COMPUTER MODELING OF CAST ALLOYS SOLIDIFICATION BY COMPUTER-AIDED COOLING CURVE ANALYSIS (CA-CCA)

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The thermal cooling curve analysis (CCA) is a high-sensitivity method of measurement for thermo-physical characteristics of substance and is widely used both in the scientific purposes, and for the practical problems solution. In the scientific purposes this method is used at studying and quantitative measurement of thermo-physical, thermodynamic characteristics of investigated materials, including metals and alloys. In practice the CCA method of cooled melt test is used for an estimation of efficiency of modifying and/or refining processing of melts, the express analysis of a chemical compound, prediction of alloys structure and properties [1].

The computer-aided cooling curve analysis (CA-CCA) includes procedure of the temperature registration of molten metal poured in a small cup during solidification as functions of time and its computation which allows accurately defining parameters of phase transitions.

The basis of a mathematical model of solidification process in most applications of computer simulation package is the basic equation of heat conduction with internal heat sources in the temperature range of liquidus-solidus. When modeling the process of solidification of alloys should be noted that in contrast to pure metals alloys crystallize in the temperature range - from the liquidus temperature T_L to solidus temperature T_S. In this zone, called a two-phase or mesh-zone, there are both liquid and solid phase. If you neglect the convective heat transfer, this equation can be written for three-dimensional case as follows [2]:

$$\rho_S(T)c_S(T)\frac{\partial T}{\partial t} + \rho_L(T)c_L(T)\frac{\partial T}{\partial t} - q\rho_S(T)\frac{\partial f_S}{\partial t} = div(\lambda(T)\nabla T) \quad (1)$$

where $c_S(T), c_L(T)$ - the specific heat of solid and liquid phases of the alloy as a function of temperature,

$\rho_S(T), \rho_L(T)$ - density of solid and liquid phases as a function of temperature;

$\lambda(T)$ - the thermal conductivity of the alloy as a function of temperature,

q - the latent heat of crystallization of the alloy;

f_s - solid fraction;

T – temperature of the alloy;

t – time.

The main assumption of two-phase zone theory is that state of the mesh-zone can be described by using the allocation functions of solid volume fraction f_S and the liquid fraction f_L:

$$f_S(t) = \frac{V_S}{V_0}, \quad f_L(t) = 1 - f_S \qquad (2)$$

where V_S, V_0 – accordingly volumes of solid phase and the alloy,

L, S – the subscripts corresponding to liquid and solid state.

It is obvious that $0 \leq f_S \leq 1$, f_S $(t < t_L) = 0$ for a liquid phase, f_S $(t > t_S) = 1$ for completely solidified alloy. Thus, correct calculation of the solid f_S phase of alloys at solidification temperatures is critical component in computer-aided modeling of casting processing.

For equilibrium solidification f_S is described by the lever rule

$$f_S = \frac{C_L - C_0}{C_L - C_S} \tag{3}$$

where C_0 is the composition of the original liquid alloy,
C_L, C_S - the equilibrium concentrations of a component dissolved in the liquid and solid phases.

The composition of the solid Cs as a function of the fraction solid transformed can be written as

$$C_S = \frac{kC_0}{f_S(k-1)+1} \tag{4}$$

where k is the partition coefficient (the ratio of the equilibrium concentrations of a component dissolved in the solid and liquid phases $k = C_S / C_L$).

The equation (4) can be re-arranged to give

$$f_S = \left(\frac{1}{1-k}\right)\left(\frac{C_S - kC_0}{C_S}\right) \tag{5}$$

If to assume that solute diffusion in the solid phase is small enough to be considered negligible and that diffusion in the liquid is fast enough to assume that diffusion is complete (this may occur because of convection, or can be aided by mechanical mixing) then eq.4 can be re-written as [3]

$$C_S = kC_0(1 - f_S)^{k-1} \tag{6}$$

and equation (5) as

$$f_S = 1 - \left(\frac{C_S}{kC_0}\right)^{\frac{1}{k-1}} \tag{7}$$

The equation (6) is known as the Scheil equation. It predicts a function of concentration that tends towards upper limit on the concentration of any solid forming. In the case where two components form a complete solid solution across the composition range, the liquid will, at some point, reach a concentration of 100 % of the second component. An alternative case arises in a binary eutectic system, where a solid eutectic structure will form when the concentration of the liquid reaches the eutectic concentration.

Such calculations are currently used within computer solidification packages [4]. However calculation f_S on the basis of the various functional dependences connecting quantity of a solid fraction with phase diagrams of alloys, often ineffectively and extremely inadequately reflects the valid character of a thermal emission for non-equilibrium conditions. The traditional calculation of solidification by the Scheil equation has quite severe restrictions when applied to multi-component alloys. It is not possible to derive this equation, using the same mathematical method with phase diagrams of alloys, if the partition coefficient, k, is dependent on temperature or composition. The Scheil equation is applicable only to dendrite solidification, can not be applied to eutectic alloys that are common type for cast alloys and can not be used to predict the formation of intermetallics during solidification. The CA-CCA technique can provide adequate calculation f_s and, therefore, all of the above disadvantages can be overcome.

All known thermal analysis methods including CCA techniques use a comparison method of data processing. The measurements are carried out from a reference state or point of comparison. It is commonly called the "baseline" or "zero curve" for thermal analysis and

its determination is the critical requirement for the CCA methods. The baseline overlaps the first derivative of the cooling curve (dT/dt) in single-phase parts of the sample cooling process, as shown in Fig.1. Usually to definition of the baseline apply polynomial or linear Newtonian and Fourier methods [1,5-9]. These methods use one or two thermocouples placed in the test sample and involves curve fitting the cooling rate (the first derivative of the cooling curve) of the liquid phase with the cooling rate of the solid phase what gives a baseline cooling rate applicable throughout the two-phase region.

The latent heat q and solid fraction f_S can be calculated for known values of specific heat of the alloy from equations [1]:
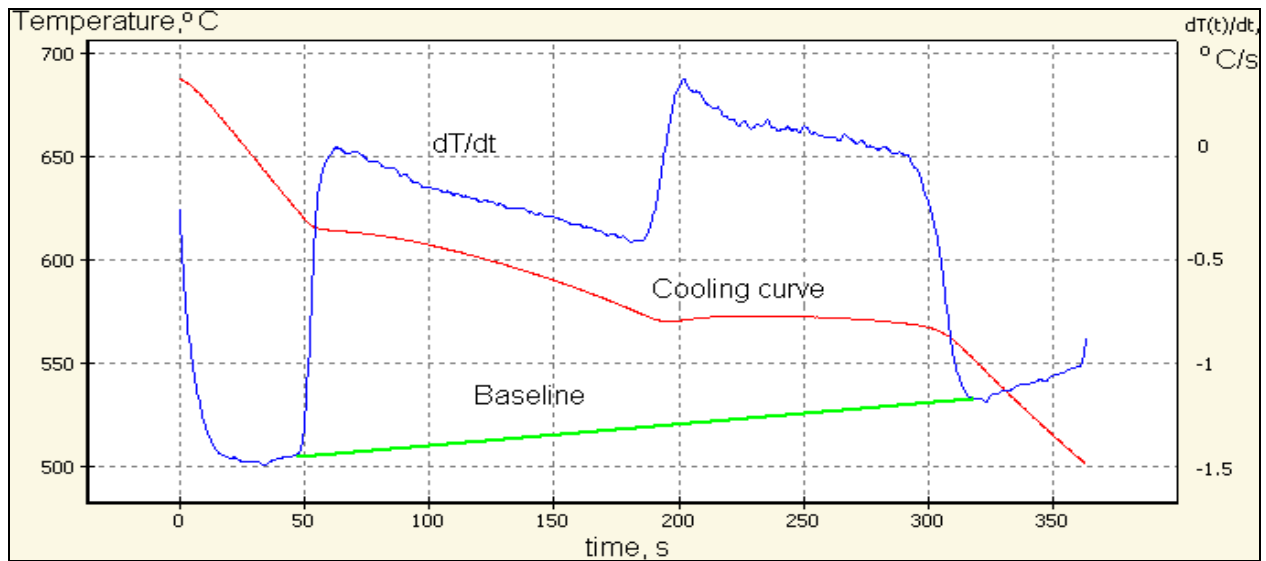
$$q = c_p \int_{t_L}^{t_S} (\frac{dT}{dt} - Z(t))dt \ , \tag{8}$$

Figure 1 *Cooling Curve of an Al-7%Si alloy*

$$f_S = \frac{c_p}{q} \int_{t_L}^{t_S} (\frac{dT}{dt} - Z(t))dt \tag{9}$$

where $Z(t)$ is the "baseline" function,

t_S and t_L are the times for the start and end of solidification.

The Newtonian methods are based on the analysis of the heat balance equation for the solidifying "sample-mould" system [1, 6]:

$$\frac{dQ}{dt} - mc_p \frac{dT}{dt} = aF(T - T_0) \tag{10}$$

where m is the mass of the sample, a is overall heat transfer coefficient, F is sample surface area, T_0 is ambient temperature, and Q is the total latent heat of solidification ($q=Q/m$).

While $dQ/dt = 0$ (no phase transformations at cooling of the sample), the first derivative of the cooling curve of the sample can be written as [1]:

$$Z(t) = \frac{dT}{dt} = -\frac{aF(T - T_0)}{mc_p} \tag{11}$$

The curve corresponding to Equation 11 represents the Newtonian baseline (Z) if no phase transformation occurs (in the single-phase regions). For mesh zone the analysis starts by fitting a line or polynomial curves, usually of the third order or higher, to the start and end solidification points of the first derivative of the cooling curve.

The Fourier methods consider the effect of thermal gradient during solidification and assume that heat transfer takes place by conduction only [8]:

$$\frac{\partial T}{\partial t} = \alpha \nabla^2 T + \frac{1}{c_V} \frac{\partial Q}{\partial t} \tag{12}$$

where α is the thermal diffusivity,
C_V is the volumetric specific heat.
Equation (12) can be rewritten as [1]:

$$\frac{\partial Q}{\partial t} = c_V (\frac{\partial T}{\partial t} - \alpha \nabla^2 T) = c_V (\frac{\partial T}{\partial t} - Z) , \tag{13}$$

where Z is Fourier baseline.

If cylindrical sample with known temperatures T_1 and T_2 at radius R_1 and R_2 in the test sample is used and assuming temperature field in a parabolic form, $\nabla^2 T$ can be calculated as:

$$\nabla^2 T = \frac{4(T_2 - T_1)}{R_2^2 - R_1^2} \tag{14}$$

The thermal diffusivity is determined through an iterative procedure, assuming it before and after solidification according to the following equation:

$$\alpha = \frac{\partial T / \partial t}{\nabla^2 T} \tag{15}$$

and solid fraction by the first order approximation as:

$$f_S = \frac{t - t_L}{t_S - t_L} , \tag{16}$$

where t_L and t_S are time of the start and end of the sample solidification determined from the first derivative curve.

The thermal diffusivity and the volumetric specific heat are calculated from iterative procedure as functions of time:

$$\alpha(t) = \alpha_L \left[1 - f_S(t) \right] + \alpha_S f_S(t) \tag{17}$$

$$c_V(t) = c_{VL} \left[1 - f_S(t) \right] + c_{VS} f_S(t) \tag{18}$$

where C_{VL} and C_{VS} are the volumetric specific heats of liquid and solid phase, respectively,
α_L and α_S are the initial and final values of the thermal diffusivity.

The latent heat and the fraction solid can be calculated as [7,8]:

$$q = \int_{t_L}^{t_S} \left(\frac{\partial Q}{\partial t} \right)(t)dt , \tag{19}$$

$$\frac{\partial Q}{\partial t} = c_V \left(\frac{\partial T}{\partial t} - Z \right), \tag{20}$$

$$f_S(t) = \frac{1}{q} \int_{t_L}^{t} \left(\frac{\partial Q}{\partial t} \right)(t)dt \tag{21}$$

A comparison of solidified volume fractions predicted by Newtonian and Fourier methods executed in [1]. According to the presented data the significant difference in the shape of zero curves is being reflected in the calculation of solid fraction and its dependence on the temperature or time. Using the average values of specific heat affect the calculations and might add to the calculation's errors, therefore, it is recommended to calculate the specific heat of the system from the volume fraction and composition of the existing phases throughout the solidification.

Thus, definition of the solid fraction by the methods considered above strongly depends on a way of carrying out of a baseline and knowledge of values the specific heat. In order to accurately measure thermal properties and solid fraction f_S using CA-CCA techniques the baseline must be removed from the calculation.

For definition of the solid fraction using CA-CCA techniques authors of the present work used the mathematical model offered in [10]. The solidification model can be calculated from the equation (10) of heat balance in a combination to Newton-Rihman's equation for heat exchange:

$$q\rho \frac{dV_S}{dt} - c_p\rho V_0 \frac{dT}{dt} = aF(T(t) - T_0) \,, \tag{22}$$

where $q\rho \dfrac{dV_S}{dt} = \dfrac{dQ}{dt}$ is the latent heat rate of solidification, $\rho V_0 = m$ is the mass of the sample.

The equation (22) can be re-written as:

$$\frac{d(V_S/V_0)}{dt} = \frac{c_p}{q}\frac{dT}{dt} + \frac{aF}{q\rho V_0}(T(t) - T_0) \tag{23}$$

Integrating (23), the solid fraction can be calculated as:

$$f_S(t) = V_S(t)/V_0 = \beta \int_{t_L}^{t} (T(\tau) - T_0)d\tau + \frac{c_p}{q}(T(t) - T_L) \,, \tag{24}$$

where $\beta = \dfrac{aF}{q\rho V_0}$ can be defined for the condition of the sample solidification from CA-CCA if $f_S=1$ and the ratio C_P/q is known.

According to [10] the casting temperature before and after solidification exponentially decreases:

$$\Delta T(t) = T(t) - T_0 = (T_f - T_0)\exp(-\alpha t) = \Delta T_0 \exp(-\alpha t) \,, \tag{25}$$

and during solidification at assuming $\alpha(t_S - t_L) \ll 1$ the temperature can be written as:

$$\Delta T(t) \approx \Delta T_0 \exp(-\alpha t) + \frac{q}{c_P}\frac{V_S(t)}{V_0} \,, \tag{26}$$

where $T_f = T(0)$ and $\alpha = \dfrac{aF}{c_p\rho V_0}$.

Thus, if the solidification is finished ($V_S=V_0$) the ratio C_P/q can be approximately estimated from (26) as

$$\frac{c_P}{q} = \frac{1}{\Delta T(t_S) - \Delta T_0 \exp(-\alpha t_S)} ,$$ (27)

The coefficient α is defined from an initial part of a cooling curve according to equation (25).

In this work, the comparative calculations of solidification were carried out for aluminum alloy Al-7%Si by the lever rule and CA-CCA methods, including on the basis of the solidification model (24-27). The alloy was melted in a electric resistance furnace. No protective salt mixes or modification agents were added to the melt. Test samples with masses from 35g ±2g to 100g±5g were melted in graphite and alundum crucibles, also were poured into standard cups with the built in thermocouples of type Quik-Cup of «Heraeus Electro-Nite» Company. For measurement the microprocessor CA-CCA system with high permission of time was used (Fig.2).

Fig. 2 *Appearance of microprocessor system for the thermal (CA-CCA) analysis of cast alloys*

The solid fraction as function of time for an Al-7% Si calculated by the lever rule (5), by Scheil equation (7) for binary Al-Si phase diagram and received with application of ProCAST software (by the lever rule method) is presented on Fig.4-5. These data show small difference in the amount of solid fraction calculated using the equilibrium Al-Si phase diagram.
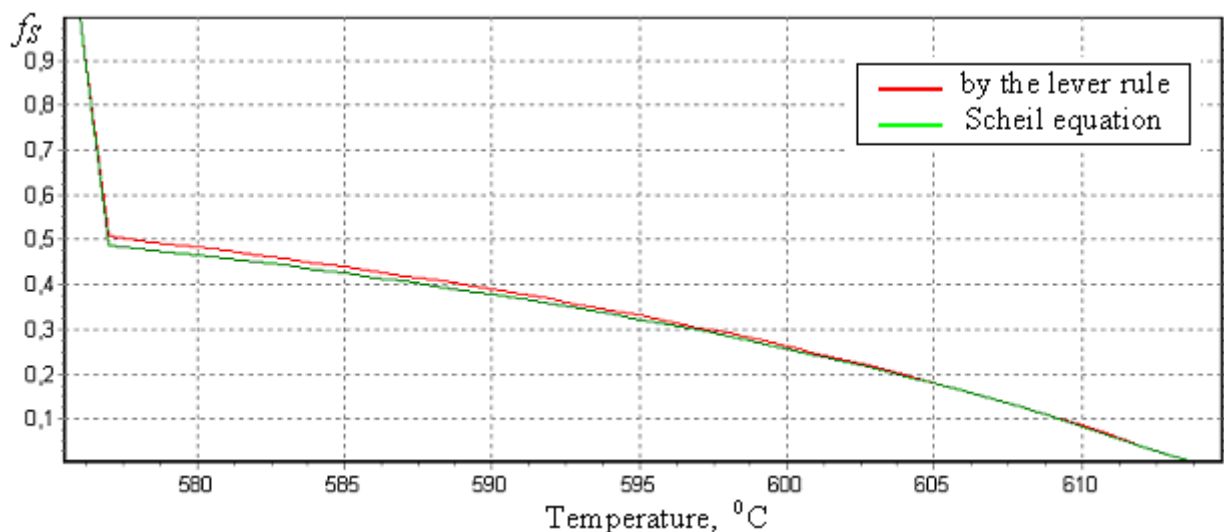

Fig. 3 *The solid fraction for an Al-7% Si calculated by the lever rule*
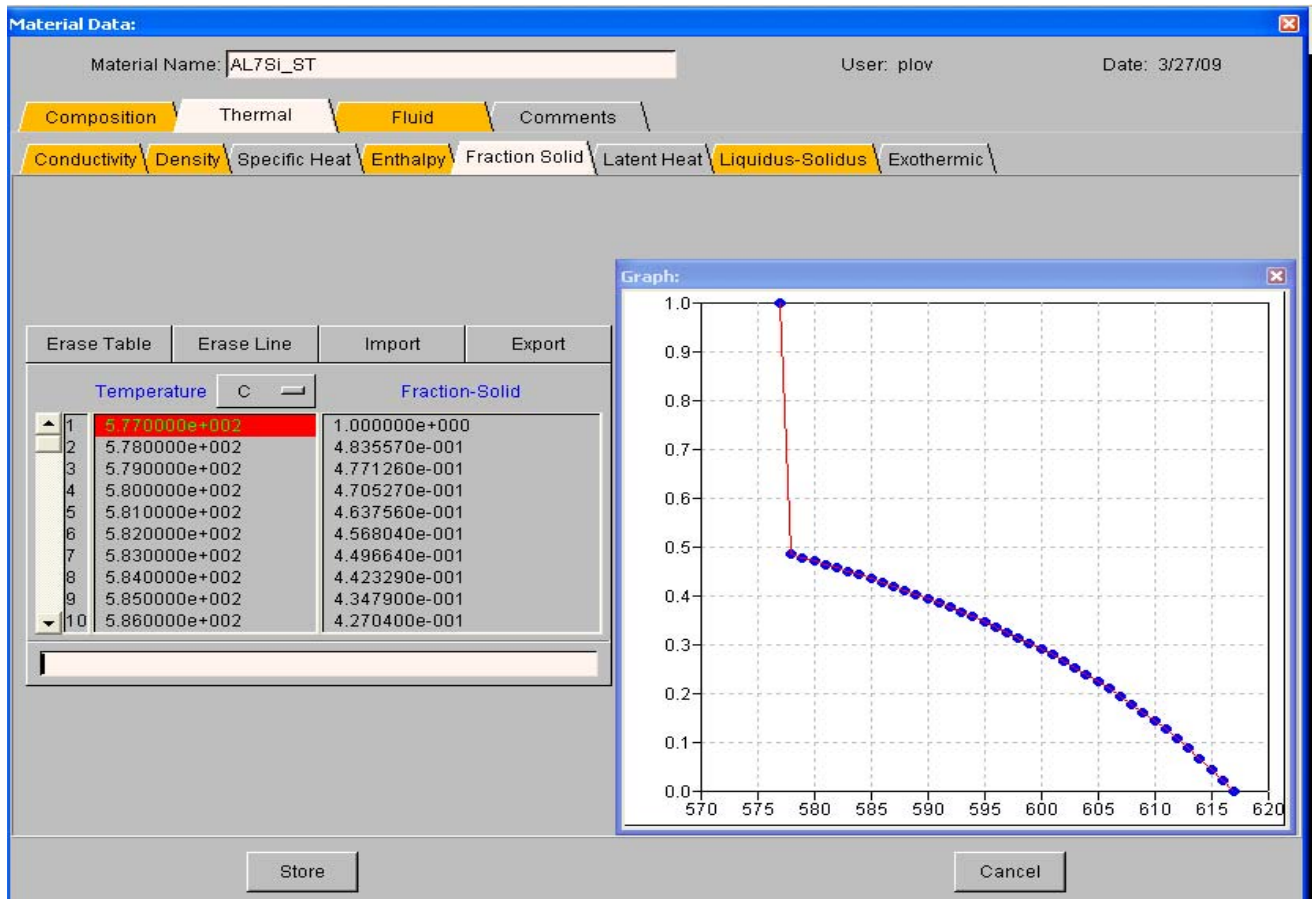
Fig. 4 *The solid fraction for an Al-7% Si calculated by ProCAST software*

The solid fraction as function of temperature for an Al-7% Si calculated by CA-CCA methods is shown on Fig.5-6.
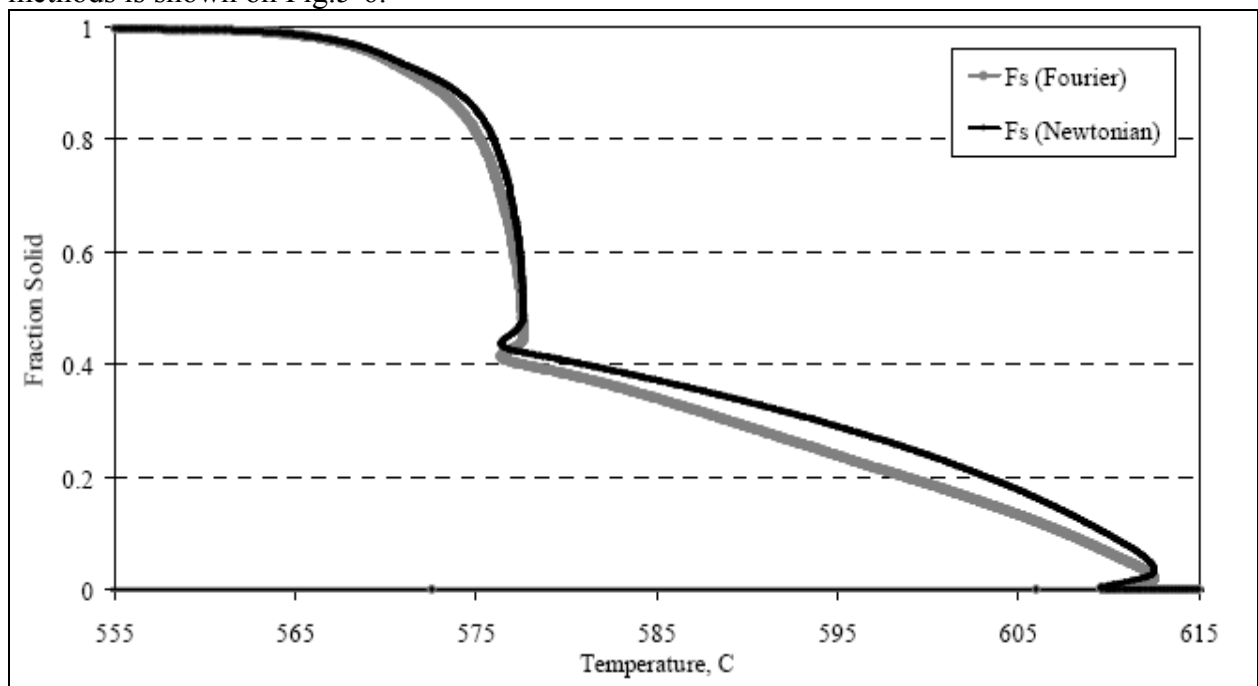

Fig. 5 *Comparisons of solidified volume fractions calculated by Newtonian (polynomial) and Fourier methods for an Al – 7 % Si alloy at a cooling rate of 0,55 ºC/s according to [1]*
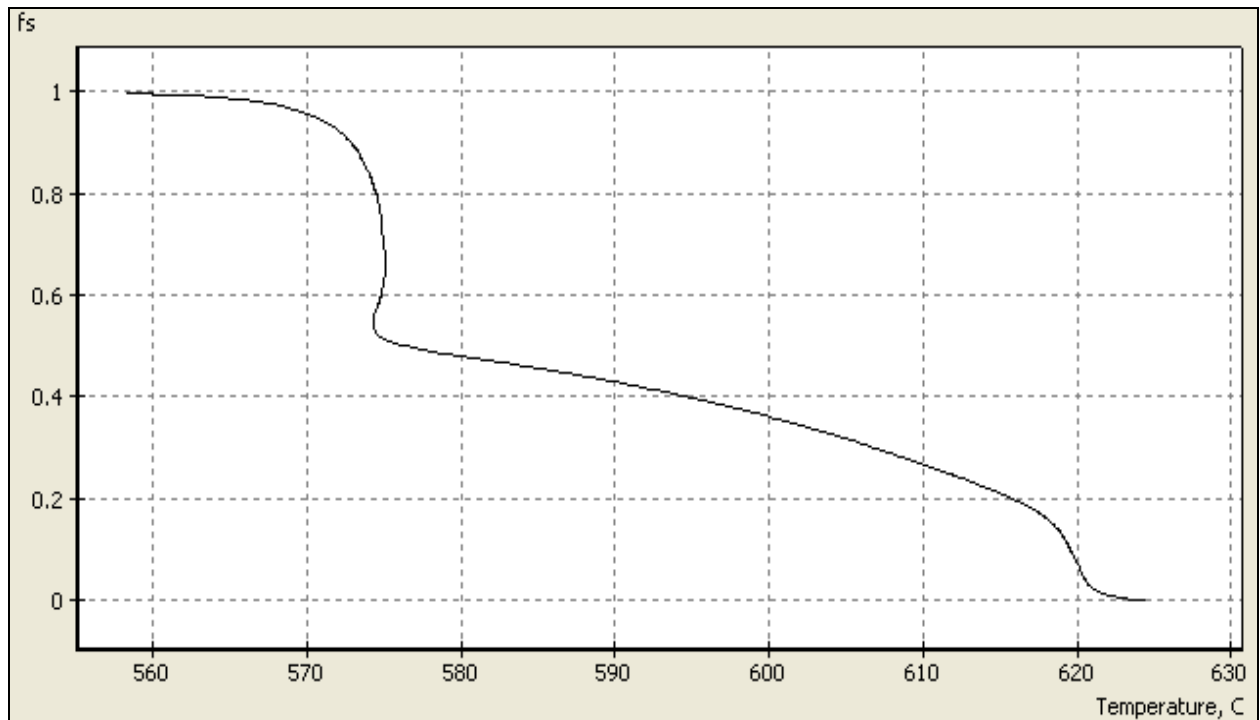
Fig. 6 *Solid fraction calculated by CA-CCA method on the basis of the solidification*
models (24)-(27) for an Al – 7 % Si alloy at a cooling rate of 2,0 °C/s

These figures show that there are small differences in the amount of fraction solid calculated using Fourier or Newtonian methods and applying solidification models (24)-(27). However, the curve of solid fraction received on the basis of the equilibrium phase diagram including data received by ProCAST software considerably differs from received by CA-CCA methods.

The comparative analysis of computer modeling of cast solidification for an Al-7%Si alloy was carried out. To estimate the influence degree of the solid fraction on results of modeling, data received by CA-CCA method have been entered as the initial data in ProCAST (Fig.7).
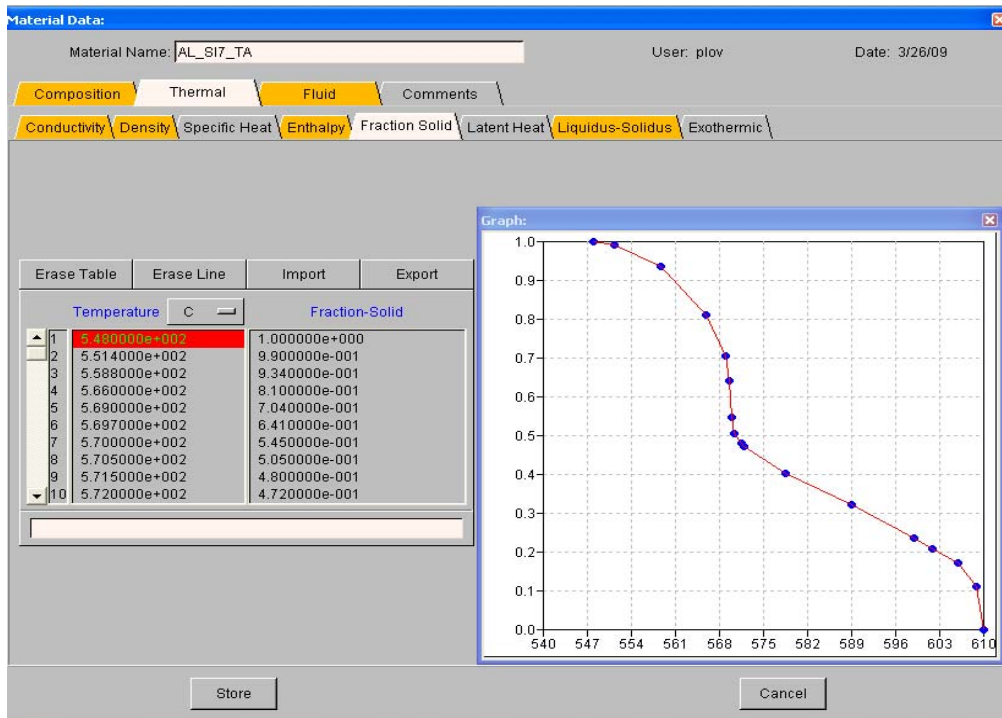
Fig.7 *The solid fraction for an Al-7% Si alloy calculated by CA-CCA and entered as the initial data for solidification modeling by ProCAST*

The performed analysis of various types of computer models carried out for solidification modeling of an Al-7%Si alloy has shown the remarkable difference between the solidification process calculated by CA-CCA method and on the basis equilibrium phase diagram Al-Si (Fig.8).
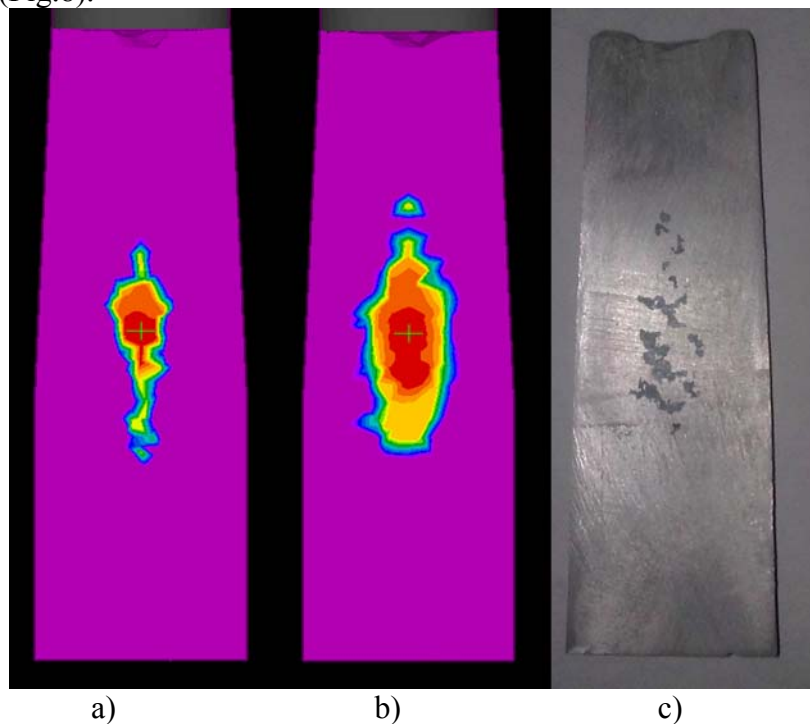

a)   b)   c)

Fig.8 *The computer models of an Al-7% Si alloy solidification: a) calculated by ProCAST according to the lever rule for solid fraction; b) calculated by ProCAST with CA-CCA method use;*
c) the casting template poured and solidified in a metal mould

In the conclusion it is important also to notice that because of a lack of the data under phase diagrams for multi-componental systems and obvious complexity of calculation of solid fraction for them, the CA-CCA method remains unique technique for adequate modeling of solid fraction of the majority of industrial alloys.

Thus, using only solid fraction f_S calculated for equilibrium solidification might add some errors to the calculation of cast alloy solidification, therefore, it is recommended to carry out computer modeling on the basis CA-CCA methods having removed from calculations the determination of the baseline for modeling of the volume solid fraction.

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