APPLICATION OF THERMAL ANALYSIS TO IRREVERSIBLE PROCESSES IN THE FIELD OF METALLURGY

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ABSTRACT

According to the publications of our coworkers M. DIRAND, F.A. KUHNAST, C. CUNAT, J.P. HILGER, as well as their students, we can prove that **irreversible** processes are often detected by the D.S.C. technique. After theoretical considerations, we describe various experiments where thermal analysis has been very helpful to understand such mechanisms.

## A FEED-BACK TO THERMODYNAMIC EQUILIBRIUM CONDITIONS

When a system is maintained in equilibrium conditions, each local subsystem exhibits interactions with its local environment. These interactions represent the various exchanges of extensive quantities entropy δS, volume δV, moles of matter δN_i. In consistency with the formalism initially proposed by J.W. GIBBS [1] such local exchanges between a local subsystem and its environment involve a variation of the internal energy of the total system :

$$\delta U = T'\delta S' + T''\delta S'' - P'\delta V' - P''\delta V'' + \sum_i (\mu'_i \delta N'_i + \mu''_i \delta N''_i) \tag{1}$$

where ' is related to the subsystem and " is related to its environment.

The entropy exchange in general conditions of transference is written $\delta S' + \delta S'' \geqslant 0$ considering the ability of a system to create some positive entropy by irreversible processes.

Now, if we assume that the system has attained its equilibrium state under external conditions (which need not necessary be specified), any internal exchange linked to the fluctuations of the system becomes a perfectly reversible one. This means that for all the local exchanges :
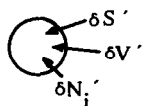
$$\delta S' + \delta S'' = 0 \tag{2}$$

$$\delta V' + \delta V'' = 0 \tag{3}$$

$$\delta N'_i + \delta N''_i = 0 \tag{4}$$

a local exchange between a small subsystem and its environment inside the total system.

GIBBS [1] has demonstrated that the general conditions of equilibrium of a system can be expressed by two equivalent formalisms, considering all the local exchanges inside the system :

$$dS_u = 0 \qquad (5)$$

$$(\delta S)_u \leqslant 0 \qquad \qquad \text{maximum position}$$

$$d^2S_u < 0 \qquad (6)$$

$$dU_s = 0 \qquad (7)$$

$$\text{or} \quad (\delta U)_s \geqslant 0 \qquad \qquad \text{minimum position}$$

$$d^2U_s > 0 \qquad (8)$$

The same demonstration can be seen in the more recent "Classical Thermodynamics" of A. MUNSTER [2].

Now, when considering independently each local exchange inside the system in the vicinity of the equilibrium, according to the conservative condition (2) $\delta S' + \delta S'' = 0$ we deduce that during reversible fluctuations the total entropy does not vary and the conditions (7) and (8) have to be satisfied.

FIRST ORDER CONDITIONS

There are an issue of the relation (7) dU = 0 with respect to the (1), (2), (3) and (4) relations :

$$dU = (T' - T'')dS' + (P' - P'')dV' + \sum_i (\mu'_i - \mu''_i)dN_i = 0 \qquad (9)$$

$$T' = T'' \qquad P' = P'' \qquad \mu'_i = \mu''_i \qquad (10)$$

All these first order conditions are **contagious conditions** that establish the uniformity of intensive parameters in the whole system, by transmission of this condition environment by environment.

SECOND ORDER STABILITY CONDITIONS

Relation (9) or (10) translates the extremum position of the system, but any extremum can be either a maximum as well as a minimum or even an inflexion point. Stability of the system is linked to a minimum for U with respect to any reversible local exchange inside the system. So the stability condition expressed with the U function is $\qquad d^2U > 0 \qquad (11)$
with d^2U given by the differential expression of (1)

$$d^2U = (dT'dS' - dP'dV' + \sum_i d\mu'_i dN'_i) + (dT''dS'' - dP''dV'' + \sum_i d\mu''_i dN''_i) \qquad (12)$$

Relation (12) implies that S', V' and N'$_i$ are really independent variables.

But the variations of all the intensive parameters of the local system dT', dP', dμ'$_i$ are much bigger than the correlative variations of the same parameters for the relatively infinite environment, dT'', dP'', dμ''$_i$ for the same extensive exchanges. For this reason the stability condition (12) can be restricted to the local subsystem :

Stability conditions are **no longer contagious conditions, but local ones.**

$$d^2U > 0 \quad \stackrel{\sim}{\sim} \quad dT'dS' - dP'dV' + \sum_i d\mu'_i dN'_i > 0 \tag{13}$$

This new expression is perfectly symmetric with respect to the variations of the intensive and extensive parameters. Therefore, it can be very useful to separate the influence of the variations of external conditions T and P from the role played by the introduction of mole of matter, inside the system.

We designate for binary systems :

$$d^2U = [dT, d(-P), dN_1, dN_2] \cdot \begin{vmatrix} \dfrac{Cp}{T} & \alpha V & 0 & 0 \\ \alpha V & V\kappa_T & 0 & 0 \\ 0 & 0 & \dfrac{\partial\mu_1}{\partial N_1} & \dfrac{\partial\mu_2}{\partial N_1} \\ 0 & 0 & \dfrac{\partial\mu_1}{\partial N_2} & \dfrac{\partial\mu_2}{\partial N_2} \end{vmatrix} \begin{bmatrix} dT \\ -dP \\ dN_1 \\ dN_2 \end{bmatrix} > 0 \tag{14}$$

This quadratic form has to be positive which is equivalent to the following set of conditions

For the closed systems :

$$\frac{Cp}{T} > 0 \quad \text{or} \quad \left(\frac{\partial S}{\partial T}\right)_P > 0 \tag{15}$$

$$V\kappa_T > 0 \quad \text{or} \quad \left(\frac{\partial V}{\partial P}\right)_T < 0 \tag{16}$$

$$\begin{vmatrix} \dfrac{Cp}{T} & \alpha V \\ \alpha V & V\kappa_T \end{vmatrix} > 0 \tag{17}$$

Considering the possibility of permutation of the derivation order into the crossed second derivates, condition (17) can be expressed in two different ways :

$$\left(\frac{\partial S}{\partial T}\right)_V > 0 \quad (18) \quad \text{or} \quad \left(\frac{\partial V}{\partial P}\right)_S < 0 \tag{19}$$

For the isothermal, isobar open binary system :

$$\left(\frac{\partial\mu_1}{\partial N_1}\right)_{P_1 T_1 N_2} > 0 \tag{20}$$

or spinodal conditions

$$\left(\frac{\partial\mu_2}{\partial N_2}\right)_{P_1 T_1 N_1} > 0 \tag{21}$$

The last minor $\begin{vmatrix} \dfrac{\partial\mu_1}{\partial N_1} & \dfrac{\partial\mu_2}{\partial N_1} \\ \dfrac{\partial\mu_1}{\partial N_2} & \dfrac{\partial\mu_2}{\partial N_2} \end{vmatrix} \geqslant 0$ does not introduce any new restriction for stability of binary systems, since this determinant is always equal to zéro when considering the Gibbs-Duhem binary isobar isothermal relations :

$N_1 \, d\mu_1 + N_2 \, d\mu_2 = 0$ from which two independent relations follow

$$N_1 \frac{\partial \mu_1}{\partial N_1} + N_2 \frac{\partial \mu_2}{\partial N_1} = 0$$
$$N_1 \frac{\partial \mu_1}{\partial N_2} + N_2 \frac{\partial \mu_2}{\partial N_2} = 0$$

which have to be satisfied simultaneously.

Nevertheless for a ternary system this determinant does not vanish but introduces a new stability condition.

APPLICATION OF SECOND ORDER STABILITY CONDITIONS TO THERMAL ANALYSIS

The most important stability conditions for thermal analysis are linked to conditions (15) and (18)

$$\left(\frac{\partial S}{\partial T}\right)_P > 0 \qquad \text{or} \qquad \left(\frac{\partial S}{\partial T}\right)_V > 0$$

In equilibrium conditions the thermal heat flow has to be of the same sign as the derivate of temperature with time (at constant pressure or at constant volume)

Experimentally this general theorem involves two different aspects often observed :

a) During exothermal heat flow (with a cooling program in DTA or DSC experiments) any increase of the temperature of the system implies an irreversible process.

b) At increasing temperatures in a system (with a heating program in DTA or DSC experiments) any exothermal heat flow implies an irreversible process.

EXPERIMENTAL

Many examples can be found in the various topics of experimental thermodynamics to illustrate these two aspects of thermal analysis.

An example in cooling DSC procedure

The irreversible conditions are generated by a delay in the germination of a solid phase inside the liquid. The apparatus is a SETARAM high temperature CALVET-type calorimeter, used in cooling conditions at the rate of (-10)K/hour. The temperature of a $Mg_5 Ga_2$ liquid mixture is recorded by a thermocouple immersed in the cell of the calorimeter. The apparatus linked to a microcomputer is able to record, every 10 seconds, simultaneously the time scale, the temperature and the heat flow signal. $Mg_5 Ga_2$ exhibits a congruent indifferent melting diagram. Figure 1a shows that the DSC-time curve is typical of a solidification process without any apparent distorsion of the exothermal versus time signal. On the contrary the DSC-temperature curve (1b) exhibits a feed-back of the temperature at the beginning of the solidification by an

irreversible transition. This $\frac{dS}{dT} < 0$ slope is characteristic of the non equilibrium conditions of solidification (I) : even if the cooling rate is extremely slow. When the general invariant conditions liquid $\rightleftharpoons$ solid are realised under constant pressure, the $\frac{dS}{dT}$ slope becomes really infinite (II) which is equivalent to $(\frac{\partial T}{\partial S})_P = 0$ for this indifferent equilibrium. After solidification the $\frac{dS}{dT} > 0$ slope (III) corresponds to the new equilibrium conditions of cooling.
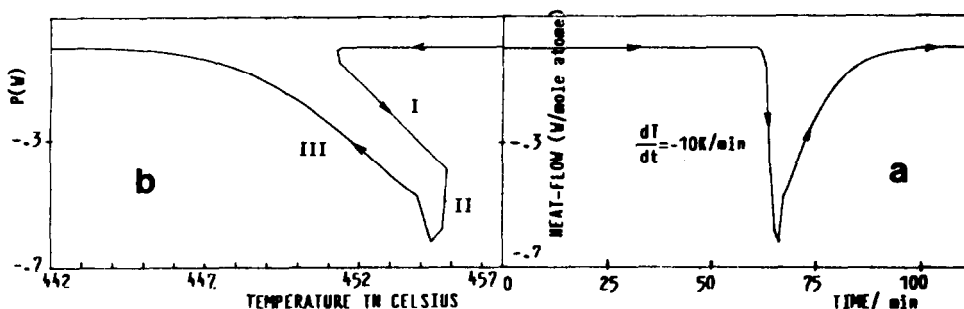

Fig. 1. Solidification of a Mg_5Ga_2 liquid mixture : a) heat flow-time curve
b) heat flow-temperature curve. Notice the irreversible feed-back $\frac{dH}{dT} < 0$ (I)

Heating DSC - Procedure

The following describes various non-equilibrium states generated by quenching the sample from high temperatures. Many examples can illustrate the general feature of the DSC curves when heating the quenched samples :

- relaxation and crystallisation of amorphous materials
- annealing of quenched steels
- elimination of vacancies
- structural hardening
- disorder $\rightarrow$ order transformations

In any case the DSC thermogram exhibits during heating, an exothermal heat flow deviation which corresponds to the irreversible process $\frac{dS}{dT} > 0$.

Figure 2 presents two different Cp curves versus temperature obtained with a SETARAM DSC 111 calorimeter. The sample is constituted of a $Ni_{.77} P_{.23}$ amorphous material obtained by electro-deposition in an aqueous mixture. Comparison of the first and the second heating shows a strong exothermal deviation of the first annealing treatment. The exothermal deviation from 380 K to about 550 K is linked to the relaxation process inside the amorphous phase. The two big exothermal peaks with high negative values of Cp represent the first crystallisation processes. After the crystallisation the two thermograms are quite identical for the two successive heatings, which means that either the equilibrium state or a metastable state is attained.

Figure 2 corresponds to a new unpublished work but many other amorphous systems have been studied previously in our laboratory : (Fe,B) [3], (Co,P) [4], (Co,B) [5] for examples.
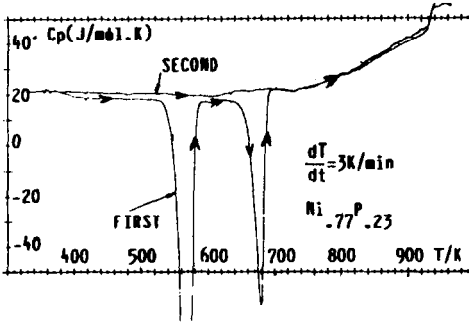

Fig. 2. Two successive annealings of an initially amorphous $Ni_{.77}P_{.23}$ alloy. Notice the exothermal deviation of Cp during the first heating.
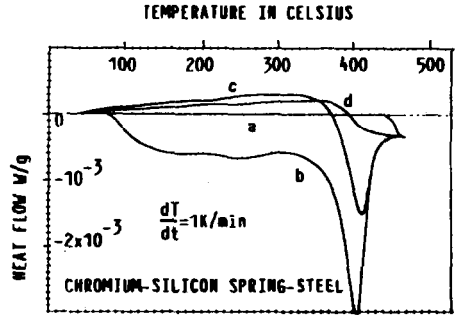
Fig. 3. Annealing of a chromium-silicon spring steel a) full annealed b) as quenched c) and d) preannealed with η or χ carbide.

Annealing of quenched spring-type steels can also be studied by the D.S.C. technique. Figure 3 shows four different thermograms obtained with a chromium-silicon steel using a BARBERI-type calorimeter. The heating rate is 1K/min. The base line d corresponds to the full-annealed sample at 460°C. The three other curves represent different states of the heat treatment.

The **a** line represents the as-quenched steel which shows in the whole range of temperature, during heating a continuous exothermal heat-flow characteristic of irreversible processes $\frac{dS}{dT} < 0$.

The **b** and **c** curves correspond to two different stages of preannealing, with precipitation of η or χ carbides [6]. For these two initial states we do not detect any more irreversible processes up to 370°C : at this temperature the metallic atoms begin to move inside the matrix. So a new irreversible process involves the diffusion of these matrix-atoms [7].

Figure 4 is a DSC curve realised in a SETARAM-CALVET-type calorimeter with a quenched FeAl ordered B2 alloy. By quenching this alloy it is possible to catch a high concentration of vacancies. The exothermal peak between 400°C and 500°C represents the elimination of these vacancies with the formation of a dense dislocation network. This network disappears between 600 and 700°C with an endothermal effect [8].

Figure 5 exhibits the DSC curve obtained with a high-sensitive BARBERI-type calorimeter when aging a lead alloy for battery grids. This alloy contains a small amount of calcium, about 0.1 weight %. The exothermal heat-flow during heating corresponds to the irreversible hardening process in the metal [9].
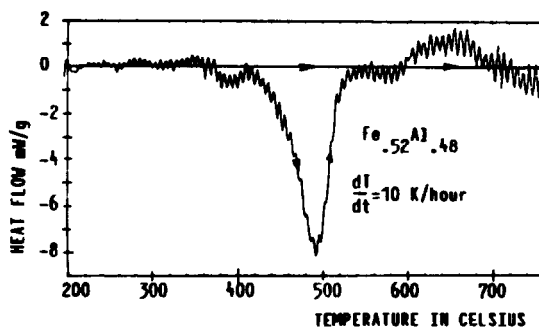
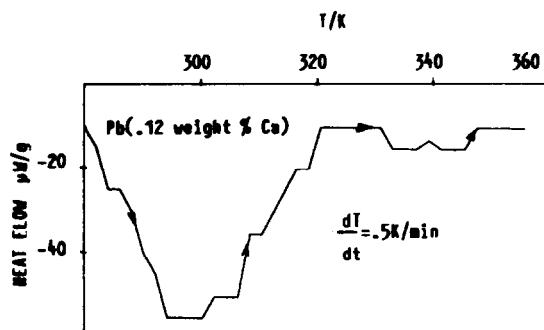Fig. 4. Elimination of quenched vacancies in an ordered B2, FeAl alloy.

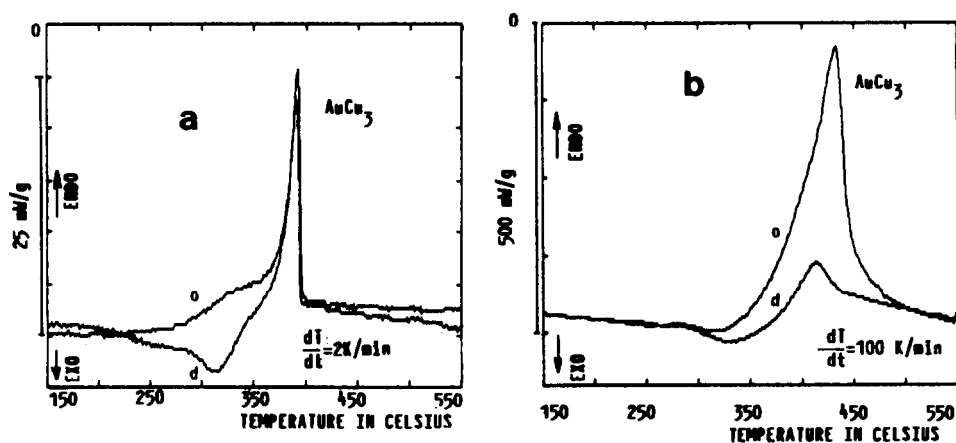Fig. 5. Exothermal heat flow linked to the structural hardening of a battery grid alloy.

Fig. 6. Ordering-disordering process when annealing a quenched AuCu3 alloy
d disordered initial state - o ordered initial state.

CREATED ENTROPY

During an irreversible transformation the increase of the entropy inside the system is higher than the exchanged entropy. Here we describe a paradoxal experiment where the **created entropy** quantity decreases with the heating rate. The sample is an $AuCu_3$ alloy initially quenched in disordered state from high temperature. DSC experiments start at low temperature in a METTLER TC 10 device. In figure 6a we observe first an exothermal deviation during heating at the rate of 2K/min (irreversible ordering), immediately followed by an endothermal peak (curve d). The o curve in the same figure corresponds to the fully ordered initial state. Figure 6b presents the same two experiments for the higher heating rate of 100K/min.

Results : From both experiments we found

$$H \text{ (disorder, } 150°C) - H \text{ (ordered, } 150°C) \simeq 15 J/g$$

But the exchanged entropies are quite different

$$\Delta S - S \text{ (created, } 2K/min) = -26 J/(gK)$$

$$\Delta S - S \text{ (created, } 100K/min) = -20 \ J/(gK)$$

Finally : S (created, 2K/min) $- S$ (created, 100K/min) $= 6 J/(gK)$.

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