# STUDY OF THE THERMAL EXPLOSION PHENOMENON IN MOLTEN COPPER-WATER SYSTEM

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Abstract-Experimental results are given of thermal explosions in a copper-water system. Measurements are presented relative to transient temperature, pressure, and reactive force with scanning frequencies up to 20 kHz. Results are described of particle size analysis and of thermal explosion debris surface measurements. Photos taken with a high-speed camera (up to 8OOOf/s) as well as pictures from the scanning electron microscope and from metallographic studies complete the experimental material.

A mechanism ofthermal explosion is assumed by which "jets", observed experimentally, of small particles from the bulk mass of the hot material trigger the phenomenon. Sudden phase transformations and combined internal stresses lead to copper fragmentation followed by a vapour explosion.

### **NOMENCLATURE**

- material parameter, equation (1);  $\overline{a}$ .
- inside and outside radius of a sphere,  $b, c$ respectively;
- heat capacity;  $C_p$ ,
- slope of the temperature reading; D.
- diameter of the particle;  $D_{\nu}$
- dilatation:  $\ell$ .
- $f_{\rm x}$ fraction of particles the diameter of which is smaller than indicated diameter  $D_n$ ;
- $h$ . enthalpy;
- Jakob number, equation (12);  $Ja.$
- elasticity and conductivity coefficient,  $K, k,$ respectively;
- enthalpy of phase transformation; L.
- characteristic dimension;  $l_{\rm{r}}$
- $\overline{M}$ material constant, equation (9);
- mass; m,
- $P, P_{ij}$ , force acting on the bottom of the thermal interaction vessel and between old- and new-phase molecules on solidification, respectively;
- $p$ ,  $p_{\text{max}}$  pressure and the maximum value of pressure, respectively;
- $q$ , stress at the boundary, equation (7);
- $T, \overline{T}$ , temperature and mean temperature, respectively;
- $t$ , time calculated from the first particle contact with the bottom of the vessel:
- $U, u$ , velocity and displacement, respectively;
- $V, v$ , volume and specific volume, respectively;
- linear dimension ;
- $\Delta T_{\text{HM, expl}}$ , fast temperature change ("jump") connected with thermal explosion (Figs. 2, 4, 5, Table 1);
- $\Delta t$ <sub>expl</sub>, duration of the temperature jump,  $-\Delta T_{\rm HM, expl}$ ;
- **"1**  linear expansion coefficient;
- $\Delta f$ . increment of  $f$ ;
- $\Delta q$ ,  $= q p$ ;
- $\delta_p$ , diameter of particle  $D_p$  (expressed in  $\mu$ m) related to  $1 \mu m$ ;
- $\Delta t_n$ , duration of the pressure peak (Fig. 5, Table 1);
- $\delta$ , Kronecker delta;
- $\varepsilon_{ij}$ , strain tensor;
- $\theta$ ,  $\theta$ <sub>c</sub>, dimensionless temperatures used in Fig. 12 and in equation (1), respectively;
- $\kappa$ , linear strain, equation (4);
- $\lambda_0, \mu_0$ , Lamé constants;
- density;  $\rho$ .
- $\Sigma$ surface tension ;
- $\sigma$ ,  $\sigma_{ii}$ , stress and stress tensor, respectively;
- $\tau$ , thermometric lag of a thermocouple.

# Subscripts

- CL, cold liquid;
- ctc, contact;
- ex, extremum;
- expl, thermal explosion;
- HM, hot material;
- MS, metastable;
- PhT, phase transformation;
- r, radial;
- S<sub>i</sub> solidification;<br>Sa, saturation;
- saturation;
- SN, spontaneous nucleation;<br>1.2. state before and after ph
- state before and after phase transformation, respectively.

# **INTRODUCTION**

THERMAL explosion is a special case of thermal interaction between a hot molten material and a relatively cold liquid. Explosive thermal interactions occur accidentally, e.g. in the metal industry, and their destructive effects have been described in the literature [20]. A possible occurrence of this phenomenon in the nuclear reactor core was recognized in 1962 during the operation of the SPERT-I test reactor when a considerable portion of the reactor fuel melted and the reactor core was destroyed unexpectedly [ZO]. In all probability

the molten reactor fuel was dispersed in the reactor coolant which gave rise to a thermal explosion. An extensive reactor safety program was initiated to study the mechanism underlying the phenomenon and to elaborate engineered safeguards.

In this study small-scale experiments were performed to gather more information about the thermal interaction of the "molten metal-water systems" and to formulate the physical model of the thermal explosion phenomenon. There is still a lack of detailed mathematicai description of the processes occurring during a thermal explosion. but this should be the next step of thermal explosion studies.

Thermal interaction can be defined as the complex of phenomena which appear when at least two substances differing considerably in temperature, come into close contact with each other and an intensive heat transfer takes place. One substance will be called "hot material" (HM). and the other "cold liquid" (CL). Two main types of thermal interaction can be specified, namely: 1-"normal course", and 2--"thermal explosion" (or "explosive thermal interaction"). A difference between both types is not always quite evident. but considering a particular "hot material-cold liquid system" for which both types of thermal interaction mentioned above arc possible, the time during which the event takes place is one order of magnitude longer in the normal course than in a thermal explosion, which means that thermal explosion is characterized by high heat-transfer rates.

The first type of thermal interaction. i.e. "normal course" is the cases when **the** hot material solidifies in a more or less regular form and no hot material fragmentation is observed. In the experiments performed in this study, the "normal course" began by film boiling, and-via transition and nucleate boiling-resulted in pure convection and ended in an equilibrium state (Fig.  $2)$  [22].

The second type of thermal interaction, i.e. thermal explosion, is characterized by rapid increase in the energy transfer rateduring thermal interaction, by short duration of the event, and by fast (in extreme cases "explosive") displacement of the interacting substances. usually coupled with fragmentation of the hot material. The thermal explosion event can be divided into two processes:  $1$ --*fragmentation* of the hot material, and 2 vapour explosion of the surrounding cold liquid. A full thermal explosion can be defined as an event with both these processes taking place.\*

Fragmentation is characterized by hot material partition or even rupture into relatively small pieces. The processes which lead to fragmentation are not yet completely understood and they will be discussed later in this study.

From previous studies of vapour explosions [10] it has been suggested that the spontaneous nucleation temperature  $[18]$  of the cold liquid must be reached for an explosion to take place. This temperature which is dependent on pressure is characteristic of a particular liquid. In the context of vapour explosions it wiil be called the "cold liquid thermal explosion temperature"  $(T_{\text{CL,exol}})$ .

"Strong" and "weak" thermal explosions can be observed in the experiment. "Strong" or "weak" means here, e.g. that the strong thermal explosion is characterized by larger heat-transfer rates as compared with the weak thermal explosion or that the debris of the strong thermal explosion consist of finer particles (after hot material fragmentation) than thedebris produced in the weak thermal explosion.

A review of the existing hypotheses on thermal explosions  $[7, 20, 22]$  and the experimental data available suggest that by its nature the thermal explosion phenomenon is a complex process and that many effects play a role. The main facts which can be stated from the literature review are:

1. For lack of sufficient experimental information and measurements a complete theory of thermal expfosion cannot be formulated.

2. The hypotheses concerning thermal explosion are more contradictory than compfementary.

3. The processes leading to the fragmentation of the hot material are not fully described and they cannot be predicted satisfactorily before the event.

3. The transplosion phenomenon? may play an important role in the fragmentation of the hot material.

?. The spontaneous nucleation temperature of the colder material may be **an** important factor when considering whether a vapour explosion can arise.

6. The triggering mechanism of thermal explosion is still not understood completely.

The aim of this study is to provide more detailed experimental data concerning the thermal explosion and to answer some of the questions raised above relative to the processes taking place in the hot material during its fragmentation.

### **EXPERIMENTAL TECHNIQUES**

The principle of the experimental technique used in this study was described in  $[22]$ . The measurement technique, however, was improved and adapted to investigations of thermal explosions. The apparatus is shown in Fig. 1. Metal particles of about 0.5-2 g of mass were heated and melted in the levitation coil. The heating process was conducted in air or in inert gas atmosphere (Ar or  $N_2$ ). Then the hot molten particle was dropped into a small vessel filled with about  $7-25$ ml of water at  $10-25$ °C. The measurements were made by standard chromel--alumel thermocouples of 0.5 mm O.D. located in the bottom of the thermal interaction

<sup>\*</sup>This description gives only a general characteristic of thermal explosions. and more details will he presented in the next sections. Some experimental facts make difficult the exact definition of a thermal explosion, e.g. impact hydrodynamic fragmentation of the hot material can result in the "normal course" of heat transfer. On **the other hand. vapour**  explosion can also take place in some situations without hot material fragmentation.

<sup>†</sup>Transition from film to nucleate boiling (with more or less short duration of transition boiling). Transplosion connected with the inverse Leidenfrost phenomenon [13] is considered in  $[23]$ .



FIG. 1. Schematic drawing of the experimental apparatus (all dimensions in mm).

vessel. The thermometric lag of the thermocouples was  $\tau = 6 - 14$  ms.\* The transient temperatures were recorded by means of a high-speed digitizing system with 0.5 kHz scanning frequency for the "normal course" of thermal interaction and with 5 kHz for thermal explosion. The pressure and force were measured by means of quartz crystal gauges (Kistler, 41.7 pC/kgf and  $-14.9$ ) pC/bar) and registered at a scanning frequency of 20 kHz. The debris of thermal explosions were investigated by use of a scanning electron microscope, and the particle size analysed by means of the mesh method. The oxygen content was determined chemically and metallographically. The debris surface area was measured using the nitrogen adsorption technique.

### **RESULTS OF MEASUREMENTS**

Results of the experiments performed in this study concern both the "normal course" of thermal interaction and thermal explosion. The experimentai information consists of: (a) transient temperature measurements in hot material and in cold liquid, carried out during thermal interaction (Figs. 2-5); (b) transient pressure and reactive force measurements for the thermal explosion (Fig. 5); (c) high-speed films of thermal explosion events (Figs.  $6, 7$ ); (d) debris of thermal interactions (Figs.  $8-10$ ), and (e) description of the phenomena observed. The following results are representative of all measurements made in these investigations.

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 $\overline{\phantom{a}}$ 

Transient temperature measurements of the "normal course" allowed a study of boiling at the surface of small copper particles [22] and they were also the basis of investigations into transplosions (Leidenfrost phenomenon) for the molten copper-water system [23]. Temperature and pressure readings of thermal explosions and the corresponding movie pictures, supplemented by other experimental material, allowed the triggering mechanism underlying the thermal explosion to be studied.

In this study, the majority of tests were made with the Cu/water system.<sup>†</sup>

In the thermal interaction zone, the following main phenomena can be observed :

1. Quiet fall in the cold liquid and then "normal course" of heat transfer on the bottom of the thermal interaction vessel.

2. Thermal explosion:  $during~ the~ fall~ in~ the~ cold$ liquid or *on the bottom* of the vessel.

3. Special effects such as hydrodynamic partition, "jets" (or "shots") of small particles from the main hot material mass, and growth of the hot material particle in the form of an "empty shell" ("fungus form").

If the metal particle is melted in an air atmosphere, all the previously indicated phenomena can be observed in a series of tests, which is due to the metal oxide

<sup>\*</sup>A correction of the temperature curve hy means of the first time derivative term  $[19]$  gave an insight into the accuracy of the method. This correction was about 5-10°C (sometimes even more) in the test series. Due to the dificulty of thermocouple calibration in all tests it was not possible to eliminate this error.

t The main arguments were that copper particles offer advantages for the experimental technique developed here and allow study of all basic regimes of boiling [22]. The debris from thermal explosions have a similar shape for the Cu/water system and for the  $UO_2/Na$  system. This suggests asimilar origin and mechanism of thermal explosion in both cases, which, however. were not investigated thoroughly in this study.



FIG. 2. Idealized temperature histories for characteristic courses of Cu/water thermal interaction. normalized for 1 g of the hot material mass.

originating in the particle [22]. If the metal particle is melted in inert gas atmosphere, only the "normal course" and, rarely, very small jets are observed.

In Fig. 2, idealized temperature histories are presented for the characteristic courses of Cu/water- thermal interaction occurring on the bottom of the vessel. The temperature curves are normalized for 1 g of hot material mass and they show temperature histories in the middle of the hot material particle. At point O, the first contact is registered with the thermocouple in the bottom of the vessel. The temperature reading jumps almost immediately to its maximum value at point A. The hot material particle is molten and, at its surface, cooling takes place through film boiling. At point B which is at about 13OO"C, the temperature slope changes and three different temperature readings are possible. Point B seems to record the beginning of solidification for the copper particle with the copper oxide content (CuO content, Appendix 1). The upper curve in Fig. 2  $(\overline{BCEPTIPW})$  illustrates the cooling history for the "normal course". At points C and E (about  $1165^{\circ}$ C and  $1050^{\circ}$ C, respectively), the temperature slope changes again.

At point F, the solidification of the hot material particle is terminated. During solidification in the temperature range between about 1300 $\degree$ C and 1100 $\degree$ C, "jets" ofsmall particles can be observed. Sometimes, the "jet" solidifies during its expulsion.\* The "solidified jet" (Fig. 8d) suggests that there exists a high heat-transfer rate in the expulsion phase, which results in its solidification, i.e. the "local liquid-liquid contact" between molten hot material and cold liquid is conceivable. A "jet" can be more complex in its shape and it is possible that a "sequence of jets" occurs. The split at the base of

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the jet shows an empty form of the particle and of the jet in this region (Fig. 8e).

Film boiling is completed as soon as transplosion takes place (Leidenfrost temperature, point L in Fig. 2). Transplosion has random character in the test series involving molten copper and it occurs in the range of temperatures between 160 and 750°C for water at about  $20^{\circ}$ C and at atmospheric pressure [23]. Then nucleate boiling (sometimes also transition boiling. point P in Fig. 2) and pure convection of nonboiling water take place. The measured temperature history for the normal course is shown in Fig. 3.

The temperature history for thermal explosion (Fig. 2, curve  $\overline{ABC}$   $\overline{C' E' F' L' P' W'}$  exhibits a negative "temperature jump" of about  $-100^{\circ}$ C at point B (Table 1). Then, similar phases as for the normal course can be recognized however, with duration shorter by one order ofmagnitude compared to the "normal course". At the moment represented by point B, thermocouples placed in water, Smm from the hot material particle, record positive temperature jumps and the high-speed film shows thermal explosion. A detailed study of the highspeed movie pictures reveals the existence of an "initiating jet" before thermal explosions. There was a delay of about  $1-10$  ms between the generation of this jet and thermal explosion (Figs.  $6, 7$ ) [22]. The time of this delay corresponds well to the duration of the " $-\Delta T$ -jump" registered at point B for the thermal explosion event (Fig. 2). The respective temperature jump of the temperature reading in water is related to the increased heat-transfer rate and it may again be the result of the "local direct liquid-liquid contact" taking place between the hot material and the cold liquid.

Fragmentation of the hot material particle seems to start between points B and C (Fig. 2). It seems that the "initiating jet" triggers the particle growth and this growth triggers the next fragmentation and vapour explosion (Figs. 6, 7). After fragmentation, a "thermal

<sup>\*</sup> These "jets" can be called "macrojets" as compared with the solidified "microjets" observed in small debris formed in strong thermal explosions (Fig. 9).



FIG. 3. Cooling history of the "normal course" of heat transfer. Melting of the copper particle in air (sample 7-02) and in inert gas atmosphere (sample 20-14). respectively.

explosion zone" is formed which consists of the hot material pieces and the vapour-water mixture.

The temperature history for an "empty shell" is illustrated by the intermediate curve in Fig. 2. Some similarities exist between this curve and the "thermal explosion curve". At point B, a negative "temperature jump"can be seen which is equal to about half the jump for thermal explosion (Figs. 2.4). Then, the temperature reading resembles the temperature reading for the "normal course". The growth of the hot material particle in the form of an "empty shell" or in the "fungus form" is observed between points B and F, i.e. when the hot particle is partly solid. Large temperature fluctuations were registered between points B and C. "Jets" can also be seen for such course of thermal interaction. The decrease in the cooling period of the hot material as compared to the "normal course" corresponds to an increase in the particle surface.

The temperature history of the copper particle previously molten in inert gas atmosphere does not exhibit the bending points B and C (Fig. 2). and solidification begins at point E (Figs. 2, 3).

The foregoing results show the occurrence of internal processes during thermal explosion, the role of the hot material components, and the role played by the heattransfer rate in the system. In a series of tests, a copper pin of 1-1.35 mm O.D. was used which should increase the heat-transfer rate between the hot copper particle and water.\* This pin was located in the bottom of the vessel and it played the role of an "artificial jet", provided the pin was properly covered by the molten hot material particle at the bottom of the vessel (Fig. 1). Molten hot material particles dropped down and deposited at the pin bottom. The pin should be "sufficiently long and thick" to bridge thermally the hot material with the liquid. The result was that the frequency and energetics of thermal explosions in test series increased (from about  $10\%$  in previous tests to about  $40\%$  for the tests with the "artificial jet").<sup>†</sup> The increased energetics of thermal explosion resulted often in the destruction of the plexiglass vessel in which the event took place (this was never observed in the previous tests [22]). Temperature readings for thermal explosion with the "artificial jet" are similar to the corresponding readings of thermal explosion with a

<sup>\*</sup> Copper alloys, as e.g. Ag +Cu-alloy, were also used to study the role of the hot material heterogeneity. Preliminary results show a violent thermal explosion for the  $(Ag+Cu)/$ water system.

tThe simple experimental technique implied a more or less statistical character of the experimental results. High temperatures in the levitation coil and a rather primitive current shut off system made difficult the exact reproduction of the initial conditions before thermal explosion. When, for example. the initial temperature was too high, the "artificial jet" melted before point B (Fig. 2) was reached during the cooling history of the hot material particle.



**FIG. 4.** Cooling **history or the** "empty **shell"** particle (sample **37-07) and 01 thermal explosion (sample 40-04), respectively which were recorded by thermocouple No. I.** (Arrows Nos. 2 and 3 indicate the slope changes of thermocouples Nos. 2 and 3, respectively.) Copper pin **of** I mm O.D. was used as an "artificial jet".

"natural jet" [22]. In Figs. 4 and 5 temperature histories are presented for thermal explosion and for the "empty shell", which are applicable to thermal interactions with "artificial jets". They provide material complementary to the experimental results given in [22].

The pressure measurement indicates a short-term peak  $(0.3-1 \text{ ms})$  of several bars  $(7-20 \text{ bars or more})$  at the moment of thermal explosion (Fig. 5). The thermal explosion zone is, however, an open system and it releases quickly the high pressure. The pressure gauge registers some very weak change occurring several milliseconds ( $\sim$ 7ms) before the pressure peak. This weak pressure change may be related to the "triggering jet" of thermal explosion. The force measurements (Fig. 5) support the foregoing observations. However, the elasticity of the apparatus has an influence on the results.

The debris of thermal explosions consist of both regular spherical and "shattered" particles. Spherical

particles are usually larger and the microscopic investigation often reveals their "empty form" as well as cracks (Fig. 8a, b). A thin shell can be noticed at their surface (Fig. 8c). In Fig. 8d, the "solidified natural jet" is shown. At its base, a crack can be seen and a second jet (or small spherical particle) seems to penetrate it. The surface of the jet shows some sort of solidified whirls (Fig. Sf) and differs from the main particle structure (Fig. 8c, d). Irregular "shattered" particles from weak thermal explosions usually have a complex shape (Fig. 9a). Microscopic investigations yield relatively large flat surfaces which seem to be grain surfaces, and a kind of "micro-jet" (Fig. 9b, d) or "pressed out" small sphere (Fig. 9c, d). Such "micro-forms" could perhaps result from the action of intergranular pressure. Debris of strong thermal explosions consist also of "powder-like" particles of less than  $10 \mu m$  size (Fig. 9e, f). Very small spheres and small "shattered" particles can be distinguished.



FIG. 5. Temperature, pressure and force-readings for thermal explosion (sample 42-07). Thermocouple No. 2 touched the surface of the hot particle. Copper pin of 1.2 mm O.D. was used as an "artificial jet".

The chemical analysis results in a mean oxygen content between 1.15 and  $2.4\%$  in the test series. But the particles of less than  $10 \mu m$  size contain more oxygen (up to  $4.6\%$ ).

In Fig. 10, micrographs are presented of spherical and "shattered" particles. Spherical particles have cavities often larger in volume than shrinkage cavities  $(Fig. 10a)$ . The particle structure is hypereutectic and it is composed of coarse and fine primary copper oxide dendrites and of a fine eutectic matrix (Fig. lob). At the surface of the spherical particle, a fine eutectic inhomogeneity (looking like a "jet-base") can be seen (Fig. lOa, c, d). The absence of dendrites and the presence of a fine structure suggest a fast solidification process.

"Shattered" particles are complex in their nature (Fig.

10e). The particle body has an inhomogeneous hypereutectic structure (Fig. IOf-h), and no dendrites can be found there. Relatively small hypoeutectic particles are dispersed in the particle body. They consist of copper dendrites in a fine eutectic matrix.

Particle size distribution curves in a differential form are presented in Fig. 11. The analysis of measurements yields two maxima of the weight contribution for particle diameters of about 50–80  $\mu$ m and 100–400  $\mu$ m, respectively. This fact corresponds well to the existence of irregular and spherical particles and for these particles the total distribution curve seems to be a sum of two partial distribution curves. The mutual relation of the maxima can be used to define the "strong" and "weak" thermal explosions. The maxima are different



FIG. 6. Sequence from a film showing development of a double thermal explosion (the weak one taken at a small distance below the water surface, and the strong one taken at the bottom of the vessel) (sample 44-04).

and they may be characteristic of various hot material; cold liquid systems. This, however, calls for further investigations.\*

The total debris surface of a strong thermal explosion which is calculated from particle size analysis, is about  $0.3-0.5 \times 10^{-2}$  m<sup>2</sup>. Adsorption measurements in nitrogen indicate about  $0.5 \text{ m}^2$  of total surface. The discrepancy between both results confirms the complex porous form of the debris.

### DISCUSSION OF THE EXPERIMENTAL RESULTS

The following conclusions can be drawn from the experiments made on the Cu/water system :

1. At the moment of thermal explosion some determined thermal conditions exist. For molten copper containing oxide a temperature range close to 1300°C was registered at the beginning of the thermal explosion in water of about  $15-20^{\circ}$ C.

2. Some internal processes occur in the hot material during the thermal interaction. In the experiments performed in this study, these processes were related to the heterogeneity of the hot material and resulted in "jets" ("macro-" and "micro-jets") jnto the cold liquid. The occurrence of such "jets" suggests the existence of internal forces which are able to eject small amounts of molten material from the whole hot material mass. However, the origin of the "macrojet" and "microjet" may be due to different causes. The growth of the hot material particle as an "empty shell" (e.g. Cu/water thermal interaction) or as a "coral" (e.g. for Sn/water thermal interaction) indicates also the existence of some internal processes.

3. The internal processes occurring in the hot material may trigger vapour explosions. The observation of the "initiating macrojet" on high-speed pictures supports this conclusion.

These arguments can be completed by the following remarks :

In the experiments performed in this study, the initial temperature of copper before thermal interaction was

<sup>\*</sup> Recalculation of the particle size distribution for  $UO_2/Na$ experiments (results e.g. from [17]) indicates the existence of two similar kinds of maxima for particles  $130-700 \mu m$  and I, l-5 mm in diameter.



FIG. 7. Sequence From a film showing development of a strong (case a. sample 42-07) and of a weak (case b. sample 44-07) thermal explosion, respectively.

about 1400°C for thermal explosion during the particle fall in the water [22], and about 1650°C for thermal explosion at the bottom of the vessel. A temperature range can be determined in which thermal explosions may occur. Such observations agree with the literature data, and for example temperature ranges of about 250-700°C [5], and of about 400-500°C [11] were registered for Sn/water and Pb/water systems, respectively.

The available literature data are limited to the initial hot material temperature before thermal interaction.

Experimental evidence [l] indicates that the hot material is entirely or partly molten during fragmentation. This conclusion is not fully supported in the literature by any temperature or other measurements. On the other hand, in some theoretical considerations [6, IS, 211, part of the hot material is assumed to be solid during the fragmentation process. Mathematical models used in such considerations are, however, based on the assumptions which do not correspond to the real physical situation. The examination of thermal explosion debris suggests that part of the hot material was molten at the moment of fragmentation producing small spherical particles (second maximum in Fig. 11) or "microjets".

It can be stated that at the moment of the thermal explosion, the hot material must have a temperature within a determined range of temperatures characteristic for the given hot material. Hot material fragmentation is the main process relevant to thermal explosion. The temperature at which the hot material undergoes the fragmentation process will be called the *hot material thermal explosion temperature*  $(T_{HM, expl})$ . This temperature can be recognized as the point at which the negative temperature slope increases abruptly on a temperature reading of the hot material for a thermal explosion history, (It can also be related in time to the sudden growth of the hot materiat on a film sequence.) Temperature  $T_{\text{HM, expl}}$  corresponds to point B in Figs. 2, 4, 5 and in Table 1 in most cases which were observed in



FIG. 8. Microscopic study of the spherical particle and of a "macro-jet" origination (sample 43-14).

this study, and occasionally to point  $C$  (Table 1. Sample No. 37-04). Points B and C can be related to lines B and C in Fig. 14 in dependence on the oxide content in the hot material.

The nature and temperature of the cold liquid also plays a role with respect to thermal explosions. Above some initial cold liquid temperature. thermal explosions either do not occur (e.g. at  $\sim 60^{\circ}$ C for the Sn/water system [3]) or only weak explosions are observed [22]. The total surface arca of the fragments depends on the initial cold liquid temperature  $[5, 11]$ . For the Cu/Na system, only fragmentation takes place without vapour explosion [2].

The temperature field in hot material and cold liquid

and the type of contact between them at the moment of thermal explosion or just before the event are not known exactly. "Direct liquid -liquid contact" is often postulated  $[1, 2, 10]$ . It is, however, not precisely defined. e.g. the contact area and the duration of the direct contact are not indicated. The "direct contact temperature" ( $T_{\text{etc}}$ ) is usually calculated with the following simple formula:

$$
\theta_c = a \tag{1}
$$

where  $\theta_c$  and material parameter  $\alpha$  are defined as follows:

$$
\theta_{\rm c} = \frac{T_{\rm ctc} - T_{\rm CL}}{T_{\rm HM} - T_{\rm ctc}}, \qquad a = \sqrt{\left[\frac{(k\rho c_p)_{\rm HM}}{(k\rho c_p)_{\rm CL}}\right]}.
$$
 (2)



FIG. 9. Microscopic study of thermal explosion debris. Formation of a "micro-jet": photos a d (sample 39-07). Small particles below  $10 \mu m$  O.D.: photos e f (sample 32-07).

Formula (1) is only valid for two semi-infinite bodies having constant thermal properties (of course it is only a calculational restriction). In Fig. 12 the "dimensionless direct contact temperature"  $\theta$  is given as a function of a, if  $T_{HM}$  and  $T_{CL}$  are kept constant. This simple calculation shows that, if such direct contact exists, a negative temperature drop  $-\Delta T$  takes place in the hot material, amounting to about 50, 400. 350°C for Cu, Cu<sub>2</sub>O and CuO, respectively (Fig. 12). So, the direct contact temperature considerably exceeds the critical temperature of water. and this fact excludes the "direct contact" in the simple sense, A vapour film is formed

around the hot material particle. It pulsates irregularly [22] and results in fluctuations of the heat transfer rate. So, the *hot material surface temperature* ( $T_{\text{HM, etc}}$ ), and the cold liquid surface temperature  $(T_{CL, ctc})$  can be introduced. They depend on the time in real situations and change with the temperature difference between the *mean hot material temperature*  $\overline{T}_{HM}$  and the *mean cold liquid temperature*  $T_{CL}$ .

Various hot material/cold liquid systems will react in different ways depending on whether  $T_{CL, \text{ctc}}$  is greater or less than  $T_{CL, expl}$  and whether  $T_{HM, cle}$  is greater or less than  $T_{HM, expl}$ .



FIG. 10. Metallographic study of weak thermal explosion debris.

# HYPOTHESIS OF THERMAL EXPLOSION FOR THE MOLTEN COPPER/WATER SYSTEM

Full thermal explosion is a combined process of hot material fragmentation and fast cold liquid vapourization (vapour explosion). It was shown **in** the previous section that some temperature conditions should be fulfilled, before the full thermal explosion occurs, i.e. some determined temperature relations (temperature field) should exist in the thermal interaction zone between the hot material and the cold liquid. It is hypothesized that thermal explosion takes place, if this temperature field is suddenly destroyed at a "sufficient speed" and the phase is transformed quickly. For the

molten copper/water system, the following development is suggested (Fig. 13):

1. Initial phase of contacting between the hot and cold substances and beginning of thermal interaction. In the small-scale drop experiments performed in this study. the vapour film appeared around the hot material particle during this phase. This phase was usually instable and related to oscillations of the vapour film thickness.

2. "Skin effect" and sudden local change of the temperature field in the thermal interaction zone. In these Cu/water drop experiments, this change of the temperature field was brought about by a "jet" ("natural"



FIG. 11. Particle size distribution of thermal explosion debris (Cu/water system). The vertical arrows show diameter  $D_p$  of  $\Sigma \Delta f = 50\%$ .

Table 1. Characteristic measurement results for strong thermal explosions of the copper/water system

				Sample Par- Water   Characteristic temp. (Fig.2), $^{\circ}$ C   Time of cooling (Fig. 2), sec													$p_{max}$		$Re -$		
No.	$\text{tic1}\sqrt{\text{col}}$ mass 8.	ml		$T$ gmp <sup><math>\cdot</math></sup> HM, $\mid$ <sup><math>\cdot</math></sup> A $ C $ c $ exp1$		$T_B$	$T_{\rm C}$	$T_{C'}$	$ T_{\rm E} $	$\vert \text{\ensuremath{\tau_{\scriptscriptstyle\text{L}}}}\vert$	$\Delta t$ <sub>exp1</sub> $t$ <sub>AB</sub> $t$ <sub>BC</sub>			$\mathfrak{r}_{\texttt{BC}}$ $\mathfrak{r}_{\texttt{CF}}$		$t_{\rm{EF}}$	$ $ t $_{\rm AL}$	$t_{LW}$	$bar$ $\sigma$ <sub>p</sub>	Imsec	lmark에
$7 - 03$	$-.57$				20 20 1287 - 1300 1287										. 246						1
$113 - 35$					$\sim$ 55 $\{25\}21$ 1297 $\sim$ 1450   1297				1022				$1.759 \times 0.004$								$\mathbf{1}$
$ 37 - 04 $					1.101 15 16 1114 - 1500 1291 1114						$\{1069\}$ 753 < 006 $\{075\}$ 043					.008 .006 .165 .087					$\overline{z}$
$139 - 07$					1,073 15 22 1228 - 1500 1228				994 438				$1.710$ $1.030$ 1					$.026$ , $.969$ , $.016$			3
$140 - 04$	.828										.024. [742. [742. [140] 712. [203. [204. - 1037] 71005 71175 7126 71175 7126 71299 - 1650 7129 71175										
$141 - 09$	1.354				7   14 $\approx$ 1400   > 1650 $\approx$ 1400				$1094$ 316			.365						.028.544.026			
$ 42 - 07 $	1.226										7   14   1313   > 1500   1313   1222   1139   1050   418   < 004   449   004							$\vert .112 \vert .095 \vert .807 \vert .030 \vert .10 \vert$		1. S.	4
$43 - 04$	1.350										7   14   1308   1309   1309   1309   1309   1309   1410   1410   1411   1421   1422   1430   1450   159 $10^-$									1.3	
$144 - 04$											1.4 1.91 1077 1092 0.037 1944 12 0.05 = 1.408 1.412 1.060 0.037 1.692 1.994 1.414 1.578 1.578 1.692 1.578 1.692 1.590 1.590 1.590 1.590 1.599 1.699 1.699 1.590 1.590 1.590 1.590 1.599 1.699 1.590 1.590 1.590 1.590 1.590 1										5
$44 - 05$	1.558										7   14. 14   1226   1230   1231   1032   1043   1053   1053   1054   1054   1054   1056   1057   1057   1057										
$144 - 09$											1008. [787. [100] 1010] 1,571 [100] 1154 [1067 [204] 126 [1067 [204] 1786] 1787 [1008 [204] 1173 [1173 [1173 ] 1173 [1173 ] 1173 [1184] 1008			$10^{-4}$							

 $\frac{1}{10}$  Early stage of experiments;  $\frac{2}{3}$  Explosion on line C Fig. 14;  $\frac{3}{10}$  relatively long;  $\frac{4}{3}$  oxide content 1.15\$ W. ce below the water surface (Fig. 6). Total debris surface after thermal explosion .5026  $m^2/g$ .



FIG. 12. "Dimensionless direct contact temperature"  $\theta$  as a function of the constant a of thermal properties, if  $T_{HM}$  and  $T_{CL}$  are kept constant.



FIG. 13. Schematic sequence of events for Cu/water thermal interaction.



postulated that the "natural jet" was due to pressur- and if it occurs in the temperature range of phase ization of the hot material mass upon solidification of transformation of the hot material. local supercooling a thin surface oxide layer.  $\blacksquare$  of this material is conceivable and fast phase trans-

tation begins upon local fast phase transformation and next step. This does not mean that each "jet" results in an action which results in the growth of the hot thermal explosion, but only that which produces a material particle. Fast phase transformation (solidifi- "sufficient" cooling rate in the "proper range" of temcation) upon fast cooling is assumed to be the cause of peratures Experiments with "artificial jets" also conthe growth and of the fragmentation process. firm this explanation.

4. A vapour explosion occurs if the amount of heat During phase transformation, the physical properties transferred to the cold liquid is sufficiently large and such as density. specific heat, thermal conductivity, are the spontaneous nucleation temperature  $(T_{SN}$  or subject to a change. Slow and fast phase transfor- $T_{\text{CL-cap}}$  of the liquid is exceeded. In these Cu/water mations can be distinguished. The slow phase transdrop experiments, it was caused by sudden "direct formation is characterized by the continuous growth contact" and/or sudden increase of the contact surface of a "new" phase and a smooth change of the crystalline between both hot and cold substances after hot structure of the body considered. With a sufficiently material fragmentation. high cooling rate, an abrupt change occurs of the

and thermal conditions prevailing immediately before thermally. thermal interaction and on the mass of substances The existence of such phase transformation stresses subjected to thermal interaction. Above a value of the can be predicted theoretically [16]. The result of the Weber number\* hydrodynamic partition, for example, quasi-stationary elastic state analysis during fast phase takes place or, for a quite different relation of the hot transformation is that a relative interphase pressure material and cold liquid mass (if  $m_{HM} \gg m_{CL}$ ), entrap-  $\Delta q$  [Appendix 2, equation (8)] exists between the "old" ment of the cold liquid is possible. In these small drop and "new" phases. It is negative for the substances experiments, it was found that these initial contact which have a negative volume effect on phase transeffects play a secondary role during thermal explosion. formation. For a sphere this pressure is equal to zero Thermal explosion at the bottom of the vessel occurred at the sphere surface and it decreases to its minimum, over some time  $(0.1-1 s)$  after the first contact of both  $M$ , in the centre of the sphere [Appendix 2, equation hot and cold substances (gold particles split hydro- (9) and Table 2]. The sphere will rupture, when the dynamically very easily but they have never exploded hot material strength is overcome for a given radius thermally). during fast phase transformation. The phase trans-

When the temperature of the hot material decreases down to the temperature range of copper oxide solidification. 'jets" of small particles are observed. The physical mechanism producing "jets" may be:

The copper oxide component which first solidifies at the surface of the hot material,<sup>†</sup> promotes the formation of a thin solid shell. The shrinkage of this shell may cause instantaneous pressurization of the hot material and may result in the generation of jets. This is a "skin effect" and it can subsequently be overcome by shrinkage of the inner hot material mass during the slow solidification process. The expansion coefficients **I** Cu+M Cu+Cu<sub>2</sub>0 cu+Cu<sub>2</sub>0 field in the thermal interaction zone are not known exactly. but the observation of 'jets" ("macro-jets") in the experiments performed within the temperature range marked by the beginning of solidification (Fig.  $\frac{1}{6.5}$  1.5  $\frac{1}{2.5}$  1.5  $\frac{1}{2$ **05 IO 15 20 25** 2) as well as photos of the surface shell (Fig. 8) are in

FIG. 14. Part of the copper oxygen phase diagram (valid for A "macro-jet" may cause some kind of local "direct quasistatic changes) [8]. contact" between the hot and cold substances. and then, a sudden local increase in the cooling rate of the or "artificial") which bridged the vapour film. It is hot material. If this cooling rate is "sufficiently high" 3. Fragmentation of the hot material. Fragmen- formation in such local supercooling zone may be the

5. Thermal interaction in the mixture consisting of specific volume during phase transformation. This may the hot material fragments, vapour and cold liquid. result in stresses possibly exceeding the hot material The initial phase depends both on hydrodynamical strength, which means that the process is controlled

<sup>\*</sup>We =  $\rho l U^2/\sum$  where  $\rho$ , *l* means the density and characteristic dimension of the substance, respectively, and  $\sum$ ,  $U$   $+$  This can be the hot material component which has a is the surface tension and relative velocity, respectively, higher solidification point than the wh is the surface tension and relative velocity, respectively, between the hot material and the cold liquid. in another hot material/cold liquid system.

formation zone for the sphere may be very thin for "sudden" phase transformation (e.g.  $x_{PhT}/x \approx 0.996$ ) for Cu<sub>2</sub>O/Cu, if  $\Delta q = 10^8$  N/m<sup>2</sup>). If a supercooling zone consists of a mixture of "old" and "new" phase molecules (or grains), some kind of "repulsion forces" may be formed between these molecules. The process is violated when the hot material is a mixture of substances having different solidification points (e.g. copper-copper oxide) due to the increase in the  $M$ value (Table 2). If the fast solidification zone is curved. expected which is the necessary condition for fragmentation of the hot material. For cooling rates in the vicinity of this critical value, other effects (e.g. violent release of dissolved gas within the molten hot material [9]) may play a role and result e.g. in an "empty shell" form of the hot material particle. However, more experimental results are required to check this explanation.

After hot material fragmentation vapour explosion occurs if the spontaneous nucleation temperature of

	Quantity Substance		Cu	Cu <sub>2</sub> O	lCu0		
$T_S$	$\circ$ <sub>C</sub>		1065	1235	1336 or 1447		
$\mathcal{O}$	$1_{kg/m}$ <sup>3</sup>	solid	$8320(1083^{\circ}C)$	6090-6260 <sub>(~20</sub> °C) 6315 <sub>(1000</sub> °C)			
		molten	$7990(1083^{\circ}C)$				
$\kappa$			$-.0204$	$\cdot$ .076 (Cu <sub>2</sub> 0/Cu)	$-.065$ (CuO/Cu)		
$c_p$	kJ/kg degC	solid	$.50_{(1083^{\circ}C)}$	$.56_{(+900}$ <sup>o</sup> C)	$\cdot$ <sup>59</sup> (~1300 <sup>o</sup> C)		
		molten.	.42	$\sim$ 1			
k	W/m degC		$310(1083^{\circ}C)$	$4.51_{(*500^{\circ}C)}$	$3.35_{(-500}$ °C)		
L	kJ/kg		209				
$\mathbb{M}^{\preccurlyeq}$	$N/m^2.10^{-8}$		$-26$	$-96$ (Cu <sub>2</sub> 0/Cu)	$-82$ (CuO/Cu)		

Table 2. Selected thermophysical properties of copper and its alloys  $[8, 12]$ 

Approximate values because of the limited data available.

the interphase forces are not equalized and may subsequently act upon the surroundings. The local fast solidification zone resulting from the local "direct contact" through a "jet" is complex and the boundary is formed by a curved surface. It is assumed that the action on the surroundings. due to the fast phase transformation zone, leads to the growth and then to the fragmentation of the hot material particle. The development of thermal explosions seen from the sequence of movie pictures shows that following a "jet", the hot material particle seems to grow with subsequent disappearance of the vapour film (Figs. 6, 7).

Because of fast particle growth, the vapour film may be broken more or less over the whole surface of the hot material particle, possibly resulting in an extension of "direct contact" on the surface. Such contact may entail fast phase transformation in the hot material mass and it may cause its fragmentation.

For real physical situations the dependence on time should be taken into account, and the cases between slow and fast phase transformations should be considered. A critical value of the cooling rate may be

the cold liquid is exceeded. By contrast, if this temperature is not reached, the hot material fragments are quickly cooled without explosive effects. The latter case is usually observed in experiments with hot material/sodium system.

Thermal interaction of the heterogeneous mixture formed after the fragmentation of the hot material is a more complex process which depends on many factors, such as the distribution of the hot material fragments, their thermodynamical state, relative velocities, etc. and it can only be predicted statistically. Temperature measurements in such a mixture show similar phases for cooling as for the "normal course", but with a duration which is shorter by one order of magnitude for the Cu/water thermal explosion. The Leidenfrost point is usually situated close to the upper limit of the temperature range in which transplosion may occur because of a strong turbulence in the thermal explosion zone [23].

Experimental facts such as the occurrence of 'jets", the time delay between the "triggering jet" and thermal explosion, the two types of particles found in thermal explosion debris, metallography of spherical and "shattered" particles, support the foregoing hypothesis. The "shattered" and spherical particles may originate from the fast solidification zone and from the "pressed out" regions, respectively. Simplified thermal calculations result in a total mass of "shattered" and spherical particles, respectively, which is similar to those derived from the particle size distribution.

# **CONCLUSIONS**

The results of this study can be summarized as follows :

1. Thermal explosions were realized experimentally and investigated for the copper/water system. Two conditions were found in which thermal explosions may occur. namely a short distance below the water surface and at the bottom of the vessel when the vapour layer (or bubble) already covers the hot material surface.

2. The experimental results (temperature and pressure plots, high-speed films, results of debris examination, observations) yield information about the phenomena which take place before and during thermal explosion. "Jets" of small particles from the hot material mass were observed and the temperature was measured at which thermal explosion begins. The temperature corresponds to the solidification point of copper oxide. This led to the conclusion that some internal processes take place in the hot material and the hot material components with different solidification points play an important role. Experiments with "artificial jets" yield more information about the triggering mechanism of thermal explosion.

3. Vapour explosions take place if the spontaneous nucleation temperature of the cold liquid is exceeded. It was demonstrated that internal processes occurring in the hot material may lead to vapour explosion in spite of the fact that the vapour film separates hot material from the cold liquid.

Special cases of separate hot material fragmentation or vapour explosion of cold liquid may take place, if some necessary temperature conditions are fulfilled.

4. A hypothesis was developed of thermal explosion for the copper/water system in which fragmentation and vapour explosion are specified as the main processes of full thermal explosion. Fast phase transformation (solidification during fast cooling) of the hot material is supposed to be the cause of fragmentation.

The fast cooling rate and sudden change of the temperature field in the thermal interaction zone may result from the "jet", The "jet" may bridge the hot material and cold fiquid over the vapour layer. The generation of a supercooling zone in the hot material and sudden phase transformation are conceivable. This results in expulsion forces acting on the surroundings and causing fragmentation of the hot material. "Direct contact" and the increased surface for thermal interaction trigger the vapour explosion of the cold liquid.

5. Besides the foregoing results the experimental technique developed in this study offers advantages if "normal" heat transfer is investigated within a broad range of temperatures.

The foregoing description of thermal explosion is based on the experimental results obtained in this study. A different course of thermal explosion is possible for different physical conditions. The dominating processes, i.e. fragmentation or vapour explosion, determine the character of the thermal explosion. Fragmentation is characterized by high interphase pressure and small volume effects. Vapour expIosion is accompanied by a large increase of volume, i.e. if a given amount of cold liquid is enclosed in the hot material, the fast increase of the cold liquid temperature may also cause rapid vapour explosion. The thermal interaction of relatively large masses of hot and cold substances may be combined with other effects, such as hydrodynamical partition, mixing of interacting substances, entrapment and entrainment, which can influence the development of the phenomenon. Also a different mechanism may lead to destruction of the vapour film and produce "direct contact" of hot and cold substances. But fast phase transformation seems to play the important role in all cases and it triggers the energetics of thermal explosion, if thermal interaction of molten substances with a relatively cold liquid takes place.

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#### **APPENDIX 1**

### **Thermophysical Properties of Copper**

The properties of copper and its alloys are well known [8]. The thermophysical properties used in this study are briefly summarized in Table 2. In these experiments. the technically pure copper particles were melted in air or inert gas atmosphere by the levitational technique. Copper particles melted in air contained up to about 2.5% oxygen  $\lceil 22 \rceil$ . The copper oxide was distributed along the radius of the particle. The temperature readings exhibit some characteristic bending points which correspond to the characteristic points of the copper-oxygen phase diagram (Figs. 3. 14). The technique used in these experiments allowed simple realization of the thermal explosion. but made difficult the exact reproduction of initial conditions. Varying oxygen contents in test series resulted in scattering of points B and C (Fig. 2) in the process of cooling of copper particles.

# **APPENDIX 2**

# Application of Elastic States Theory to Phase Transformations

The first order approximation of the phase transformation stresses is obtained from the analysis of elastic states during phase transformations. If a simple closed system. a pure substance consisting of two phases. and only equilibrium states are assumed, the following Clausius-Clapeyron relation, based on the Maxwell relations  $[14]$ , can be derived:

$$
(h_2 - h_1)/(v_2 - v_1) = T dp/dT
$$
 (3)

where *h*, *v*, *p*, *T* are the enthalpy, specific volume, pressure, and the absolute temperature of the system. respectively. Subscripts 1 and 2 mean the coexisting phases before- ("old phase") and after phase transformation ('new phase"), respectively. Equation (3) links three commonly measured quantities, namely the "pressure temperature" relation for two phases in equilibrium, the latent heat  $(h_2 - h_1)$ , and the volumetric change  $(v_2 - v_1)$  corresponding to phase transformation. The Clausius-Clapeyron relation yields the formula

$$
(\rho_1/\rho_2) - 1 = (\rho_1(h_2 - h_1)/T)(dT/dp) = 3\kappa
$$
 (4)

 $\overline{1}$ 

where  $\rho$  means the density, and  $3\kappa$  is the volumetric strain related to phase transformation in the neutral state, and  $\kappa$ is the linear strain for  $\kappa \ll 1$ . Assuming linearity, the stressstrain relation for the new phase can be written in the following form:

$$
c_{ij} = 2\mu_0 \varepsilon_{ij} + (\lambda_0 e - 3K(\kappa + \gamma T))\delta_{ij}
$$
 (5)

where *i*,  $j = 1, 2, 3, \sigma_{ij}$  means stress tensor;  $\mu_0$ ,  $\lambda_0$  the Lame constants,  $K = \lambda_0 + 2\mu_0/3$ ,  $\varepsilon_{ij} =$  strain tensor.  $e = e_{kk}$  the dilatation.  $\gamma$  the coefficient of linear expansion, and  $\delta_{ij}$  the Kronecker delta. Equation (4) is a generalization of the constitutive relation of thermoelasticity [16]. The form of equation (4) illustrates the complexity even of the elastic problem, if other effects than only phase transformation stress are taken into consideration. Assuming that the fragmentation process takes place during solidification of the hot material,  $\kappa = 0$  can be written for the molten phase ("old phase").\*

At the phase boundary between the liquid and solid phases in the hot material, the continuity of displacements  $u_i$  ( $i = 1, 2, 3$ ), and of normal and shear stress components should be maintained.

For the Cu/water drop experiments, the hot molten particle submerged in the cold liquid can be described by a symmetrical phase transformation problem in a sphere,  $0 \leq x \leq 1$ . In this case, the displacement equation has the following form [4] :

$$
u_{,xx} + 2u_{,x}/x - 2u/x^2 - \rho \ddot{u}/2\mu_0 = 0 \tag{6}
$$

where comma "," means differentiation on the space coordinate x, and point  $\ddot{\ }$ " means the differentiation in time. For "abrupt"' phase transformation, one can put  $\ddot{u} \equiv 0$  (quasi-stationary state). This assumption is valid, if high cooling rates exist during phase transformation ("fast solidification").

Assuming that the hot material particle is a hollow sphere.  $b \leq x \leq c$ , with the boundary radius of phase transformation  $x_{\text{PhT}}$  (i.e.  $b \le x_{\text{PhT}} \le c$ ) and supposing an "old phase region", if  $x \in [b, x_{PhT})$  and a "new phase region", if  $x \in (X_{PhT}, b]$  with the following boundary conditions:

$$
u|_{x_{\text{Ph1}}-c} = u|_{x_{\text{Ph1}}+c}, \quad \sigma_r|_{x_{\text{Ph1}}-c} = \sigma_r|_{x_{\text{Ph1}}+c} \stackrel{\text{def.}}{=} q
$$
\n
$$
\text{if} \quad c \to 0
$$
\n
$$
\sigma_r|_b = -p_b, \quad \sigma_r|_c = -p_c
$$
\n(7)

where  $\sigma_r$  is the radial stress and  $\epsilon$  is a small number, the following solution of the simplified equation (6) can be obtained [16]:

$$
\Delta q = -M((c^3 - x_{\rm PhT}^3)(x_{\rm PhT}^3 - b^3))/x_{\rm PhT}^3(c^3 - b^3)
$$
 (8)

where  $\Delta q = q - p$ ,  $p = p_b = p_c$  and q is the *interphase pressure of phaw transfiwnation* calculated from the simplified relation (5).

$$
M = 4\mu_0 \kappa/(1 + 4\mu_0/3K) \tag{9}
$$

is a characteristic material constant which determines the absolute value of  $\Delta q$ .

When  $x_{\text{PhT}} = (bc)^{0.5}$ ,  $\Delta q$  has its extremum at:

$$
\Delta q_{\text{ex}} = -M[(c/b)^{1.5} - 1]/[(c/b)^{1.5} + 1].\tag{10}
$$

For a full sphere ( $b \equiv 0$ ), equation (8) reduces to the simple form :

$$
\Delta q = -M(1 - (x/c)^3). \tag{11}
$$

<sup>\*</sup>Phase transformation stresses occur also, if e.g. "solidsolid" phase transformation takes place with abrupt change of the specific volume.



FIG. 15. Effect of curvature on origination of expulsive forces during sudden solidification (Schematic).  $P_{ij}$ -interphase force between "i"- and "j"-particles.  $P_{i\Sigma}$  -result explosion force" acting on "*i*"-particle. B-B-ph" boundary between phase transformation zone and liquid (molten) surrounding.

If the sudden solidification zone is composed of two kinds of molecules (or grains) with different solidification points. the interphase forces originate in this zone and act between the "old-" and "new-phase" components. If the boundary of the sudden solidification zone is curved. expulsive forces appear which act on these components and may cause the extension or fragmentation of the zone. This may explain both origination of the "empty shell" and the fragmentation process, respectively, for molten copper/water experiments. Copper oxide- and copper molecules would be the "new-" and "old-phase" molecules, respectivel (Fig. 15). Figure 14 shows also that for the Cu/water system. two "hot material thermal explosion temperatures" are possible which depend on the oxide content (compare points B and C in Fig. 2 with lines B and C in Fig. 14). This is verified by the experimental results (Table I).

# APPENDIX 3

#### Metastuble Srures in Hot Materiul und Cold *Lipid*

The calculation of the transient temperature field existing during fast phase transformation is a complex nonlinear problem and requires knowledge of the contact character

at the boundary between hot and cold substances, the distribution of components as, e.g. oxide, and material properties in the high temperature region. Large heattransfer rates promote supercooling in the hot material or superheating in the cold liquid before phase transformation. Then, if a limit of the metastable state is reached, spontaneous phase transformation takes place. The phenomenon can be characterized by the following "transient Jakob number":

$$
Ja(t) = h_{\rm MS}(t)/h_{\rm PhT}(t) \tag{12}
$$

where :

$$
h_{\rm MS}(t) = \int_{V_{\rm MS}(t)} c_p \rho_1 \left( T_{\rm PhT} - T(t) \right) \mathrm{d}V \tag{13}
$$

means the heat accumulated in volume  $V_{MS}$  of the liquid in the metastable state,  $T_{\text{PhT}}$  means the temperature of phase transformation (solidification temperature of the hot material or saturation temperature of the cold liquid),  $T(t)$  is the transient temperature field,  $\rho_1$  the density before phase transformation. The expression:

$$
h_{\text{PhT}}(t) = \int_{V_{\text{PhT}}(t)} \rho_2 L \, \mathrm{d}V \tag{14}
$$

means the enthalpy of spontaneous phase transformation in volume  $V_{\text{PhT}}$ , *L* the specific enthalpy of phase transformation, and  $\rho_2$  density after phase transformation.

The metastable state may arise in the two following situations:

I. Locally, if a "jet" produces "local direct contact" between the hot material and the cold liquid (Fig. 13), and

2. "Globally" as a consequence of the hot material particle growth and after "direct contact" on the total or "almost total" surface of the particle with the cold liquid (Fig. 13).

Restricting the discussion to "sudden phase transformation" in the hot material (quasi-static description, i.e.  $Ja<sub>HM</sub> = 1$ ) and assuming a spherical form of the particle, a homogeneous distribution of the oxide in the hot material particle and of the temperature at the moment of thermal explosion, as well as supercooling of about  $-100^{\circ}$ C of the hot material (Table l), the predicted spontaneous solidified mass  $m_{\text{PhT}}$  is about 20% of the total mass of the particle. Assuming also that sudden solidification results in finely shattered debris of thermal explosion, good correspondence with the results of particle size measurements is observed, e.g. for sample 42-07 (Fig. 11), the integral portion of small particles is about  $24\%$ .

### ETUDE DU PHENOMENE D'EXPLOSION THERMIQUE DANS UN SYSTEME CUIVRE FONDU-EAU

Résumé-On présente des résultats expérimentaux sur l'explosion thermique dans un système cuivre-eau. Les mesures de température transitoire, de pression et de force de réaction ont été effectuées à des fréquences de balayage atteignant 20 Hz. On décrit les résultats des analyses granulométriques et des mesures relatives à la surface des débris produits par l'explosion thermique. Les données expérimentales sont complétées par des photographies prises à l'aide d'une caméra très rapide (jusqu'à 8000f/s) ou obtenues au microscope électronique à balayage ainsi qu'à partir d'études métallographiques.

On suppose un mécanisme d'explosion thermique produisant des "jets" constitués de petites particules éjectées de la masse du matériau chaud qui sont observés dans l'expérience et déclenchent le phénomène. L'action combinée des changements de phase soudains et des tensions internes conduit à la fragmentation du cuivre suivie d'une explosion de vapeur.

### UNTERSUCHUNG DER THERMISCHEN EXPLOSION FÜR EIN SYSTEM AUS GESCHMOLZENEM KUPFER-WASSER

**Zusammenfassung--Es** werden experimentelle Ergebnisse fiir die thermische Explosion eines Kupfer/ Wasser-Systems angegeben. Die Messungen der Veränderlichen: Temperatur, Druck, und Reaktionskraft mit einer Abtastfrequenz bis zu 20 kHz werden beschrieben. Die Ergebnisse einer Korngrößenanalyse und der Messungen der Gesamtoberfliche von Explosionsprodukten werden dargestellt. Bilder. aufgenommen mit Hochgeschwindigkeitsfilmen (bis zu 8000 B/s) und mit dem Raster-Elektronenmikroskop sowie Aufnahmen von metallographischen Untersuchungen ergänzen das experimentelle Material.

Es wird ein Mechanismus der thermischen Explosion vorgeschlagen, in welchem die experimentelle Beobachtung von kleinen "jets" aus der Hauptpartikelmasse als eine Zünderscheinung angenommen wurde. Die Notwendigkeit der schnellen Phasenumwandlung und der damit verbundenen inneren Spannungen zur Erzeugung einer Explosion wird unterstrichen.

# ИССЛЕДОВАНИЕ ЯВЛЕНИЯ ТЕПЛОВОГО ВЗРЫВА В СИСТЕМЕ РАСПЛАВЛЕННАЯ МЕДЬ-ВОДА

Аннотация - Приводятся данные по экспериментальному исследованию тепловых взрывов в системе медь-вода. Измерения нестационарной температуры, давления и реактивной силы проводились при частоте до 20 кгц. Представлены результаты измерения размеров частиц распада и общей поверхности продуктов теплового взрыва. Приводятся фотографии (отснятые со скоростью до 8000 кадров/сек.), а также диаграммы электронного микроскопа по металлографической обработке исследуемого материала.

Предполагается, что механизм теплового взрыва состоит в том, что экспериментально наблюдаемые «струйки» мелких частиц выбрасываются из массы горячего материала, вызывая этот эффект. Внезапные фазовые превращения и сложные внутренние напряжения вызывают дробление меди и взрыв пара.