

Variable Temperature Laser Light Scattering Microscopy (VTLLSM) Studies on 10-100 μm Size High Purity Gold and Commercial Grade Zinc Grains*

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ABSTRACT

The VTLLS microscopy studies were made on high purity gold and commercial grade zinc grains in a temperature range of 30-230°C. Differential area ω and surface activity S_a were estimated from photomicrographs. The ω vs dT/dt (rate of heating) curve was seen to differ from those of silver and titanium. The nature of curve between normalized ω and dT/dt was seen to be non-exponential. The characteristic relation between sectorized differential area ω_{sec} and mean temperature was examined. The present study further establishes the simplicity and versatility of the VTLLS technique, in studying the defect-sub-structure of metal particles such as Au and Zn in presence of an imposed temperature gradient in a reasonable way. As such an attempt was made to connect the ω and defect-sub-structure related parameters.

Keywords: Variable Temperature, Laser Light Scattering Microscopy, Au and Zn Grains, Defects

1. Introduction

Studies on defects in materials and metals have been a fascinating subject and many techniques were developed to support such investigations. Triftschauer and Kogel [1] developed a positron annihilation technique to study defect structure in metals in the vicinity of surfaces. Recknagel and Wichert [2] reported a perturbed angular correlation study on point defects in metals. NMR studies on point defects in Al and Cu were reported by Minier and Minier [3]. Mossbauer studies of defectimpurity interactions in metals were carried out by Vogl *et al* [4]. Peisl [5] made X-ray scattering studies on defects in metals. Earlier, the present authors [6] made variable temperature laser light scattering microscopy (VTLLSM) studies on relatively larger grains of aluminum, copper and silver in a small temperature interval and established the effectiveness of the technique. The technique was similar to the variable oblique incidence reflection microscopy (OIRM) reported by the present authors [7].

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Later on, the approaches were modified and the VTLLSM was used to investigate structural variations of high purity silver [8], titanium [8], gold [9] and (commercial grade) Pb-Sn alloy [9] grains having sub-millimeter dimensions (within the range of 10-100 μm) as a function of the temperature (in a wider temperature range). The new technique consists of the Fourier space interference images (resulted from light scattered by particles), which is the intermediate step in the formation of a holographic image. Such an image is composed of black and white contrast regions, which were attributed to surface micro-facets of the particles. The present authors used these contrasts and their variations with temperature as the signature of particle's structural changes in terms of internal defects such as voids and dislocations.

A large working distance (LWDO) optical microscope with water cooled heat shield [10,11], a zero thermal expansion (in upward direction) table (V⁺ZET) to function as sample holder [12] and a beam path cooler (BPC) to stabilize image formed by scattered laser light at high temperature [13] were developed for the VTLLSM stud-

ies. Gold and zinc are too well known; a complete introduction on them is therefore not attempted. Briefly, Doremus [14] studied optical adsorption by gold particles. Granqvist and Hunderi [15] studied optical properties of ultra fine gold particles. Hassam *et al.* reported [16,17] equilibrium phase diagram of some mixed systems, that contained gold as a component.

Investigations were made on 10-100 μm size gold and zinc grains, by employing variable temperature laser light scattering microscopy (VTLLSM). Results are presented in this report.

2. Experimental

As received Sigma-Aldrich (USA) made agglomerated (+ 99.999% pure) 10-100 μm size gold grains and commercial grade purity zinc grains (prepared one hour before the commencement of each experiment) were employed in the present study. The experimental procedure and data analysis were almost identical to those reported earlier [8,9,18]. A 10 mW, 670 nm laser, a zero thermal expansion hot stage (V^+ZET) coupled with a beam path cooler (BPC), were employed [12,13]. Thermocouple based thermometry was used to measure the temperatures. Fused silica optical flat was used as sample holder; linear thermal expansion coefficients [19,20] of fused silica, gold and zinc are $0.4 \times 10^{-6} \text{ k}^{-1}$, $14 \times 10^{-6} \text{ k}^{-1}$ and $11.6 \times 10^{-6} \text{ k}^{-1}$ ($\perp C$ axis) and $64.20 \times 10^{-6} \text{ k}^{-1}$ ($\parallel C$ axis) respectively. In order to suppress the back ground scattering, amorphous MnO_2 was employed in the form of thin layer. Reflection coefficients [21] of carbon black, gold and zinc are 0.003, 0.75 and 0.45 respectively in the visible spectrum. The coefficient of reflection of MnO_2 may be equal or very close to that of carbon black. The metal grains were heated on V^+ZET and a series of photomicrographs were recorded at different temperatures. Measurements were made from such photographs. The same fused silica optical flat has been used in the studies

on Ag, Ti, Pb-Sn, Al, Zn and Au [8,9,18], in order to eliminate the influence of substrate, if any, while comparing the results on grains of different metals.

3. Results

The VTLLS microscopy images of Au grains at three different temperatures are shown in **Figure 1**. The images of zinc grains are similar to that of gold grains. The areas of bright patches (BPs [13]) were measured from a given photomicrograph and summed up, giving total area (A_{TOT}). Differential area ω , defined as $2(A_{max} - A_{min}) / (A_{max} + A_{min})$, where A_{max} and A_{min} were maximum A_{TOT} and minimum A_{TOT} respectively in a heating-run, were estimated. The ω values, obtained in five heating-runs vs rate of heating (dT/dt) are shown in **Figure 2**. The curve ω vs dT/dt of Au and Zn (**Figures 2(a,b)**) shows an initial increase and then a constant decrease in the average value of ω of two grains, as the rate of heating was progressively increased. The relation between normalized differential area ω/a_1 vs dT/dt of Au is shown in **Figure 3(a)**. The curve joining most of the points (dashed line; **Figure 3(a)**) has negative slope (similar to the curve in **Figure 2(a)**, between $dT/dt = 0.26$ and 0.66).

$$\log \omega = (dT/dt)^{-1} \tan \phi \quad (1)$$

may describe the straight line (**Figure 3(a)**). It is a deviation from earlier observations, that exponential curves (connecting ω and dT/dt) with positive and negative slopes were noticed in case of grains of silver [8] and titanium [8]. In order to handle the experimental data, it may therefore be useful to use a general equation, such as,

$$Y = (1 - K)e^{\pm \phi x} + Kmx^{\pm 1} \quad (2)$$

where $Y = \omega$, $x = dT/dt$ and ϕ is a constant. K is a parameter that probably defines the state of a grain and can assume a value 0 or 1. It is assumed that the value of

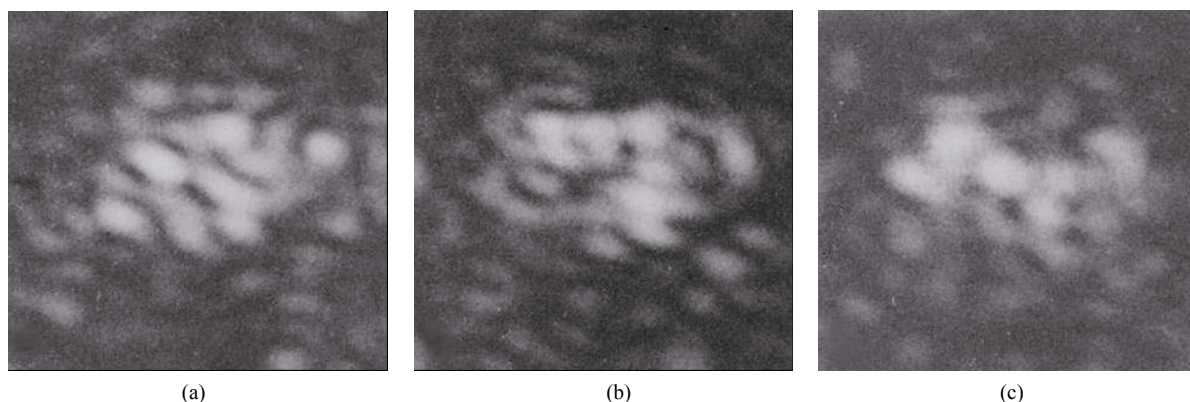


Figure 1. VTLLS microscopy images of Au grains. (a) 29°C, (b) 130°C, (c) 230°C; $dT/dt = 0.46^\circ\text{C}/\text{min}$. 500X.

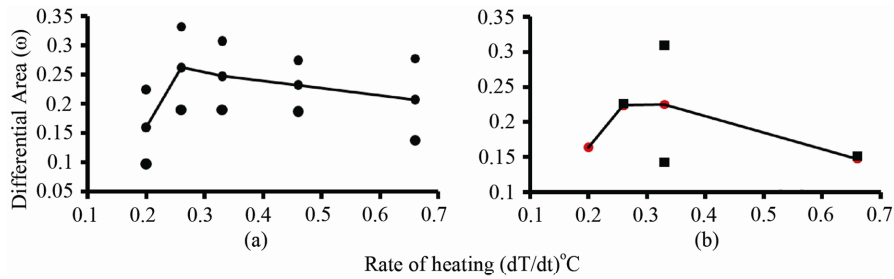


Figure 2. Differential area ω vs. dT/dt ; (a) Case of Au and (b) Case of Zn.

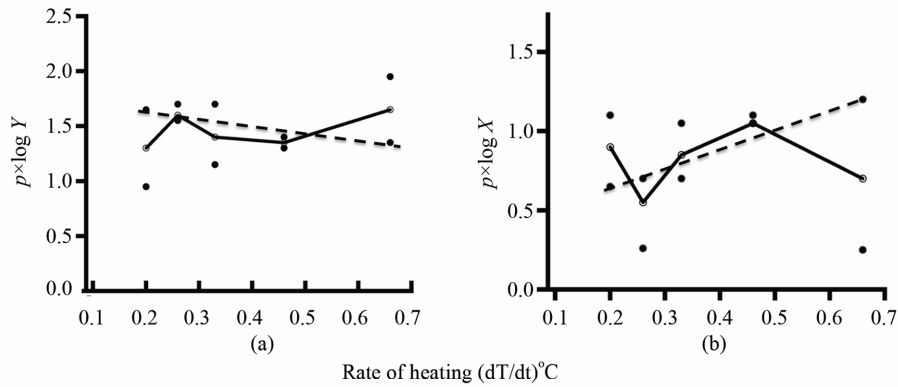


Figure 3(a). Normalized ω (curve a) and normalized S_a (curve b) of Au grains. In the graph: $p \times \log X = 10^{-3} \times [\log(S_a/a_1)]$ and $q \times \log Y = 10^{-5} \times [\log(\omega/a_1)]$.

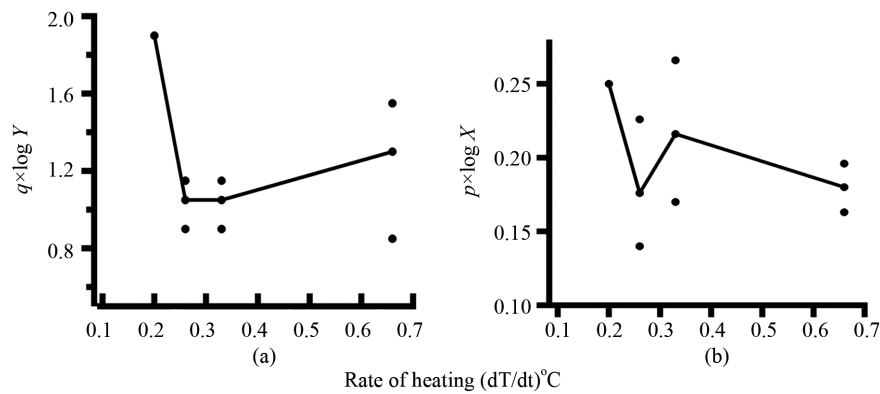


Figure 3(b). Normalized S_a (curve a) and normalized ω (curve b) of Zn grains. In the graph: $p \times \log X = 10^{-4} \times [\log(\omega/a_1)]$ and $q \times \log Y = 10^{-3} [\log(S_a/a_1)]$.

The profile of distribution of bright patches (BPs) was noticed to change with temperature [12]. A term surface activity S_a was defined, while taking the decompositions and recombinations of BPs into consideration. The surface activity S_a was proposed to be given by an empirical relation

$$S_a = (N_{HBPs} - N_{LBPs})^2 (N_o - 1)^{-1} \left[1 - (N_{TBPs})^{-1} \right] \left[1 - (1 + T_m - T_h)^{-1} \right] \quad (3)$$

where N_{HBPs} and N_{LBPs} are highest and lowest number of BPs respectively, found in photomicrographs of a heating-run; N_o and N_{TBPs} are total number of (photomicrograph) frames and total number of bright patches respectively. T_m and T_h are melting temperature (of the metal) and highest temperature reached (in a given heating-run) respectively and expressed in $^{\circ}\text{C}$.

It may be stated that S_a indicates the level of internal and external activity promoted by thermal pressure. It is known that atomic migration takes place at a much faster

rate on a (metal) crystal surface, than through the lattice and that such difference is a consequence of surface activation energy being lesser than the lattice activation energy.

Normalized surface activity (S_a/a_i) vs dT/dt curve suggests increase in surface activity with increase in rate of heating (dashed line; **Figure 3(a)**). The results obtained in case of zinc grains (**Figure 3(b)**) are much similar to the results obtained on Au grains (**Figure 3(a)**). Sectorized differential areas (ω_{sec}) were also estimated in case of Au, by grouping every three consecutive A_{TOT} (in each heating-run) as a set and by picking up A_{max} and A_{min} among them. Curves were drawn (**Figure 4(a)**) between ω_{sec} and mean temperature (mean of a set of three values). The curves showed both positive and negative peaks. Data on peak positions is shown in **Figure 4(b)**, which indicates that there is a temperature-wise combination of peaks with respect to the rates of heating. These observations have relevance to the meaning of curves shown in **Figures 2,3** and needs a detailed presentation. As such it

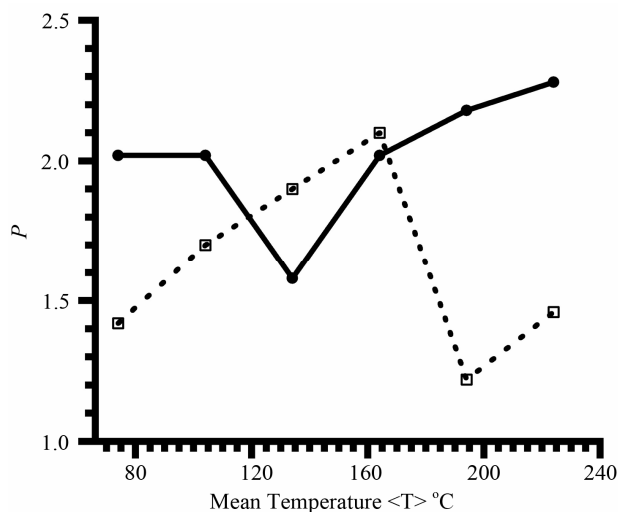


Figure 4(a). Sectorized differential area ω_{sec} vs. mean temperature $\langle T \rangle$ in case of Au. In the graph: $p = 10^{-3} \times [\log \omega_{sec}]$.

	DT/dt 0.20	0.26	0.33	0.46	0.66
T_{mean}					
190					o
160	o		o	o	o
130		o		o	o
100	o	o	o		o

• (+) ve peak; o (-) peak

Figure 4(b). Peak formation due to two grains of Au, for different values of dT/dt , is illustrated. The o, • peaks on each vertical axis belong to the same grain in that heating-run (fresh grains were used in each heating-run).

shall be discussed elsewhere, while considering the grains of Al, Au, Ti and Zn [18].

4. Discussion

It may be noted that the optical absorption of small gold particles at 436 nm was found to be independent of size of particles [14]; the absorption spectra of aqueous gold sols showed [14] that the absorption touched zero in the vicinity of 700 nm. The variation in absorption coefficient in a temperature range of 25-514°C was negligibly small at 700 nm [14]. Therefore, it may be stated that the variations in the A_{TOT} of BPs were not due to optical absorption effects. Similar results were obtained in case of zinc. The following considerations may probably explain the observations (curves showed in **Figures 2,4**).

It is well known that any real crystalline material can be treated as a combination of two physical states: 1) Ideal (defect free) crystal structure, with well defined symmetry and 2) Defect-sub-structure. The thermal expansion behavior of any material in a temperature interval ΔT is described by the classical equation [22],

$$V = V_o (1 + \gamma \Delta T) \quad (4)$$

where V_o and V are the volumes of a material at low and high temperature; γ represents the coefficient of thermal expansion and may vary over wider range of temperature [23]. It was proposed [9] that classical Equation (4) might be modified (while taking the relaxation time into consideration), as Equation (5) such that V shall also be a function of time 't'.

$$V = V_o [1 + \gamma \Delta T f(t)] \quad (5)$$

In the context of defect-sub-structure, basically two types of defects can be thought of 1) Locked-in defects, formed during the synthesis or mechanical handling (of the grain) and preserved, 2) Born-defects, generated due to heating of a grain and decay on further heating [24-26]. These two types of defects are volume defects, and only differ in the nature of their origin.

Let the rate of generation of defects (b) = number of volume defects with smallest volume, generated per second, per °C temperature rise, per unit volume of the grain. Equation [24] of the rate of vacancy generation in metals was given in terms of $d(C_a)/dt$, where C_a and t were average vacancy concentration and time respectively, at a temperature T . The term b of Equation (6) is either similar or identical to C_a (depending on whether formation of a combination of different types of defects, or only vacancies, is described by (b)). Let the rate of decay of defects (d) = number of volume defects, with smallest volume, decaying per second, per °C temperature rise, per unit volume. Such that $b \geq d$. Total contri-

tribution to the volume (of defect free metal grain) due to birth and decay of defects in a temperature interval ($t - t_o = \Delta T$) is,

$$V^{(1)} = V_o (b - d) \Delta T \quad (6)$$

It is assumed logically that $d = f(r_m, r_r, T)$, where r_m is rate of migration of defects to surface, r_r is the rate of recombination, and T is temperature. Let the concentration of locked-in defects (number of defects per unit volume) = Γ . Based on the fact that the physical properties of metals vary, depending on the nature of preparation [27], it may be stated that the value of Γ depends on the process of synthesis of grains. Decay of locked-in defects due to rise of temperature may be represented by a decay factor D (= number of defects decaying per unit volume per $^\circ\text{C}$ rise of temperature). Therefore, total change in excess initial volume due to decay of locked-in defects is given by,

$$V^{(2)} = V_o (\Gamma - D\Delta T) \quad (7)$$

The real volume of grain is given by the sum of Equations (5-7) and may be written as:

$$V_{real} = V_o \{ (1 + \Gamma) + \Delta T [\gamma f(t) + (b - d) - D] \} \quad (8)$$

On differentiating Equation (8) with respect to time and equating $d(V_{real})/dt$ to zero (since expansion reaches maximum after a certain length of time) it may be written after simplification,

$$dV_{real} = V_o \{ 1 + \Gamma + (dT/dt)^{-1} \Delta T^2 [F_{der}] \} \quad (9)$$

where derivative factor $F_{der} = d[\gamma f(t) + (b - d) - D]/dt$.

It was shown [6] that the differential area ω , defined as $2(A_{max} - A_{min})/(A_{max} + A_{min})$, could give thermal volume-strain variation $\omega = 2(V_{max} - V_{min})/(V_{max} + V_{min})$, where V_{max} and V_{min} were maximum and minimum total volumes respectively, exhibited by a grain, during a heat-run. It may therefore be written that $dV_{real} = V_{max} - V_{min}$ and $V_o \approx (V_{max} + V_{min})/2$, then Equation (9) may be written as

$$\omega = (2/5) \{ \Gamma + (dT/dt)^{-1} \Delta T^2 [F_{der}] \} \quad (10)$$

By using Equation (10), values of F_{der} were calculated for a few assumed values of Γ in case of the grains of zinc; the results are shown in **Figure 5**. Expectedly, F_{der} exhibits large variations, for relatively larger concentration of locked-in defects.

It may therefore be expected that, in case of small metal grains, variations in the volume with systematic changes in temperature, can be strongly influenced [28,29] by the crystal-defects related parameters. It may be

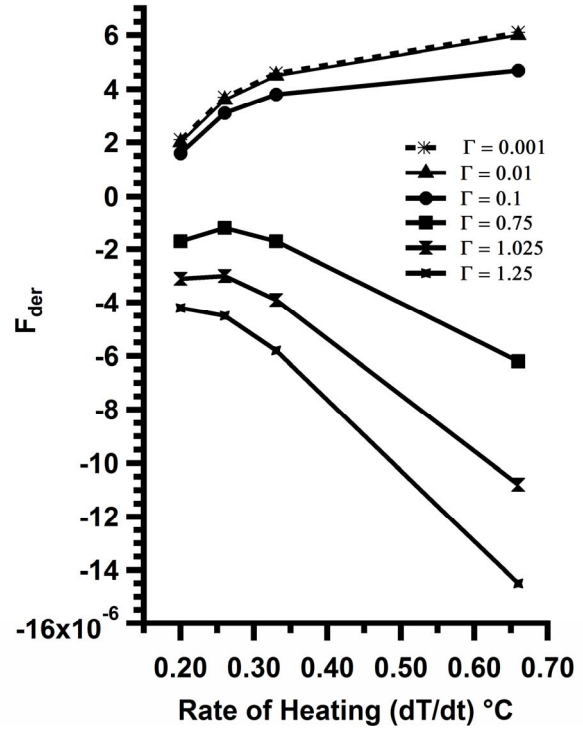


Figure 5. Variation of F_{der} with dT/dt , for different values of Γ ; case of Zn.

pointed out that, 1) Since no two metal grains (formed under identical conditions) can have identical defect-sub-structure, they exhibit non-identical response to the injected heat energy. (It may be recalled that non-uniform behavior is a frequent occurrence in crystallization [30-32], when individual cases are considered); and, 2) Yet, the defect-sub-structure parameters may vary within an upper and lower limits, permitted by the parameters, controlling the nucleation and growth of grains. These two factors coupled with the macroscopic physical properties of a given material, lead to a sort of uniformity in diversity-like condition. Individual metal grains, studied by VTLLS microscopy, appear to have anarchic behavior. But, when the behavior of a good number of grains is considered, a systemization surprisingly surfaces. Such diversity in the behavior should become more dominant, with further reduction in the size of metal grains. It can be pointed out that the observed behavior of the grains is their intrinsic character and not due to any secondary influences. Because, unlike the conventional techniques, such as electron microscopy and X-ray techniques (where the probing beam can interact with the material and modify its state [33]), VTLLS microscopy is powerful, yet passive. In the sense that it does not modify the state of metal (or non-metal) grain, if the beam energy is not too high (as in the pre-

sent case). The VTLLSM technique is most suited for studies on surfaces and small grains.

5. Conclusions

The VTLLS microscopy technique can be effectively employed to study the response of small metal grains (in 10-100 μm size range) to an imposed temperature gradient and the results can be interpreted in a reasonable way, by taking the defect-sub-structure related parameters into consideration.

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