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SOME MODELS ON PHASE TRANSFORMATIONS ON A WIDE RANGE OF TEMPERATURE CHARACTERIZING DISSIPATIVE PROCESSES

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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 feature about elastic-plastic properties, like the hardening. We emphasize some retrospective results along a temperature scale. Some considerations about the phase transitions are made for a 0,8 %C steel, a cast ingot steel at 1500^0C subject to the prescribed cooling conditions, supposing a non isotherm process. Along a large interval of temperature the steel changes some typical interne structures: volume - centered cubic, face -centered cubic, again volume- centered cubic, according to the phases followed by the steel in a cooling process: liquid - δ , austenite, perlite, martensite, so on.*

The microstructure is dominated by the dendrite structure, as a result between the two intimate phenomena which arise during the cooling process: the nucleation of the new phase and crystal growing of the dendrite network, the result of this competition is a dendrite structure. For a local study we extract an elementary representative volume (ver), to whom we can attribute some thermo-dynamical or geometrical parameters. During manufacturing process it is acted by a sequence of transformations which define the particular constitutive laws underlying by the ver in phase transitions of the material. 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.

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1. INTRODUCTION

2.

For a 0,8%C steel, we make a study on cast ingot steel at 1500^0C in prescribed cooling conditions, supposing a non isotherm process. During this process, along a large interval of temperature the steel changes some typical interne structures, according to the phases followed by the steel in a cooling process. The microstructure reveals a dendrite design, so we have in view a schema from figure 1.

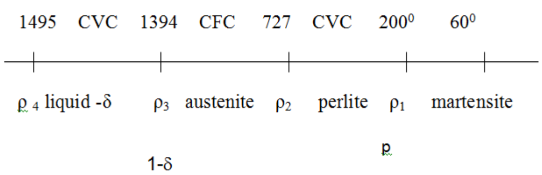

Figure 1. The cooling structure diagram of the steel

The microstructure is dominated by the dendrite structure, as a result between the two intimate phenomena which arise during the cooling process: the nucleation of a new phase and crystal growing. The mathematical literature have tried to realize an agreement between a dendrite structure of the metal and a lattice structure of the processes and implicitly of the elementary domains set, as an ingredient which appears in the mixture of an intermediate zone.

For a local study we extract an elementary representative volume (*erv*), 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 *erv*. 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.

Obviously, the liquid-solid transitions are governed by the reversible processes (without dissipation of internal energy). The phase transitions in solid materials (so called *solid-solid transforma-tions*) are connected to the thermo-dynamical processes with hysteresis, leading to the dissipative models. The analysis of a loop of hysteresis reveals some features about elastic-plastic properties of the materials, like hardening.

2. ENERGETIC ACCUMULATION DURING THE TRANSITION PROCESSES

We have considered a metal melting in liquid-δ phase, as a fluid and at the same time, as a 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 corresponding to a scale of temperatures (a cooling range) can be explained by the *heat accumulation* concept (dissipation of heating) associated to one process; this concept is viewed as a measure of the accumulated heat (lost heat).

The most liquid - δ- austenite transitions are described by the free boundary value problems of *Stefan type* in different studies about the thermodynamics of dissipative materials. Here, the behavior of the interface characteristics reveals the phase growing. The model equations are compatible with the principles of thermo-dynamics, see *C. Truesdell*, 1984, *M. E. Gurtin*, 1983, 1990, *R. N. Hills*, *D. E. Loper* & *M. E. Gurtin*, 1989, *S. Luckhaus* & *L. Modica*, 1989.

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

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

For a *erv*-system $\sigma^{-1}(P)$, which lies in the process *P*, the *absorption* or the *emission phenomenon* can be characterized by the distributions C^+ , $C^- : \mathcal{P} \to \mathcal{G}_+$.

Definition 2.1. The heat accumulation of the *erv* along the transformation *P*, from the fiber $P(\sigma^{-1}(P))$, is the quantity $C(P) = C^+(P) - C^-(P)$.

We will associate to the union operation $\oplus$ another application π, named a projection over the processes compatible with the union, $\pi : P(\oplus K) \to\ \mathcal{P} \times \mathcal{P}$, π 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* $I, I \in \mathcal{H}$, such that $\chi_{\{h \in H / h \le I\}} := h_I$, where χ_A is the characteristic function of the set *A*, so $\chi_A(x) = \begin{cases} 1, x \in A \\ 0, x \notin A \end{cases}$.

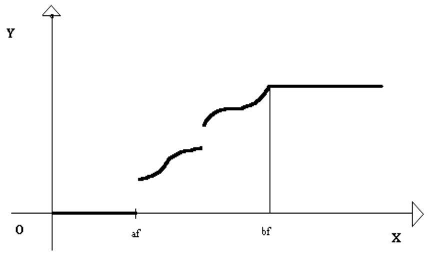

Figure 2. *An example of the accumulation function*

In all that follows, the set of non decreasing, right continuous functions will be of a great importance, as the example from the *figure* 2, $f : (0,\infty) \to (0,\infty)$, for which there exist $a_f, b_f \in R$, $a_f \le b_f$, such that $f(x) = \begin{cases} 0, x < a_f \\ \bar{f}, x \ge b_f \end{cases}$. Based on the positive and continuous functions we can introduce the family of bounded variation functions $\mathcal{F} = F^+ - F^-$.

Definition 2.3. We name an *integral accumulation* with density $f \in \mathcal{F}$, 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 2.1. If the density function *f* lies in the distributional space $C_0^\infty([0,+\infty))$, then $A_c(f) = \int_0^\infty \frac{1}{x^2} f(x) dx$.

Considering a united process consisting in elementary processes compatible with the family $\mathcal{U}$ of *erv*-systems from the intermediate zone of the material, denoted $P \in P_\oplus$, which is endowed with a heat accumulation $C(P)$ (emitted, or absorbed quantity), $C(P) = C^+(P) - C^-(P)$ and a temperature scale $\rho \in \mathcal{G}_+$, we perform a *heat distribution* of the system $\sigma^{-1}(P)$ along the process *P*, using a temperature scale ρ as $C_\rho(P,.) = C(P) \circ \rho^{-1} \in \mathcal{F}$. We give

Definition 2.4. Let $A : \mathcal{P} \to R$, $A(P) = A_c(C_\rho(P,.))$, $\rho \in \mathcal{G}_+$, to be the *heat accumulation* of the *erv*-system $\sigma^{-1}(P)$, along the process *P*, in the scale ρ.

3. THE ANALYSIS OF THE MOLTEN METAL (LIQUID δ)

From the point of view of our research, we have investigated the heat change into the molten metal, assimilating the fluid with a union of *erv*-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 the measure of heating change from the material. Suppose that the quantity

$q(\alpha(t)) := C \circ \varphi^{-1}(\alpha(t))\dot{\alpha}_2(t) + p \circ \varphi^{-1}(\alpha(t))\dot{\alpha}_1(t)$
can be considered as a specific heat of the fluid (molten alloy) and

$$I(\alpha, T) = \{t \in [0, \infty) / \alpha_2(t) < T\}$$

is called the *temporal level* imposed by the temperature *T*.

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

Theorem 3.1. For any curve $\alpha \in C$, identified with the composed process $i\alpha \in P_\oplus$, for any $\varphi \in Hom(H, R)$ 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 $S = \int_\alpha \frac{dq}{T}$)

Remark 3.2. At this stage we can define the particular transformations of a *erv*-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 *erv*-system $\sigma^{-1}(i\alpha) \in \mathcal{U}$; if any part $\tau \in P([0,1])$ satisfies the relation $\int_\tau q(\alpha(t))dt = 0$, then $\alpha \in C$ is an adiabatic curve along the $i\alpha$ process for the *erv*-system $\sigma^{-1}(i\alpha) \in U$; if $\alpha(0) = \alpha(1)$, then α corresponds to a cyclic process.

Corollary 3.1. Let $\alpha \in C$ be a curve of the transformation, such as $i\alpha \in \mathcal{P}_C$, then $A_\varphi(i\alpha) = 0$, i.e. any cyclic process is realized without heat accumulation.

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

3.1. The austenitic transform-transition from liquid state δ to solid (austenite)

We make some thermo-dynamic considerations about the transition process of the *erv*-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 *erv*-system occupies a bounded measurable domain $\mathcal{B}$ 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, see figure 3.

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

$$\theta = T - T_M = \varphi(h) - \varphi(h_M).$$

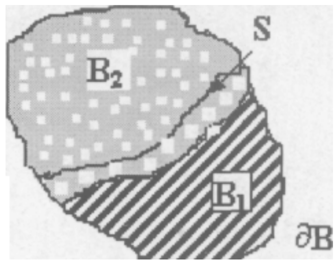

Figure 3. *Sketch of an erv*

The *erv*-system has an internal energy during the phase transition as an absolute continuous measure (obviously a distribution) according to the *Jordan* measure on the $\mathbf{R}^3$-space. The heat transfer is realized between connected *erv*-systems if there exists one difference of hotness between some two systems and can be characterized by the *q* heat flux vector. Denote by θ_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 θ_0 and the transformation from the liquid to solid can't take place, one says that the system presents 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* $\chi : \mathcal{E} \to R_+$, $\chi(t,x) = \begin{cases} 1, x \in B_1(t) \\ 0, x \notin B_1(t) \end{cases}$, 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 takes 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 *erv*-system. We have supposed that the *erv* is submitted to a transition governed by the *Fourier* law; here K is the *thermal conductibility* of the material. Thus the states space of the *erv* is

$$\Sigma = \{(\theta,\chi) / \theta \in C^0(B \times R_+, \chi \in D'(B) \times R_+)\}$$

and ε, q are scalar function and vector function, respectively on Σ, $D'(B)$ is the distributional space on $\mathcal{B}$.

Some results of the phase transitions applied on freezing water, on steel solidification, including *super thermal states* have been obtained by *G. Caginalp*, 1986, *A. Visintin*, 1986, 1987, *G. Caginalp & J. T. Lin*, 1987, *M. E. Gurtin*, 1986, 1987, *J. Chadam, S. D. Howison & P. Ortoleva*, 1987.

An important parameter characterizing the state of the *erv*, 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 *erv*, denoted A_v, 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 an *erv* – system consists in the equilibrium of total energy, which is

$$\left\{\int_{erv} \varepsilon(t,x)dx\right\}' = -\int_{Fr(erv)} q(t,x)n d\sigma + \int_{erv} r(t,x)dx,$$

where the *r* function represents the heat supply, and it will count as an external energy.

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

$$\left\{\int_{erv} \eta(t,x)dx\right\}' \geq \int_{Fr(erv)} \frac{q(t,x)n}{\theta(t,x)} d\sigma + \int_{erv} \frac{r(t,x)}{\theta(t,x)} dx.$$

We suppose that the θ function is continuous on the domain $\mathcal{B}$, but all the other functions: ε, q, K, η 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 *erv*-system

(e) $\dot{\varepsilon}(t,x) = -div q(t,x) + r(t,x)$, almost everywhere $(t,x) \in R_+ \times B$, and the *Clausius-Duhem* inequality

(i) $\dot{\eta}(t,x) \geq -div \dfrac{q(t,x)}{\theta(t,x)} + \dfrac{r(t,x)}{\theta(t,x)}$, a.e. $(t,x) \in R_+ \times B$.

Assumption 3.1. The *erv*-system is endowed with an internal energy ε, which is taken as *primitive variable* characterizing the physical state, consequently all other parameters depend upon ε. Let $\theta = \tilde{\theta}(\varepsilon)$, $\eta = \tilde{\eta}(\varepsilon)$, $q = -\tilde{K}(\theta)\nabla\theta$ be dependent variables, where $\tilde{\theta}$, $\tilde{\eta}$, $\tilde{K} \in D'(R)$, and $\tilde{K}$ is a positively defined matrix on R^3.

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

$$\dot{\eta} - \frac{\dot{\varepsilon}}{\theta} \geq \frac{1}{\theta^2} q \nabla \theta = -\frac{1}{\theta^2} grad\,\theta . K . grad\,\theta \geq 0$$

and it underlines another nonlinear characteristic of the *erv*-system $\gamma(\varepsilon) = \frac{1}{\tilde{\theta}(\varepsilon)^2} \nabla \tilde{\theta}(\varepsilon) K \nabla \tilde{\theta}(\varepsilon)$, named the local *productivity of entropy* accumulated by the *erv*-system in a liquid-solid transition, otherwise the last inequality becomes $\tilde{\eta}'(\varepsilon) . \tilde{\theta}(\varepsilon) \geq 1$.

Definition 3.1. During a transition, the process P whose characteristics $\tilde{\theta}$ and $\tilde{\eta}$ satisfy the relation $\tilde{\eta}'(\varepsilon)\tilde{\theta}(\varepsilon) \geq 1$, it is a *dissipative process* and the *transition is irreversible*; if $\tilde{\eta}'(\varepsilon)\tilde{\theta}(\varepsilon) = 1$ holds then the *process is conservative* and the transition is named a *reversible transition*.

The last two relations ensure the inequality $\tilde{\eta}'(\varepsilon) > 0$, that is the entropy of the *erv*-system is a strictly increasing function with respect to internal energy. In order to preserve the estimation of the mechanical work consumed means only to assume that dissipation cannot increase the work done.

Assumption 3.2. The density of entropy η hasn't positive second derivative, i.e. $\eta''(\varepsilon) < 0$, meaning that η is a concave function.

For a reversible transition a simple calculus assure

$$\theta'(\varepsilon) = \frac{d}{d\varepsilon}\left(\frac{1}{\eta'(\varepsilon)}\right) = -\frac{\eta''(\varepsilon)}{\eta'(\varepsilon)^2} > 0,$$

then, the θ function is an invertible function on ε, such that $\varepsilon = \tilde{\varepsilon}(\theta)$. I have referred to lack of dissipation for *ervs* capable to follow only reversible processes.

Definition 3.2. The variation of the $\tilde{\varepsilon}$ function according to the temperature, that is the quantity $C(\theta) = \tilde{\varepsilon}'(\theta)$, which is named the specific heat of the *erv*-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 *erv*-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 (ε, η) diagram corresponding to figure 4, the concavity of the function $\tilde{\eta} = \begin{cases} \tilde{\eta}_1, & in\ B_1 \\ \tilde{\eta}_2, & in\ B_2 \end{cases}$ near the critical value ε^* of the energy, having the common slope at ε_1 for the function $\tilde{\eta}_1$, at ε_2 for the function $\tilde{\eta}_2$.

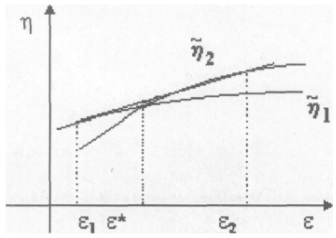

Figure 4. *Convexification of the entropy*

Using the definition of the specific heat, the equilibrium equation becomes

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

But the liquid δ-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 a new function $L = \varepsilon_2 - \varepsilon_1$.

Later on the free energy of the *erv*-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 *erv*-system. First, we have

$$\tilde{\Psi}_1(\varepsilon_1)=\varepsilon_1-\theta_0\tilde{\eta}(\varepsilon_1),$$
$$\tilde{\Psi}_2(\varepsilon_2)=\varepsilon_2-\theta_0\tilde{\eta}(\varepsilon_2)$$

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 smooth real function) =L+ $\theta_0\tilde{\eta}'(\bar{\varepsilon})L=L(1+\theta_0\tilde{\eta}'(\bar{\varepsilon}))$, where $\bar{\varepsilon}\in(\varepsilon_1,\varepsilon_2)$, because the slope is the same on the tangent line, $\tilde{\eta}_1{}'(\varepsilon_1)=\tilde{\eta}_2{}'(\varepsilon_2)=\tilde{\eta}'(\bar{\varepsilon})=0$, therefore the relation holds.

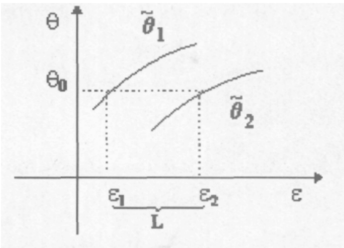

Figure 5. Variation of free energy

The particular case of the phase transition at the constant energy ε^* appears a discrepancy between the individual phase energies, which assures a super thermal state of the *erv*-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 $\{x\in B/\varepsilon_1(t,x)<\varepsilon(t,x)<\varepsilon^*, t\in R_+\}$ another part of the mushy zone stated in *super-heating*, the two parts are non equilibrium regions of the *erv*-system.

We affirm that any transition into the *erv* at constant energy ε^* 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 3.1. Some features about the shape of the free energy can be viewed, doing simple calculus, $\tilde{\Psi}'(\varepsilon)=1-\tilde{\theta}'(\varepsilon)\tilde{\eta}(\varepsilon)-\tilde{\theta}(\varepsilon)\tilde{\eta}'(\varepsilon)$ (the *erv*-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 increasing, for $\tilde{\eta}>0$, $\tilde{\Psi}$ is a decreasing function, a fact that justifies the variation given in diagram (η,Ψ).

3.3 Integral and entropy solution for a thermal conservation law

A partial differential equation of the form $u_t+\ divF(u)=f$, in $R^n\times(0,+\infty)$ is called a *conservation law* with unknown *u* and the flux function $F=(F^1,F^2,...,F^n)$. 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) $\quad u_t+divF(u)=0$, in $R^n\times(0,+\infty)$,
$u=g$ 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

Definition 3.3. We say that $u\in L^1{}_{loc}$ is an integral solution of (CL) if there exists $\int_0^\infty\int_{R^n}\{uv_t+F(u)\nabla u\}dxdt+\int_{R^n}gv(.,0)dx=0$, for all $v\in C_c^1$, where C_c^1 is the space of real valued function with compact support.

Now we introduce a thermo-dynamical notion

Definition 3.4. Let Φ, Ψ be a real valued function and a vector valued function, respectively, we call (Φ,Ψ) an *entropy/ entropy flux pair* for the conservation law

(CL) provided Φ is convex and Ψ satisfies $\Psi' = bgrad\Phi$.

We consider an approach problem: for $\varepsilon > 0$ find $u_\varepsilon \in L^1{}_{loc}$ satisfying the non homogeneous problem $u_{\varepsilon t} + divF(u_\varepsilon) = \varepsilon \Delta u^\varepsilon$.
Compute

$$\Phi(u^\varepsilon)_t + \nabla(\Psi(u_\varepsilon)) = \Phi'(u_\varepsilon)u_{\varepsilon t} + \Psi'(u_\varepsilon)\nabla u_\varepsilon$$
$$= \Phi'(u_\varepsilon)\{-b(u_\varepsilon)\nabla u + \varepsilon\Delta u_\varepsilon\} + \quad \Psi'(u_\varepsilon)\nabla u_\varepsilon =$$
$$= \varepsilon\Phi'(u_\varepsilon)\Delta u_\varepsilon = \varepsilon\nabla(\Phi'(u_\varepsilon)\nabla u_\varepsilon) -$$

$\varepsilon\Phi''(u_\varepsilon)|\nabla u_\varepsilon|^2$ (Φ is a convex function, $\Phi'' \le 0$) $\le \varepsilon\nabla(\Phi'(u_\varepsilon)\nabla u_\varepsilon)$.

Taking into account some regularity conditions and convergent results we obtain

$$\frac{d}{dt}\Phi(u) + \nabla\Psi(u) \le 0 .$$

Definition 3.4. We say that u is an *entropy solution* of the conservation law providing that $\frac{d}{dt}\Phi(u) + \nabla\Psi(u) \le 0$, in the distribution sense for each pair (Φ, Ψ).

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

$u_t + divF(u) = 0$, in $R^n \times (0, +\infty)$,

where the unknown is $u = (u^1, u^2, ..., u^m)$ and the flux function $F = \begin{pmatrix} F_1^1 & ... & F_n^1 \\ ... & ... & ... \\ F_1^m & ... & F_n^m \end{pmatrix} \in M(m, n)$ is given. The initial value problem

$u_t + divF(u) = 0$, in $R^n \times (0, +\infty)$, $u = g$ on $R^n \times \{t = 0\}$, 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 3.5. We say that $u \in L^1{}_{loc}$ is an integral solution of (CL) if there exists

$$\int_0^\infty \int_{R^n} \{uv_t + F(u) : \nabla v\} dxdt + \int_{R^n} gv(.,0)dx = 0 ,$$

for all $v \in C_c^1$, where C_c^1 is the space of real valued function with compact support.

Definition 3.6. We call (Φ, Ψ) an *entropy/entropy flux pair* of the conservation law provided $\Phi : R^m \to R$ is convex, $\Psi = (\Psi^1, \Psi^2, ..., \Psi^n)$ satisfies $\nabla\Psi = B\nabla\Phi$, for $B = \nabla F$.

At the end of section we gives

Definition 3.7. We say that u is an entropy solution providing that $\frac{d}{dt}\Phi(u) +$ $\nabla\Psi(u) \le 0$, in the distribution sense for each pair (Φ, Ψ).

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 θ_0 . We have also like in the previous section $\tilde{u}_1(\varepsilon_1) = \tilde{u}_2(\varepsilon_2) = 0$, $\tilde{\varphi}_1(\varepsilon_1) = \tilde{\varphi}_2(\varepsilon_2) = ct$, 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.

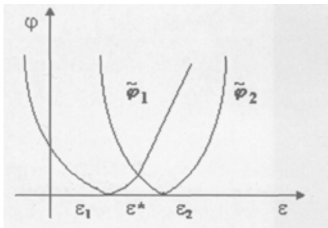

Figure 6. *Evolution of potentials Gibbs of the two phases*

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 χ can characterize the distribution of the solid germs into *erv*-system. In this way, the internal energy ε is consistent with the function χ, that is ε is continuous similar to χ, 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 (φ, u) taking account for the independent variable χ,

$$\tilde{\varphi}(\varepsilon,\chi)=\chi\tilde{\varphi}_1(\varepsilon)+(1-\chi)\tilde{\varphi}_2(\varepsilon),$$

$$\tilde{u}(\varepsilon,\chi)=\chi\tilde{u}_1(\varepsilon)+(1-\chi)\tilde{u}_2(\varepsilon),$$

$$q=-\chi\tilde{K}_1(u)\nabla u-(1-\chi)\tilde{K}_2(u)\nabla u,$$

u being continuous on $\mathcal{E}$, a.e. $\varepsilon\in R_+$. The energy and the entropy of the interface are neglected. The thermodynamics of the *erv*-system assure relations in a local form:

$\dot{\varepsilon}=-divq+r$, $\dot{\varphi}+div(uq)-ru\le 0$, in $B-S(t)$, where S(t) is the free interface, $[\varepsilon]v=[q]m$, $[\varphi]v\ge u[q]m$ on C,

where v is the displacement speed of the interface, m an outer unit normal of S(t).

The quantity defined by

$$\Gamma(ver)=\left\{\int_{erv}\varphi dx\right\}'+\int_{Fr(erv)}uqnd\sigma-\int_{erv}urdx,$$

is the *dissipation functional* of the *erv*-system. Obviously, we have $\Gamma(erv)\le 0$. The non dissipative phenomenon of the interface can be expressed by the stability conditions of the functional $\Gamma(erv)$: $\lim_{n\to\infty}\Gamma(erv_n)=0$, when $\lim_{n\to\infty}mes(erv_n)=0$, or locally $Lv=[q]m$. 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 *W.W. Mullins& R.F. Sekerka*, 1963, *R.F. Sekerka*, 1968, *N. 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 *erv*-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:

$$f_1(t)=Lvol(B_2(t))+a\int_B u(t)dx,$$

$$f_2(t)=\beta\sigma(S(t))+\frac{a}{2}\int_B u^2(t)dx+\alpha L\int_B c(t)dx;$$

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 θ greater then ρ_2 the austenite phase is stable, when $\rho_1<\theta<\rho_2$ appears a perlite phase (bainite) and for θ less then ρ_1 and nearest for ρ_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 ρ_2 value to ρ_1 value. Models of solid-solid phase transition were studied by *A. Visintin*, 1987, *R. Abeyaratne* & *K. Knowles*, 1992, *M. E. Gurtin*, 1993, *P. Cermelli* & *M. E. 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 *G. Ruddock*, 1994.

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

Let $\theta\in[\rho_1,\rho_2]\to F(t)\in[0,1]$ be a vector valued function, we define $\phi(\theta,t)=F(t)=1-e^{-b(\theta)t^{a(\theta)}}$, 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 θ decrease near $\rho 1$ the nucleation falls and the element size of the structure grows. In this case we obtain a *column structure*. When θ 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 *erv*-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 μ a scale factor, we introduce the energetic equilibrium equation

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

6. CONCLUSIONS

We have investigated some models of phase transition on the range of temperature from 60° to 1495°C. By their balance equations and their own characteristics, these models answer to the exigencies of the thermodynamics. We recall a model of an elastic-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 compacity of Nonlinear Analysis.

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