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To cite this version:
L.F. Donà Dalle Rose. ULTRASHORT HEAT TRANSIENTS IN METALS UNDER LASER IRRADIATION. Journal de Physique Colloques, 1983, 44 (C5), pp.C5-469-C5-479. <10.1051/jphyscol:1983569>. <jpa-00223154>

HAL Id: jpa-00223154
https://hal.archives-ouvertes.fr/jpa-00223154
Submitted on 1 Jan 1983

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ULTRASHORT HEAT TRANSIENTS IN METALS UNDER LASER IRRADIATION

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Abstract - Among the different types of ultrashort heat flow transients which involve melting and boiling of metal samples, only those not showing convective-type effects are amenable to quantitative discussion. The structure of these transients is described and discussed in terms of several experimental results.

1. Introduction

The ultrashort heat transients in metals, as induced by directed and pulsed energy beams, ranging between 5\(\cdot\)100 ns in duration (sometimes up to 300 ns) and within 1\(\cdot\)15 J/cm\(^2\) in energy density, show considerable differences in their characterization. Basically, with increasing energy density, four different regimes may be defined and experimentally studied: transients in solid phase, transients in solid and liquid phase, transients involving quiet vaporization and/or boiling from the liquid phase, transients which involve convective motion and violent boiling of the molten phase.

The heat flow transients are accompanied and related to transients in other relevant physical quantities like surface state, reflectivity, surface and bulk temperature, transport properties of embedded impurities, or mixing at the boundary of a layer deposited over bulk substrate. The reflectivity transient has a special importance, since it determines the actual amount of observed energy under pulsed laser irradiating (PLI) and therefore the main features of the associated heat flow transient (like molten phase duration and maximum molten depth). Unfortunately very few measurements are available about such a transient. There is also an initial reflectivity problem which depends on the surface preparation technique. For example, rolling of the sample surface may cause scratches which under laser irradiating act as preferential centres for light absorption (see Fig. 1). Similar events may occur on chemically (polished and) pitted surfaces, sometimes provoking even early heating and localized evaporation from the surface. In other cases implantation of species to be studied under matrix heat transients may quite alter the initial reflectivity, as clearly shown by Fig. 2, where regions a,b,c are respectively virgin surface, Cr (7 at %) implanted region, Cr implanted plus pulsed laser treated region (ruby laser, at 3. J/cm\(^2\), 25 ns); region d which was laser treated but not implanted does not show any particular feature. Region c shows a wrinkle pattern, with a characteristic wavelength \(\sim 40 \mu m\), which is probably due to
Fig. 1 - Evidence for preferential light absorption along rolling scratches in virgin Al under PLI at 3.5 J/cm², 15 ns (ruby laser). Courtesy of Padua CNR-GNSM group on energy beam treatment of materials.

Fig. 2 - Transition region of an Al sample from virgin (left) to Cr implanted (right) after PLI with ruby laser; see main text for details about region a, b, c, d. Courtesy of Padua CNR-GNSM group.

a laser diffraction pattern inducing melting only at the light maxima; the absence of such a pattern in region d clearly calls for a greater absorbed energy, i.e. a reduced reflectivity, in the implanted region. These and similar observations demand attention when adopting literature data about reflectivity. Apart from direct (during transient) measurements, some indirect methods have been discussed
to assess the surface reflectivity in a given experiment, either by looking \(^2\) at the characteristic fringes which sign the melt threshold, this latter being then compared with heat flow calculations, or by using a calorimetric method \(^4\) to measure the total absorbed energy. This very method allows detection of reflectivity changes when passing from a solid to a liquid sample surface (e.g. a slight decrease, in the case of Al). An additional melt threshold indicator is given by the damage (i.e. \(X_{\text{MIN}}\)) behaviour with increasing absorbed energy \(^5\), which shows a peak (due to increased slip deformation at melt threshold). Finally a consistency check about an effective (i.e. all over the pulse duration) reflectivity assignment may be carried out whenever a set of impurity profiles (as implanted as well as after transient profiles, at several energy densities) are available. It is then generally possible to locate the melt threshold and, by means of a combined solution of the heat and impurity diffusion equations, to assign definite values to the impurity normal diffusion coefficient \(D\). By now several diffusion coefficients have been determined in this way \(^5\), \(^8\), \(^9\), \(^10\), their value being \(\approx 10^{-4} \text{ cm}^2/\text{sec}\), which is widely recognized as the typical liquid phase value, mainly on the basis of other measurements \(^11\), carried out under conditions much nearer to thermal equilibrium. An interesting point here concerns the diffusion coefficient dependence on the transient absorbed energy, which in turn may be related to the temperature dependence of the diffusion process and to the as yet undecided question whether the coefficient \(D\) increases linearly or exponentially \(^11\). For instance, Sb diffusion in Al \(^12\) yields a value \(D = 5 \times 10^{-3} \text{ cm}^2/\text{sec}\) under a situation where a high average temperature is achieved during the transient (a concentration gradient higher than usual might also introduce corrections to the linear theory). Some earlier determinations \(^12\), \(^13\) provided values for \(D\) up to \(10^{-1} \text{ cm}^2/\text{sec}\). Such rather extreme results are now interpreted as a piece of evidence for convective type motions under PLI. This is further supported (see Fig. 3): i) by the after transient metal surface which shows quite a rough aspect as compared to the surface smoothness found after lower energy density transients (and which in turn correlate with \(D\) values for implanted impurities equal to \(\approx 10^{-4} \text{ cm}^2/\text{sec}\)) and ii) by the deep impurity profile tails which often extend well beyond the detectable limits, thus preventing any check based on the conservation of the total impurity amount and at the same time confirming the general idea according to which convective motions may quite increase the depth over which a molten phase appears. The true nature of this violent, convective type motion has not yet been understood completely, the main difficulty being the quite longer time scale needed in conventional convective motion \(^14\). A nice evidence for the existence of these two quite different diffusion regimes is found in ref. 12, where both a simple liquid phase diffusion profile and a convective-type flat profile are shown, as measured by means of a RBS microbeam, within the same laser spot, which has a gaussian intensity distribution. For some reasons (perhaps radial thermal gradient) the peripheral circular region, which achieves lower average temperatures, shows evidence for convective-type motion both because of the rough surface and of the Sb flat profile shape; on the other hand the central region, which achieves highest absorbed energy, is smooth and the corresponding Sb profile is simply diffusion like.

In the following we shall restrict our discussion only to transients which either relate to simple heating and melting of the irradiated metal (lower absorbed energy transients) or involve quiet evaporation and/or boiling from the liquid phase (higher absorbed energy transients).
Fig. 3 - Lower (above) and higher (below) absorbed energy transient effects on the state of a La implanted Ni surface and on the La profile (courtesy of Padua CNR-GNSM group; see also ref. 10). Both transients were induced by a ruby laser pulse, 16 ns Fwhm.

2. Structure of the heat transient

2.1. Lower absorbed energy transients

As it is well known \(^{15}\), in metals it is possible to assume an instantaneous conversion into heat of the energy absorbed from the primary beam, at least for the times under consideration here. Then the heat flow is governed by the (unidimensional) conduction equation

\[
C \rho \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left[ K(T) \frac{\partial T}{\partial x} \right] + Q(x,t)
\]  

where \(C\), \(\rho\), \(K\) are the sample specific heat, density and thermal conductivity (depending on the temperature \(T\), on the state, whether solid or molten, and possibly on the amount of embedded impurities and damage). \(Q(x,t)\) represents the source term. Equation (1) must be solved together with the boundary conditions:

\[
T(x,0) = T_b \quad ; \quad T(\infty,t) = T_b
\]  

\((2a,b)\)
\[ \rho H_{fus} \dot{x} = K_{sol} \frac{\partial T}{\partial x} \bigg|_{x^+} - K_{liq} \frac{\partial T}{\partial x} \bigg|_{x^-} \]  

(3a)

plus, during resolidification,

\[ \dot{x} = \frac{1}{\beta} (T_i - T_M) \]  

(3b)

Conditions (2a,b) takes into account the external bath at \( T = T_b \) (often, but not always, room temperature), while conditions (3a) and (3b) refer to the melt front (whenever it shows up), more precisely to its velocity \( \dot{x} \), which varies in such a way as to conserve the balance of ingoing and outgoing heat flux (eq. 3a, where \( H_{fus} \) is the latent heat of fusion/resolidification) and which has to satisfy the undercooling constraint as required by crystal regrowth thermodynamics (eq. 3b, where \( T_i \) is the liquid-solid interface temperature and \( T_M \) the melting temperature; \( \beta \) is a proportionality constant). The constant \( \beta \) is very small in metals as compared to the semiconductor case. According to a simple argument \( 16 \), the interface undercooling obeys

\[ \frac{T_M - T_i}{T_i} \approx \frac{v_{\text{Stefan}}}{v_{\text{res}}} \]

where \( v_S \) is the metal sound velocity and \( v_{\text{res}} \) is the resolidification velocity as determined by the pure heat flux conservation (i.e. eq. 3a which determines a Stefan boundary problem if acting alone). As a consequence since \( v_{\text{Stefan}} \approx 20 \text{ m/sec} \) in most calculated transients in metals, and \( v_S \approx 5000 \text{ m/sec} \), \( \Delta T_i \approx 0.5 \% \) of \( T_M \), i.e. negligible. The resolidification velocity in metals is then controlled only by heat flux.

As a matter of fact, heat transients in metals may be calculated by using appropriate average values for \( C, \rho, K \), which are slowly varying functions of \( T \) in a given state (solid or molten). Keeping into account their actual variation would only change the results by some percents, while increasing much the computer time. Recent papers \( 15,17 \) have described the detailed nature of the heat transient at lower absorbed energy. The source term may quite influence its structure. Roughly speaking the molten phase duration may be divided into two subsequent stages, an earlier one which is quite warmer (its average temperature being at an intermediate value between \( T_M \) and the normal boiling temperature \( T_{eb} \)) and a second one characterized by an almost constant temperature (actually \( T_M \)) all over the molten layer. Depending on the used source (i.e. with laser but not with e-beam) the former stage is also characterized by very high thermal gradients in liquid phase (up to \( 10^7 \text{ °K/cm} \)). These two stages may be experimentally observed by looking at several properties of impurities embedded in the host metal sample through either implantation or sandwiching of a thin impurity layer. While normal diffusion may occur during both stages, there are other phenomena which are characteristic of one stage or the other. The first stage offers the unique combination of high concentration gradients (as due to ion implantation or mixing of a layered structure) and extreme liquid phase gradients: their product controls \( 18 \) a term in the impurity diffusion equation which is usually negligible, but which may play an observable role in some cases (Soret diffusion). Appreciable effects have been observed for Cu and Zn in Al and Au in Ni. The second stage, on the other hand, may be quite apt for impurity precipitation occurrence; this may be understood \( 19 \) by looking, for example, at the Al-rich portion of the equilibrium phase diagram for the Al-Sb binary and by noticing
that, for Sb concentration of a few atomic percents, the time spent by the cooling
AR molten phase within the temperature interval associated with a two phase state
(i.e. liquid plus AR-Sb precipitate) may be long enough to cause precipitation in
certain transients. A beautiful experiment 4) which controlled the second stage
duration under PLI by acting on the ambient temperature $T_a$ was able to show in
the very case of the AR(Sb) system, with initial Sb concentration equal to 2. at %,
that precipitate nucleation and growth occurred within 15 ($\pm$10) ns.

Another phenomenon which may take place along both stages, at lower absorbed ener-
gies, is impurity surface oxidation. The corresponding surface peak has been de-
tected in the after transient profile of some impurities implanted in Ni; Hf 20),
La and Eu 10) are good examples in this respect. For Hf and La, laser irradiating in
Helium atmosphere or under $10^{-2}$ torr vacuum yields quite a reduction in the peak
height. In addition the heat of formation of La$_2$O$_3$ and Hf$_2$O$_3$ is negative and much
larger, in absolute value, than NiO. This means that in these cases surface impu-
ritiness oxidation is an energetically highly favoured process, even though the exact
way, in which it actually develops at high temperatures, is subject to a delicate
and as yet not explored balance between the reaction rate and the Le Chateliers
principle (about exothermic reactions). Eu seems not to be an altogether different
case, even though no check was performed on it by varying the oxygen atmosphere 10).

An impurity surface peak may be originated by several mechanisms: beside surface oxidation, impurity segregation during resolidification 13), changes in the reso-
lidification velocity when the impurity distribution is flat 21), preferential evaporation of the host metal which causes impurity enrichment of the surface
layer 10), and finally different combination of the transport coefficients
(normal and Soret diffusion, segregation, surface capture rate, ...) which may
be used in the experimental profile fitting procedure. Here we only remind the
reason why segregation effects, which are so abundant in pulse induced transients
in silicon, are not observed in metals under similar conditions. This is due to
the fact that the impurity residence time $\tau_{res}$ at the regrowing interface is much
too long, as compared to the regrowth time $\tau_{reg}$, in order to avoid trapping. As
a consequence, if $D_i$ is the impurity diffusion coefficient just at the regrowing
interface, the condition for segregation to occur:

$$\frac{\tau_{res}}{\tau_{reg}} = \frac{\lambda^2/D_i}{\lambda/v_{res}} = \lambda \frac{v_{res}}{D_i} << 1$$

($\lambda$ being the monolayer characteristic length), is not satisfied under PLI, since
$v_{res}$ is quite high as compared to silicon (this being due to the fact that metals
have higher thermal conductivity and lower latent heat of recrystallization).

Estimates of the ratio $\tau_{res}/\tau_{reg}$ give 8 for Sn in AR (ref. 22) or 62 for Eu in
Ni (ref. 10). We may finally quote the fact 19,5,18,22) that Sb,Cr,Cu,Sn,(and
perhaps Pb) 9), all show an effective segregation coefficient in AR equal to 1,
even though the equilibrium segregation coefficient is either very large (Sb,Cr)
or very small (Cu,Sn). A similar statement holds for Eu and La in Ni 10).

A further support to the absence of segregation in metals under the present
conditions is the fact that no cell structure has yet been observed, this fact again
being related to the high $v_{res}$ value (see Mullins-Sekerka criterion 23)).

Other topics which might be discussed in the present context of transient structure
are defect formation in single crystal liquid phase epitaxy and impurity defect
interaction. As to them and to the related question of metastable solid solutions
see ref. 10 and references therein.
2.2. Higher absorbed energy transients

In these cases, the heat flow equation must satisfy some additional boundary conditions. Denoting by $S$ the instantaneous evaporating front position with respect to a reference frame fixed in the bulk of the sample, then it is

$$\rho H_{\text{vap}} \frac{\partial S}{\partial t} = K \frac{\partial^2 S}{\partial x^2} \bigg|_{x=S}$$ (4)

$H_{\text{vap}}$ being the (constant) heat of vaporization; equation (4) states by itself another Stefan boundary problem. The thermodynamical condition on the surface front velocity $\dot{S}$ is given by one of the following two relationships, stated in terms of the surface temperature $T_S$:

$$\dot{S} = U \exp\left(-M \frac{H_{\text{vap}}}{k T_S}\right), \quad \begin{cases} 
U \exp\left(-M \frac{H_{\text{vap}}}{k T_S}\right), & T_S < T_{eb} \\
\text{as given by eq. (4),} & 
\end{cases}$$ (5a,b)

Here $M$ is the mass of the metal atoms, $k$ the Boltzmann constant and $U$ a velocity of the same order as sound velocity in metals. We shall refer to (5a) and to (5b) as to surface and bulk evaporation respectively. Case (5b) corresponds to ordinary boiling. Ultrashort laser induced evaporative transients may be discussed from the point of view of the so called developed or intense evaporation regime. Such a regime, when heat diffusion may be assumed as unidimensional, corresponds to a conversion of the absorbed energy into heat of vaporization only and is characterized by an evaporated thickness $S_{\text{ev}} \gg \sqrt{2kT_p/\rho c}$ ($T_p$ is the pulse duration). In terms of laser pulse intensity there is a threshold intensity value for achieving the intense evaporation regime, given by $I_{\text{thr}} = (\rho H_{\text{vap}}/(1-R))^{\frac{1}{3}} K/\rho c T_p$, ($R$ is the reflectivity). In Fig. 4 (r.h.s.) we plot such a threshold intensity as a function of $T_p$ for some metals (Al, Ni and Sb); as it may be seen the

![Diagram](image)

Fig. 4 - (r.h.s.) Developed evaporation regime threshold as a function of pulse duration for Al, Ni, Sb together with the PLI region, (l.h.s.) Temperature of the stationary front (abscissa) as a function of incident laser energy (ordinate); arrows refer to critical temperatures (see side table).
PLI region is below threshold for Al and Ni, but for Sb it is just on top of the transition region from a weak to an intense evaporative regime. Notice that for a given $\tau_p$ and for an intensity $I$ above $I_{th} (\tau_p)$, a stationary regime is reached with constant vaporization front temperature $T_o$ and front velocity $S_o$.

$$T_o = M \frac{H_{vap}}{\ln \left[ \frac{\rho H_{vap}}{U/I(1-R)} \right]} \quad S_o = (1-R) I / \rho H_{vap}$$

In the l.h.s. of Fig. 4, $T_o$ is plotted as a function of $I$, for the same metals as in r.h.s., up to their critical temperature ($\approx 8600 \, ^\circ K$ for Al and estimated to be about 4.7 times $T_{eb}$ in the other cases). Qualitatively it is then plausible that PLI may lead to a high surface superheating, provided an adequate pressure prevent surface boiling: while in this respect ambient pressure seems negligible, radiation and recoil pressure might play a role. Plasma formation may also be important. The situation seems quite open to investigation. From the general structure of the heat flow equation solution, it is found that the evaporative/boiling transient is always nested in the warmer stage of the heat transient itself. A parameter which assesses its importance is the ratio between the energy used for it and the total absorbed energy. As an example, in the case of surface evaporation (5a), such a ratio is 2% and 81% for Sb under PLI at 0.41 and 2.1 J/cm$^2$ respectively (7 ns Fwhm, $R = 0.63$). For Al under PLI at 5 J/cm$^2$ (15 ns Fwhm, $R = 0.79$) the same ratio is 6%, corresponding to 100 Å evaporated thickness. If the surface temperature is clamped at $T_{eb} = 2740 \, ^\circ K$ (bulk evaporation, see (5b)), then the ratio rises up to 51%, and about 900 Å boil off.

Experimental study of these transients may be carried out by means of a layered structure, e.g. Pb overlayers deposited on bulk Al. The structure of the transient, with evaporation/boiling located in the early part of the global transient, is well illustrated by experiments using two different energy sources, ruby laser which causes heating up just at the(external) surface of the Pb layer, characterized by a definitely poorer thermal conductivity with respect to the Al substrate, and e-beam which on the contrary may deposit energy over several different ranges well inside the Al substrate, thus offering differentiated heating up opportunities. In Fig. 5, RBS spectra are shown as obtained from a 500 Å thick Pb layer vacuum evaporated over a pure Al matrix, after treating by means of a monochromatic (15 keV) e-beam pulse, 50 ns Fwhm, and at energy densities equal to 0.11, 0.16, 0.43 J/cm$^2$. It is seen that at the lowest energy density Al and Pb mix together and no Pb loss is detectable, at 0.16 J/cm$^2$ both mixing and Pb loss occur, while at 0.43 J/cm$^2$ only Pb loss (i.e. evaporation or boiling) occurs. We suggest the following mechanism for a competition between mixing and evaporation, on the basis of the general structure of the ultrashort heat flow transient. The heat of solution of a Pb gram into Al is (positive, i.e. absorbed and) equal to 236 J/gr and has to be compared with 24 J/gr for the heat of fusion and 863 J/gr for the heat of evaporation. In the actual transient, evaporation or boiling, if any, occurs early and once started consumes much of the deposited energy which then cannot be used for mixing processes.

This is just the case in the hottest transient. On the other hand "colder" transients allow mixing to occur as soon as both Pb and Al are molten. A correlated mechanism may also offer a key to the behaviour of the Pb losses under PLI vs. Pb layer thickness, at a constant energy density (Fig. 6). From the RBS spectra (not shown), it may be seen that at lower thickness almost no mixing occurs, while at thickness ≥ 750 Å both loss and mixing occur: in this case the Al matrix, because of its higher thermal conductivity, acts as a heat pump, which is
Fig. 5 - RBS spectra (1.8 MeV He\(^+\)) of Pb (500 Å)/Al system as evaporated and after different e-beam induced transients (cooperation Padua-Lecce).

Fig. 6 - Pb loss under PLI of a 500 Å thick Pb layer over pure Al (results from Padua GNSM-CNR group).

more effective at lower Pb thickness, thus preventing mixing. In Fig. 6 we clearly see a saturation of the loss mechanism, roughly above 500 Å layer thickness. A possible explanation is that, when mixing has occurred up to the sample surface, Pb evaporation becomes more difficult. We are then faced with the problem of evaporation of a single atom, which has neighbours different from itself. In the
limit of a very dilute alloy this problem may be tackled by means of the macroscopic atom model. Preliminary results, to be presented in a later paper, show that the ratio of the impurity (A) to matrix (B) evaporating flux is

$$\frac{\Phi_A}{\Phi_B} = C_A \frac{\Phi_A}{\Phi_B} \exp \left[ -\left( \frac{H_{A_{\text{in}B}}}{RT_{\text{vap}}} - \frac{H_{B}}{RT_{\text{vap}}} \right) \right]$$

where $C_A$ is the impurity concentration, the dotted fluxes refer to pure metals A and B, while $H_{A_{\text{in}B}}$ is a rather simple function of the surface tensions of A and B and of the heat of solution of A in B. Here R is the gas constant. Actual calculations show that $H_{A_{\text{in}B}}$ for Pb in Al or Al in Pb are very similar: thus it seems that both species may evaporate once they have mixed up to the surface.

3. Conclusions

As a conclusion, in the present work we have discussed the physical processes which allow detecting of a structure in the heat flow transient induced in metal samples by ultrarapid pulsed energy beams. Many of these processes are clearly related to the temporal evolution of the heat flow transient; the situation is quite complex offering interplay of different mechanisms in the two experimental regimes which may be referred to as lower and higher absorbed energies. In the former, transport properties of implanted impurities have by now been studied in many cases: perhaps what is called for now is an attempt to systematize and give a macroscopic foundation to many different facts. The latter regime, which seems more difficult to describe in a detailed quantitative manner, naturally offers the opportunity for a direct comparison between different directed energy sources: this very fact may be of great value, mainly for studying the reflectivity problem under PLI at high energy densities.

Acknowledgements

I would like to thank all the staff of GNSM-CNR groups in Padua and Lecce Universities for their assistance while writing this paper up and for providing useful experimental material, to be published in coming works. A particular thank to V.N. Kulkarni, A. Miotello and D. Guidolin for useful discussions, to P. Meneghelo for cooperation in evaporative transient calculations and to P. Troncon for aid in the problem of preferential evaporation. A warm thank to A. Rampazzo for his drawings.

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