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On the behavior of Au and Pb-Sn metal grains subjected to heat: A variable temperature laser light scattering microscopy study

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ABSTRACT

Detailed investigations were carried out on sub-millimeter sized metal (Au) and alloy (Pb-Sn) grains by employing VTLLSM technique. The studies were made in an extended temperature range (ambient to 200°C), at different heating rates. Observations were also made, while keeping the temperature constant at elevated levels. Changes noticed in the areas of facets of grains are interpreted as due to growth of new facets. Re-crystallization at substantially lower temperatures and the possible influence of defects are considered. Modifications noticed in Au grains are compared with Pb-Sn grains.

INTRODUCTION

The changes occurring in larger Ag, Al and Cu metal grains were studied in a temperature range of 30-70°C, by employing laser light scattering microscopy (which is essentially Oblique Incidence Refection Microscopy –OIRM[1]) and the variations in the expansion behavior were discussed in terms of influence of defects[2]. The studies were extended in terms of temperature range and size of metal grains. For such studies, a large working distance microscope was designed and fabricated[3]. A stage with zero thermal expansion in positive vertical direction (V^+ZET) was designed and fabricated[4]. The thermal gradients between the V^+ZET and objective of the microscope triggered instabilities in the image of grain, formed by scattered light. A beam path cooler (BPC) was designed and fabricated, which eliminated the instabilities[5]. A scheme for the interpretation of images was also out lined[6]. In view of high surface reflectance and stability against oxidation, Au metal grains were chosen for initial investigations. Pb-Sn alloy was chosen due to its low melting temperature (T_m). The results on Au were compared with that of Pb-Sn, since the general behavior of Au should match with that of Pb-Sn, in certain temperature range. The results obtained are presented in this report.

EXPERIMENTAL

Materials and/or equipment.

Sub-millimeter sized Au metal grains (Sigma-Aldrich, USA make; 99.999% pure) were studied by employing variable temperature laser light scattering microscopy[2,3].

A 10 mW, 670nm laser beam was used to illuminate the grain at an oblique angle θ (θ = 62.4°, with respect to the Z-axis), while positioning the grain on V^+ZET. Temperature was increased in small steps, from room temperature to 200°C and a good number of photomicrographs were recorded (at different temperatures) in every run. Figure 1 shows the typical image of grain.

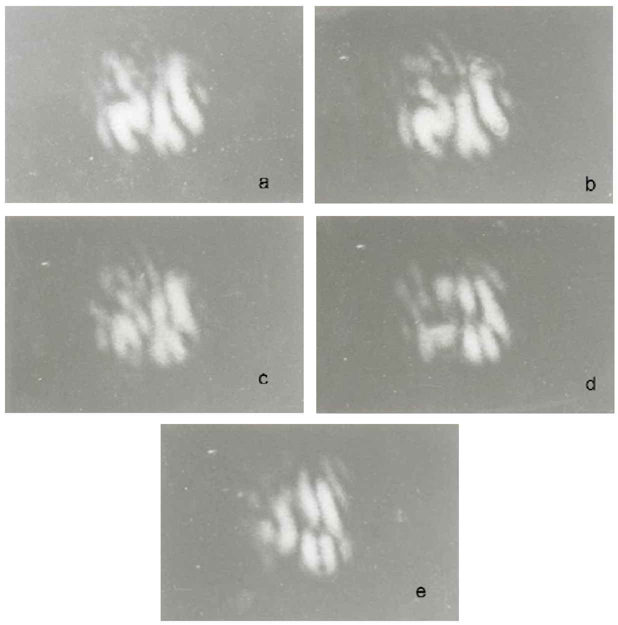

Figure 1 : Laser light scattering microscopy images of Au metal grains at progressively increasing temperature are illustrated: (a) 23.4°C, (b) 53.1°C, (c) 103.4°C, (d) 153.5°C, (e) 200°C. 500X

Disappearance of existing bright patches (BPs) and appearance of new BPs were noticed. The BPs were identified as facets acting as specular reflectors, reflecting at that particular angle determined by the oblique incidence angle of the laser beam[6]. The number of facets appearing and disappearing was estimated from the photomicrographs (Figure 2a). Areas of BPs should be proportional to the areas of the reflecting facets[6]. Therefore, areas of BPs were measured from photomicrographs; the three BPs whose areas were measured were relatively wide patches. Fluctuations were noticed in the areas (Figure 2b). Au metal grains were also subjected to heating-cooling cycles. The image of a grain recorded after cooling it down to room temperature did not coincide with its initial (pre heating) image; it was an indication that the grain underwent irreversible surface changes, during a heating-cooling process. Fragmentation and recombination of BPs were noticed to take place (Figure 3a-c). The lines (in Figure 3a-c) with positive slopes (inclined towards left) and negative slopes (inclined towards right) are due to fragmentation (break down) and recombination respectively. The diagrams (Figure 3a-c) explicitly indicate the activity occurring at the surface of grains. The integrated areas of the same grain (sum of areas of all BPs of the grain at any temperature), during the cyclic heating-cooling process are shown in Figure 3d. Interestingly the fluctuations in the integrated areas, was low during the first run and became considerable during the second and third heat-runs.

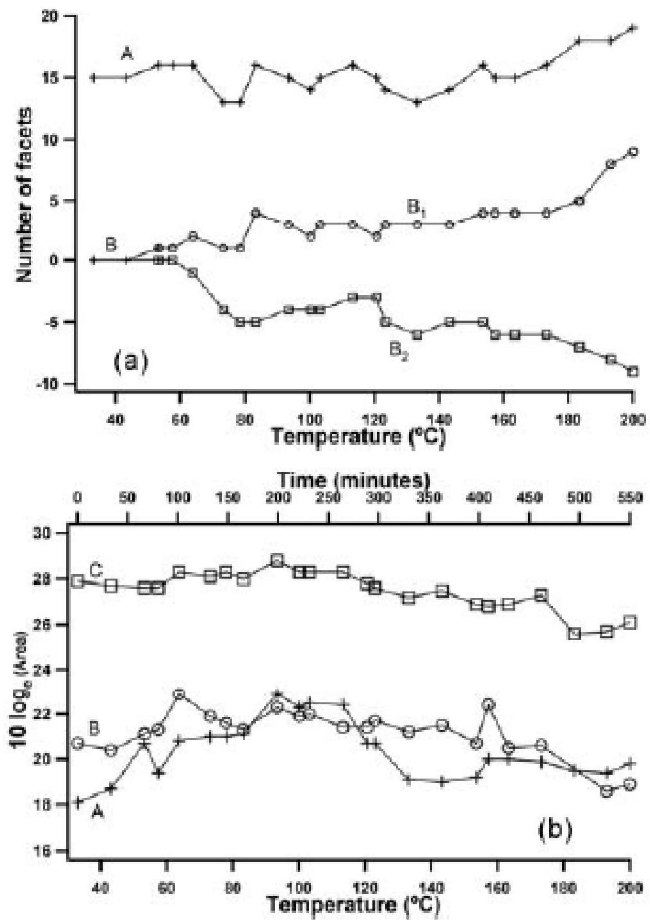

Figure 2 : Au metal grain: (a) Number of bright patches (facets) appearing (curve-B_1) and disappearing (curve-B_2) at progressively increasing temperature. Curve-A indicates the total number of facets at any given temperature. (b) Slow decrease in the areas of facets.

Studies were also made on sub-millimeter sized grains of commercial grade Pb-Sn alloy, in view of its low T_m (123°C). Some of the results obtained in case of Pb-Sn are shown in Figure 4. The activity of splitting and recombination of facets was seen (Figure 4) to be initiated at about 75°C (in the first heat-run it self), while the T_m was just 28°C away.

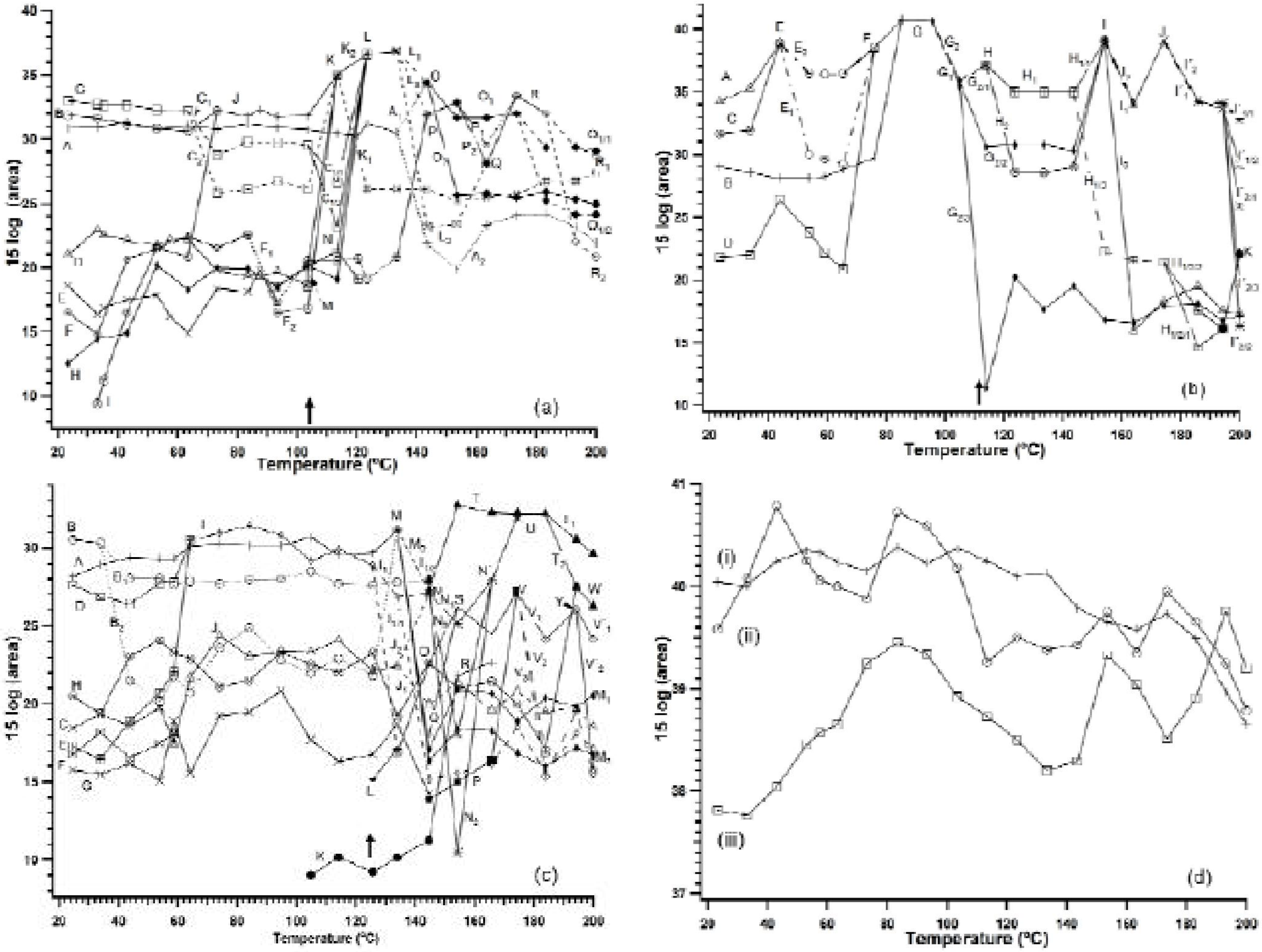

Figure 3 : (a) Areas of BPs vs temperature; Au grain during 1st heat-run. (b) The same grain during 2nd heat-run. (c) The same grain during 3rd heat-run; increased surface activity evident from the increased number of lines with positive and negative slopes. On-set of activity is indicated by heavy arrows. (d) Integrated areas (I_a) of the grain during 1st, 2nd and 3rd heat-runs. Fluctuations in I_a are evident.

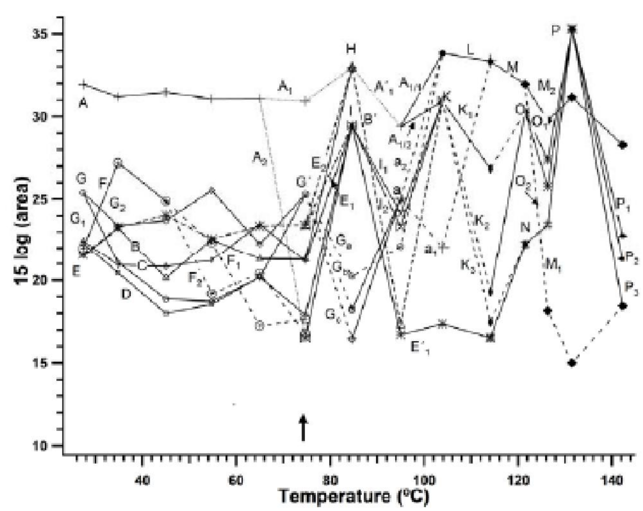

Figure 4 : Case of Pb-Sn alloy grain; on-set of activity at lower temperature (75°C) is evident (heavy arrow).

RESULTS AND DISCUSSIONS

Kave et al[7] showed from theoretical considerations that when two micrometer sized particles, having equal dimensions were at different distances from each other, the light scattering profiles exhibit variations, both in number and width of bright bands. It was pointed out[6] that BPs were composed of bright and dark fringes. Such fringes were formed as a result of interference. In view of larger size of the grains considered here (sub-millimeter), the observations of Kave et al[7] may not be completely applicable to the present situation. At the same time, the observed variations (i) increase and decrease in the areas of BPs and (ii) fragmentation and recombination of BPs, might not be completely explained only in terms of thermal expansion (which can be prominent at lower temperatures, as it could be the only available process). As such, facet growth and related mechanisms (that are active in the present temperature ranges) may have to be considered. It is also important to note, that if optical interference effects were the reasons for the observed fluctuations in the integrated areas (I_a), then the curve-i (Figure 3d), corresponding to the first heat-run should also exhibit such fluctuations. In view of the absence of fluctuations (in curve-i), it may be stated safely that the fluctuations are not entirely due to interference effects. It appears that migration of material (added to or withdrawn from the surroundings defining the surfaces) could be the possible reason for the fluctuations.

It may be noted that polygonization (process of redistribution of dislocations, giving rise to the formation of sub-grains in single and poly-crystals) can noticeably change the structure of a deformed material on heating and also it is the most low temperature process[8]. At lower temperatures, dislocations move by slip and from stable boundaries and at higher temperatures, diffusion climb becomes dominant and promotes boundaries having relatively high mobility, formed in the process of polygonization. It was reported[9], based on electron microscopy studies that cyclic heating of Al grains led to development of sharp faceting. Under favorable conditions, polygonization may be considered as pre-re-crystallization state[8]; the reduction of volume energy is the principal driving force. During such process, triggered by increasing temperature, nuclei formed in the deformed matrix grow at the expense of starting matrix, forming distortion free matrix, with the same cell structure[8] (as such no phase changes are involved).

In the present case, therefore, it seems that the response of a grain to temperature depends on the level of stress that exists in it, generated probably during the process of formation of grain it self. Further, during heating-cooling cycles, dislocations should invariably be formed, thus generating stress. Interfacial defects can migrate and also increase in density[10-12]. Such newly generated stress dictates the grain to behave differently (via polygonization, recrystallization etc.) in successive heating-cooling cycles.

In case of high purity metals[8], T_r = (0.25 to 0.35)T_m; where T_r and T_m are recrystallization and melting temperatures respectively. And, in case of commercially pure metals[8], T_r = (0.35 to 0.45) T_m; the increase in T_r is due to inhibition of mobility of dislocations by impurity atoms[8]. It may also be noted that plastic working under certain conditions can lower T_r substantially in metals[8]. The T_m of Au is[13] 1064.43°C. Therefore, the expected T_r = 1064.43 x 0.25 = 266.1°C. The onset of activity in Au grains at about 105°C, 110°C and 125°C during 1st, 2nd and 3rd runs (heavy arrow marks in Figures 3a,b,c) respectively indicate substantial lowering of re-crystallization related activity. Clearly, here the size of grain also plays important role. In view of smallness of grain, larger energies, consequently higher temperatures may not be needed to move out dislocations, that are not large in number (in comparison to the bulk material), in order to promote growth of wider facets, in a pre-re-crystallization condition. It is known that smaller grains melt at lower temperatures, which is the size effect[14,15].

We define the surface activity (S_a), as a process of breaking down and recombination of specular and scattering facets. The manifestations due to thermal expansion, facet growth, influence of different types of defects etc. are collectively represented by surface activity. The surface activity is given by the following empirical equation:

$$S_a = (N_B + N_C)\{1 - N_t [N_I (1 + T_m - T_h)]^{-1}\} \quad (1)$$

Here, N_B and N_C are number of fragmentations and re-combinations recorded in a heat-run, when the grain was heated slowly from ambient temperature to (a high temperature) T_h. Further, N_t and N_I are total number and initial number of points on the graph respectively. By making use of this equation, surface activity of the Au grain during the three heat runs was estimated. The obtained values were: (i) 40.59, (ii) 38.61 and (iii) 47.42.

Further, transformation of a NaCl aerosol particle to a (water) solution droplet was studied[16] by employing light scattering technique and large variations in scattering intensity were noticed around transformation state and intensity profiles assumed stable state (after the transformation), which corresponds to scattering from spherical particles. In case of Pb-Sn system, it can be seen (Figure 4) that the surface of grain was quite active, before it attained T_m (= 123°C) and after crossing the transition temperature, the system became relatively tranquil. Obviously, there is a parallelism at least to the first approximation) between the behavior of Pb-Sn grain and NaCl aerosol particles, around the corresponding phase transitions.

Also, it is well known[17] that high purity and high annealing temperatures result in smaller dislocation densities and in case of alloys, the dislocation density is high and dislocations are effectively random. Therefore, the on-set of activity in Pb-Sn at 75°C may be seen as a manifestation of the dislocation-motion-promoted subgrain boundary migration leading to widening of subgrain surfaces and surface activity. As temperature advances, on-set of re-crystallization takes over, till the temperature reaches T_m. Once Pb-Sn grain melts, a few micro-drops of liquid alloy are formed; they appear to be relatively docile, as seen in Figure 4. (It may be added here that probably the static light scattering experiments may not be able to reveal the activity that goes on at the surface of a liquid drop). Broadly speaking, the behavior of Pb-Sn system indicates the way in which Au grains may probably behave at higher temperatures (during the first heat run).

CONCLUSIONS

This study illustrates the temperature induced surface modifications, in case of Au, via the influence of dislocations, at temperatures that are far below the melting temperature. The observations made on Pb-Sn alloy grains corroborate the results obtained on Au grains.

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