction with it won't change electrochemical properties of sacrificial alloys that allow attributing them to group of neutral elements. At production of metal matrix composites these elements will also not have a negative effect on operational properties due to their low content in primary aluminum.

Elements of group VI. Chrome, oxygen and sulfur differently interact with aluminum. Presence of chromium in solid solution based on aluminum practically does not alter its stationary potential. Whereas chromium content in primary aluminum is thousandths of a percent it is possible to expect formation only of solid solution in structure of such alloy and to consider chrome as neutral impurity. Oxygen is present at primary aluminum in the form of insoluble oxide in amount of 0.02-0.07%. Aluminum oxide mixed into the melt influences on the physical-mechanical and technological properties of aluminum alloys and also on their gas content. At

production of sacrificial alloys their electrochemical properties will be determined by content of oxides and gases, whereby oxygen in the form of oxide inclusions should be attributed to group of harmful elements. However, at producing of aluminum matrix composites finely-divided oxide Al_2O_3 by using of special processing methods in the conditions of exogenous or endogenous reinforcing can be a reinforcing phase [6]. Sulfur and its compounds with aluminum are unstable in the melt and don't influence on structure and properties of castings.

Elements of VII group. Manganese content in aluminum is in range from 0.001 to 0.05%. At such concentrations manganese practically always is in solid solution with aluminum and does not deteriorate alloy properties. Sources of fluorine and chlorine in aluminum are electrolyte of electrolysis cells and different fluxes. However, due to the high activity of these elements relative to aluminum at their interaction formed low-boiling halides of aluminum which are removed from the melt in the form of gas bubbles. It should be noted a positive role of aluminum purging with gaseous fluorine and chlorine for removal hydrogen from the melt. For these reasons and due to the low concentration of fluorine and chlorine in primary aluminum their impact on properties of functional alloys can be neglected.

Elements of VIII group. According to experimental data [7], increasing of iron content results in monotonous decreasing of potential and electrochemical capacity of aluminum. Presence of iron impurity in aluminum sacrificial alloys promotes formation of Fe_nAl_m type compounds, which are cathodes in relation to aluminum [8]. For these reasons, iron must be attributed to the group of harmful impurities in sacrificial alloys. At production of aluminum matrix composites by mechanical stirring there are examples of use of iron powder as a reinforcing phase for improving of tribological properties [9]. Presence of nickel and cobalt in aluminum worsens electrochemical characteristics of alloys owing to formation of a number of chemical compounds like Ni_nAl_m and Co_nAl_m . At production of aluminum matrix composites nickel powder has been successfully tested as a precursor for the endogenous intermetallic compounds. Reactions of synthesis of these compounds are exothermic and promote wetting and assimilation of entered exogenous ceramic particles, including nanosized components [10].

3. Classification of elements in primary aluminum

Taking the foregoing into consideration, in Table 1 is provided classification of elements which are present in aluminum ingots by their influence on operational properties of castings from functional alloys.

Table 1. Classification of elements in primary aluminum by their influence on the operational properties of alloys for functional purposes

Groups of elements according to their influence on operational properties	Sacrificial alloys	Antifriction composite alloys
Useful	Mg, Zn, Mn, Be, Na, Li, K, Ca, Ba, Zr, Ti	Mg, Si, Cu, Na, Li, Be, B, Ti, Zr, C, V, Cr, O, Fe, Ni, Co
Neutral*	Sr, Cd, Sc, Y, La, B, Ga, C, Si, Ge, Pb, V, P, As, Sb, S, Cr, F, Cl	K, Ca, Zn, Sr, Ba, Cd, Sc, Y, La, Ga, Ge, Pb, P, As, Sb, S, Mn, F, Cl
Harmful	Cu, Fe, Ni, Co, H, O	H

* Assignment of elements to the neutral category in most cases caused by their low content in the primary aluminum.

4. Conclusions

- Depending on the desired complex of properties of functional alloys, impurities in primary aluminum can be assigned to different groups on influence on operational properties of products.
- In addition to regulated by Russian standards harmful impurities of iron and copper, at production of sacrificial alloys it is necessary to additional attribute hydrogen, oxygen, nickel and cobalt to harmful elements, that testifies to expediency of application for preparation of such alloys of high grades of aluminum.
- In aluminum matrix composites for tribotechnical purposes as harmful element from attendees in primary aluminum it is necessary to consider only the hydrogen promoting formation of gas porosity and worsening assimilation of the reinforcing phase. Therefore for their manufacturing use of aluminum of lower grades is allowed.
- At production of aluminum-based functional alloys for ensuring of high quality of castings it is necessary to

include operation of melts refining from dissolved hydrogen in technological process.

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THE TIME FACTOR IN THE SPHEROIDIZING AND GRAPHITIZING MODIFICATION AND CAST IRON CRYSTALLIZATION

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ABSTRACT: This work was carried out studies on the effect of different ways of modifying the microstructure and mechanical properties of cast ductile irons identical to the final chemical composition. For comparative studies have chosen three ways of modifying the molten iron, characterized the time interval between the introduction of additives into the melt and crystallization of iron – autoclave method, processing method in an open ladle ("Sandwich process") and a method of in-mold melt processing ("Inmold-process").

It is found that the process mold inoculation molten iron a more effective compared to other methods studied, by reducing the time interval between entering modifier in liquid iron and the onset of crystallization. This in turn enables the production of castings of several grades of ductile iron in the total process stream without additional alloying and heat treatment.

Results of research testify in favor of the fluctuation hypothesis about straight line graphitization of cast iron during primary crystallization.

KEYWORDS: HIGH-STRENGTH CAST IRON, MODIFIER, METHOD OF MODIFYING, MICROSTRUCTURE, STRENGTH, HARDNESS, INMOLD- PROCESS, SANDWICH-PROCESS, AUTOCLAVE METHOD.

Structure and mechanical properties of ductile iron with nodular graphite in cast condition defined by four technological factors and may be substantially changed by heat treatment of castings. Influence of chemical composition of the base alloy, amount and absorption degree of spheroidizing magnesium and graphitizing silicon introduced into the liquid iron, as well as the cooling rate of the metal in the mold for the modification results in a sufficiently studied full [1-5]. Fourth factor influencing these results – the time interval between the input modifiers in liquid melt and the beginning of crystallization – most researchers pay negligible importance. Meanwhile it is well known that in contrast to the alloying efficiency of modification during isothermal exposure worsens: increased cast iron tendency to metastable

system crystallization " $\text{Fe-Fe}_3\text{C}$ " and reduced the degree of graphite nodularity [1,2].

In the process of sequential replacement on four industrial enterprises autoclave method of ductile iron production (fig. 1, a) first by ladle (fig. 1, b), and then in-mold (fig. 1, c) accumulated extensive statistical material on the technical and economical efficiency of these methods of modification. Analysis of the results proved conclusively advantage of in-mold method of input magnesium and silicon in liquid iron, as compared with previous methods, and that was the main reason for its implementation in the production of complex thin-walled castings of hydraulic equipment weighing up to 180 kg of ferritic spheroidal graphite cast iron.

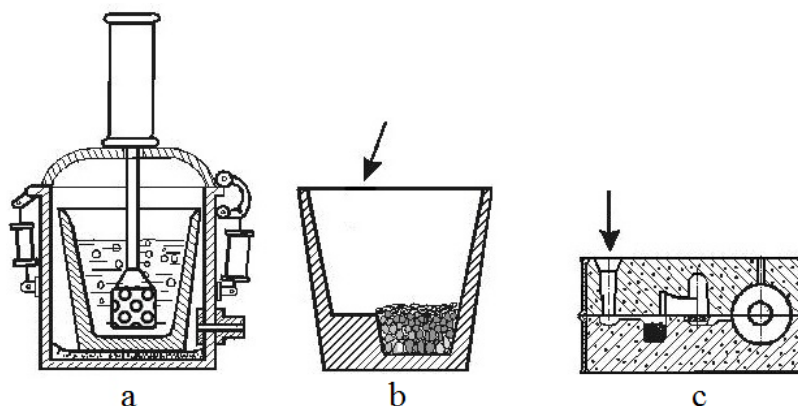


Fig. 1. Methods of complex spheroidizing and graphitizing modifying of cast iron in a sealed autoclave (a), in open ladle by "sandwich" process (b) and directly in the casting mold by "in-mold" process (c).

From the data array of plant laboratories accumulated during great enough time for analysis selected only the results of meltings, in which iron chemical composition meets the conditions listed in tab. 1. All three methods of modification provided a high (96...98%) degree of nodularity in metal castings suitable.

The microstructure of cast iron was determined on the templates made of the middle part of cylindrical samples of 140 mm and a diameter of 6 to 40 mm, as well as standard samples for mechanical testing, made from the casting samples of 10...12 kg of the working part having a thickness of 25 mm. Values of the mechanical characteristics of the cast irons set by standard methods.

Table 1. Chemical composition of initial and modified cast-irons and amount of the silicon and magnesium entered in initial cast-iron

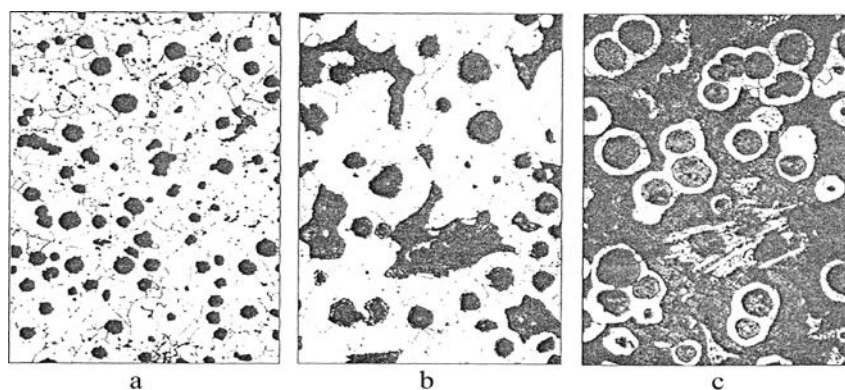
Object of analysis		Chemical composition,% (weight percentage)					
		C	Si	Mn	S	P	Mg
Initial cast iron		3,70 ±0,08	2,15 ±0,07	0,32 ±0,02	0,029 ±0,002	0,070 ±0,002	–
Modifier, introduced	into the mold reaction chamber	–	1,01 ±0,07	–	–	–	0,23 ±0,07
	into the open ladle	–	1,14 ±0,04	–	–	–	0,19 ±0,01
	into the ladle in the autoclave	–	0,95 ±0,05	–	–	–	0,23 ±0,01
Iron, modified	into the mold	3,64 ±0,06	3,06 ±0,05	0,32 ±0,02	0,018 ±0,002	0,070 ±0,002	0,058 ±0,008
	into the ladle	3,58 ±0,04	3,18 ±0,07	0,32 ±0,02	0,012 ±0,002	0,070 ±0,002	0,042 ±0,004
	into the autoclave	3,62 ±0,08	2,92 ±0,07	0,32 ±0,02	0,008 ±0,002	0,070 ±0,002	0,062 ±0,008

According to the results of dispersion analysis comparing the experimental and tabulated values of Fisher's exact test with a coefficient of 95% found that the amount of silicon and magnesium, which is added to the molten metal, as well as the chemical composition of the studied cast irons modified by various methods did not significantly affect the microstructure and mechanical properties of the alloy. At the same time, these characteristics in the cast state essentially depend on the method of modification.

Mean values and the dispersion of mechanical characteristics of the cast iron modified into the reaction chamber of the mold by "in-mold"-process, into the ladle bottom lining open by "sandwich"-process and into the ladle placed in the autoclave mark "KM-2" are shown in tab. 2. Typical

microstructure of cast iron in the relevant standard samples is illustrated in fig. 2.

Found that in the cast iron in-mold modified, the amount of graphite spheroids in 1 mm² area microsection 40% more than in the iron modified in the ladle, and 60% more than in the iron modified in an autoclave. With the same carbon content, average diameter of the spheroids is respectively 50, 65 and 85 μm. In cast iron, modified in an autoclave, there are separate sections ledeburitic eutectic, which are absent in cast irons, modified in-mold or in the ladle. Percentage of ferrite in cast iron in-mold modified is 85...95% and a metal matrix of cast iron, modified in the autoclave, preferably pearlitic with a fine ferrite rim around the graphite spheroids.

**Fig. 2.** The microstructure of the cast iron casting in-mold modified (a), in an open ladle (b), in an autoclave (c). × 100.**Table 2.** The mechanical properties of cast iron in-mold modified, in a ladle or in the autoclave in the cast state

Name of the mechanical characteristics	Arithmetic mean and the dispersion of the mechanical characteristics of cast iron		
	modifying		
	into the mold	into the ladle	into the autoclave
Tensile strength $\sigma_{t,s}$, MPa	513 ± 23	553 ± 24	603 ± 28
Yield strength $\sigma_{y,s}$, MPa	342 ± 20	348 ± 28	394 ± 18
Relative elongation δ , %	13,5 ± 1,8	7,0 ± 1,2	2,4 ± 0,8
Impact elasticity KC, kJ/m ²	750 ± 210	350 ± 90	120 ± 60
Hardness HB	156...170	197...207	302...321

Microstructures difference (fig. 2) makes a significant difference of the mechanical properties of cast irons, modified by various technological options. Found by dispersion analysis that the process of in-mold modification provides production of casts with high plastic properties without bleaching in thin sections of the walls in the cast state more reliably than the process of modifying in an open ladle or in an autoclave. At the same time,

due to the increased dispersion of graphite and eutectic grains of metal matrix, the strength characteristics of ferritic iron in-mold modified, to stabilize at a high level. From tab. 2 shows that by modification in the form of as-cast iron is obtained with a tensile strength $\sigma_{t,s}$ of more than 500 MPa and elongation δ more than 12%. This corresponds to the iron requirements of ДСТУ 3925-99 (standart) for industrial marks ВЧ 420-12, ВЧ 450-10, ВЧ 450-5,

B4 500-7, B4 500-2. Mechanical characteristics of cast iron, modified in an autoclave in the cast state do not meet the requirements of ДСТУ 3925-99 to mark B4 600-3 ductility, and to mark HF 700-2 strength. Therefore, to achieve the desired combination of strength and ductility of autoclave casts, depending on the desired mark, factories generally subjected to further ferrite annealing or perlite normalizing.

Thus, by method of in-mold modifying under certain conditions can stably produce castings from nodular iron several brands in the general process flow without additional alloying and heat treatment.

It confirms metallographic analysis of the microstructure of cast irons in the cylindrical samples of different diameters. In the in-mold modified cast irons, in the samples of 6 mm diameter graphite spheroids number reaches 500...800 units per 1 mm² area microsection (fig. 3, curve 1) at their size 15...20 μm (fig. 4, curve 1). With the increase in the diameter of the sample, i.e. with reduced cooling rate, the amount of graphite spheroids rapidly decreases with a corresponding increase of their size in samples of 40 mm diameter to 45...55 μm. In cast iron, in an open ladle is modified or modified in the autoclave, the samples of 6 mm diameter graphite inclusions sizes are 20...25 μm, i.e. only slightly exceed the graphite dimensions of similar samples of cast iron, in-mold modified. However, the low degree of graphitization their amount does not exceed of 125 units per 1 mm² area microsection (fig. 3 and 4, curves 2 and 3). In cast iron samples with a diameter of 6 mm, in-mold modified, a eutectic cementite is absent (fig. 5, a), whereas in the cast iron in the ladle or in the autoclave modified, main part of carbon in samples connected to the needle cementite of ledeburitic eutectic (fig. 5, b, c). In the ladle modified cast iron, the eutectic cementite disappears only in the samples of 20 mm diameter (fig. 5, e). In the autoclave modified cast iron, individual inclusions of

ledeburitic eutectic observed even in samples of 40 mm diameter (fig. 5, f). At the same diameter of cylindrical samples microsection area occupied by ferrite in cast iron, in-mold modified (fig. 6, curve 1), significantly more than in the ladle modified cast iron (fig. 6, curve 2). Cast iron metal matrix structure modified in the autoclave, in all the samples mostly pearlitic with fine ferrite rim around the graphite spheroids (fig. 6, curve 3).

Ceteris paribus, the main technological difference between the three methods of modification lies in the different time interval between introduction of modifier elements into the molten metal and the beginning of crystallization in the mold. To reduce the pressure in the autoclave to atmospheric, opening the autoclave and removed from him the ladle, slag removal, transportation and casting modified cast iron in form in a manufacturing conditions is spent 8...12 minutes. If the total time for these operations is more than 14...16 minutes, the propensity of cast iron to graphitization and degree of graphite nodularity in the modified cast iron begins to decrease rapidly. The removal of slag, transportation and metal pouring spent 4...6 minutes after modifying in the open ladle. Gist of the in-mold modifying cast iron method reduces that interval up to several tens of seconds, regardless of which form the first poured and which latter.

Thus, in the cast state with the same chemical composition and the same cooling rate inclination to graphitization during eutectic and eutectoid transformation, the amount of graphite inclusions, graphite spheroids dispersity, eutectic grain dispersion in the cast iron in-mold modified higher than in the cast iron, modified in ladle, and significantly higher than in the cast iron modified in the autoclave. The difference of these indicators is particularly evident at high cooling rate (fig. 3...6).

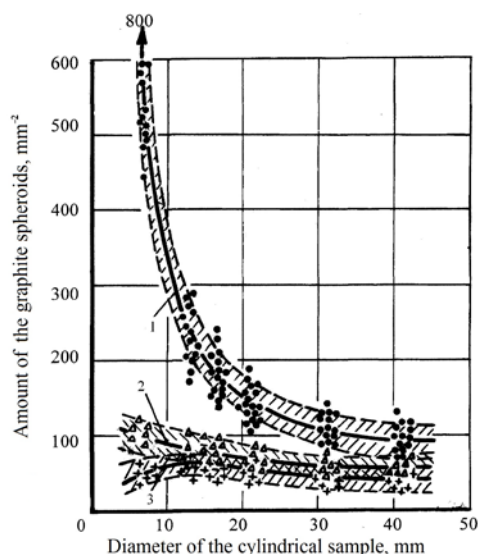


Fig. 3. The cooling rate influence (diameter of the cylindrical sample) by the amount of graphite spheroids in 1 mm² area of cast iron microsection modified into the mold (1), into an open ladle (2), into an autoclave (3).

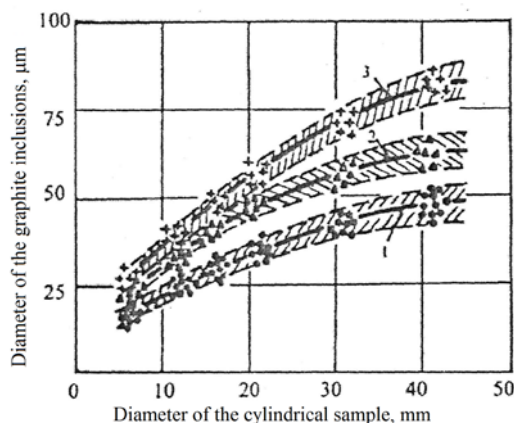


Fig. 4. The cooling rate influence (diameter of the cylindrical sample) by the diameter of the graphite spheroids in the cast iron modified into the mold (1), into an open ladle (2), into an autoclave (3).

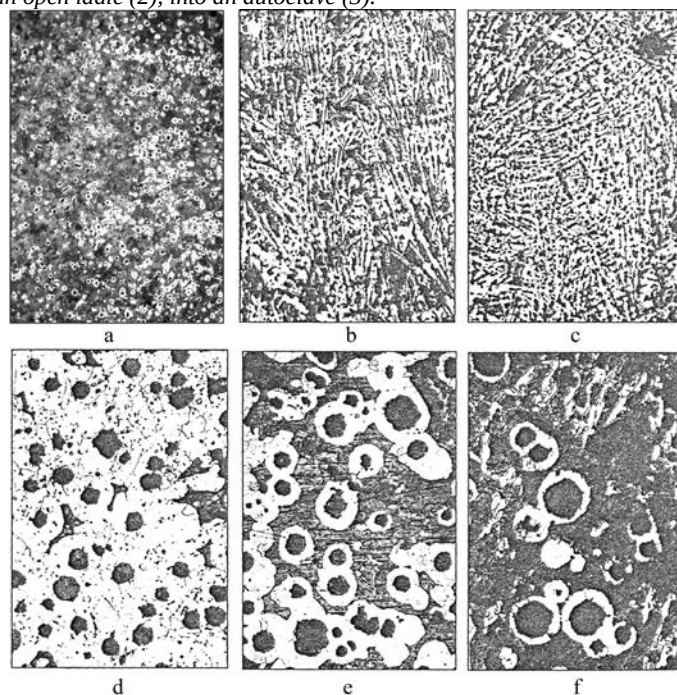


Fig. 5. The microstructure in cast iron specimens of 6 mm (a, b, c) and 40 mm diameter (d, e, f) modified: a, d – into the mold; b, e – into an open ladle; c, f – into an autoclave. $\times 100$

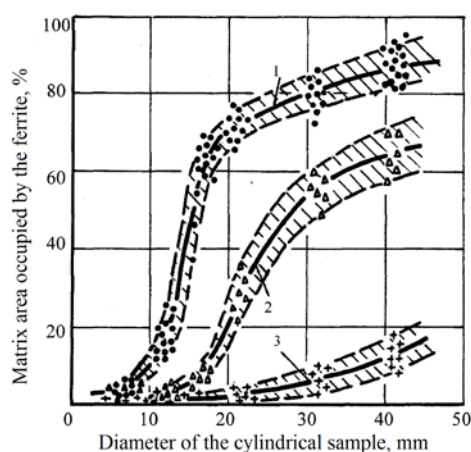


Fig. 6. The cooling rate influence (diameter of the cylindrical sample) by the relative microsection area occupied by ferrite in the cast iron modified into the mold (1), into an open ladle (2), into an autoclave (3).

Tendency to crystallize on a metastable system "iron-cementite" mainly explaining by the fact that when the cast iron temperature drops to eutectic mean, probability of phase fluctuations with carbon concentration, approximate to the 6,67%, significantly higher than the probability of micro volumes with carbon concentration, approximate to 100%. But, from the point of view of thermodynamics, the minimum value of the free energy corresponds more stable equilibrium of "iron-graphite" system. Therefore, the propensity to structure formation by stable, metastable or mixed system primarily depends on the length of cast iron stay in the solid-liquid state at the eutectic solidification, which determined by the rate of heat transfer between the micro-volume of the alloy in the wall section of the casting and the mold. The smaller section of the wall of the casting, the greater the rate of its cooling, the shorter the duration of the isothermal eutectic crystallization, the less the probability of increasing carbon concentration from 6,67 to 100% in its fluctuation groupings in the residual liquid and the greater the probability of formation unstable cementite in ledeburitic eutectic.

Results of the study are in good agreement with the fluctuation hypothesis and contradict to the inoculation hypothesis about the mechanism and kinetics of graphitizing modification and structure formation of cast iron in the primary crystallization.

According to the inoculation hypothesis additional nucleant of crystallization of solid graphite phase during eutectic crystallization of cast iron are refractory silicon carbides, iron silicides or complex iron-carbon-silicon chemical compounds which forming in the melt by modifying by the ferrosilicon or ferrosilicon-magnesium. According to this hypothesis is difficult to explain the effect of time factor on structure formation between the introduction of additives in the alloy and the beginning of the eutectic crystallization. The more uncertain the mechanism and kinetics of deactivation refractory inoculators that leads to gradual demodification of molten cast iron.

Fluctuation hypothesis assumes that the microparticles of graphitizing modifier containing 45...75% of the silicon during the dissolution time replacing part of the carbon in alloy from the surrounding them microvolume of equilibrium solution of carbon and silicon in the liquid iron. Depleted carbon and enriched silicon fluctuation microvolumes of liquid become additional potential nucleuses of primary austenite grains. Liquid in microvolumes distant from ferrosilicon particles overloading repressed carbon, fluctuation groups which are close to 100% concentration and become additional potential nucleuses of graphite phase in crystallizes eutectic. During the relatively long exposure in ladle concentration fluctuations of carbon and silicon gradually uniformly distributing in the volume of liquid cast iron

and efficiency of graphitizing modification respectively reduced to zero. During cast iron modification directly into the mold such exposure does not exceed ten seconds. Therefore, the graphitizing efficiency of adding even small amounts of silicon in molten cast iron is shown at the maximum level.

The results of experiment are not quite consistent with the hypothesis mediated cast iron graphitization. According to this hypothesis, the eutectic crystallization of cast iron always takes place at a metastable system, followed by dissociation of the formed solid ledeburite cementite to austenite and graphite by "self-annealing" by the heat of the casting, cooling in the mold, similar to high temperature annealing white cast iron at malleable. In samples with a diameter of 6 mm made of cast iron in-mold modified cooling which occurs with the high speed inclusions of cementite or it "self-annealing" remains isn't observed (fig. 4, a). Probably, under certain conditions graphite separation directly from the residual liquid without forming an intermediate cementite during eutectic crystallization takes place. However, at higher cooling rate, a low content of carbon and silicon, the presence of chromium or other carbide stabilizing elements, absence the operation of modification or long exposure of the modified alloy to it beginning of crystallization conditions are taking shape for full or partial crystallization by a metastable system. Thus, the hypothesis of a direct graphitization from liquid phase has the same right to exist as the hypothesis of iron mediated graphitization.

CONCLUSIONS

Technological process of spheroidizing and graphitizing modification directly into the mold provides a tendency of cast iron to graphitization at the eutectic and eutectoid transformation, the refinement of austenite grains and graphite spheroids, increased ductility with high strength cast iron more efficiently and reliably than the process of modification in the ladle or in an autoclave.

The researching shows the benefit of the fluctuation hypothesis of graphitizing modification and hypothesis about the possibility of a direct cast iron graphitization from liquid phase at the primary crystallization.

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EVALUATION OF FATIGUE LIMIT FOR ALUMINIUM ALLOYS BY ULTRASONIC MEASURING

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Abstract : The evaluation of fatigue limit - σ_{-1} for AlSi7Mg, AlCu6Mn aluminum alloys is frequently encounter in material testing. In this method there is necessity of manufacture of test-tube from tested material or detail and made tension test.. There is destructive method. For many details there is not acceptable. Calculated in the usual ways fatigue limit appear only their statistical averaging between a number of structural factors indicating the influence. In material testing there is interest to non-destructive evaluation of fatigue limit σ_{-1} for the specimens and details. In this paper is lock at possibility for non-destructive evaluation of fatigue limit σ_{-1} by means measure velocities of propagation of longitudinal and transversal ultrasonic waves - V_L and V_T in tested materials and details.

KEY WORDS: NON-DESTRUCTIVE EVALUATION OF FATIGUE LIMIT, ALLUMINIUM ALLOYS, VELOCITIES OF PROPAGATION OF ULTRASINIC WAVES

1.Introduction

Destruction of fatigue in aluminum alloys can occur in an area of elastic deformation. Even adding modifiers and higher plastic limit leads to destruction without structural changes and a clear boundary- σ_{-1} . Under the action of cyclic stresses brittle fracture occurs. Fatigue of material, ratio is dependent on the dimensions of the dendrites (Solid solution of Si in Al).

2. Structure of aluminum castings alloys and ultrasound

Aluminum alloys AlSi7Mg, AlCu6Mn have a structure shown in Figure 1. There are α -matrices and Si eutectic in the form of fiber in inter dendritic field. Phases of Gine-Preston after heat treatment of Mg_2Si , $\theta-Al_2Cu$. By the relationship (1) are defined: Grain size- $\overline{D}_{Al}$: about AlSi7MgSr [Popov] .It was receive $(24 \div 35) \mu m$ and silicon eutectic - $(1,2 \div 4,0) \mu m$. . It is AlCu6Mn alloy, the grain size $\overline{D}_{Cu}$ is in the range $(29,03 \div 132,86) \mu m$. The relationship between $\overline{D}_{Al}$ and acoustic characteristics $(V_L; V_T; \alpha_L)$ is [1]

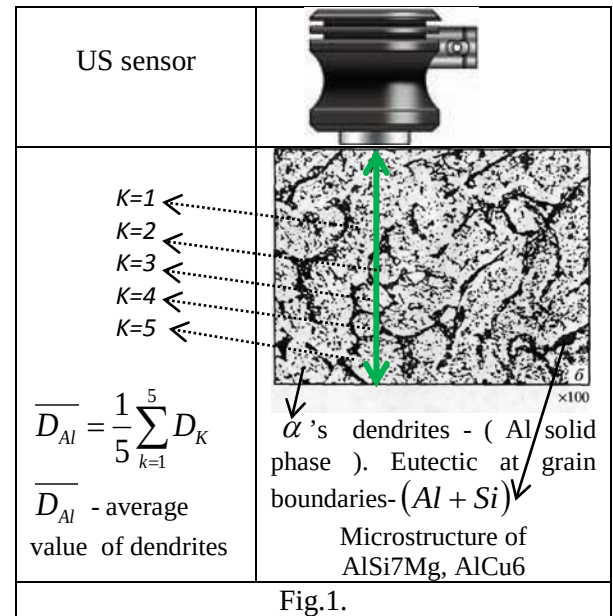
$$(1) \quad W(V_L; V_T) \cdot f^4 \cdot (\overline{D}_{Al})^3 - \alpha_L = 0$$

$$\text{where } W(V_L; V_T) = \frac{4\pi^2}{1125} \frac{V_T^4}{V_L^3} \left(\frac{2}{V_L^5} + \frac{3}{V_T^5} \right) \text{ and}$$

$(V_L; V_T; \alpha_L)$ is respectively longitudinal and transversal velocity and attenuation in ultrasonic wave propagation ASTM E 494: 2010.

3.Empirical correlations

The materials science used to dependence. [2]



$$(2) \quad \sigma_{-1} \approx 0.19HB$$

where: HB is Brinell's hardness.

This article consider the microstructure's factors as to destruction of fatigue. The fatigue of the grain size- $\overline{D}_{Al}$ of the Al- phase. In literature [3] is given depending $\sigma_{-1}(\overline{D})$. It is shown explicitly.

$$(3) \quad \sigma_R = \sigma_{ir} + K_R \cdot (\overline{D})^{-1/2}; R = -1$$

where $\sigma_{ir}; K_R$ - material constants. To obtain explicit constants in (3) for cast aluminum alloys AlSi7MgSr, AlCu6Mn considering the relationship:

a) Hol-Petch's relationship [4]

$$(4) \quad \sigma_S = \sigma_0 + K_y^{(Al)} (\overline{D})^{-1/2}$$

where: $\sigma_0^{(Al)} = 50 \text{ MPa}$ $K_y^{(Al)} = 8.5 \text{ MPa} \cdot \text{mm}^{1/2}$.

b) From Solution of Business's problem [5]

$$(5) \quad \tau_{\max} \approx \phi(\nu)HB$$

$$\text{where } \nu = \frac{0.5 - (V_T / V_L)^2}{1 - (V_T / V_L)^2};$$

$$\phi(\nu) = \left\{ \frac{1}{2}(1 - 2\nu) + \frac{2}{9}(1 + \nu) \cdot [2 \cdot (1 + \nu)]^{1/2} \right\}$$

c) Tresca's condition for plasticity [2]

$$(6) \quad \tau_{\max} = \sigma_s / 2$$

Therefore there is relationship

$$(7) \quad \sigma_s \approx \phi(\nu)HB$$

4. Derivate of relationship $\sigma_{-1}(\overline{D_{Al}})$

From equations (2) and (7) follows

$$\frac{\sigma_{-1}}{\sigma_s} = \frac{0.19HB}{\phi(\nu)HB} = 0.19\phi^{-1}(\nu) \text{ and therefore}$$

$$(8) \quad \sigma_s = \frac{\sigma_{-1}}{0.19\phi^{-1}(\nu)}$$

After substitution (8) in (4) it was obtained

$$\frac{\sigma_{-1}}{0.19\phi^{-1}(\nu)} = \sigma_0^{(Al)} + K_y^{(Al)} (\overline{D_{Al}})^{-1/2} \text{ and}$$

$$(9) \quad \sigma_{-1} = \tilde{\sigma}_0^{(Al)} + \tilde{K}_y^{(Al)} (\overline{D_{Al}})^{-1/2}$$

$$\text{where } \tilde{\sigma}_0^{(Al)} = \frac{0.19\sigma_0^{(Al)}}{\phi(\nu)}; \tilde{K}_y^{(Al)} = \frac{0.19K_y^{(Al)}}{\phi(\nu)}$$

5. Conclusion

In this paper the relationships (7) $\sigma_s \approx \phi(\nu)HB$ and (9) $\sigma_{-1}(\overline{D_{Al}})$ are obtain.

The material constants in (9) are $\sigma_{iR} \equiv \tilde{\sigma}_0^{(Al)}$ and $K_R \equiv \tilde{K}_y^{(Al)}$. Because there is $\nu = \nu(V_L; V_T)$ then coefficients are

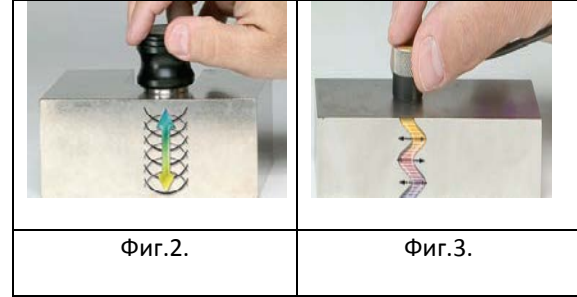
$$\tilde{\sigma}_0^{(Al)} = \tilde{\sigma}_0^{(Al)}(V_L; V_T); \tilde{K}_y^{(Al)} = \tilde{K}_y^{(Al)}(V_L; V_T).$$

It is non-destructive evaluation of material constants.

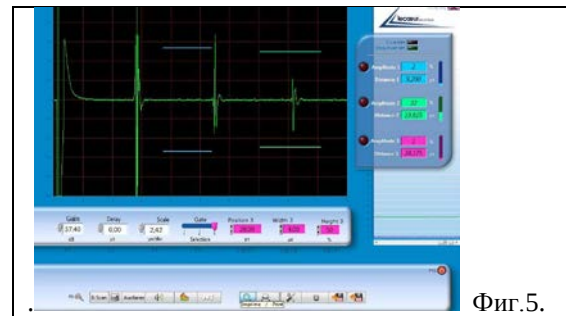
$$\sigma_{iR}; K_R.$$

6. Измерване на V_L и V_T

За измерване на величините V_L и V_T се използват ултразвукови осезатели с пиезопластини (ПП) X - срез и фиг.2., Y- срез, фиг.3. на ф-ма PANAMETRICS – САЩ



За измерване на величините $t_{L,T}, \mu s$ се използва ултразвуково устройство US Key (ф-ма LECOEUR ELECTRONIQUE, Франция). Точността на измерване на времето на $t_{L,T}, \mu s$ е $0.01 \mu s$.



Микрометър Digimatic Micrometer (MITUTOYO, Япония). Обхват 0-30 mm. Този микрометър, единствен в света, измерва с точност на отчета 0.0001 mm и точност на измерването $\Delta S \pm 0.5 \mu m$.

Величините V_L и V_T се изчисляват от зависимостите, съгласно ASTM E 494-2010

$$(10) \quad V_{L,T} = \frac{2.l, mm}{(t_{L,T}), \mu s}$$

където l, mm - делелина на измервания образец,
 $t_{L,T}, \mu s$ - съответно времена на разпространение на
 надлъжни и напречни ултразвуксови вълни.
 Използва се доверителен интервал за $V_{L,T}$ е [3]

$$(11) \quad \overline{V_{L,T}} \pm \left(\frac{1}{n}\right)^{1/2} T(n; \alpha) S_{V_{L,T}}$$

Използва се толерантен интервал за $V_{L,T}$ е [3]

$$(12) \quad \overline{V_{L,T}} \pm \left(1 + \frac{1}{n}\right)^{1/2} T(n; \alpha) S_{V_{L,T}}$$

Където $\overline{V_{L,T}}$ и $S_{V_{L,T}}$ са съответно средна стойност и
 стандартно отклонение за измерената скорост, n –
 брой на измерванията, $T(n; \alpha)$ - разпределение на
 Стюдънт при вероятност $Pr = 1 - \alpha$.

7.Literature

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