The behavior of gold nanoparticles at high temperatures

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ABSTRACT

Many materials of technological interest contain metallic nano-particles and their high temperature properties are very important in modern materials science. In the present work we report a in-situ Transmission Electron Microscope studies of coalescence behavior of gold nano-particles at high temperatures. At temperatures greater than 800°K a new mechanism for coalescence was found. This phenomenon occurs in a time scale many times faster than the normal sintering of grains reported by Flueli et. al. [6]. Before the coalescence the particles undergo shape convulsions of the type described by lijima and Ichihashi [1] which has been termed "quasimelting", then a very fast coalescence ocurrs and the newly formed particle also undergo convulsions until stabilized by the substrate. This new mechanism implies that at this temperature the liquid and solid phases might coexist.

KEYWORDS:
Microscopy of materials; Small particles; Coalescence of clusters.

1. INTRODUCTION

One of the most intriguing phenomenon that has been discovered in recent years [1] is the fluctuation of metal nanoparticle structure under an electron beam in the electron microscope. Iijima and Ichihashi [1] indicated early that particles size of ~ 20 Å can not be heated by the electron beam higher than ~ 100°C. Therefore the origin of the phenomenon is not direct heating. (at least for particles < 100 Å).

Several models were put forward to explain this phenomenon such as a quick cycle of melting are recrystallization events (many times per second) which are due to Auger losses [2] or Coulomb explosions [3]. However, Marks and Ajayan [4] in their recent work have reported that the energy needed to sustain the quasi-molten state, previously defined by Dundurs et. al. [5], is much lower than expected. In any case the quasi-molten state might be dependent of the mean energy of the particle. Therefore appears interesting to study this phenomenon at higher temperatures around half of the bulk melting point (Tm).

In the present work we report studies of the quasi-molten state in gold particles which are produced by evaporation and coated by carbon film and then observed at high temperature with a TEM. We found that at these temperatures there is spontaneous ultra-fast coalescence of some of the particles. This ultra-fast coalescence is always preceded and followed by quasimelting oscillations in the particles.

2.EXPERIMENTAL

Gold particles were prepared by vacuum evaporation on a NaCI substrate between room temperature and 400°C., samples were covered with amorphous carbon and then floated and mounted on TEM grids. The samples were observed on a JEOL100-CX microscope using a side entry heating stage. Samples were heated at temperatures up to ~~800°C. Despite the instability of the heating stage which impeded to obtain a high resolution images, a very valuable information about this phenomenon was obtained.

Images were recorded in a VTR with a time resolution of 1/60 sec. and transferred to an image processing system. The final processed images were photographed from the TV monitor of the processing unit.

3. EXPERIMENTAL RESULTS

3.1 General

A typical image of the initial state and particle size distribution of the sample are shown in Figs 1a and 1b. Once the temperature was raised to ~800°C. It is clearly noticed that particle size increased with the heating time. After 3 hours of heating the size distribution corresponds to a bimodal distribution, as shown in Fig. 2b.

However when the heating is continued it was observed that some individual particles start to fluctuate at very high frequency often higher than >60 Hz. This fluctuations always led to the coalescence of at least two particles. The particle formed by coalescence keeps on with the fluctuations, usually at smaller frequency, until eventually comes to rest and remains stable. It is very noticeable that the majority of the particles in a specific do not present fluctuations. From about 100 particles, which correspond usually to a frame on the screen, only two or three presented fluctuations simultaneously. In the following sections some typical cases observed willbe described.

3.2 Coalescence between two particles of different size

The first example of coalescence is shown in Figs 3a-c which shows a particle of ~1000Å diameter and two smaller of about 500Å. The total event took place in few seconds. As can be observed the smaller particles become in contact with the larger ones and then are swallowed by the larger ones, merging as a single particle. (The time needed for this process is lesser than 0.1 sec. It is worth to point out that coalescence do not take place in this case by the usual process of "neck" formation due to surface diffusion, since is much slower than the one observed here. (For a full description on the standard behavior see references 6-7). It is also very interesting to note

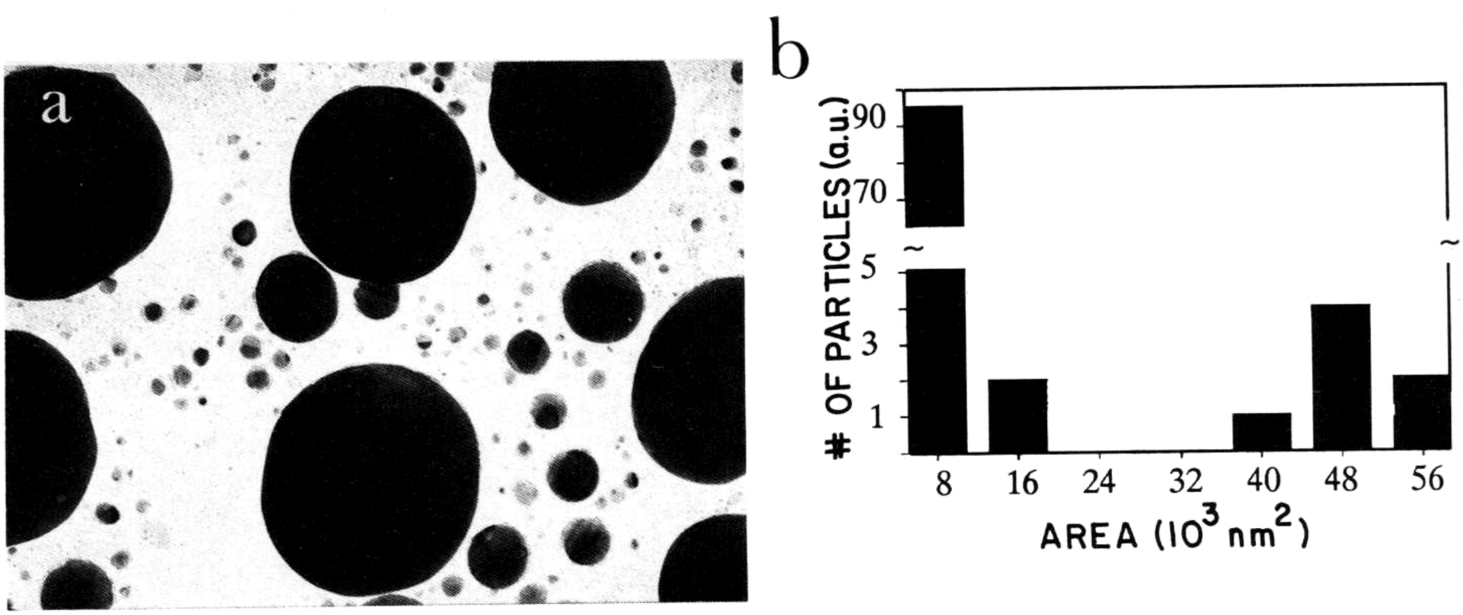


Figure 1. a) Typical image of the sample before in-situ heating. b) Corresponding size distribution

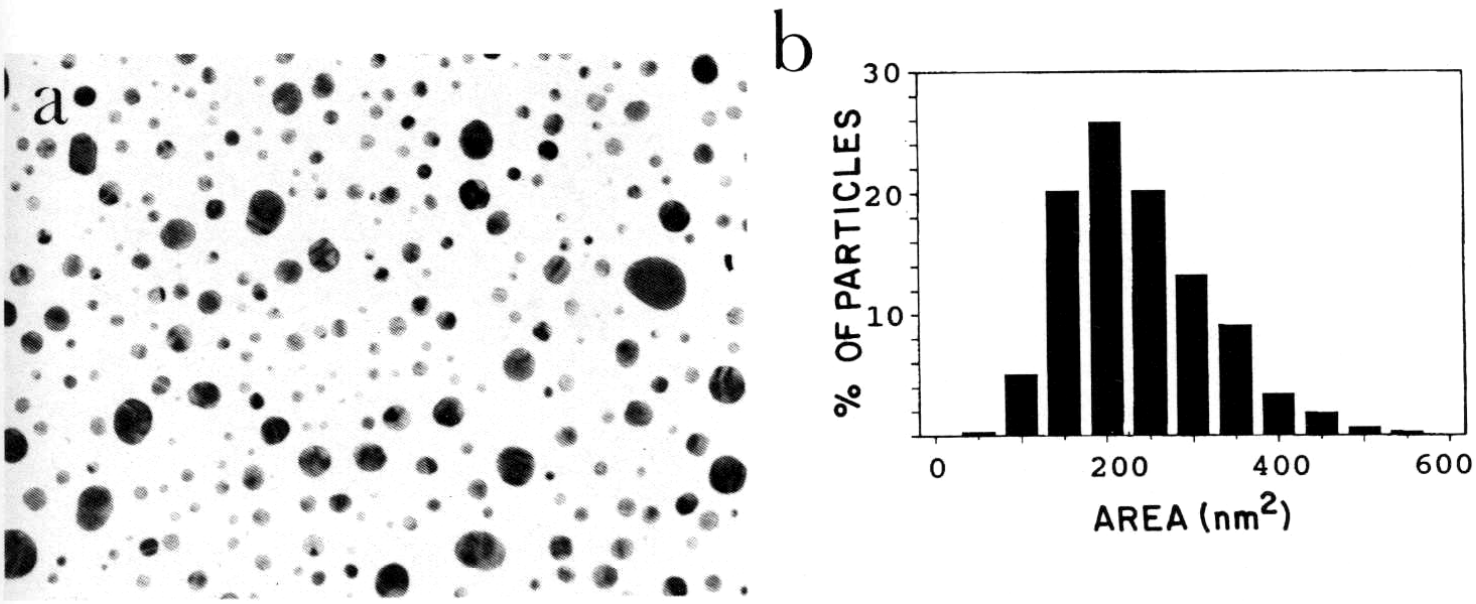


Figure 2. a) Image of the same sample after heating at 800ºC during 3 hours. b) Corresponding size distribution.

that in the upper part of the micrograph it is represented another group of two small and one large particles at similar distances, which do not show ultra-fast coalescence. Although it can not be noticed on the micrographs presented the rides tape indicated that the particle showed quasimelting fluctuations for some time after coalescence until comes to stable position.

3.3 Coalescence of two similar sized particles

An extremely interesting sequence shown in Figs. 4a-d corresponds to the bright field image. Figs 4e-h show the corresponding image after that computer processing has been performed. In particular, in this case pseudo-coloring has been used to enhance the contrast. In the first step the particles start to fluctuate and then come in contact Figs. 4a and 4e. After a short time they become an elongated particles as shown in Figs. 4b and 4f and finally the particle becomes rounded. The whole sequence is extremely fast and happens in few milliseconds. The final rounded particle remains fluctuating this is clearly indicated by the difference between the images 4c and 4d and its corresponding pseudo-colored images. Note that particles surrounding this pair are not altered at all. The resulting particle of this flash coalescence is only 26% larger in diameter than the original particles, fact which strongly suggests that the particle is not a solid (or at least in not behaving like one), since its size increase is typical of liquid droplets. Indeed in many examples of coalescence cited in the literature the size of a compound particle is sum of the sizes correspondidg to the individual particles. A typical example is the double icosahedron studied by Marks and Smith [8]. The particle appears to be a liquid and the coalescence process is controlled by the minimization of surface tension. It should be noted that in the processed images a different contrast arises around the surface of the particle which might indicate that some of material that surrounds the particle is in a different state. Very likely in a liquid state. However considerable caution should be taken before any conclusion is made because the contrast changes in this picture can not be straightforward interpreted as thickness variations.

3.4 Coalescence with extreme changes on shape

The next example of flash coalescence is perhaps the most dramatic and it is shown in the Figs. 5a-j in direct image and in Figs. 5k-t in processed image. The sequence starts with two particles that are in contact indicated by arrow in Fig. 5a) and they start to fluctuate and eventually coalesce. Then a triangular shaped particle, which is formed by the coalescence, starts to change in shape becoming rounded and then triangular again. Along the whole sequence it can be seen in neighbour particles that they get in touch first then are separated again. This kind of behavior is not the case of a normal growth by

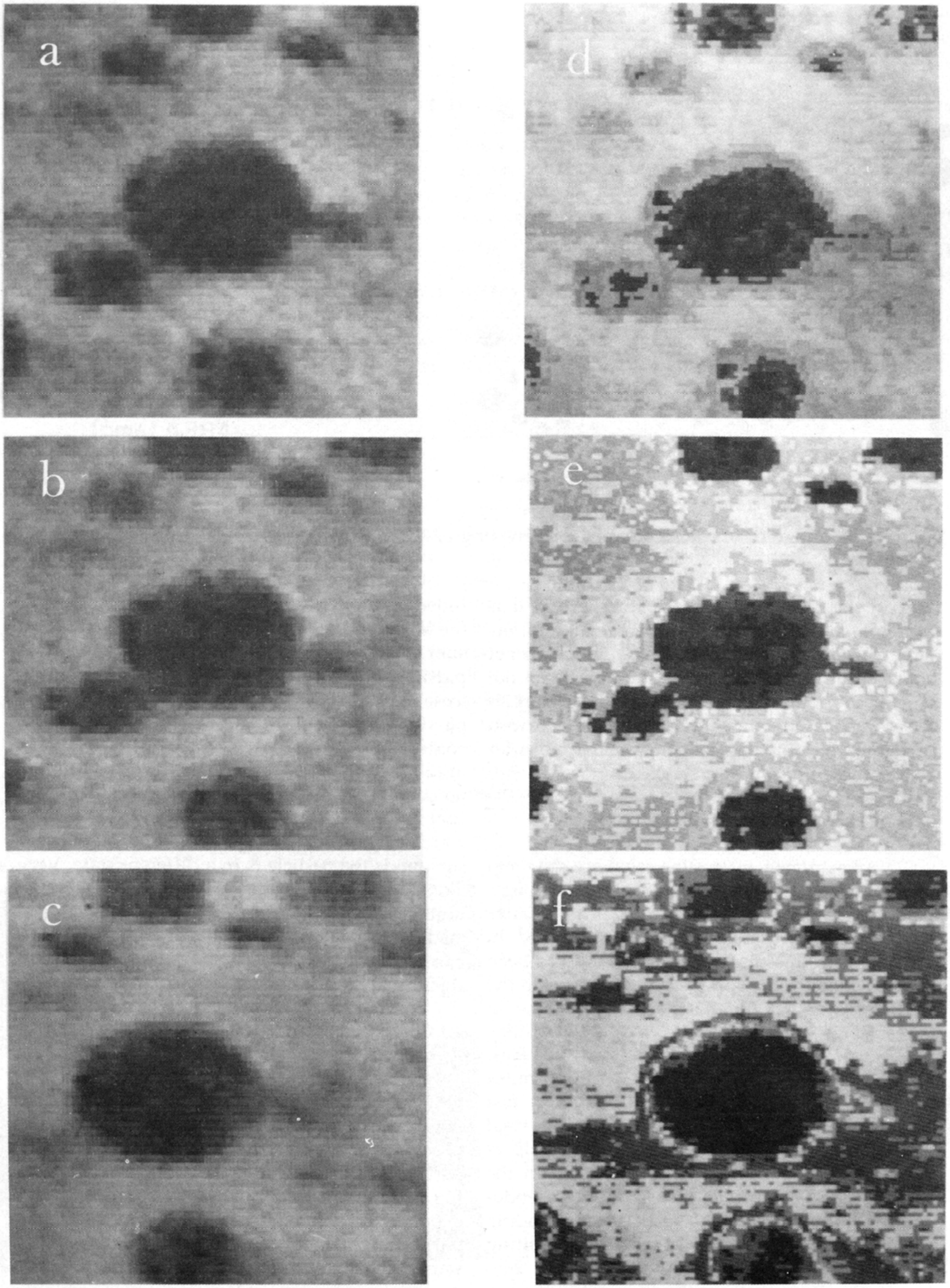


Figure 3. Coalescence event in which the small particles coalesce with a larger one. a)-c) shows different stages of the coalescence d)-f) shows the images with pseudo-coloring. The time frame between pictures is 16.6 ms.

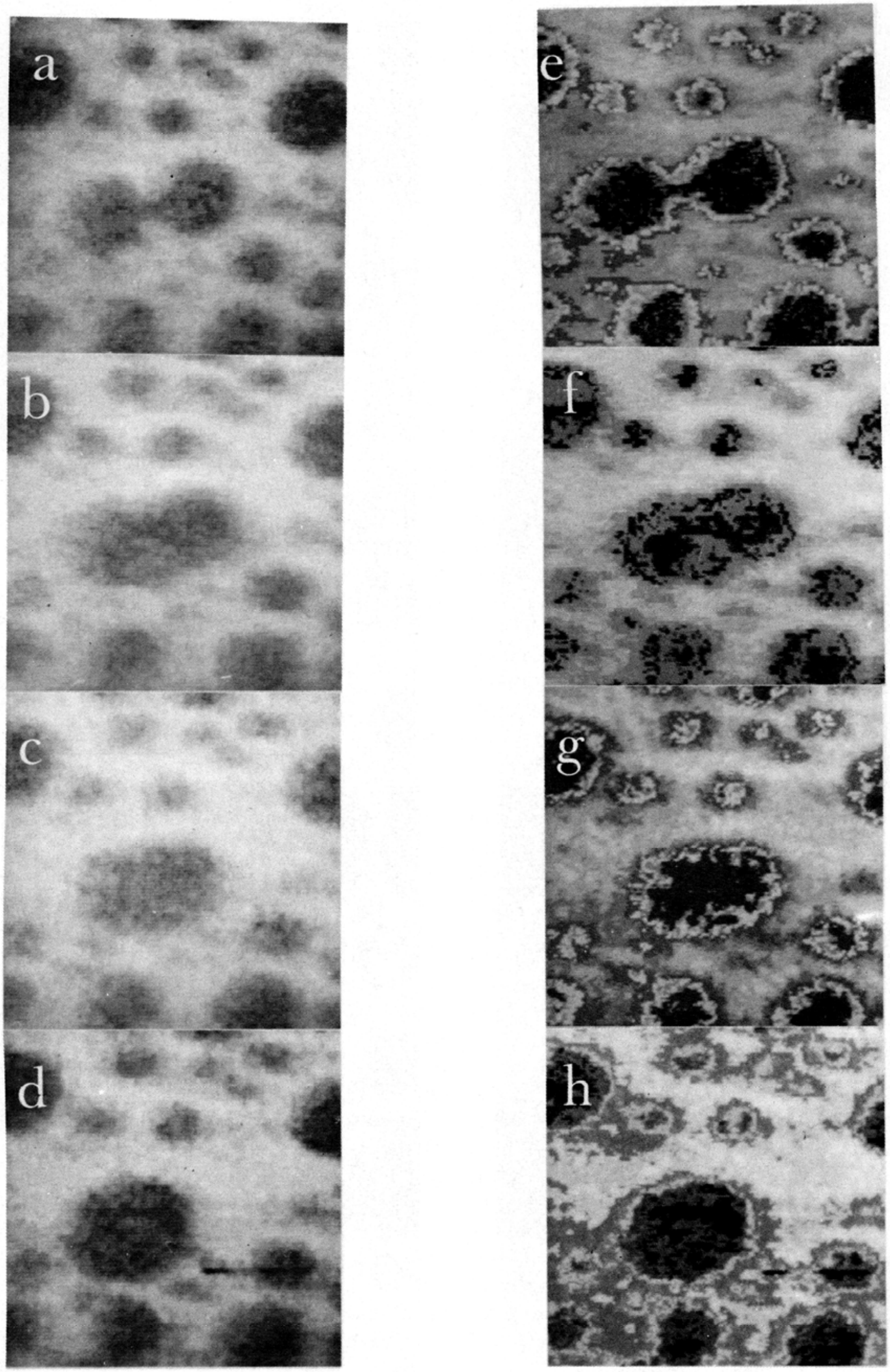
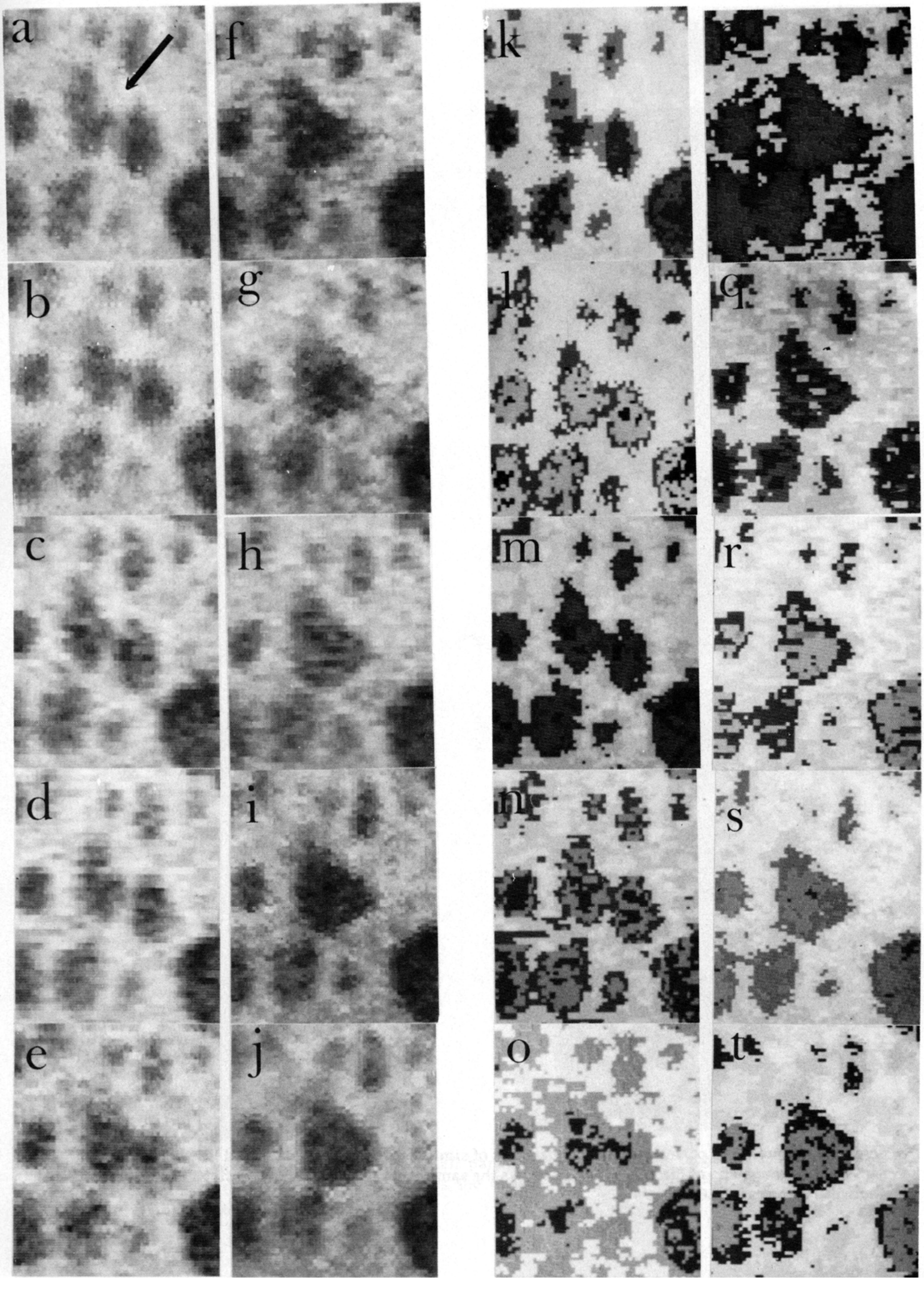


Figure 4. Sequence of coalescence of two particles of similar size suggesting a liquid like behavior. a)-d) shows different steps of the process. e)-h) shows the same event after image processing. The time frame between pictures is 16.6 ms.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surface diffusion in which particles once in contact do not separate. This strongly suggest the possibility of charging on the particles being çonnected with the shape fluctuations as recently suggested [9]. This sequences clearly illustrates the principle that shape fluctuations always occurs before and after flash coalescence.

3.5 Coalescence involving several particles

A final example of flash coalescence is given in Figs. 6a-f in this case two particles come in contact (arrow) and then fluctuate. However, the contact is broken and the one of the particles coalesce with another one on top. This case again illustrates the fact that contact between particles do not necessarily limpies coalescence and also suggests the possibility of strong repulsive forces that start to act suddenly. These forces can of course, be related to the charging of the particles. Moreover, it has been observed that two particles which are fluctuating are in contact with each other for a long period of time with no coalescence neither repulse.

4.Discussion

The results presented so far clearly shown the peculiar behavior of nanoclusters when the temperature is raised to ~800°C, therefore many aspects of the problem should be analyzed. In the first place it should be considered the influence of the electron beam heating on the observed phenomenon. In the case of room temperature observation we do not notice any particle fluctuation at the dose used for the sample. In order to observe fluctuations it was necessary to increase the beam current to ~100Å/cm^2 during a few minutes [4]. This clearly indicates that most of the particles were in a deep potential well in the substrate and are therefore stable. When the temperature was raised to 550°C., most of the particles on the observation field remain stable. The lowest possible electron beam current that can be used for the observations is ~1Å/cm^2. Under this condition few particles start to fluctuate and then undergo different types of coalescence. When the temperature of the substrate is raised might be induced a loose thermal contact with the substrate and then electron beam heating might become important (specially for larger particles). This point is very hard to prove or disprove since it was not noticed any special orientation or geometry of the particles that start to fluctuate.

Flash coalescence of the type described in this work is totally different from the normal sintering of grains which was described in the classical work of Pashley et. al. [10]. In the recent work of Flueli et. al. [6], in which the phenomenon was induced by the electron beam heating, the grains of gold become in contact by surface diffusion. The contact occurs along (111) faces, and then surface diffusin goes on until a neck is formed. The coalescence continues along the neck until a single particle, frequently deffective, is formed. Even in latter stages the planar defects more along the particle the composite crystal builds up by the migration of atoms on the surface of aggregates. The total process might take ~10-15 sec. The present case corresponds to a qualitative different situation. The flash coalesce is a extremely fast phenomenon which occurs in less 0.1 sec and therefore can not be explained by regular surface diffusion.

On the other hand the behavior observed in Fig. 4 clearly suggests a liquid like behavior. In fact, it is known from experiments with liquid mercury droplets [11] that when two similar size droplets collide the resulting droplet has a diameter about 26% larger than either dropled. This is exactly what was observed in the Fig. 4. On the other hand, the fact that the particle becomes rounded suggests a minimization of their surface tension.

This would have allow us to determine whether the particle is in a true molten state or remains as a solid (as in the case of pure quasimelting fluctuations) but there are, however, some other indications that support the idea of a mixed state which will not correspond enterely to a liquid or solid state. In particular the Fig. 5 shows a particle that after coalescence becomes triangular (probably a flat platelet). This is inconsistent with the idea of the particle being already in a solid state since the triangular

Figure 5. Sequence of images showing the ultra-fast coalescence of two particles and the subsequent fluctuations on the resulting particle. a)-j) shows the image with proccesing and k)-t) the same sequence but with pseudo-coloring. The time frame between pictures is 16.6 ms.

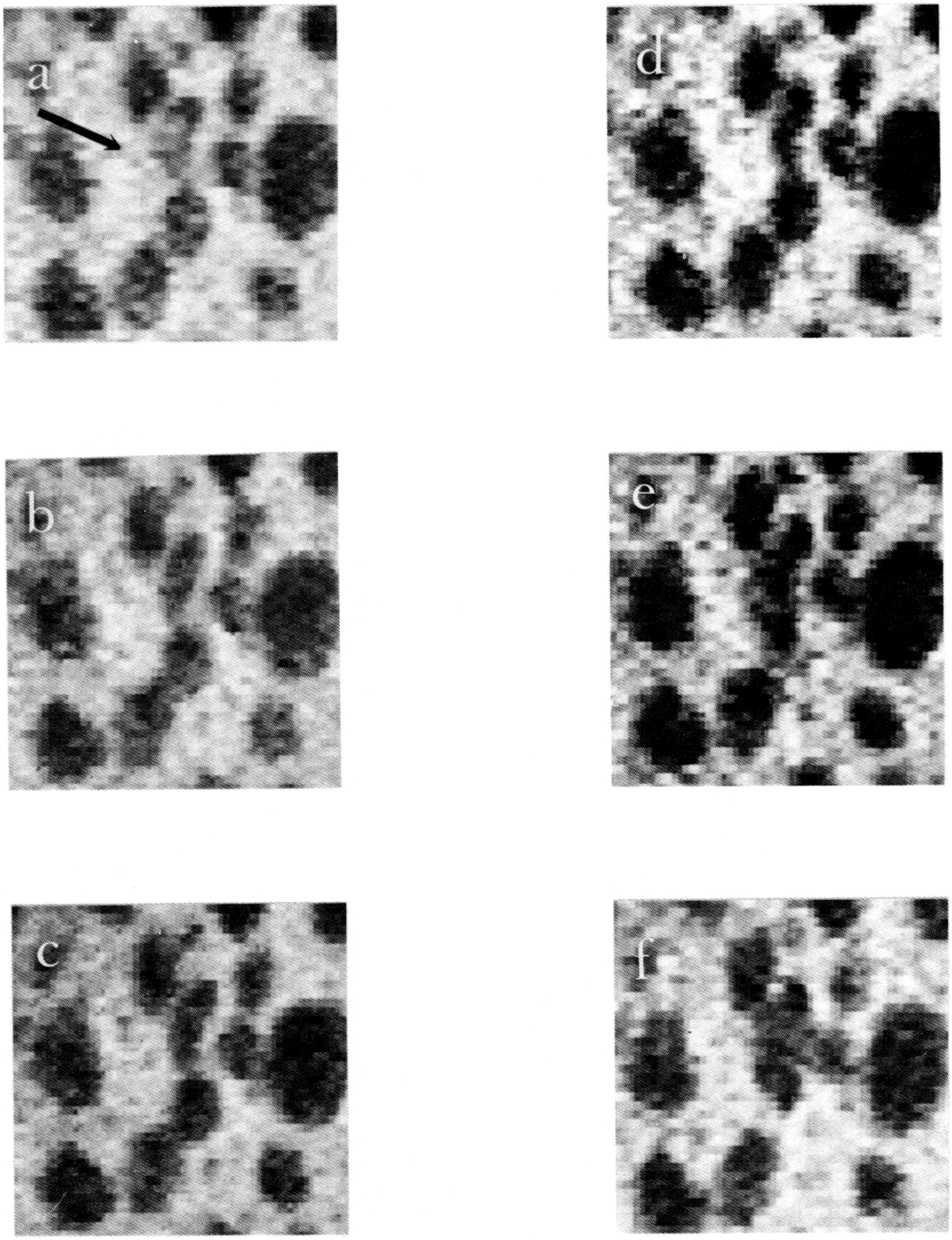

Figure 6. Sequence of images a)-f) which indicates that a particle in contact with a particle can finally coalesce with a different particle.

shape will not represent a minimum surface tension configuration. Therefore it appears that at high temperatures (0.5 Tm) the cluster is already a mix between solid an liquid [12]. Some of the results presented can be understood using the theoretical calculations of Ercolessi et. al. [13] who demonstrated that melting started at the surface of cluster and the nucleated to the rest of the particle. They predict that (111) surfaces will remain ordered up to melting. However, in other faces there are premelting effects such as high atomic diffusion of those located at edges between facets, i.e.; surface melting preceed bulk melting.

5. CONCLUSION

It has been observed a mechanism of particle coarsening which occurs in a shorter period of time than the classical case described by Pashley et. al. [10] and is always preceded and followed by quasimelting oscillations in the particle structure. This phenomenon occurs at T>1/2Tm. It appears that surface enhanced diffusivity related to surface melting might explain the fact that this coalescence occurs faster than the one reported by Pashley et. al. [10]. The phenomenon described in the present investigation might have relevant consequences for catalytic reactions which occur, generally, at high temperature.

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