Abstract. The phase transitions in solid materials (called solid-solid transformations) are connected with the thermo dynamical processes with hysteresis, leading to the dissipative models. Obvious, the liquid-solid transitions are governed by the reversible processes (without dissipation of internal energy). The analysis of a loop of hysteresis reveals some features about elastic-plastic properties, like the hardening. We give some retrospective results of these transformations along a temperature scale.

Keywords: elementary representative volume, integral accumulation, entropy/entropy flux pair, weak formulation of the Perrin principle.

1. INTRODUCTION

In this paper are made some considerations about the phase transitions for a 0.8 %C steel, cast ingot steel at 1500 °C in prescribed cooling conditions. There are supped a non isothermal process. During this process, the steel changes some typical internal structures: volume-centered cubic, face-centered cubic, again volume-centered cubic, along a large interval of temperature. These phenomena are in accordance with the phases followed by the steel in a cooling process: liquid-δ, austenite, perlite, martensite, so on. The microstructure reveals a disposal on dendrites; we have in mind a schema from Fig. 1.

![Fig. 1. The cooling structure diagram of steel.](image)

The microstructure is dominated by the dendritic structure, as a result between the two intimate phenomena which arise during the cooling process: the nucleation and crystal growing. The circumstances of the priory evolution of one phenomenon or another are analyzed by physicians and other scientists. The mathematical literature have tried to realize an agreement between a dendritic structure of the metal and a lattice structure of the processes and implicitly of the elementary domains set, which appears in the mixture of an intermediate zone.
For a local study we extract an *elementary representative volume* (ver), to whom we can attribute some thermo dynamical or geometrical parameters, it is acted by a suite of transformation processes, which define the particular constitutive laws underlying phase transitions of the ver.

![Fig. 2. Sketch of a ver.](image)

The mathematical models of phase transitions are described by the nonlinear problems of the heating diffusion (the cooling of the molten metal), by the mass and heat transfer problem (solidification), by the elastic-plastic deformation with phase transition into the solid materials.

### 2. ENERGETIC ACCUMULATION DURING THE TRANSITION PROCESSES

We have in view a metal melting in liquid-δ phase, as a fluid. At the same time it is presume as an union of elementary volumes, each of them submitted at the thermal process, the thermal change develops by the loss of heat at different hotness.


The mechanism of heat changing correspond to a scale of temperatures (a cooling range), it can be explained by the heat accumulation concept (dissipation of heating) associated to one process. This concept is equivalent to the measure of the accumulated heat (lost heat).

We intend to introduce an abstract formalism adequate to thermodynamics. Denote by $U$ a family of the elementary representative volumes, $V \in U$ is a ver and $P$ a family of the transition processes which are submitted the systems of $U$. We take as a subfamily of $P$ the set of conservative processes (cyclic processes), denoted $P^c$. Our aim is to define a lattice structure associated to the material, viewed as molten, so we form a vector bundles $(U, P, \sigma)$, where $\sigma : P \to U$ is a surjective application, the image $P(V) = \sigma^c(V)$ is a fiber of the all processes compatible with the ver $V$, $P_c(V) = P(V) \cap P_c$ it is also the fiber of the cyclic processes. We will introduce an union of the ver- systems and also an union of the processes.
which are compatible with them: for \( K \subset U \times U \) define \( \oplus : K \to U \), \((K_1, K_2) \to K_1 \oplus K_2 \in U \).

Denote by \((H, \leq)\) a total ordered set, called the variety of hotness applied to the family \( U \), which is isomorphic to \((R, \leq)\); for each hotness we associate a temperature. Any homeomorphism \( h \in \text{Hom}(H, R) \) is a temperature scale, we denote by \( G_+ \) the scale family of positive temperatures, \( G_+ = \{ \rho \in \text{Hom}(H, R) / \rho : H \to [0, +\infty) \} \).

For a ver-system \( \sigma(P) \), which lies in the process \( P \), the absorption or the emission phenomenon can be characterized by the distributions \( C^+, C^- : P \to G_+ \).

**Definition 2.1.** The heat accumulation of the ver along the transformation \( P \), from the fiber \( P(\sigma(P)) \), is the quantity \( C(P) = C^+(P) - C^-(P) \).

We will associate to the union operation \( \oplus \) another application \( \pi \), named a projection over the processes compatible with the union, \( \pi : P(\oplus K) \to P \times P \), \( \pi \) is injective, here \( P_{\oplus} = P(\oplus K) \) is the family of the united processes associated to united systems (enchained systems) \( \oplus K \).

**Definition 2.2.** We name the reference hotness threshold \( I, I \in H \), such that \( \chi_{\{h \in H / h \leq I\}} := h_I \), where \( \chi_A \) is the characteristic function of the set \( A \), so.

In all what follows, the set of non increasing, right continuous functions will be \( \chi_A(x) = \begin{cases} 1, & x \in A \\ 0, & x \notin A \end{cases} \) of a great importance, as the example from the figure 2, \( f : (0, \infty) \to (0, \infty) \), for which there exist \( a_f, b_f \in R \), \( a_f \leq b_f \), such that \( f(x) = \begin{cases} 0, & x < a_f \\ f(x), & x \geq b_f \end{cases} \).

Based on the positive and continuous functions we can introduce the family of bounded variation functions \( F = F^+ - F^- \).

**Definition 2.3.** We name an integral accumulation with density \( f \in F \), denoted \( A_c(f) = \int_0^\infty \frac{1}{x} df(x) \), the numerical value given by this Stieltjes-Riemann integral of the ratio \( \frac{1}{x} \) according to \( f \).

**Remark 2.4.** If the density function \( f \) lies in the distributional space \( C_0^\infty ([0, +\infty)) \),

\[
A_c(f) = \int_0^\infty \frac{1}{x^2} f(x) dx
\]
then
Considering an united process consisting in elementary processes compatible with the family \( U \) of ver-systems from the intermediate zone of the material, denoted \( P \in \mathcal{P}_\oplus \), which is endowed with a heat accumulation \( C(p) \) (emitted, or absorbed quantity), \( C(p) = C^+(p) - C^-(p) \) and a temperature scale \( \rho \in G_+ \), we perform a heat distribution of the system \( \sigma(p) \) along the process \( p \), using a temperature scale \( \rho \) as \( C_\rho(p) = C(p) \circ \rho^{-1} \in F \). We give

**Definition 2.5.** Let \( A : P \to R \), \( A(p) = A_\rho(C_\rho(p)) \), \( \rho \in G_+ \), be the heat accumulation of the ver-system \( \sigma(p) \), along the process \( p \), in the scale \( \rho \).

### 3. THE MOLTEN METAL (LIQUID \( \delta \))

From the point of view of our research we have investigated the heat change into the molten melt, assimilating the fluid with an union of ver-systems, but the change with the exterior medium have been approached by a suite of small changes at different hotness. We recall the idea of Serrin (see C. Truesdell, 1984) regarding the accumulation along the process, corresponding to a temperature scale and we will introduce a classical capacity, which is the same as a measure of heating change from the material. Suppose that the quantity \( \int_0^t q(\alpha(t)) \, dt \) can be considered as a specific heat of the fluid and \( I(\alpha, T) = \{ t \in [0, \infty) / \alpha(t) < T \} \) is called the temporal level imposed by the temperature \( T \).

Supposing the molten as an ideal fluid satisfying the law \( p(V, L) = R \varphi(L) \), for all \( \varphi \in G_+ \), \( L \in H \), \( V \in R_+ \), we derive the central result.

**Theorem 3.1.** For any curve \( \alpha \in C \), identified with the composed process \( i\alpha \in \mathcal{P}_\oplus \), for any \( \varphi \in \text{Hom}(H, R) \) a temperature scale, the integral accumulation \( A_\varphi(i\alpha) \) can be expressed by

\[
A_\varphi(i\alpha) = \int_0^1 \frac{q(\alpha(t))}{\alpha_2(t)} \, dt
\]

(see also the classical expression of the entropy \( S = \int \frac{dq}{T} \)).

**Remark 3.2.** At this stage we can define the particular transformations of a ver-system: if \( \alpha_2(t) = T \), for all \( t \in [0, 1] \), then \( \alpha \in C \) is an isotherm curve of \( T \) level along the \( i\alpha \) process for the ver-system \( \sigma(i\alpha) \in U \); if any part \( \tau \in \mathcal{P}([0, 1]) \) satisfies the relation \( \int q(\alpha(t)) \, dt = 0 \), then \( \alpha \in C \) is an adiabatic curve along the \( i\alpha \) process for the ver-system \( \sigma(i\alpha) \in U \); if \( \alpha(0) = \alpha(1) \), then \( \alpha \) correspond to a cyclic process.
Corollary 3.3. Let $\alpha \in C$ be a curve of the transformation, such as $i\alpha \in P_0$ then $A_\varphi(i\alpha) = 0$, i.e. any cyclic process is realized without heat accumulation.

![Fig. 3. An example of the accumulation function.](image)

In what follows, the accumulation function permits us an irreversible or a reversible treatment of the subject.

### 3.1. THE AUSTENITIC TRANSFORM-TRANSITION FROM LIQUID STATE $\Delta$ TO SOLID (AUSTENITE)

We make some thermodynamic considerations about the transition process of the ver-system, where the heat diffusion is made by the thermal conduction, a non isotherm process governed by a classical problem of Stefan type. Consider that the ver-system occupies a bounded measurable domain $B$ in the physical space, denoting by $B_1$ the sub domain occupied by the solid phase and the complementary sub domain by $B_2$ and $S = \overline{B_1} \cap \overline{B_2}$ is the separation interface. For a transition hotness $h_M$ we associate a reference temperature $T_M = \varphi(h_M)$, called the solidification temperature, later we use a reduced temperature $\theta = T - T_M = \varphi(h) - \varphi(h_M)$. The ver-system has an internal energy during the phase transition as an absolute continuous measure (a distribution) according to the Jordan measure on the $\mathbb{R}^3$-space. The heat transfer is realized between connected ver-systems if there exists some difference of hotness between the two systems and can be characterized by the $q$ heat flux vector. Denote by $\theta_0$ the reduced equilibrium temperature of the two phases and we take $l = \varepsilon_2(\theta_0) - \varepsilon_1(\theta_0)$ the difference of energy at the phase transition, named the solidification latent heat.
Sometimes the temperature can decrease under the value $\theta_0$ and the transformation from the liquid to solid can’t take place, one say that the system lies in the super thermal state, which is named a sub cooling of the interface. The existence of the super thermal zone leads us to impose the presence of the mushy zone, which is a mixture of phases in equilibrium. Analytical characterization of the mushy zone needs the introduction of the fraction solid function $\chi$: $B \rightarrow R_+$, it can be understood as a measure of nucleation phenomenon near the separation interface. In this way a thin free interface (as a surface of null volume) must be replaced by an entire mixture zone, where the germs of the new phase arise and where their growing take place. We adopt the new expressions for the internal energy and heat flux according to the transition process with nucleation,

$$
\varepsilon(\theta, \chi) = \chi \varepsilon_1(\theta) + (1 - \chi) \varepsilon_2(\theta),
q(\theta, \nabla \theta, \chi) = -\chi K_1(\theta) \nabla \theta - (1 - \chi) K_2(\theta) \nabla \theta
$$

for one ver-system. We have supposed that the ver is subjected to a transition governed by the Fourier law, here $K$ is the thermal conductivity of the material. Thus the states space of the ver is $\sum = \{ (\theta, \chi) / \theta \in C^0(B \times R_+, \chi \in D'(B) \times R_+) \}$ and $\varepsilon$, $q$ are scalar function, vector function respectively on $\sum$, $D'(B)$ is the distributional space on $B$.


An important parameter characterizing the state of the ver, more used in the treatment of the Stefan problem, also counting the super thermal states, is the integral accumulation of Clausius type, named the global entropy of the ver, denoted $A_N$, whose density according to Jordan measure on Euclidian space $R^3$ is the function $\eta(t, x)$, the density of entropy.

The first law of thermodynamics for a ver–system consists in the equilibrium of total energy, which is

$$
\int_{\text{ver}} \varepsilon(t, x) dx = -\int_{\text{Fr(\text{ver})}} q(t, x) n d\sigma + \int_{\text{ver}} r(t, x) dx,
$$

where the $r$ function represents the heat supply, will means the external energy.

The second law of thermodynamics explains the increase of the entropy which accompanies the arise of the new free interface. Here we have the Clausius-Duhem inequality

$$
\int_{\text{ver}} \eta(t, x) dx \geq \int_{\text{Fr(\text{ver})}} \frac{q(t, x) n}{\theta(t, x)} d\sigma + \int_{\text{ver}} \frac{r(t, x)}{\theta(t, x)} dx
$$

We suppose that the $\theta$ function is continuous on the domain $B$, but all the other functions: $\varepsilon, q, K, \eta$ have some discontinuities across the interface. Despite this difficulty we can apply the Gauss-Ostrogradski Theorem and we obtain the local relations of equilibrium for the ver-system.
\[
\dot{\varepsilon}(t,x) = -\text{div}(q(t,x)) + r(t,x),
\]
almost everywhere \((t,x) \in \mathbb{R}_+ \times B\), and the Clausius-Duhem inequality

\[
\eta(t,x) \geq -\text{div} \frac{q(t,x)}{\vartheta(t,x)} + \frac{r(t,x)}{\vartheta(t,x)} \quad \text{a.e.} \quad (t,x) \in \mathbb{R}_+ \times B.
\]

**Assumption 3.4.** The \textit{ver}-system is endowed with an internal energy \(\mathcal{E}\), which is taken as primitive variable characterizing the physical state, consequently all other parameters depend upon \(\mathcal{E}\). Let \(\vartheta = \tilde{\theta}(\mathcal{E})\), \(\eta = \tilde{\eta}(\mathcal{E})\), \(q = -\tilde{K}(\vartheta)\nabla \vartheta\) \(q\) be, where \(\tilde{\vartheta}, \tilde{\eta}, \tilde{K} \in D'(\mathbb{R})\), and \(K\) is a positively defined matrix on \(\mathbb{R}^3\).

We suppose that the hotness increases, then the temperature of the \textit{ver}-system increases too and consequently the internal energy grows strictly monotone. We have considered the temperature continuous on \(B\), therefore \(\tilde{\vartheta}\) is a invertible function. We eliminate the \(r\) function between the two relations (e) and (i) and we obtain the inequality

\[
\dot{\eta} - \frac{\dot{\varepsilon}}{\vartheta} \geq \frac{1}{\vartheta^2} \nabla \vartheta \cdot K \nabla \vartheta = \frac{1}{\vartheta^2} \nabla \vartheta \cdot K \nabla \vartheta \geq 0,
\]

and it underlines another nonlinear characteristic of the \textit{ver}-system

\[
\gamma(\mathcal{E}) = \frac{1}{\vartheta(\mathcal{E})^2} \nabla \tilde{\vartheta}(\mathcal{E}) K \nabla \tilde{\vartheta}(\mathcal{E})
\]

\(,\) named the local productivity of entropy accumulated by the \textit{ver}-system in a liquid-solid transition, otherwise the last inequality becomes \(\tilde{\eta}'(\mathcal{E})\tilde{\vartheta}(\mathcal{E}) \geq 1\).

**Definition 3.5.** During a transition, the process \(P\) whose characteristics \(\tilde{\vartheta} \) and \(\tilde{\eta}\) satisfy the relation \(\tilde{\eta}'(\mathcal{E})\tilde{\vartheta}(\mathcal{E}) \geq 1\), it is a dissipative process and the transition is irreversible; if \(\tilde{\eta}'(\mathcal{E})\tilde{\vartheta}(\mathcal{E}) = 1\) holds, then the process is conservative and the transition is named a reversible transition.

The last two relations assure \(\tilde{\eta}'(\mathcal{E}) > 0\), that is the entropy of the \textit{ver}-system is a strictly increasing function with respect to internal energy. In order to preserve the estimation of the given work means only to assume that dissipation cannot increase the work done.

**Assumption 3.6.** The density of entropy \(\eta\) has a no positive second derivative, i.e. \(\eta''(\mathcal{E}) < 0\), meaning a concave function.

For a reversible transition a simple calculus assure

\[
\vartheta'(\mathcal{E}) = \frac{d}{d\mathcal{E}} \left( \frac{1}{\eta'(\mathcal{E})} \right) = -\frac{\eta''(\mathcal{E})}{\eta'(\mathcal{E})^2} > 0
\]

\(,\) then the \(\vartheta\) function is an invertible function on \(\mathcal{E}\), such that \(\mathcal{E} = \tilde{\vartheta}'(\mathcal{E})\). I have referred to dissipationless \(\textit{ver}\) capable to follow only reversible processes.
Definition 3.7. The variation of the $\varepsilon$ function according to the temperature, that is the quantity $C(\theta) = \tilde{\varepsilon}'(\theta)$, which is named the specific heat of the ver-system.

Obviously, $C(\theta) > 0$, because $\tilde{\varepsilon}$ is a monotone function.

### 3.2 ENTROPIC ANALYSIS OF A PHASE TRANSITION

We take again the idea of the two phases in a ver-system, the heat conduction produce an irreversible transition along the manifestation of a process $P$, also counting the monotony of the entropy, that in a $(\varepsilon, \eta)$ diagram correspond to figure 3, the concavity of the function $\tilde{\eta} = \begin{cases} \tilde{\eta}_1, & \text{in } B_1 \\ \tilde{\eta}_2, & \text{in } B_2 \end{cases}$ near the critical value $\varepsilon^*$ of the energy, having the common slope at $\varepsilon_1$ for the function $\tilde{\eta}_1$, at $\varepsilon_2$ for the function $\tilde{\eta}_2$. Using the definition of the specific heat, the equilibrium equation becomes

$$C(\theta)\dot{\theta} = \text{div}(\tilde{K}(\theta)\nabla \theta) + r.$$ 

But the liquid-$\delta$ austenite transition is a reversible one, thus $\tilde{\theta}_1(\varepsilon_1) = \frac{1}{\tilde{\eta}_1(\varepsilon_1)} = \frac{1}{\tilde{\eta}_2(\varepsilon_2)} = \tilde{\theta}_2(\varepsilon_2) = \theta_0$, considered as a transition value of the temperature, which generates a convex hull of the entropy function and at the same time gives the initial reduced temperature of the liquid-solid transition. We generalize the notion of latent heat adding the new function $L = \varepsilon_2 - \varepsilon_1$.

![Fig. 4. Convexification of entropy.](image)

Later on the free energy of the ver-system will be very useful, presented as a discontinuous function, having a jump across the separate interface, revealed in figure 5, $\Psi(\varepsilon) = \varepsilon - \theta_0 \eta(\varepsilon)$. We connect this notion with the super thermal states of the ver-system. First, we have

$$\tilde{\Psi}_1(\varepsilon_1) = \varepsilon_1 - \theta_0 \tilde{\eta}(\varepsilon_1), \quad \tilde{\Psi}_2(\varepsilon_2) = \varepsilon_2 - \theta_0 \tilde{\eta}(\varepsilon_2),$$
the two values corresponding to the minimum of the Gibbs potentials, passing to the small variations which lead us to the equality $\tilde{\Psi}_1(\varepsilon_1) = \tilde{\Psi}_2(\varepsilon_2) + L$, indeed, $\tilde{\Psi}_1(\varepsilon_1) - \Psi_2(\varepsilon_2) = \varepsilon_1 - \varepsilon_2 - \theta_0(\tilde{\eta}_1(\varepsilon_1) - \tilde{\eta}_2(\varepsilon_2)) \approx$ (using a Lagrange formula for a regular function) $+ L + \theta_0 \tilde{\eta}'(\varepsilon)L = L(1 + \theta_0 \tilde{\eta}'(\varepsilon))$, where $\varepsilon \in (\varepsilon_1, \varepsilon_2)$, because the slope is the same on the tangent line, $\tilde{\eta}_1'(\varepsilon_1) = \tilde{\eta}_2'(\varepsilon_2) = \tilde{\eta}'(\varepsilon_2) = 0$, therefore the relation holds.

The particular case of the phase transition at the constant energy $\varepsilon^*$ appears a discrepancy between the individual phase energies, which assures a super thermal state of the ver-system. The domain $\{x \in B/\varepsilon^* < \varepsilon(t,x) < \varepsilon_2(t,x), t \in R_+\}$ constitute the part of the mushy zone stated in sub cooling of interface and another part of the mushy zone stated in the super heating, the two parts are non equilibrium regions of the ver-system.

We affirm that any transition into the ver at constant energy $\varepsilon^*$ governs the entropy production described by a positive quantity $\gamma(\theta) > 0$, therefore the material presents the super thermal regions under small variations of some other characteristics.

**Remark 3.8.** Some features about the shape of the free energy can be viewed, doing a simple calculus, $\tilde{\Psi}'(\varepsilon) = 1 - \tilde{\theta}'(\varepsilon)\tilde{\eta}(\varepsilon) - \tilde{\theta}(\varepsilon)\tilde{\eta}'(\varepsilon)$ (the ver-system is submitted at reversible transformation) $= - \tilde{\theta}'(\varepsilon)\tilde{\eta}(\varepsilon)$, but the function $\tilde{\theta}$ is an increasing function on $R_+$ and for $\tilde{\eta} < 0, \tilde{\Psi}$ it is also increasing, for $\tilde{\eta} > 0, \tilde{\Psi}$ is a decreasing function, a fact that justifies the variation given in diagram $(\eta, \Psi)$.

### 3.3. INTEGRAL AND ENTROPY SOLUTION FOR A THERMAL CONSERVATION LAW

A partial differential equation of the form $u_t + div F(u) = f$, in $R^n \times (0, +\infty)$ is called a conservation law with unknown $u$ and the flux function $F = (F^1, F^2, \ldots, F^n)$. We can write this equation into non divergence form $u_t + b(u)\nabla u$, for $b = F'$. We will focus on the initial homogeneous value problem

$$(CL)\quad u_t + div F(u) = 0, \text{ in } R^n \times (0, +\infty), \quad u = g \text{ on } R^n \times \{t = 0\},$$

where $g \in L^1_{loc}$ is the initial value of $u$. Our aim is to use the variational method in treating of this problem. First of all we introduce a notion.

**Definition 3.9.** We say that $u \in L^1_{loc}$ is an integral solution of (CL) if there exists
\[ \int_0^t \int_{\mathbb{R}^n} (u' v + F(u) v) \, dx \, dt + \int_{\mathbb{R}^n} g v(\cdot, 0) \, dx = 0, \quad \text{for all } v \in C^1_c, \] where \( C^1_c \) is the space of real valued functions with compact support.

Now we introduce a thermodynamical notion

**Definition 3.10.** Let \( \Phi, \Psi \) be a real valued function and a vector valued function respectively, we call \((\Phi, \Psi)\) an *entropy/entropy flux pair* for the conservation law (CL) provided \( \Phi \) is convex and \( \Psi \) satisfies \( \Psi' = b \Phi' \).

We consider an approach problem: for \( \varepsilon > 0 \) find \( u_\varepsilon \in L^1_{loc} \) satisfying the nonhomogeneous problem

\[ u_\varepsilon + \text{div} F(u_\varepsilon) = \varepsilon \Delta u_\varepsilon. \]

Compute

\[ \Phi(u_\varepsilon) + \nabla \Psi(u_\varepsilon) = \Phi(u_\varepsilon) u_\varepsilon + \Psi(u_\varepsilon) \nabla u_\varepsilon = \Phi(u_\varepsilon) (-b(u_\varepsilon) \nabla u + \varepsilon \Delta u_\varepsilon) + \Psi'(u_\varepsilon) \nabla u_\varepsilon = \varepsilon \Phi(u_\varepsilon) \Delta u_\varepsilon - \varepsilon \Delta \nabla (\Phi(u_\varepsilon) \nabla u_\varepsilon) - \varepsilon \nabla \Phi''(u_\varepsilon) \nabla u_\varepsilon \]

\( \leq \varepsilon \nabla (\Phi'(u_\varepsilon) \nabla u_\varepsilon) \). Taking account some regularity conditions and convergent results we obtain

\[ \frac{d}{dt} \Phi(u) + \nabla \Psi(u) = 0. \]

**Definition 3.11.** We say that \( u \) is an *entropy solution* of the conservation law provided

\[ \frac{d}{dt} \Phi(u) + \nabla \Psi(u) \leq 0, \quad \text{in the distribution sense for each pair } (\Phi, \Psi). \]

This definition can be extended on the conservation laws defined by the system

\[ u_i + \text{div} F(u) = 0, \quad \text{in } \mathbb{R}^n \times (0, +\infty), \quad \text{where the unknown is } u = (u^1, u^2, \ldots, u^n) \]

and the flux function

\[ F = \begin{pmatrix} F_1^1 & \ldots & F_n^1 \\ \vdots & \ddots & \vdots \\ F_1^m & \ldots & F_n^m \end{pmatrix} \in M(m, n) \]

is given. The initial value problem \( u_i + \text{div} F(u) = 0 \),

\[ \text{in } \mathbb{R}^n \times (0, +\infty), \quad u = g \quad \text{on } \mathbb{R}^n \times \{ t = 0 \}, \quad \text{for a given } g \in L^1_{loc}, \]

has an integral solution and the entropy/entropy flux pair in the same manner as above.

**Definition 2.5:** We say that \( u \in L^1_{loc} \) is an integral solution of (CL) if there exists

\[ \int_0^\infty \int_{\mathbb{R}^n} (u' v + F(u) \nabla v) \, dx \, dt + \int_{\mathbb{R}^n} g v(\cdot, 0) \, dx = 0, \quad \text{for all } v \in C^1_c, \] where \( C^1_c \) is the space of real valued functions with compact support.

**Definition 3.12.** We call \((\Phi, \Psi)\) an *entropy/entropy flux pair* of the conservation law provided \( \Phi: \mathbb{R}^m \rightarrow \mathbb{R} \) is convex, \( \Psi = (\Psi^1, \Psi^2, \ldots, \Psi^n) \) satisfies \( \nabla \Psi = B \nabla \Phi \), for \( B = \nabla F \).

At the end of this section we give
Definition 3.13. We say that \( u \) is an entropy solution provided \( \frac{d}{dt} \Phi(u) + \nabla \Psi(u) \leq 0 \), in the distribution sense for each pair \((\Phi, \Psi)\).

4. Analysis of the Gibbs Potential

We take the Gibbs function \( \varphi = \varepsilon - \theta_0 \eta \), see figure 6 and the reduced temperature \( u = \frac{\theta - \theta_0}{\theta_0} \), otherwise \( u \) is a local perturbation near the transition value \( \theta_0 \). We have also like in the previous section \( \tilde{u}_1(\varepsilon_1) = \tilde{u}_2(\varepsilon_2) = 0 \), \( \tilde{\varphi}_1(\varepsilon) = \tilde{\varphi}_1(\varepsilon) = c_t \), indeed \( \tilde{\varphi}(\varepsilon) = 1 - \theta_0 \tilde{\eta}(\varepsilon) \), particularly \( \tilde{\varphi}_1(\varepsilon) = 1 - \theta_0 \tilde{\eta}_1(\varepsilon) \) and \( \tilde{\varphi}_2(\varepsilon) = 1 - \theta_0 \tilde{\eta}_2(\varepsilon) \), thus \( \tilde{\varphi}_1(\varepsilon_1) = \tilde{\varphi}_2(\varepsilon_2) \), consequently \( \tilde{\varphi}_1(\varepsilon_1) = \tilde{\varphi}_2(\varepsilon_2) \), after doing void potential value. As in the previous section where we used the entropic analysis, we can define the super thermal states according to Gibbs potential.

![Fig. 5. Variation of free energy of the two phases.](image)

Physically, it exists there a solid dispersed phase into the matrix of liquid phase at the level of mushy zone, perhaps the mixture zone occupies a thin domain, therefore it can be considered of null measure. We have seen that the solid fraction function \( \chi \) can characterize the distribution of the solid germs into ver-system. In this way, the internal energy \( \varepsilon \) is consistent with the function \( \chi \), that is \( \mathcal{E} \) is continuous similar to \( \chi \), but the internal energy has at most discontinuities of the first kind. For our transformation governed by a thermal conduction process we adopt the framework of the two parameters \((\varphi, u)\) taking account for the independent variable \( \chi \), \( \tilde{\varphi}(\varepsilon, \chi) = \chi \tilde{\varphi}_1(\varepsilon) + (1 - \chi) \tilde{\varphi}_2(\varepsilon) \), \( \tilde{u}(\varepsilon, \chi) = \chi \tilde{u}_1(\varepsilon) + (1 - \chi) \tilde{u}_2(\varepsilon) \), \( q = -\chi \tilde{K}_1(u) \nabla u - (1 - \chi) \tilde{K}_2(u) \nabla u \), \( u \) being continuous on \( \mathbb{B} \), a.e. \( \varepsilon \in \mathbb{R}_+ \). The energy and the entropy of the interface are neglected.
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Fig. 6. Evolution of potentials Gibbs.

The thermodynamics of the ver-system assure relations in a local form:
\[ \dot{\varepsilon} = -\text{div}q + r, \quad \phi + \text{div}(uq) - ru \leq 0, \quad \text{in} \quad B - S(t), \]
where \( S(t) \) is the free interface,
\[ [\varepsilon]^\nu = [g]^m, \quad [\phi]^\nu \geq u[g]^m \quad \text{on} \ C, \]
where \( \nu \) is the displacement speed of the interface, \( m \) an outer unit normal of \( S(t) \).

The quantity defined by
\[ \Gamma(\text{ver}) = \int_{\partial B} \phi \, dx + \int_{F_{\text{ver}}(\text{ver})} \eta \, d\sigma - \int_{\text{ver}} ur \, dx \]
is the dissipation functional of the ver-system. Obviously, we have \( \Gamma(\text{ver}) \leq 0 \). The non dissipative phenomenon of the interface can be expressed by the stability \( n \to \infty \), conditions of the functional \( \Gamma(\text{ver}) \): when \( n \to \infty \), or locally \( L \nu = [g]^m \). We don’t detail other results about the dynamic models of the phase transition in metals with mass transport of Mullins-Sekerka type. Such models were initiated by Mullins, Sekerka, 1963, Sekerka, 1968, Goldenfeld, 1969. We made an energetic and mass balance from which derive the global growth relations of the area of interfaces and the phase volumes. For this particular model the state of the ver-system is characterized by the parameters \( \{u, c\} \in \Sigma \), where \( u \) is a reduced temperature, \( c \) is a concentration of dissolved element in excess from liquid phase.

Moreover, the state point \( \{u, c\} \) is a steady point for the functionals: \( f_1(t) = \text{Lvol}(B_2(t)) + a \int_B u(t) \, dx; f_2(t) = \beta \sigma(S(t)) + \alpha \int_B c(t) \, dx; f_3(t) = \int_B c(t) \, dx \)

5. SOLID-SOLID TRANSITION: AUSTENITE-PERLITE

The cooling process austenite-perlite develops over the interval of temperature \( [\rho_1, \rho_2] \) and defines an irreversible transformation during a time period. For a temperature \( \theta \) greater then \( \rho_2 \) the austenite phase is stable, when \( \rho_1 < \theta < \rho_2 \) appears a perlite phase (bainite) and for \( \theta \) less then \( \rho_1 \) and nearest for \( \rho_1 \), an instantaneous and reversible transition holds. The austenite fraction transformed in martensite grows at the same time as
the rapidly decreasing of the temperature from $\rho_2$ value to $\rho_1$ value. Models of solid-solid phase transition were studied by Visintin, 1987, Abeyaratne & Knowles, 1992, Gurtin, 1993, Cermelli & Gurtin, 1994, taking account for the nonlinear constitutive laws. Some processes for the transformations of the mixture using as variable the concentration was investigated by Ruddock, 1994.

The austenite-perlite transition as an isotherm process (with liberation of latent heat) is governed by the Johnson-Avrami-Mehl law.

Let $\theta \in [\rho_1, \rho_2] \rightarrow F(t) \in [0,1]$ be a vector valued function, we define $\phi(\theta,t) = F(t) = 1 - e^{-b(\theta)t}$, where $b$ is a rate function of nucleation of the perlite phase, and $a, b \in C^0([\rho_1, \rho_2])$, $a(0) > 0$, $b(\rho_2) = 0$. When $\theta$ decrease near $\rho_1$ the nucleation falls and the element size of the structure grows. In this case we obtain a column structure. When $\theta$ tend to $\rho_2$ the nucleation became greater and the germ size growing develops slowly. In this way we obtain an equi-axe structure. We characterize the ver-system transition from the nucleation point of view and the growing of the new phase taking as an internal energy $\varepsilon(t,x) = C \theta(t,x) + \lambda F(t,x) + \mu$, where $C$ is the latent heat at constant volume, $F$ is the austenite fraction transformed and $\mu$ a scale factor, we introduce the energetic equilibrium equation

$$\rho(C(\theta)\theta(x,t) + \lambda F(x,t)) - K \Delta \theta(t,x) = h(t,x), \text{a.p.t.} \ (t,x) \in [0,T] \times B = Q.$$ 

We have the main result.

**Theorem 5.1.** Let $\theta$ be, where

$$g(\theta(x,t)) = f^{-1}\left(\frac{\theta(x,t)}{\theta_0}\right), \ f(0) = 0,$$

$f$ is a non-increasing concave function on $[0,1]$, derivable on $(0,1)$, with $\lim_{t \to +\infty} f'(t) = +\infty$, then the Cauchy problem for the equation $\rho(C(\theta) \theta + \lambda F)^\circ - K \Delta \theta = h$ has an unique weakly solution (integrable in Benilan sense); the dependence from the initial data is continuous and monotone. More over, if $h \in \text{bv}(0, T, L^1(B))$, with $\Delta h \in L^1(B))$, then $U$ is Lipschitz continuous.

**CONCLUSIONS**

We have investigated some models of phase transitions on the range of temperature from $60^\circ$ to $1495^\circ$C. By their balance equations and their own characteristics, these models answer to the exigencies of the thermodynamics.

We recall a model of an elasto-plastic deformation consisting in a weak formulation compatible to the *Perrin principle*, a new formulation of the second principle of
thermodynamics, which says: The state parameters change along a phase transition, their initial values differ from final values.

The treatment of the equations of Stefan type corresponding to these models was made by the classical variational technics, using results of monotony and compactness of the Nonlinear Analysis.

REFERENCES