Group 3

Mathematical model of crystallization of two-component alloys at presence of nanoparticles

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Abstract.
Mathematical model of the crystallization of two-component alloys is studied, analyzed and solved numerically. We have used this model to find the temperature distribution depending on time for three different alloys, in particular aluminium alloy, cast iron and carbon steel. It has been found that increasing the number of centers of crystallization by adding nanosized particles reduces the overcooling and thus improves the properties of the alloys.

Keywords: mathematical modelling, crystallization, overcooling, two-component alloys, nanoparticles

3.1 Introduction

The crystallization is a process of formation and growth of crystals that are melted from pure substances, alloys, liquids or gas phases. The transition from liquid to solid state is called primary crystallization. In equilibrium conditions the crystallization proceeds with constant temperature or in a temperature range. In pure metals only the first case is possible, and both of them in the alloys.

The process begins with pouring the melt into a mould. The temperature T_0 to which the metal is overheated depends on the material, the shape and the size of the mould. During the crystallization process there are three zones called a liquid zone, a two-phase zone and an eutectic zone.

The liquid zone starts at the temperature of casting T_0 and ends at the liquidus temperature T_L. It is known that the crystallization does not begin at the equilibrium liquidus temperature T_L but at a lower temperature T. The value $\Delta T = T_L - T$ is called overcooling.

The two-phase zone starts at the temperature T_L and ends at the temperature T_E of the eutectic. The eutectic zone starts at T_E.

The process is non-linear due to the complex temperature change in the two-phase zone where the centers of crystallization are formed and grow. If the process is divided into the three phases mentioned above, only the process in the liquid zone can be treated as linear.

We solve the problem numerically. The purpose of the numerical simulation is to analyze the effect of submission of nanoparticles as additional centers of crystallization. It is shown that the inclusion of new centers of crystallization reduces the overcooling and thus improves the physical properties of the alloys.

3.2 Mathematical model

We consider a small enough specimen about which the temperature T depends only on time t and the spatial coordinates are ignored. Using the condition of heat balance and assuming the case of nonisothermal volume crystallization [1],

the following mathematical model is obtained:

$$C\rho V_0 \frac{\mathrm{d}\,T}{\mathrm{d}\,t} = L\rho \frac{\mathrm{d}\,V}{\mathrm{d}\,t} - \alpha F(T - T_f) \tag{3.1}$$

where α is the coefficient of heat transfer, T_f is the temperature of the mould, L is the crystallization heat, C is the heat capacity, ρ is the relative density, V_0 is the volume of the melt, F is the area of the melt, t is time, V is the volume of the solid phase in the volume of the melt.

According to the statistical theory of the volume crystallization of metals created by Kolmogorov [2], the volume V can be determined depending on the velocity of growing of the crystals and the velocity of generation of the centers of crystallization:

$$V = V_0(1 - e^{-\omega}). \tag{3.2}$$

Here the variable ω is defined as

$$\omega = \varphi N \left(\int_{t_0}^{t} K_V \Delta T d\tau \right)^3 \tag{3.3}$$

where N is the number of the crystallization centers, K_V is the crystallization constant, $\varphi = \dfrac{4\pi}{3}$ for spherical crystals. According to [3] in the case of two-component alloys considered here the overcooling is given by

$$\Delta T = T_L - T = T_A - T - \beta_0 C_0 f_L^{k-1}, \tag{3.4}$$

where C_0 is the concentration of the component whose quantity is less in the melt, $f_L = e^{-\omega}$ is the content of the liquid phase in the two-phase zone, T_A is the melting temperature of the pure metal, β_0 is the modulus of the liquidus line slope coefficient on the equilibrium diagram of the added component and the basic metal, k is a coefficient of distribution. Using (3.2) we have

$$\frac{V}{V_0} = 1 - f_L = 1 - e^{-\omega}. \tag{3.5}$$

Taking into account equations (3.1)-(3.5) we obtain:

$$\frac{\mathrm{d}\,\Delta T}{\mathrm{d}\,T} = \frac{\alpha}{R\rho_i C_i} \left[T_A - T_f - \Delta T - \beta_0 C_0 f_L^{k-1} \right] + \tag{3.6}$$

$$\left[\frac{L}{C_i} + \beta_0 C_0 (1 - k) f_L^{k-2} \right] \frac{\mathrm{d}\,f_L}{\mathrm{d}\,t}, \tag{3.7}$$

Here $R = \dfrac{V_0}{F}$ is the ratio of the volume of the melt V_0 to the area of the melt F, $i = 1, 2, 3$, $i = 1$ corresponds to the liquid zone, $i = 2$ - to the two-phase zone, $i = 3$ - to the eutectic.

Now we formulate the mathematical model of the crystallization process in each of the three zones [4].

- *Differential problem in the liquid zone, $T_0 \geq T \geq T_L$.*

  In the liquid zone $f_L = e^{-\omega} = 1$. Using this in (3.7), the temperature distribution is described by the following differential problem:

$$\begin{cases} \dfrac{\mathrm{d}\,T}{\mathrm{d}\,t} = -\dfrac{\alpha_1}{R\rho_1 C_1}(T - T_f), \, t \in (t_0; t_L] \\ T(t_0) = T_0. \end{cases} \tag{3.8}$$

  We set $t_0 = 0$. The value of t_L is the time for which the temperature of the liquidus T_L is reached.

- *Differential problem in the two-phase zone, $T_L \geq T \geq T_E$.*

  In the two-phase zone $f_L = e^{-\omega}$ and the distribution of the temperature is described by the following initial-value problem

$$\begin{cases} \dfrac{\mathrm{d}\,\Delta T}{\mathrm{d}\,t} = \dfrac{\alpha_2}{R\rho_2 C_2} \left[T_A - T_f - \Delta T - \beta_0 C_0 \left(e^{-\omega} \right)^{k-1} \right] - \\ \left[\dfrac{L}{C_2} + \beta_0 C_0 (1-k) \left(e^{-\omega} \right)^{k-2} \right] e^{-\omega} \dfrac{\mathrm{d}\,\omega}{\mathrm{d}\,t}, \qquad t \in (t_L; t_E] \\ \Delta T(t_L) = 0, \end{cases} \tag{3.9}$$

$$\Delta T = T_A - T - \beta_0 C_0 f_L^{k-1}, \tag{3.10}$$

$$\omega = \varphi N \left(\int_{t_L}^{t} K_V \Delta T \, \mathrm{d}\,\tau \right)^3. \tag{3.11}$$

- *Differential problem in the eutectic zone, $T_E \geq T \geq T_{end}$.*

  Here $\dfrac{V}{V_0} = \dfrac{V_E}{V_0} = 1 - f_E$, where V_E is the volume of the solid eutectic, f_E is the content of the liquid eutectic:

$$f_E = e^{-K_E \int_{t_E}^{t} (T_E - T) \, \mathrm{d}\,\tau},$$

  K_E is the crystallization coefficient of the eutectic, t_E is the time, at which the metal alloy reaches the temperature of eutectic, T_{end} is the temperature, at which the crystallization finishes, $T_{end} = T(t_{end})$. The differential problem is

$$\begin{cases} C_3 \rho_3 \dfrac{\mathrm{d}\,T}{\mathrm{d}\,t} = -L\rho_3 \dfrac{\mathrm{d}\,f_E}{\mathrm{d}\,t} - \dfrac{\alpha_3}{R}(T - T_f), \, t \in (t_E; t_{\text{end}}] \\ T(t_E) = T_E. \end{cases} . \tag{3.12}$$

  The times t_L and t_E are not known beforehand and are obtained in the process of numerical solving.

3.3 Numerical methods

We describe the numerical methods used in the three zones and illustrate the results on the example of an aluminium alloy.

- *Liquid zone*

  The analytical solution of the equation in the liquid zone is

  $$T(t) = T_f + (T_0 - T_f)e^{\dfrac{\alpha_1}{R\rho_1 C_1}(t_0 - t)}. \tag{3.13}$$

  The numerical one is calculated within the interval $[t_0 = 0 \text{ s}; 30 \text{ s}]$ by the embedded **Matlab** function `ode45`. On figure 3.1 we show the graphs of the analytical solution (3.13) and the numerical one calculated by Matlab. The absolute difference between both solutions is 10^{-12}. The value of the
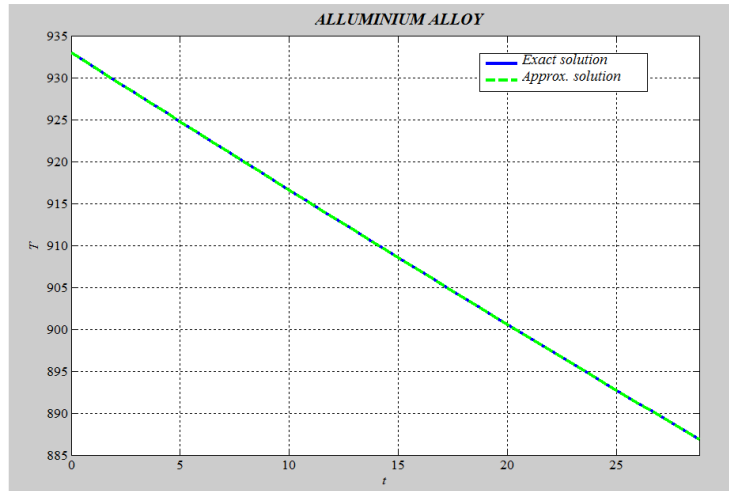
Figure 3.1: *Comparison between the numerical and the analytical solution in the liquid zone for aluminium alloy*

  time t_L for which the temperature of the metal alloy reaches the liquidus temperature is found approximately. We seek for a time t_i such that $| T(t_i) - T_L | < \varepsilon$ for a given small ε. For $\varepsilon = 10^{-4}$ we obtain

  $$t_L \approx 28.7830 \text{ s}.$$

- *Two-phase zone*

  Since in this case the equation is non-linear with respect to the temperature we use a finite difference method. The explicit Euler method is suitable for this aim [5]. We introduce a grid in the interval [28.7830 s; 130 s]:

  $$\overline{\omega}_h = \left\{ t_{i+1} = t_i + h, \, i = 0, 1, \ldots, n - 1; \, t_0 = t_L, \, h = \frac{t_n - t_0}{n} \right\}$$

and define the mesh function y, the discrete analogue of ΔT. The finite difference scheme is:

$$y_{i+1} = y_i + \frac{h\alpha_2}{R\rho_2 C_2}\left[T_A - T_f - y_i - \beta_0 C_0\left(e^{-\omega_i}\right)^{k-1}\right] -$$
$$h\left[\frac{L}{C_2} + \beta_0 C_0(1-k)\left(e^{-\omega_i}\right)^{k-2}\right]\cdot e^{-\omega_i}\cdot\frac{\omega_i - \omega_{i-1}}{h},$$
$$i = 1,\, 2,\, \ldots,\, n-1;\; y_0 = \triangle T(t_L) = 0. \quad (3.14)$$

For evaluating y_2 we need the values of y_0 and y_1. Since

$$\frac{\mathrm{d}\,\omega}{\mathrm{d}\,t} = \varphi N\cdot 3\left(\int_{t_L}^{t} K_V \Delta T\,\mathrm{d}\,\tau\right)^2\cdot K_V \Delta T(t),$$

then we have

$$\frac{\mathrm{d}\,\omega}{\mathrm{d}\,t}(t_L) = 0.$$

From here we calculate

$$y_1 = y_0 + \frac{h\alpha_2}{R\rho_2 C_2}\left[T_A - T_f - y_0 - \beta_0 C_0\left(e^{-\omega_0}\right)^{k-1}\right].$$

We already know the values of y_0 and y_1. Returning to the explicit Euler method (3.14) we successfully obtain the rest of the values of y in the mesh nodes.
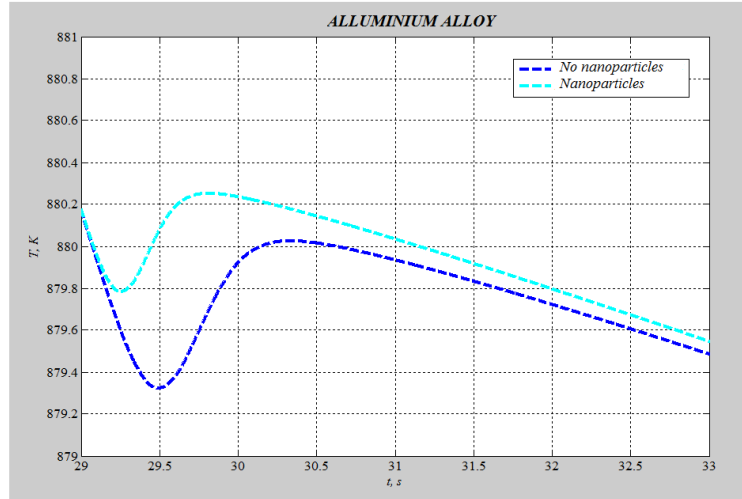

Figure 3.2: *Comparison between the numerical solutions found with and without added nanoparticles for aluminium alloy (zoom)*

The results of the numerical simulations are shown on figure 3.2. The solution of the problem is accomplished with the following values of N:

$N = 2.562 \cdot 10^3$ m^{-3} corresponds to the case without added nanoparticles and $N = 2.562 \cdot 10^9$ m^{-3} corresponds to the case with added nanoparticles. Increasing N we model the increasing of the centers of crystallization as a result of the added nanosized particles. The graph of the numerical solution of problem 3.2 shows that the increasing of N reduces the overcooling. The magnitude of the supercooling is related to the refining of the microstructure of the alloy and, hence, it improves its mechanical properties.

We find a time t_E such that $|T(t_E) - T_E| < \epsilon$ for arbitrarily small ϵ. For $\varepsilon = 10^{-2}$ we obtain

$$t_E \approx 106.03 \text{ s}.$$

- *Eutectic zone*
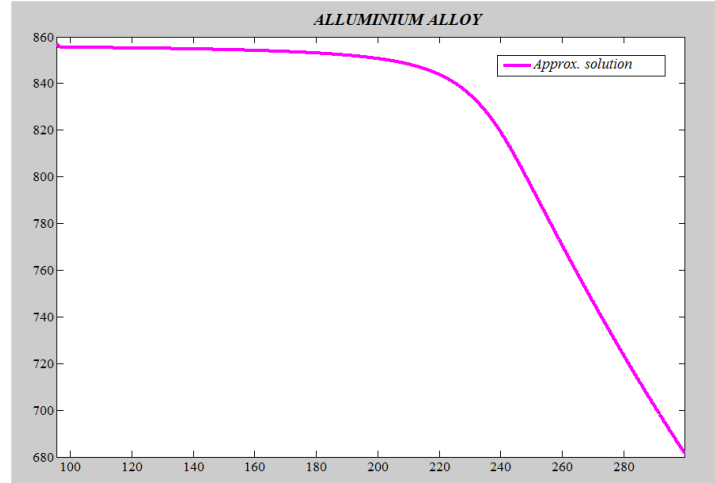
Figure 3.3: *Results from the numerical simulation of the temperature as a function of time in the eutectic zone for aluminium alloy*

We solve the differential equation (3.12) within the interval [106.03 s; 300 s]. As in the two-phase zone the equation is non-linear with respect to the temperature and we use again the explicit Euler method. We introduce a uniform mesh

$$\overline{\omega}_h = \{t_{i+1} = t_i + h, \, i = 0, 1, \ldots, n-1; \, t_0 = t_E, \, h = \frac{t_n - t_0}{n}\}.$$

The numerical scheme takes the following form:

$$\begin{cases} \dfrac{y_{i+1} - y_i}{h} = \dfrac{L}{C_3} \, K_E \, (T_E - y_i) \, e^{-K_E \, s_i} - \dfrac{\alpha_3}{RC_3\rho_3} \, (y_i - T_f) \\ y_0 = T_E. \end{cases} \qquad (3.15)$$

Here s_i is a notation for the integral

$$\int_{t_E}^{t_i} (T_E - T)\,\mathrm{d}\,\tau.$$

At first we initialize $s_0 = 0$. Then for each step i we add the value the integral $\int_{t_{i-1}}^{t_i} (T_E - T)\,\mathrm{d}\,\tau$ to the current value of s_{i-1}:

$$s_i = \int_{t_E}^{t_i} (T_E - T)\,\mathrm{d}\,\tau = \int_{t_E}^{t_1} (T_E - T)\,\mathrm{d}\,\tau +$$
$$\int_{t_1}^{t_2} (T_E - T)\,\mathrm{t}\,\tau + \cdots +$$
$$\int_{t_{i-2}}^{t_{i-1}} (T_E - T)\,\mathrm{d}\,\tau + \int_{t_{i-1}}^{t_i} (T_E - T)\,\mathrm{d}\,\tau$$
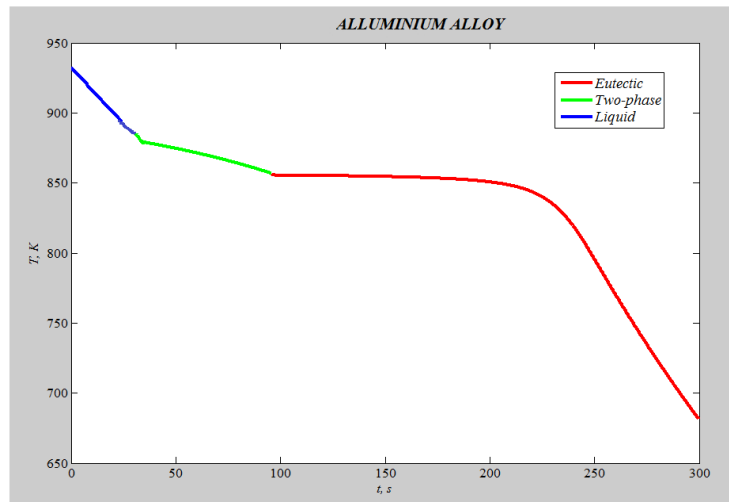
Figure 3.4: *Results from the numerical simulation of the temperature as a function of time in the liquid zone, in the two-phase zone and in the eutectic zone for aluminium alloy*

The results of the numerical solving of the problem in the region of eutectic are shown in figure 3.3. The overall look of the temperature dependence for all investigated zones of the crystallization process is shown in figure 3.4.

3.4   Some more numerical results

Numerical simulations of the crystallization of two more metal alloys were carried out in order to consolidate the hypothesis that the addition of nanoparticles

leads to decrease in the overcooling. Comparison between the temperatures with and without addition of nanoparticles are shown in figures 3.5 and 3.6 for cast iron and carbon steel respectively. For both alloys the simulations were performed for $N = 1 \cdot 10^3$ m^{-3} (no nanoparticles) and $N = 5.28 \cdot 10^6$ m^{-3} (with added nanoparticles). The results show again substantial decrease in the overcooling when nanoparticles are being introduced to the melted alloys. So in the frames of the given model the crystallization proceeds smoother when crystallization centers are added. The overall pictures of the cooling process in the liquid phase, two-phase and the eutectic phase are presented in figures 3.7 and 3.8 for cast iron and carbon steel respectively.
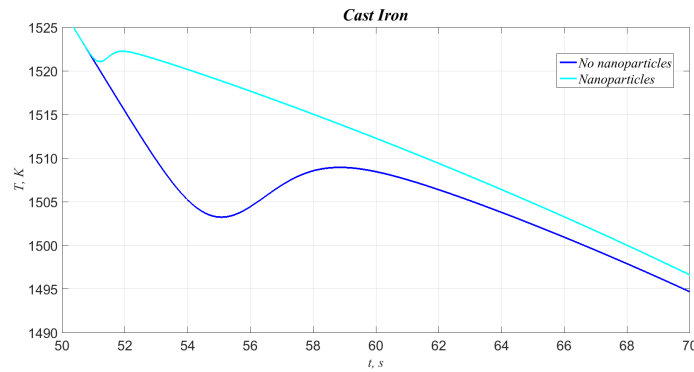
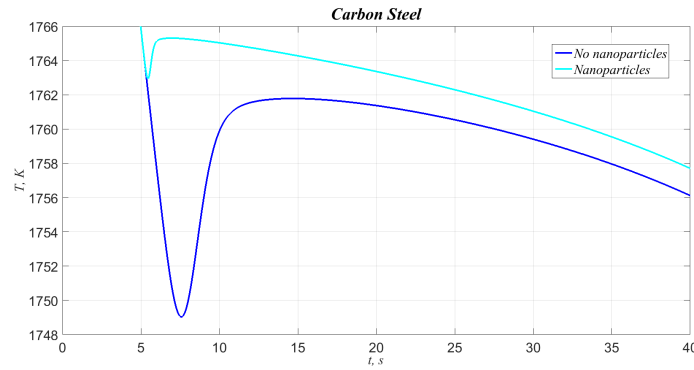Figure 3.5: *Comparison between the numerical solutions found with and without nanoparticles for cast iron.*

Figure 3.6: *Comparison between the numerical solutions found with and without nanoparticles for carbon steel*

3.5   Conclusions

We have developed an appropriate method for solving the mathematical model of crystallization of metal alloys. The temperature dependence on time has
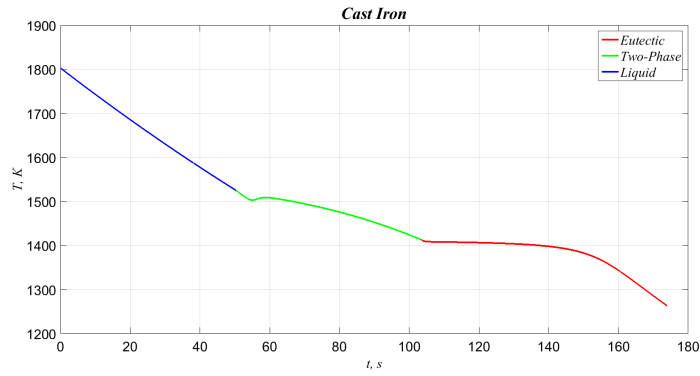
Figure 3.7: *Results from the numerical simulation of the temperature as a function of time in the liquid zone, in the two-phase zone and in the eutectic zone for cast iron*
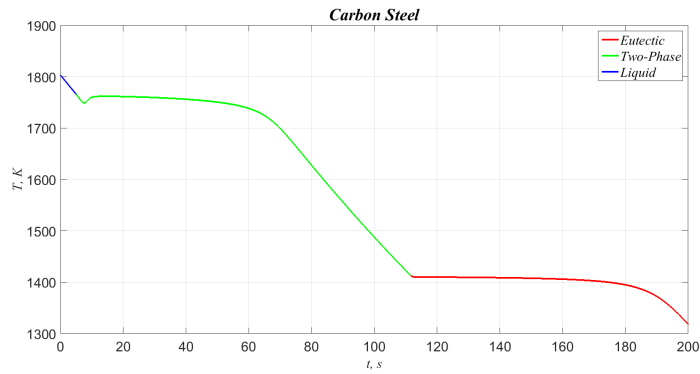

Figure 3.8: *Results from the numerical simulation of the temperature as a function of time in the liquid zone, in the two-phase zone and in the eutectic zone for carbon steel*

been obtained in the interval from the temperature of melting till the end of the crystallization process for aluminium alloy, cast iron and carbon steel. The decrease in overcooling with the addition of nanoparticles was observed with the presented model.

3.6 Appendix

The values of the physical parameters for the three alloys are given below.

1. *Aluminium Alloy*

   $T_0 = 933$ K, $T_L = 886.85$ K, $T_E = 857$ K, $T_f = 293$ K, $T_A = 933$ K

   $\alpha_1 = 48 \ \dfrac{\text{W}}{\text{m}^2\text{K}}$, $\alpha_2 = 75 \ \dfrac{\text{W}}{\text{m}^2\text{K}}$, $\alpha_3 = 85 \ \dfrac{\text{W}}{\text{m}^2}\text{K}$,

   $\rho_1 = 2.6$ kg/m$^3 \cdot 10^3$, $\rho_2 = 2.45$ kg/m$^3 \cdot 10^3$, $\rho_3 = 2.45$ kg/m$^3 \cdot 10^3$,

   $C_1 = 1000$ J/(kg $\cdot$ K), $C_2 = 1050$ J/(kg $\cdot$ K), $C_3 = 1050$ J/(kg $\cdot$ K),

   $\beta_0 C_0 = 52.3$ K, $k = 0.14$, $R = 0.0071$ m, $\varphi = \dfrac{4\pi}{3}$, $N = 2.562 \cdot 10^3$, $N = 2.562 \cdot 10^9$,

   $K_V = 1.515 \cdot 10^{-4}$ m/(s $\cdot$ K), $K_E = 0.005 \ \dfrac{1}{\text{K} \cdot \text{s}}$, $L = 4.02 \cdot 10^5$ J/kg .

2. *Cast Iron*

   $T_0 = 1803$ K, $T_L = 1525$ K, $T_E = 1413$ K, $T_f = 293$ K, $T_A = 1803$ K

   $\alpha_1 = 80 \ \dfrac{\text{W}}{\text{m}^2\text{K}}$, $\alpha_2 = 80 \ \dfrac{\text{W}}{\text{m}^2\text{K}}$, $\alpha_3 = 80 \ \dfrac{\text{W}}{\text{m}^2}\text{K}$,

   $\rho_1 = 7.0$ kg/m$^3 \cdot 10^3$, $\rho_2 = 7.05$ kg/m$^3 \cdot 10^3$, $\rho_3 = 7.1$ kg/m$^3 \cdot 10^3$,

   $C_1 = 680$ J/(kg $\cdot$ K), $C_2 = 570$ J/(kg $\cdot$ K), $C_3 = 460$ J/(kg $\cdot$ K),

   $\beta_0 = 91.7 \ \dfrac{\text{K}}{\%}$, $C_0 = 3.3$ %, $k = 0.78$, $R = 0.00416$ m, $\varphi = \dfrac{4\pi}{3}$,

   $K_V = 3.0 \cdot 10^{-4}$ m/(s $\cdot$ K), $K_E = 0.005 \ \dfrac{1}{\text{K} \cdot \text{s}}$, $L = 1.38 \cdot 10^5$ J/kg .

3. *Carbon Steel*

   $T_0 = 1803$ K, $T_L = 1766$ K, $T_E = 1413$ K, $T_f = 293$ K, $T_A = 1803$ K

   $\alpha_1 = 100 \ \dfrac{\text{W}}{\text{m}^2\text{K}}$, $\alpha_2 = 100 \ \dfrac{\text{W}}{\text{m}^2\text{K}}$, $\alpha_3 = 100 \ \dfrac{\text{W}}{\text{m}^2}\text{K}$,

   $\rho_1 = 7.1$ kg/m$^3 \cdot 10^3$, $\rho_2 = 7.45$ kg/m$^3 \cdot 10^3$, $\rho_3 = 7.8$ kg/m$^3 \cdot 10^3$,

   $C_1 = 680$ J/(kg $\cdot$ K), $C_2 = 580$ J/(kg $\cdot$ K), $C_3 = 480$ J/(kg $\cdot$ K),

   $\beta_0 = 91.7 \ \dfrac{\text{K}}{\%}$, $C_0 = 0.49$ %, $k = 0.78$, $R = 0.00416$ m, $\varphi = \dfrac{4\pi}{3}$,

   $K_V = 5.0 \cdot 10^{-4}$ m/(s $\cdot$ K), $K_E = 0.005 \ \dfrac{1}{\text{K} \cdot \text{s}}$, $L = 2.7 \cdot 10^5$ J/kg .

3.7 Acknowledgments

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