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Irreversible Thermodynamics of Metals under Stress (***)

1. INTRODUCTION

The objective of this paper is to show that the understanding of the mechanical behaviour of metals can be improved by the application of the methods of the non linear thermodynamics of irreversible processes. In this context the metal is treated as a closed (non isolated) system subjected to external flow of mechanical energy.

For the sake of simplicity we refer hereafter to the tensile test of a metal sample. It is known that for stresses below the critical resolved shear stress the behaviour of the sample is characterized by an elastic deformation: the Hooke law applies and the thermoelastic effect occurs [1]. This behaviour is accounted for by thermoelasticity, that is nothing but a branch of the linear thermodynamics of irreversible processes: we refer here to the proportionality between thermodynamic forces and fluxes. When the applied stress is increased, the thermoelastic branch eventually becomes unstable (yield phenomenon): a bifurcation occurs from the linear thermodynamic branch to plastic flow, while dislocation motion and multiplication set in. An application of the non-linear irreversible thermodynamics to the plastic deformation occurring as a « dissipative structure » [2] in the metal is presented in the following.

In Section 2 thermoelasticity of metals is briefly reviewed. In Section 3, after a schematic outline of the phenomenology, physical features of the thermo-elastic-plastic instability are presented. In Section 4 a critical assessment of the limits of applicability of irreversible thermodynamics to plastic flow is formulated. In particular, the meaning to be attached to the expressions "thermo-dynamic state" and "entropy" for an interpretation of the thermal response

of metals to mechanical stimuli during plastic flow is discussed, and an empirical expression is suggested of the entropy production, in terms of dissipation of the applied plastic mechanical power. In Section 5 preliminary results are presented, about the use of the thermal response for the measurement of the dissipation parameter in a material under stress.

In Section 6 some conclusive remarks are reported.

2. Thermoelasticity of metals

Any elastic deformation involves a configurational entropy change; in quasi-adiabatic conditions this change provokes a temperature variation, known as thermoelastic effect. The effect was discovered by Lord Kelvin in 1851; in a tensile test is shown up as a cooling (typically of the order of the tenth of a degree) in the elastic regime.

The thermoelastic effect can be rigorously treated within the general frame of linear irreversible thermodynamics of elastic deformations of metals. We start with the second principle of thermodynamics written in local form:

$$\frac{\partial s}{\partial t} + \text{div} \left(\frac{\vec{q}}{T} \right) = P[s] \geqslant 0 \qquad (1)$$

where the existence of a local entropy per unit volume s is postulated under the local equilibrium approximation [3]; $\vec{q}$ is the heat flux density vector, T the absolute temperature, and P[s] the entropy production per unit time and unit volume.

In a metal subjected to deformation the entropy production is given by two contributions: the first one is due to the flow of heat along a non-vanishing thermal gradient ($P_{th}[s]$); the second one is due to the dissipation of mechanical energy into thermal energy involved in the creation, annihilation and motion of defects ($P_{def}[s]$).

$P_{th}[s]$ is given by the product of the heat flux density vector $\vec{q}$ (flow) and its conjugated force, grad (1/T)

$$P_{th}[s] = \vec{q} \cdot \overrightarrow{\text{grad}} (1/T)$$

(the relevant kinetic coefficient is here kT², k being the thermal conductivity coefficient). Since

$$\text{div} (\vec{q}/T) = \vec{q} \cdot \overrightarrow{\text{grad}} (1/T) + (1/T) \text{ div } \vec{q} ,$$

eq. (1) can be written in the form of a heat balance equation

$$T \frac{\partial s}{\partial t} = - \text{div } \vec{q} + T \, P_{def} \, [s] \qquad (2)$$

In a general formulation, which will be fully exploited in Section 4, we consider s as a function of T and of a set of mechanical variables, collectively indicated by $\{\xi_i\}$:

$$s = s \, (T, \, \xi_i) \qquad (3)$$

The ξ_i represent both measurable quantities (like e.g. the elastic strain tensor components) and "hidden" coordinates (like e.g. dislocation densities). Eq. (3) leads directly to

$$\frac{\partial s}{\partial t} = \left(\frac{\partial s}{\partial T} \right)_{\{\xi_i\}} \frac{\partial T}{\partial t} + \sum_i \left(\frac{\partial s}{\partial \xi_i} \right)_T \frac{\partial \xi_i}{\partial t} ; \qquad (4)$$

introducing the specific heat per unit volume, at constant configuration $\{\xi_i\}$

$$C_{\{\xi_i\}} = T \left(\frac{\partial s}{\partial T} \right)_{\{\xi_i\}}$$

eq. (2) can be rewritten as

$$C_{\{\xi_i\}} \frac{\partial T}{\partial t} + \text{div } \vec{q} = T \, P_{def} \, [s] - T \sum_i \left(\frac{\partial s}{\partial \xi_i} \right)_T \frac{\partial \xi_i}{\partial t} ; \qquad (5)$$

introducing also Fourier law $\vec{q} = - k \, \text{grad } T$, eq. (5) becomes an effective Fourier equation for the temperature field:

$$C_{\{\xi_i\}} \frac{\partial T}{\partial t} - K \, \nabla^2 T = Q_d + Q_c \qquad (6)$$

where two heat sources are present:

$Q_d = T \, P_{def} \, [s]$ is the specific dissipated power per unit volume associated with the creation and motion of defects;

$Q_c = - T \sum_i \left(\dfrac{\partial s}{\partial \xi_i} \right)_r \dfrac{\partial \xi_i}{\partial t}$ is the "effective heat source" associated with configurational entropy changes.

In this section we confine ourselves to the thermoelastic regime in an isotropic medium, neglecting the elastic deformation field associated with im-

mobile dislocations. In this case Q_s is negligible, and the only relevant ξ_i is the elastic relative volume variation, i.e. the trace of the elastic strain tensor ϵ_{ii}^{el} [4]:

$$S = S_o(T) + \frac{\alpha}{K_T} \epsilon_{ii}^{el} \tag{7}$$

$$Q_s = -\frac{\alpha T}{K_T} \dot{\epsilon}_{ii}^{el} = -\gamma T C_v \dot{\epsilon}_{ii}^{el} \tag{8}$$

where $S_o(T)$ is the thermal entropy of the undeformed reference state, α is the volume thermal expansion coefficient, K_T the isothermal compressibility, γ the Grüneisen parameter and C_v the specific heat per unit volume at constant volume. In eq. (8) the equation of state of solids

$$\frac{\alpha}{K_T C_v} = \gamma \tag{9}$$

has been exploited.

In the case of a metal sample undergoing a tensile test

$$\epsilon_{ii}^{el} \approx (1 - 2\nu) \, (\sigma/E) ,$$

where E is the Young modulus, ν the Poisson ratio and σ the applied stress, so that eq. (6) reads

$$\frac{\partial T}{\partial t} - \chi \nabla^2 T = -\gamma T_o \frac{(1-2\nu)}{E} \frac{d\sigma}{dt} \tag{10}$$

where the thermal diffusivity $\chi = k/C_v$ has been introduced.

Experimental methods, based on eq. (10), have been developed to measure γ and χ [11, 12, 13].

3. The thermoelastic-plastic instability (TEPI)

At the upper limit of the thermoelastic thermodynamic branch, Q_s becomes important, because of the dissipation promoted by the motion and multiplication of dislocations responsible for plastic flow (see [1] and references therein). This is manifested by the temperature behaviour of a metal sample under tensile stress: after the cooling characteristic of the thermoelastic effect, the temperature suddenly increases (Fig. 1).

One might wonder how closely does this instability resemble other more deeply understood processes, such as the nonequilibrium phase transformations,
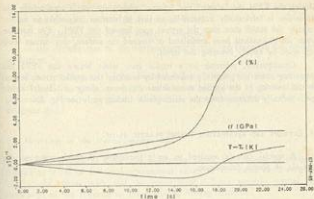
Fig. 1 — Time dependence of temperature variation (T-T$_o$) and deformation (ϵ) of an AISI 316 steel sample subjected to a tensile test at the constant stress rate $\dot{\sigma}$ = 9.6 MPa·s^{-1}.

e.g. the convective Rayleigh-Bénard instability, or the equilibrium phase transitions.

First order phase transitions are controlled by an applied external parameter. Their critical point occurs when a static balance is reached between the value of a state variable (e.g. the temperature in a liquid undergoing solidification) and a critical value of the same variable, characteristic of the stability of the internal organization of the system.

On the contrary, in non equilibrium phase transformations, the bifurcation occurs when a balance is reached between the applied rate of energy (power) and the characteristic limiting value of the energy rate that can be dissipated by the dynamical structure of the system [5].

The TEPI occurs in a metal brought away from equilibrium. The critical state or bifurcation occurs when a balance is reached between the applied external rate (generating a local shear strain energy density) and a limiting internal value of the stress itself, characteristic of the microstructure of the metal. The above critical state is reached even if the stress is increased at a vanishing rate. Under this respect the TEPI closely resembles first order equilibrium phase transitions such as melting.

Actually the similarity of the TEPI with ordinary first order phase transitions is limited by the fact that while in these transitions the simultaneously present phases (e.g. solid and liquid) are in equilibrium at the critical point,

during the TEPI the "elastic" and "plastic" phases are not in equilibrium: the transition is intrinsically irreversible, so that it becomes impossible to recover exactly the initial state once the system goes beyond the TEPI. For instance, once the dislocations have annihilated or reached the surface, they cannot show up again by merely lowering the stress.

Consequently, referring to a tensile test, while before the TEPI the preceding states are practically recovered by lowering the applied stress, beyond it the lowering of the applied stress drives the system along an "elastic" return path radically different from the elastic-plastic loading path (see Fig. 2).

4. ENTROPY AND DISSIPATION DURING PLASTIC FLOW

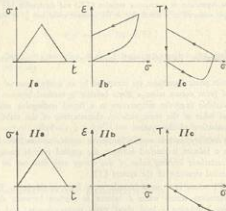A special care is required to apply irreversible thermodynamics to the domain of plastic deformation.

Fig. 2 — Two subsequent identical loading histories (Ia and IIa) for a tensile test are shown, starting from apparently identical initial states ($\varepsilon_{initial} = 0$, $T_{initial} = T_0$, see also Ic and IIc). The first loading (Ia) brings the sample beyond the TEPI, into the plastic regime, and then back to initial (T, and zero) values of the "state variables" temperature and stress, respectively (Ic). Nevertheless, the second loading history (IIa), although identical to the first one, is now completely confined within the elastic regime (IIb), while the response (IIb and IIc) is radically different from Ib and Ic, showing the dependence on the preparation or previous loading history of the system.

The main difficulties are in:

— the definition of the thermodynamic state;

— the identification of the entropy variation;

— the identification of the thermodynamic forces and fluxes in the entropy production.

These problems are briefly discussed below. As a result, an operational definition of the entropy production in terms of specific applied mechanical power is proposed, following a suggestion originally offered by Bridgman [6].

4.1. *Definition of the thermodynamic state*

The actual state of a material undergoing plastic flow cannot be uniquely defined in terms of the local instantaneous values of the usual state variables — e.g. the stress tensor and the temperature —, but requires instead the knowledge of the response to the preceding loading histories.

In the plastic regime, all states are nonequilibrium states in the sense of classical thermodynamics. Departure from any of them cannot be exactly recovered. Local equilibrium is not guaranteed since the relaxation times of the system of defects might exceed the characteristic times of mechanical stimuli (e.g. in strain ageing). It is however assumed that the presence of dislocations increases the free energy of the system above the reference level corresponding to the defect-free metal. Nevertheless, at low temperatures and low stresses annealing of these defects occurs at such a low rate that metastable states can be safely treated as time independent equilibrium states.

4.2. *Identification of the entropy variation*

According to Clausius theorem, in order to evaluate the entropy variation of a system undergoing an irreversible transformation from an initial equilibrium state A to a final equilibrium state B, one should identify any reversible path $\mathcal{R}$ connecting these two states and compute the quantity

$$\Delta S = \int_{\mathcal{R} \ (A \to B)} \dbar Q/T \tag{11}$$

where $\dbar Q$ is the infinitesimal heat quantity flowing into the system.

From Sec. 4.1 it is clear that, should the TEPI occur between A and B, no reversible path exists connecting the two states. Actually, each state beyond the TEPI is like "an island in a sea of irreversibility" [9].

In order to cope with this difficulty, in principle one should try to define a local entropy depending on hidden coordinates (see Sect. 2) and then verify

whether this function would deserve this name (e.g. from the point of view of statistical mechanics). However, the entropy variation associated with hidden coordinates is not readily experimentally available: for instance no method seems yet practicable to evaluate in real time the configurational changes of the dislocation network in thin samples.

Nevertheless, to interpret the experimental data shown below, we adopt the empirical operational approach described in the following section.

4.3. Entropy production

Entropy production is a key concept in irreversible thermodynamics [2]: in fact it provides a measure of the irreversibility of the transformation.

In general the entropy production $P[s]$ is expressed as a product of thermo-dynamic forces and fluxes. Near equilibrium proportionality holds between the two. Around the instability it is reasonable to expect deviations from this behaviour: a sudden rise of $P[s]$ occurs toward the value absorbed by the dissipative structure (in our case: plastic flow) [7].

From the previous sections it appears that in the absence of a simple picture of the connections between the defective microstructure and the macroscopic variables, it is not possible yet to identify the relevant thermodynamic forces and fluxes involved in the TEPI.

A reasonable operative empirical ansatz is adopted here. Since $P_{def}[s]$ turns out to be also a measure of the dissipation, we define, with reference to a tensile test,

$$P_{def}[s] = f \frac{\sigma \dot{\varepsilon}^{pl}}{T} .$$ (12)

The above equation can be generalised easily to states of multiaxial deformation, using the shear components of both the stress and plastic strain rate tensors. In eq. (12) σ is the applied tensile stress, and $\dot{\varepsilon}^{pl}$ is the plastic strain rate, so that $\sigma \dot{\varepsilon}^{pl}$ is the applied mechanical plastic specific power. The empirical quantity f is a dissipation coefficient providing the fraction of the plastic power immediately converted into "heat". This quantity turns out to be a function of the stress, the strain rate, the temperature and the previous history. Should $f(\sigma, \dot{\varepsilon})$ be small, the plastic work would be stored predominantly as frozen potential internal energy, local stress intensification would occur, dislocation mobility would be low.

Among the mechanisms responsible for dissipation, following Nicholas [8] we merely quote the following ones:

1) kinetic energy of moving dislocations;

2) damping of dislocation motion by local thermoelastic effect, radiation damping and scattering of sound waves;

3) creation and annihilation of dislocations;

4) creation and annihilation of point defects.

The determination of the amount of dissipated energy during plastic flow remains an open problem, as clearly pointed by the two following quotations:

"Although it is established that nine-tenths of the work done in plastically deforming a metal at room temperature is at once converted into heat, little is known of the mechanism of this conversion" [9].

"The plastic energy is absorbed predominantly by internal structural changes at an atomic level. These changes entail progressive dislocation entanglement, the creation of new dislocations and the interaction of dislocations with grain boundaries, vacancies, foreign atoms etc. The entire process, which makes dislocation motion progressively more difficult and hence leads to the observed increase of yield stress with plastic strain is called work hardening. As indicated work hardening absorbs most of the plastic energy; a small proportion (typically about 10%) is liberated as heat" [10].

5. PRELIMINARY RESULTS ON THE DISSIPATION COEFFICIENT f ACROSS THE TEP1

According to Eq. (12), in the case of a solid undergoing a uniaxial homogeneous elastic-plastic deformation, Eq. (6) can be written as follows:

$$\frac{\partial T}{\partial t} - \chi \nabla^2 T = - \gamma T \frac{1 - 2\nu}{E} \frac{d\sigma}{dt} + f \frac{\sigma}{C_\varepsilon} \frac{d\varepsilon^{st}}{dt}$$ (13)

Eq. (13) is used as the basis for the determination of f (σ) by deformation calorimetry [7, 16], for a sample of AISI 316 austenitic stainless steel.

The same instrumentation already used to assess the Grüneisen parameter [11, 13], the thermal diffusivity [12, 13] and the thermoelastic-plastic limit stress σ_1 [14] and strain ε_1 [15] has been utilized as a deformation calorimeter, with a temperature resolution down to $2 \cdot 10^{-6}$ K [17].

Loading histories consisting in stress ramps are applied and the thermal and mechanical responses, T (t) and ε (t) respectively, are measured. In Fig. 1 typical responses of AISI 316 steel are reported.

Once T (t) and ε (t) are known for the initial segment of the thermo-elastic regime, from the measured temperature rate $\dot{T}$ one can separate the plastic contribution $\dot{T}^{st}$ related to the dissipation parameter f.

In other words taking advantage of the linarity of eq. (13) with respect to temperature, implying the superposition principle for the thermal responses, one can decompose $\dot{T}$ as

$$\dot{T} = \dot{T}^{el} + \dot{T}^{st}$$ (14)

where

$$\dot{T}^{el} = -\gamma T \frac{1-2\nu}{E} \dot{\sigma} + \chi \nabla^2 T^{el} \qquad (15)$$

would describe a purely thermoelastic cooling in the presence of heat diffusion, and

$$\dot{T}^{pl} = f \frac{\sigma \dot{\epsilon}^{pl}}{C_v} + \chi \nabla^2 T^{pl} \qquad (16)$$

would describe a purely plastic heating.

The plastic strain rate is obtained as

$$\dot{\epsilon}^{pl} = \dot{\epsilon} - \dot{\sigma}/E \qquad (17)$$

while the plastic specific power is

$$W_p = \sigma \dot{\epsilon}^{pl} \qquad (18)$$

and the specific power accordingly dissipated is

$$W_d = f W_p = C_v (\dot{T} - \dot{T}^{el}) \qquad (19)$$

The adopted testing time (determined by the applied stress rate) and the geometry of the sample imply a practical adiabaticity of the deformation process, so that the laplacians in eqs. (15) and (16) are negligible. From the data of Fig. 1, using eqs. (15) to (19), one thus obtains W_p, W_d and the dissipation function f as functions of the applied stress (see Fig. 3).

An interpretation of f in terms of the dislocation motion and multiplication will be reported elsewhere.

6. Conclusions

This paper provides the present approach of the authors to the characterization and understanding of the mechanical behaviour of metals under stress in terms of irreversible thermodynamics. The role of thermal response is analyzed in detail and experimentally exploited by temperature measurements during mechanical tests.

Additional information becomes thus available. From the thermoelastic response fundamental parameters (such as the Grüneisen parameter and the thermal diffusivity) can be determined. From the temperature behaviour during plastic flow since its onset, the thermoelastic-plastic limit stress (related to the yield phenomenon) is pinpointed; furthermore, access is opened to the evaluation
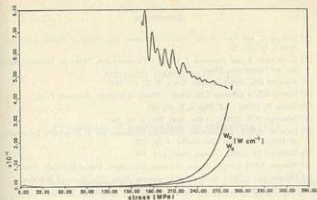
Fig. 3 — Stress dependence of the specific plastic power W_p, the specific dissipated power W_a and the dissipation function $f(\sigma, \dot{\sigma}, T)$. The oscillations in the f vs. stress curve are only due to numerical instabilities in taking the ratio between two quantities arising from digital derivatives of sampled data: thus only the mean behavior of f is physically meaningful.

of the dissipation of mechanical work into thermal energy. To this end, a dissipation parameter $f(\sigma, \epsilon | T)$ is defined and measured as a function of the applied stress. The value of f for AISI 316 tends to the very average of the conjectured values, 10% and 90% (see [7] and [8] respectively).

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