

BEHAVIOUR OF EMBEDDED METALS AND ALLOYS AT SMALL SIZES

K. Chattopadhyay
Department of Metallurgy, Indian Institute of Science
Bangalore – 560 012, India

Abstract

Nanomaterials represent a field of vigorous activity in recent time. Although not new to metallurgists, the current widespread interests do provide opportunities to look at the issues in a new light. Drawing from the recent research and experience of the present author and his group, the article provides some thoughts on the challenges and opportunities that exist for one class of nanomaterials, namely, nano embedded materials. The article highlights the basic issues, resolution of which are necessary for the future application of these materials

BEHAVIOUR OF EMBEDDED METALS AND ALLOYS AT SMALL SIZES

K. Chattopadhyay
Department of Metallurgy, Indian Institute of Science
Bangalore – 560 012, India

Introduction

It is well known for quite some time to the community of metallurgists that scaling down of the size of the second phase like precipitates improves properties. However, understanding of the effect of size on the materials properties gained momentum with the emergence of technological needs of small scale systems and in particular what is today known as nanotechnologies. It is increasingly realized that reducing the scale and distribution of grains and phases yields properties which is significantly different from the bulk properties. Thus, a new class of materials has emerged in recent times, which are popularly known as ‘ultra fine materials’ or ‘nanomaterials’.

The nanomaterials can be classified by size, dimensions and morphologies of the grains or phases. From the viewpoint of basic understanding they are often classified in terms of the dimension of the smallest length scale. Thus one can have zero, one, two or three dimensional nanomaterials. The examples of these are shown in figure 1. The classical example of zero dimensional nanomaterials is quantum dot. The thin films and multilayers, nanotubes or nanowires and the nanograined materials are examples of one, two and three-dimensional nanomaterials. The change in the property of the nanomaterials is a function of the length scale. As the length scale decreases, the surface and interface areas increase. For a bulk materials the energy contribution from the surfaces and interfaces are relatively small and are generally ignored for any discussion related to the energetic of the system. However, decreasing the grain size increases the importance of these areas. The materials behavior is significantly influenced by the surface and interface energies. It is possible to quantitatively evaluate the increase in the surface area as a function of size using simple geometrical criterion. Let us take a bulk object of a given dimension r_0 , break it into smaller pieces of size r_1 and reassemble it back. Assuming spherical geometry and a thickness ‘T’ to the interface (as shown in the figure2a), one can obtain a functional relation between the size of the reduced size of the fragments and the additional volume of the surface regions that are created when they are assembled back into the original shape. This is given by the following equation

For sphere, $A=3$

$$V_B = \frac{AV_0}{r_1} T \quad 2$$

As can be seen in fig.2b the volume occupied by the surface regions scale inversely with size of the smaller subunit. At smaller size, it can be a significant fraction of the volume. Thus, the properties of these interface regions start dominating the properties of the materials.

At still smaller size, quantum mechanical effects start appearing and the size begins affecting the density of states and band structure. The confinement of the electrons in small dimension leads to a discrete solution to the energy state and opens up gap in the density of state plot, which depends on the dimension. Typically the quantum effect starts dominating at sizes below $\sim 2\text{nm}$ while for sizes larger than this, additional energies due to interfaces and surfaces influence the properties. Figure 3b shows schematically the different domains of behaviour of the nanomaterials while fig3b shows the gaps in the energy state of electrons as the dimension of the materials decreases in one, two and three dimensions.

Nanomaterials can also contain more than one phase with different length scale for each phase. These are often termed as nanocomposites. Although the basic reasons for the property change remain unaltered, there can be significant difference in the behaviour of materials for the different class of nanomaterials. In this article we shall describe only one class of nanomaterials and endeavour to show some special properties that develop due to the reduction in the length scale. Nanosized particles dispersed in a matrix, which may or may not have nanoscaled grains, represent an important class of nanoscaled materials. This class of materials is often described as nanoembedded materials, nanocomposite or granular materials. Unlike free nanoparticles where additional surface energy due to increased surface area dominates the energetic, the interface energy between the matrix and the particles contribute to an additional energy for nano embedded particles. The contribution, therefore, comes from both the particle and the matrix. Thus, a change in the matrix can alter the properties of the particles. The interface energy consists of both structural and chemical contributions. The latter is generally ignored for free particles. However, it can significantly influence the properties of the embedded nanoparticles as well as their alloying behavior. Therefore, nanoembedded particles provide opportunities for materials development, which are often unique. In order to exploit these materials, it is necessary to understand the transformation behavior of these embedded particles. Again the behavior is often not an extension of what has been observed in free

nanoparticles. The present article illustrates some of the understanding that has been achieved through examples drawn from our work as well as from the research of other groups.

Synthesis of nanoembedded particles

Before we embark on the issues related to phase transformation and properties, it may be worthwhile to discuss briefly the various routes that have been utilized to synthesize this class of materials. The properties often depend on the route that has been followed to synthesize the materials. Even if we achieve similar scaling of the sizes of the embedded particles through different synthesis routes the materials behavior may not be identical. This is primarily due to the nature of the particle matrix interfaces, which is a strong function of the processing routes.

The two most popular synthesis routes in recent times for manufacturing these nanocomposites are rapid solidification processing and ion implantation. Both the processes are extremely effective if the embedded particles form immiscible systems with matrices. In case of rapid solidification, which is associated with a typical cooling rate of 10^6K/s , the high cooling rate is achieved through a conductive heat transfer process. On rapidly quenching a melt through an immiscible domain, the melt phase separates and forms a transient emulsion of two liquids. Subsequently, the larger fraction solidifies as matrix, thereby, producing a distribution of nanosized liquid particles dispersed in this matrix. Finally, the liquid particles solidify to yield the final product. The solidification process of the liquid droplets is profoundly influenced by the surrounding matrix [1]. The matrix catalyses the nucleation of solid and hence determines the crystallography of the particle-matrix interface. In most cases, one observes an epitaxial relationship between the embedded particles and the matrix. During ion implantation, the high-energy ions dissipate the energy by local disordering of the matrix [2]. The rearrangement process takes place in the solid-state and is strongly influenced by the crystal orientation of the matrix. Consequently, one often observes a strong epitaxial relation between nanoparticles and the matrix. In contrast, the formation of nanoembedded particles by mechanical alloying involves breaking down of both the matrix and the embedded particles by a process of repeated fracturing and re-welding in the solid state [3]. This results in complete randomization of the orientations of the embedded particles. The interfaces in such cases are completely incoherent having higher energies.

Embedded nanoparticles can also be prepared in relatively thicker films by multilayer deposition employing physical vapour deposition techniques. Particles are deposited on a thin film by controlling deposition parameters. These are finally capped by depositing another layer of matrix material. It is also possible to synthesize nanoembedded particles by Sol-gel route [4]. This is a particular effective route for ceramic matrices and can yield a very uniform distribution of particles. To illustrate we have presented in figure 4 a composite of microstructure of embedded Pb nanoparticle obtained through different processing routes.

Influence of matrix and shape transformation in nanoembedded particles

As the nanoparticles are embedded in a matrix, the chemical stability requires that the chemical potential across the interface should be the same. If we treat the problem in a macroscopic framework, one can immediately infer that the equilibrium will be shifted from that expected in bulk cases due to Gibbs Thomson effect. This leads to a situation where the compositions of the embedding particles could be different from that of the bulk cases. Microscopically, as the size decreases, contributions of edges, corners, and defects like steps to the surface energy become significant. These are ignored in the bulk situation.

Decrease in length scale also exerts influence on the timescale needed for the completion of the kinetic processes associated with the achievement of equilibrium and other relevant phase transformations. As the required diffusion distance decreases due to the small size of the particles, equilibrium can be achieved in a very short time. Thus one expects the embedded particles to acquire equilibrium shape.

Experimentally, the expectation of equilibrium shape is often validated particularly for pure metals. Figure 5 shows the shape of an embedded In particle. This has a metastable cubic structure and the expected equilibrium shape is a cuboctahedron. This is precisely what has been observed in the experiment. Similarly, Pb in Al exhibits cuboctahedral symmetry. The equilibrium shape for an embedded particle however, must take into account the crystallography of the matrix in addition to the particles. The intersection group of these two gives the equilibrium shape [5]. Thus the orientation relationship between the matrix and the particle plays a crucial role in determining the shape of the particles. For example, same Pb particle embedded in a Zn matrix does not exhibit cuboctahedral shape [6]. The orientation relationship in this case is such that the closed packed planes in the two structures are parallel. An

analysis of the interaction group indicates that the point group symmetry of the equilibrium shape is 6/mmm. The observed shape is a truncated hexagonal biprism, which conforms to this point group as shown in figure 6. A consequence of the above reasoning is the following. If one of the phase is liquid or amorphous, which has point group symmetry of ($\infty\infty\infty$) corresponding to a spherical shape, the shape of the embedding particle will be dictated by the crystallography of the second phase. Thus, embedded liquid of nanometric size is expected to be bounded by a cavity representing the equilibrium shape of the matrix. This has indeed been the case. Figure 7 shows a lead particle at 350°C embedded in aluminium matrix [7]. The particle is actually molten but exhibit well defined crystallographic shape. It is relevant to explore at this point what happens at very small sizes when edges and corner energies dominate. As chemical potential of the edges and corners will be slightly higher, these particles will have roughening transition at much lower temperature than the comparatively bigger particles. No study exist which points to a shape transition due to this factor. In principle one can expect that there may be a situation where alternate shapes with the same point group symmetry but with lesser number of edges and corners may get stabilized at small sizes. In most of the experiments and analysis of the results concerning nanoembedded particles, the role of elastic energy is ignored. However, it can have significant influence. In a remarkable work, it is recently shown that elastic energy can influence the size that can exist. The work predicted certain so called ‘magic sizes’ that only can exist in nanoembedded condition [8]. This is verified by experiment as shown in figure 8.

Shape of alloy particles

In recent times increasing success has been achieved in synthesizing embedded nanoparticles of alloys. Alloying can lead to formation of either single or multi-phase alloys. In the former case, the shape is governed by the change in free energy due to alloying. In particular the change in surface energy due to segregation at the boundary can play profound role. For example, the shape of single phase InPb particle is shown to have an octahedral shape instead of cubeoctahedral shape [9]. A more challenging problem is the size dependence of shape of multiphase particles. The nanoparticles in general, exhibit bi or tri crystals. Figure 9 shows example of such alloy particles of Pb and Sn [10]. Understanding the shape evolution of these particles pose major challenge

to both electron microscopist as well as theoreticians. We shall revisit this aspect latter in this article.

First order transformation in nano embedded particles: The case of solidification

The process of nucleation and growth characterizes the first order structural phase transformations. Low melting nanoembedded particles provide opportunities to study these processes, especially the phenomena of nucleation in a controlled manner. In a celebrated experiment, Turnbull [11, 12] dispersed the melt of mercury into a large number of droplets and studied their solidification behavior to establish the validity of the classical theory of homogeneous nucleation. On the basis of success of this theory, this was further adopted to yield what is known as theory of heterogeneous nucleation by replacing the homogeneous fluctuations by heterogeneous fluctuations at preexisting catalytic interfaces. Although, the theory is believed to be successful, several attempts to get experimental verification in the line of the experiments for homogeneous nucleation failed. The nanoembedded particles have provided opportunities to carry out such experiments. Following a theoretical development to adopt the nucleation theory to the case of embedded particles by Kim and Cantor [13], experiments carried out in our laboratory using embedded nanoparticles of Pb in Zn matrix could provide first experimental verification of the theory [14]. However, the most important consequence of solidification experiments is the understanding reached for diffuse liquid to solid transformation. Careful calorimetric experiments often indicate that at nanoscale this transformation is often diffuse and occurs over a very large temperature range. As a consequence, sometimes it is difficult to record the thermal effect due to such transformation. Insitu electron microscopic studies [9] have confirmed that different particle in the same grain solidifies at different temperature representing different undercooling behavior. Further, for the same particle, the effect is not reversible and changes with cycling. A careful analysis coupled with high-resolution imaging indicates the prominent role of the interface defects, which catalyze the nucleation. The defects can be modeled in terms of a spread in contact angle [15], which takes into account the contribution of the defects. This has resulted in a satisfactory match of the experimental results and the simulated thermal curves. The next challenge lies in identifying these defects and determining the energies associated with them in a more quantitative manner through experiments and simulation.

Understanding melting: Opportunities due to nanoembedded particle

Melting is a first order phase transformation associated with large change of energies. However, the mechanism of melting is not clear. Till to date there is no clear evidence of classical nucleation of melt in the solid matrix. Lindemann [16] in the beginning of the century has proposed Debye instability of the interface for the initiation of melting. Nanoembedded particles offer wonderful opportunities for studying melting for various reasons. The most prominent of them is the possibility of insitu study of the melting processes inside the electron microscope. The second and equally important window of opportunity that nanoembedded particles present, relates to the possibility of tuning the Debye vibration of the interface utilizing the constraining effect of the matrix. This can be done by changing both the crystallographic orientation of the embedded particles as well as by changing the matrix itself. The main experimental results of the melting behavior of the nanoembedded particles [17] can be summarized as follows:

- (i) In case where the particles exhibit good epitaxial relations with the matrix, some of the particles show superheating.
- (ii) Superheating is directly related to the achievement of perfect defect free interfaces. Presence of defects, which can act as sites for larger Debye vibrations, eliminates superheating.
- (iii) For embedded particles showing random orientation, one observes depression of melting point. The effect is similar to the size dependent depression of the melting point observed in the free nanoparticles.
- (iv) The observed superheating cannot be explained in terms of pressure effects that one anticipates due to the constraining influence of the matrix.
- (v) Insitu transmission electron microscopy indicates that the initiation of melting takes place from the edges and corners of the particles. However, no direct evidence of the formation of nuclei could be observed.

Combining all the evidences that have been accumulated through studies on the nanoembedded particles, Lindemann's criteria of melting still seems to provide the most satisfactory answer to the observed facts. However, quantitative confirmation still eludes the scientific community. There are attempts to make quantitative estimation by coupling Lindemann's criteria to the theoretical

developments due to Mott [18] and Born [19] using molecular dynamics simulation. Despite the progress [20], this issue is still open to both experimental and theoretical fraternities.

Transformation in multiphase nanoembedded alloys

As mentioned in the beginning, the phase diagram delineates the region of stability of different phases need to be modified for nanosized particles. Recently, such a modification has been attempted for Bi-Sn system. As can be seen from the figure 10, there is a dramatic change in the phase coexistence with significant depression of eutectic point [21]. This was verified by the observation of molten layer on submicron Bi-Sn particles [22]. Recently, a series of experiments have been carried out by a group led by Mori [22, 23, and 24] at electron microscopy laboratory in Osaka University. They used a novel technique of insitu metal deposition within the electron microscope to study alloying behavior of the nanosized particles. It was shown that when Bi is deposited on Sn nanoparticles spontaneous alloying takes place driving a crystalline to amorphous transition. Similar results were also observed in the case of Sn deposition on In particles. On the other hand, in systems like Au-Zn [25], spontaneous alloying leads to the formation of solid solution and intermetallic compounds Au_3Zn and $AuZn$. These investigations highlight the size dependent phase transformations that are possible in alloy nanoparticles.

Solid state transformation in embedded nano particles

There exist limited studies on the solid-state transformation behavior of the nano embedded particles. The understanding is very limited and the possibilities are immense. It is well known that at small sizes, some of the metal particles undergo phase transformation. The copper nanoparticles embedded in iron matrix are reported to undergo FCC to 9R transformations [26]. One of the simplest size dependent transformations can be observed in In particles embedded in Al matrix [26]. At small size, tetragonal indium becomes face centered cubic when constrained by a fcc aluminium matrix. A similar result was observed in thallium nanoparticles embedded in aluminium matrix. Although thallium exhibits an hcp structure in bulk, the nanosized inclusions exhibit with decreasing size bcc and fcc structures [28]. In recent times there are reports of several metals and intermetallic

particles undergoing phase transformations where they are deposited as layers sandwiched between layers of different materials [29]. One expects these transformations to occur as a function of decreasing size in the embedded nanomaterials. This line of research gains added importance due to the advent of GMR and Spintronics. For example, dispersion of FeCo nanoparticles in Cu matrix yields good GMR properties. However, at low temperatures some of these particles undergo martensitic transformation as shown in figure 11 thus altering the transport properties [27].

Recently, we have explored the effect of size on the pressure dependent transition in Bi by embedding Bi in different matrices. These experiments, although at a preliminary stage indicates a change in transformation behavior influenced both by the size and the embedding matrix. Magnetic behaviors of embedded nanoparticles provide both scientific and technological challenges. The advent of superparamagnetism with decreasing size is well established. However, the interaction of embedded particles through the embedding matrix is less understood and can lead to decrease in magneto crystalline anisotropy and exchange coupling. This had led to the development of new class of magnetic material with the trade name FINEMET where soft magnetic ordered FeSi particles embedded in iron based amorphous matrix are responsible for development of very high permeability [30]. Replacement of hard magnetic particles like FeNdB as embedding particles in iron rich matrix on the other hand leads to the development of very high coercivity due to exchange interaction. This class of materials is known as exchange spring magnets.

Superconducting transition in Nanoembedded materials

Embedded nanoparticles provide unique opportunities to study the superconducting transition at small length scale. Known as granular superconductor, this class of materials is subject of increasing interest in recent times. Two length scales are important in such materials. They are size of the particles and inter particle separation. The former is important for the study of size dependent depression of the superconducting transition. Using a combination of detailed electron microscopic characterisation and measurement of magnetization as a function of temperature, we are successful in obtaining first quantitative estimate of depression of transition temperature as a function of size for Pb

particles embedded in an amorphous matrix [31]. Currently, we are exploring the effect of embedding matrix on the superconducting transformation temperature. The results suggest a significant influence of matrix on the nature of the size dependent depression of the transition temperature [32] as shown in figure 12. The transport studies indicate increase in proximity induced coupling of superconducting particles. For a given distribution, there exists a critical temperature for superconducting percolation threshold below which the entire composition behaves like a single superconductor [33]. A major challenge in granular superconductors is to understand the size dependence of the type II superconducting transition and in particular the influence of size on H_c . The work in this direction has just begun and we expect progress in near future.

Conclusions

We have tried to illustrate in this presentation the challenges and opportunities that embedded nanoparticles present to the researchers. These materials can potentially exhibit new properties and therefore the technological implications are immense. Understanding of stability and phase transformation of these particles are central to designing meaningful future applications. In India, we have an early lead in this class of materials and if pursued vigorously, can yield rich dividend.

Acknowledgement

The author acknowledges gratefully the contributions of his research students Dr. R. Goswami, Dr. N. Ravishankar, Dr. P. Bhattacharya and Ms. V. Bhattacharya and his friends and collaborators Prof. B. Cantor, Prof. W.T.Kim, Prof. A.P.Tsai, Prof. D.L.Zhang, Prof. P.Ramachandrarao, Prof. S.N.Ojha and Prof. S.Ranganathan

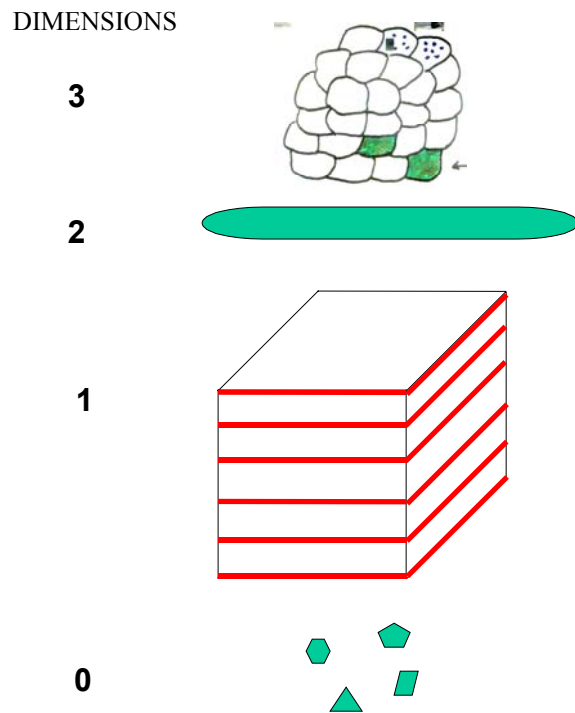
References

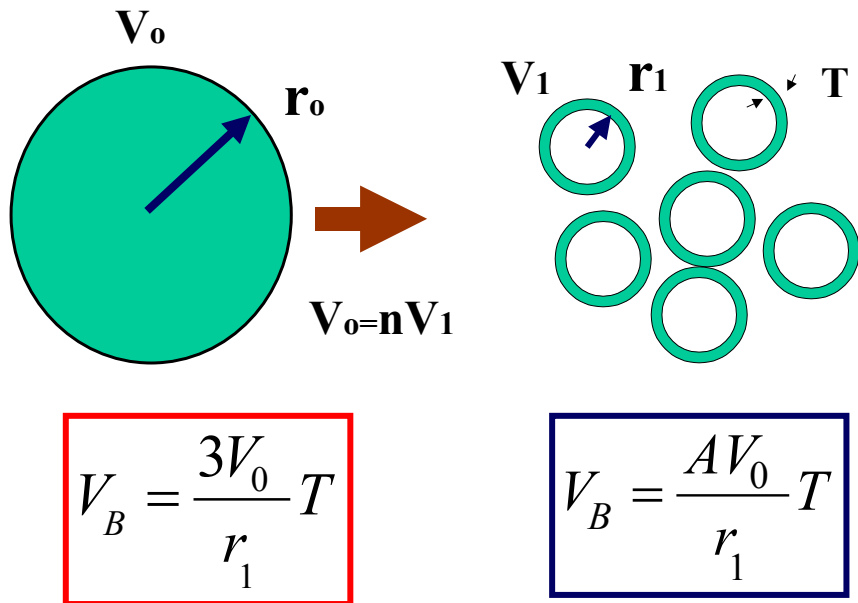
- [1] K. Chattopadhyay, Bull. Mater. Sci., 15, 515, (1992)
- [2] E. Johnson, V.S. Touboltsev, A. Johansen, U. Dahmen, and S. Hagege, Nucl. Instr. and Meth. in Phys. Res. B., 127/128, 727, (1997)
- [3] H.W. Sheng, G. Ren, L.M. Peng, Z.Q. Hu and K. Lu, Phil. Mag. Lett., 73, 4, 179 (1996)

- [4] P. Bhattacharya, and K. Chattopadhyay, *Materials Transactions JIM*, 39, 75, (1998)
- [5] J.W. Cahn, and G. Kalonji, *Proc. International Conference on Solid → Solid Phase Transformations*, The Metallurgical Society of AIME, 3, 1982
- [6] R. Goswami, and K. Chattopadhyay, *Phil. Mag. Lett.*, 68, 215, (1993)
- [7] K. I. Moore, K. Chattopadhyay and B. Cantor, *Proc. R. Soc. Lond.*, A414, 499, (1987)
- [8] U. Dahmen, S.Q. Xiao, S. Paciornik, E. Johnson and A. Johansen, *Phys. Rev. Lett.*, 78, 3, 471, (1997)
- [9] P. Bhattacharya, B. Mazumdar, and K. Chattopadhyay, *J. Elec. Micro.*, 48(Suppl.) 1047, (1999)
- [10] Victoria Bhattacharya, P. Bhattacharya and K. Chattopadhyay, *Materials Science Forum*, 386-388, 427, (2002)
- [11] D. Turnbull, and J. C. Fisher, *J. Chem. Phys.*, 17, 71, (1949a)
- [12] D. Turnbull, *J. Appl. Phys.*, 20, 817, (1949b)
- [13] W.T. Kim, and B. Cantor, *Acta Metall. Mater.*, 40, 3339, (1992)
- [14] R. Goswami, K. Chattopadhyay, W. T. Kim and B. Cantor, *Metall. Trans. A*, 23, 3207, (1992)
- [15] R. Goswami and K. Chattopadhyay, *Acta Mater.*, 44, 6, 2421, (1996)
- [16] F. A. Lindemann, *Z. Phys.*, 11, 609, (1910)
- [17] R. Goswami, and K. Chattopadhyay, *Acta Metall. Mater.*, 43, 2837, (1995)
- [18] Q. Jiang, Z. Zhang and J. C. Li, *Acta Mater.*, 48, 4791, (2000)
- [19] Z.H. Jin, P. Gunbsch, K. Lu and E. Ma, *Phys. Rev. Lett.*, 87, 055703, (2001)
- [20] R.W. Cahn, *Nature*, 413, 582 (2001)
- [21] G. L. Allen, and W. A. Jesser, *Journal of Crystal growth*, 70, 546 (1984)
- [22] J. G. Lee, H. Mori, and H. Yasuda, *Phys. Rev B*, 66, 012105, (2002)
- [23] J. G. Lee, H. Mori, and H. Yasuda, *Phys. Rev B*, 65, 132106, (2002)
- [24] J. G. Lee, H. Mori, and H. Yasuda, *Phys. Rev B*, 64, 004101, (2001)
- [25] H. Mori, and H. Yasuda, *Phys. Rev. Lett.*, 69, 26, 3747, (1992)
- [26] S.N.Ojha and K. Chattopadhyay, *Trans. IIM*, 30(1977)423
- [27] N. Ravishankar, J. Park, K. Aoki, and K. Chattopadhyay, *J. Appl. Phys.*, 86, 2733, (1999)

- [28] A. H. Sorensen, E. Johnson, K.K. Bourdelle, A. Johansen, H. H. Andersen and L. Sarholt-Kristensen, *Phil. Mag. A.*, 75, 6, 1533, (1997)
- [29] R. Banerjee, R. Ahuja, and H. L. Fraser, *Phys. Rev. Lett.*, 76, 3778, (1996)
- [30] M. Manivel Raja, K. Chattopadhyay, B. Majumder, and A. Narayanasamy, *J. Alloys Compounds*, 297, 199, (1999)
- [31] A.P. Tsai, N. Chandrasekhar, and K. Chattopadhyay, *Appl. Phys. Lett.*, 75, 15, (1999)
- [32] K. Chattopadhyay, V. Bhattacharya and A.P. Tsai, *Materials Research Society Symposium Proceedings*, Vol.703, V13.22.1, (2002)
- [33] R. Goswami, S. Banerjee, K. Chattopadhyay and A.K. Raychaudhuri, *J. Appl. Phys.*, 73, 2934, (1993)

Fig.1 A schematic showing the examples of the possible objects of reduced dimension





A - Geometric constant

Figure 2a. Schematic of the surface created during the fragmentation of a spherical particle into 'n' number of smaller particles.

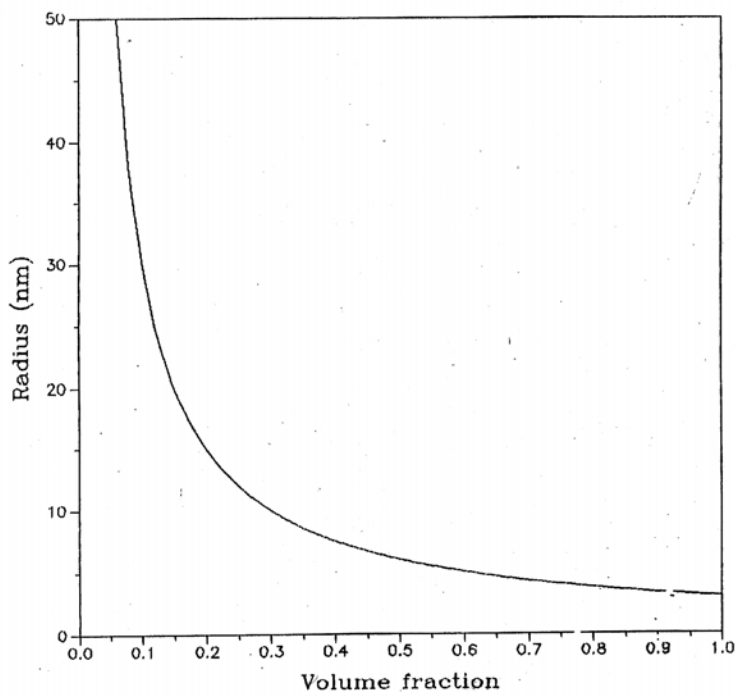


Figure 2b. A plot of estimated volume fraction of grain boundary volume versus grain size

Bulk Properties



100 nm

Surface energy dominated

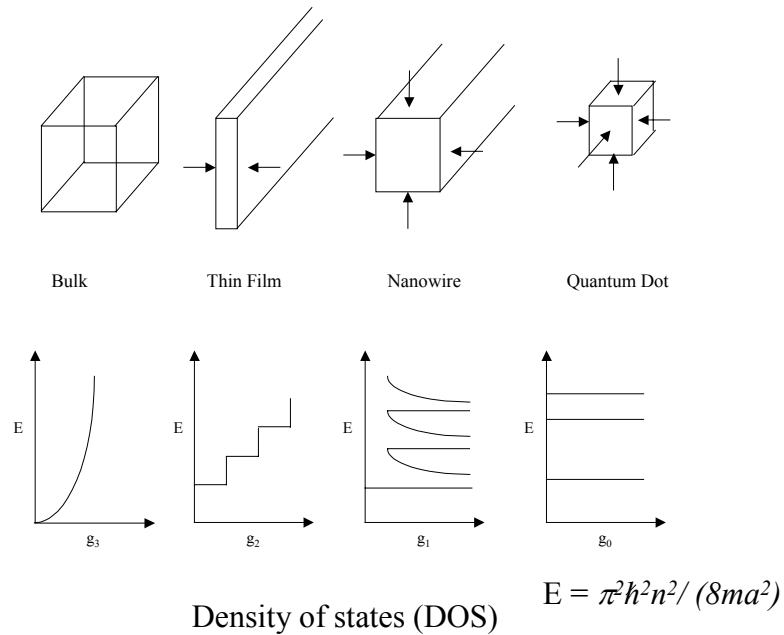


1 nm

Change in electronic state Quantum effect



Figure 3a. Schematic of the dominant mechanism controlling the change in properties as a function of the reducing size.
 b. A schematic diagram showing discretisation of the density of states as the dimension of the crystal is reduced



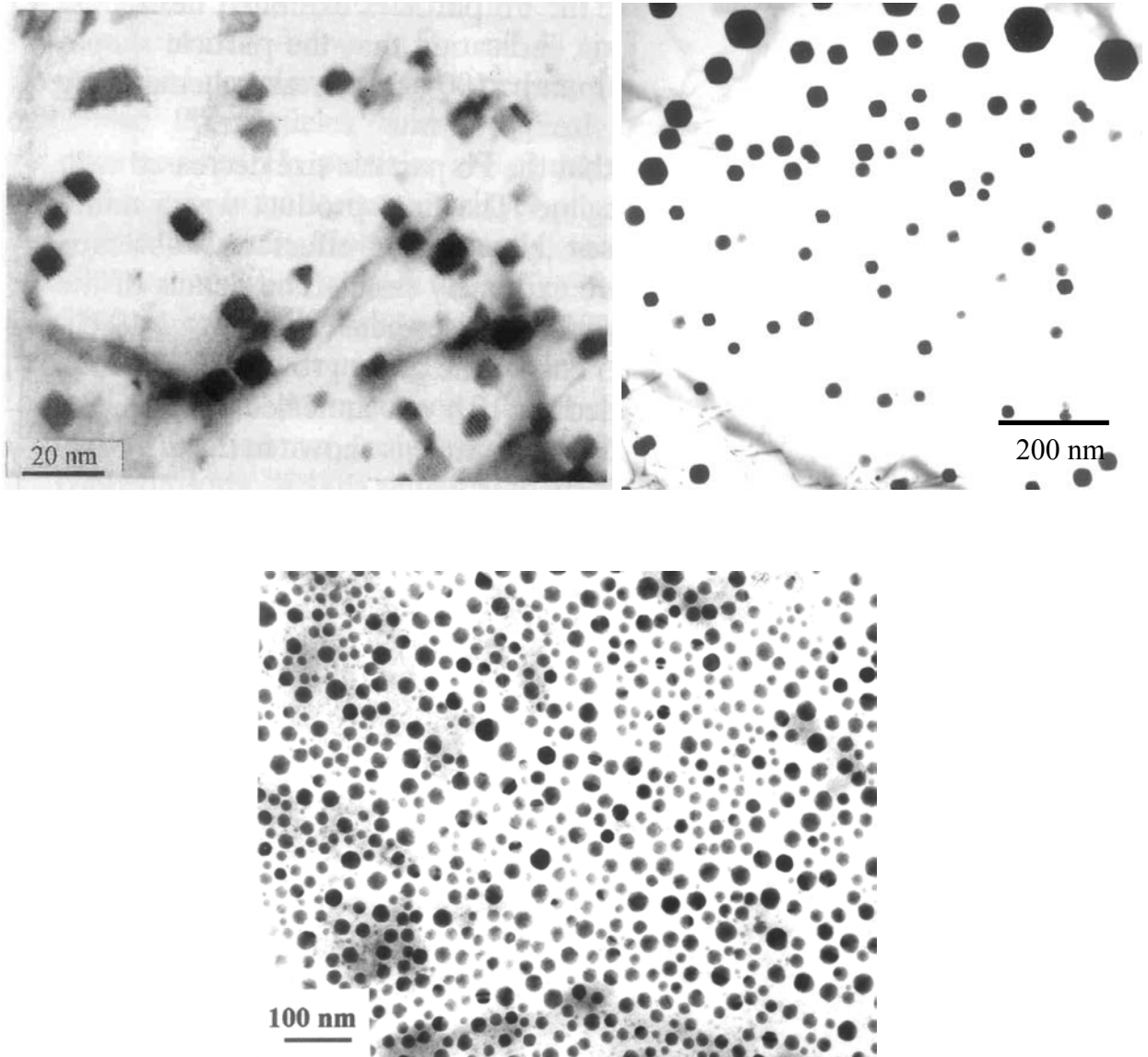


Figure 4(a) Electron micrograph showing distribution of lead particles in mechanically alloyed Al-Pb samples (Sheng et al, 1996) [3] (b) Electron micrograph showing distribution of Pb particles in melt spun Al-Pb ribbon (V. Bhattacharya, 2001) (c) Typical bright field transmission electron micrograph showing Pb dispersed in $\gamma\text{Al}_2\text{O}_3$ matrix (P. Bhattacharya, 1998) [4]

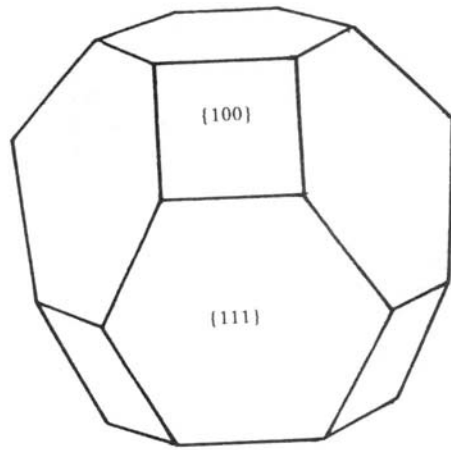
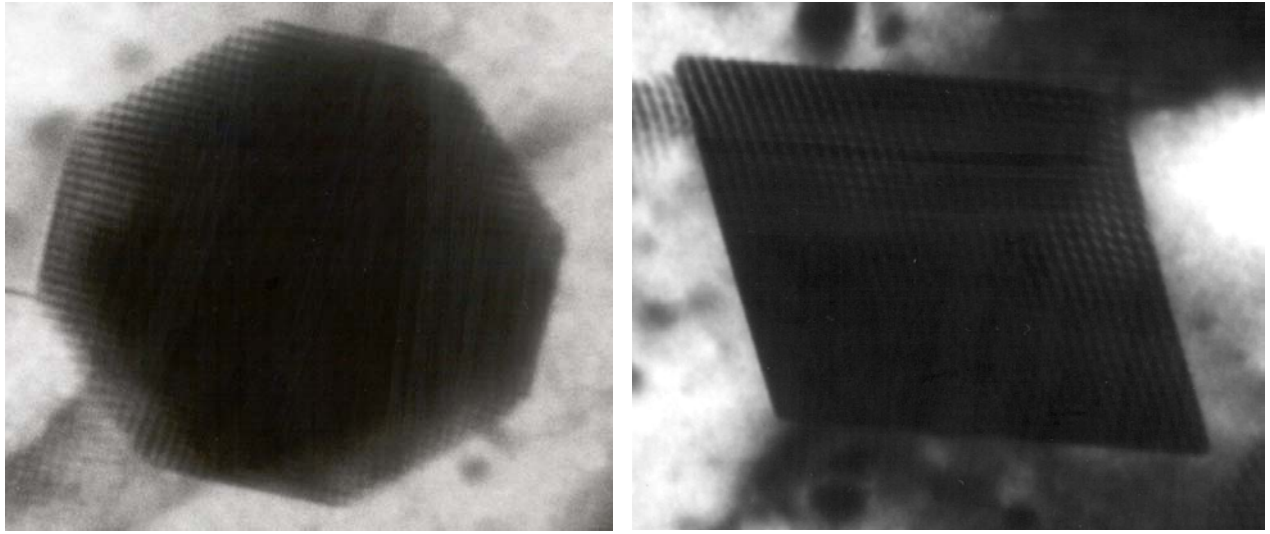


Figure 5. Electron micrograph shows a typical In particle in an Al matrix. The In particles shows both cubeoctahedral and octahedral symmetry

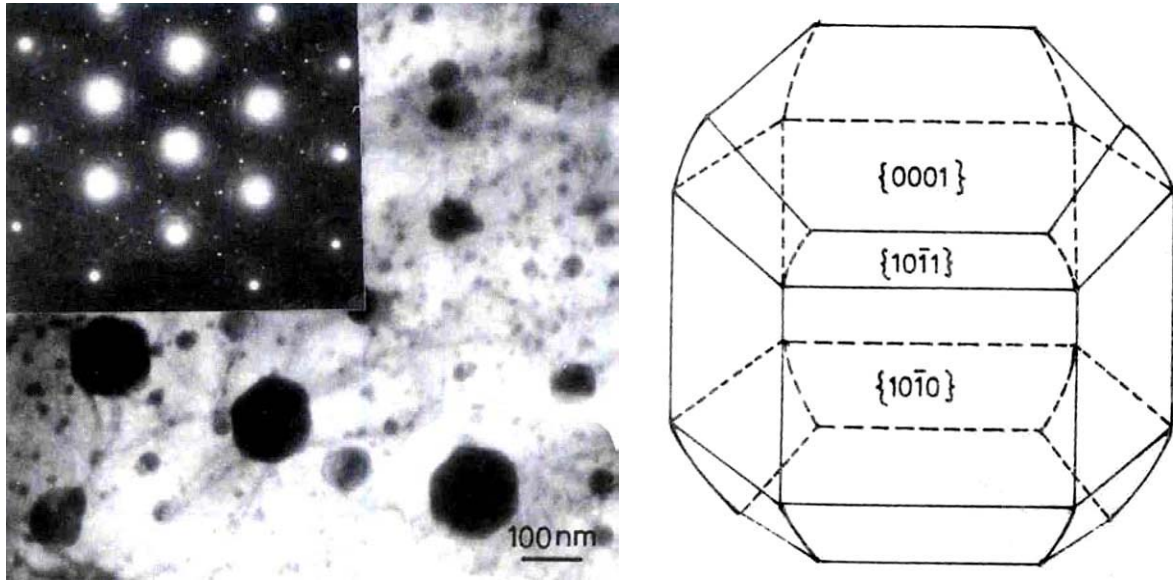


Figure 6(a) Electron micrograph showing Pb distributed in a Zn matrix (Goswami et al, 1993) [6] (b) Schematic showing the symmetry of a Pb particle which correspond to bi-prism symmetry.

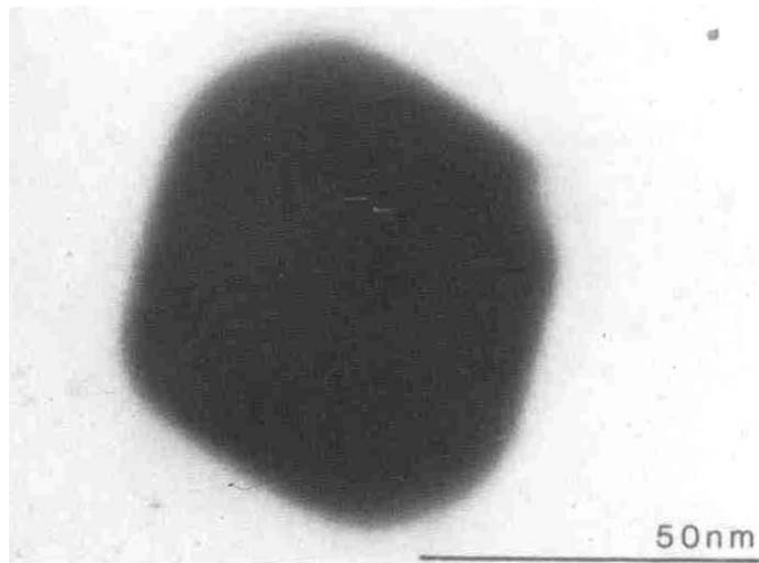


Figure 7. In situ observation of Pb particles at 350°C, 23°C above the melting point shows that the particle still exhibits well defined crystallographic shape (Moore et al, 1987) [7]

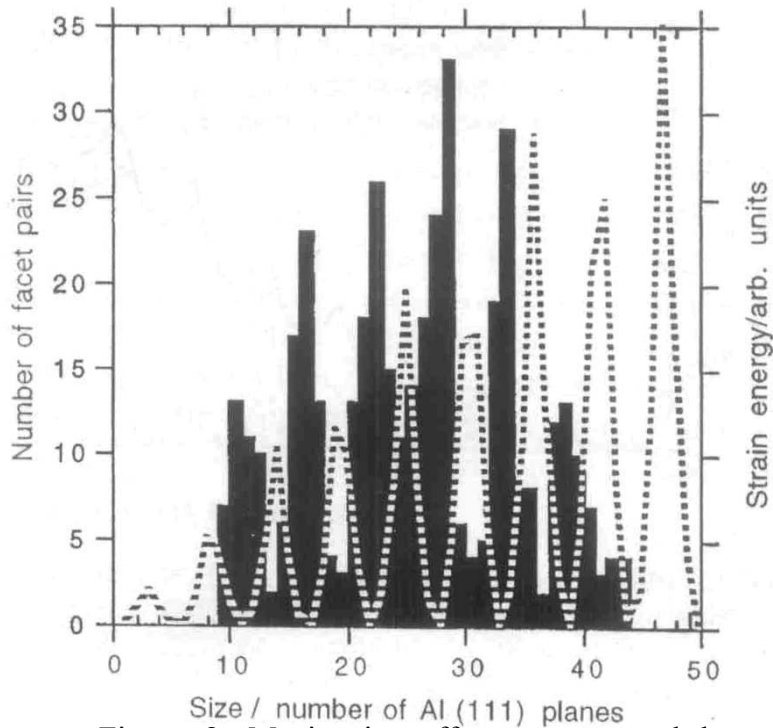


Figure 8. Magic size effect as proposed by Dahmen et al, 1997 [8]. Comparison of oscillation in observed size distribution (solid histogram) with residual strain energy (dotted line) as a function of size. Gaps in the histogram coincide with peaks in the elastic strain energy

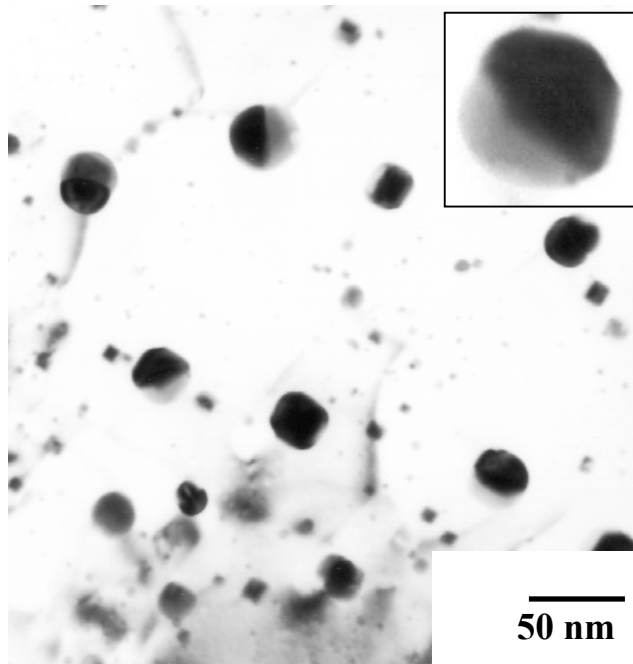


Figure 9. A typical micrograph showing dispersion of bi-phase Pb-Sn alloy inclusions embedded in aluminium matrix (V. Bhattacharya, 2002) [10].

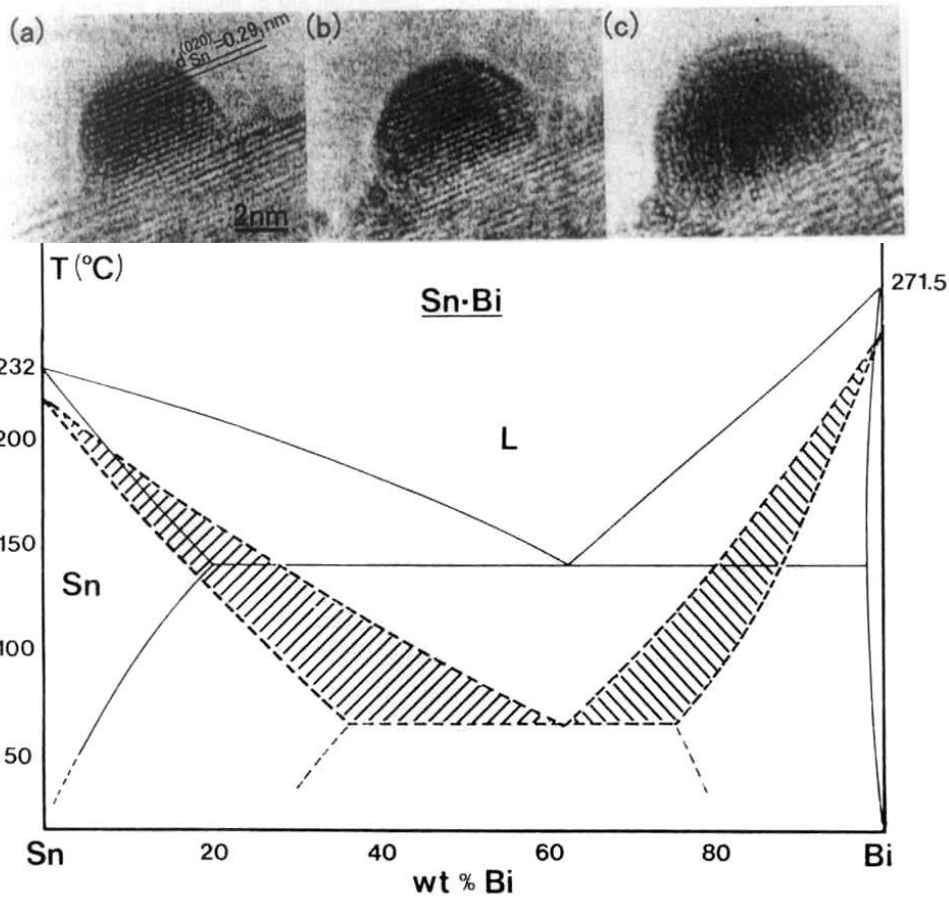


Figure 10. Experimentally determined phase diagram for Bi-Sn nanoparticles with diameter of about 40nm superimposed over the bulk phase diagram (Allen et al, 1984)[21]. The insets shows sequence of video recording of the alloying process of bismuth into nanometer sized tin particles which shows a transition from crystalline to amorphous phase as proposed by Mori et al, 2002 [22].

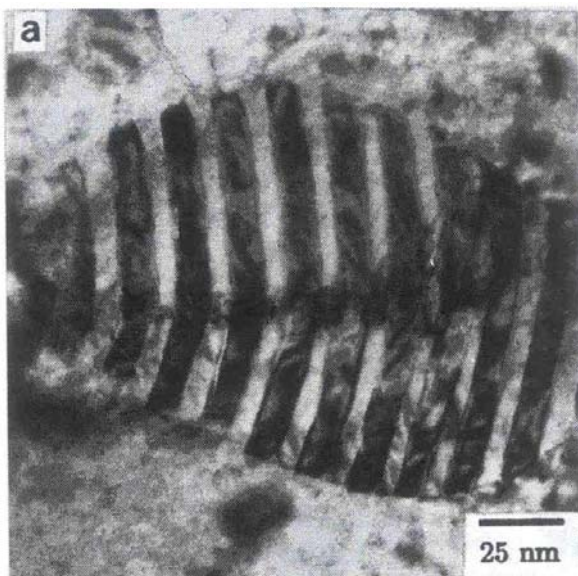


Figure 11. Dispersion of nanoparticles embedded in Cu particles yield good GMR properties (Ravishankar et al, 1999) [26]

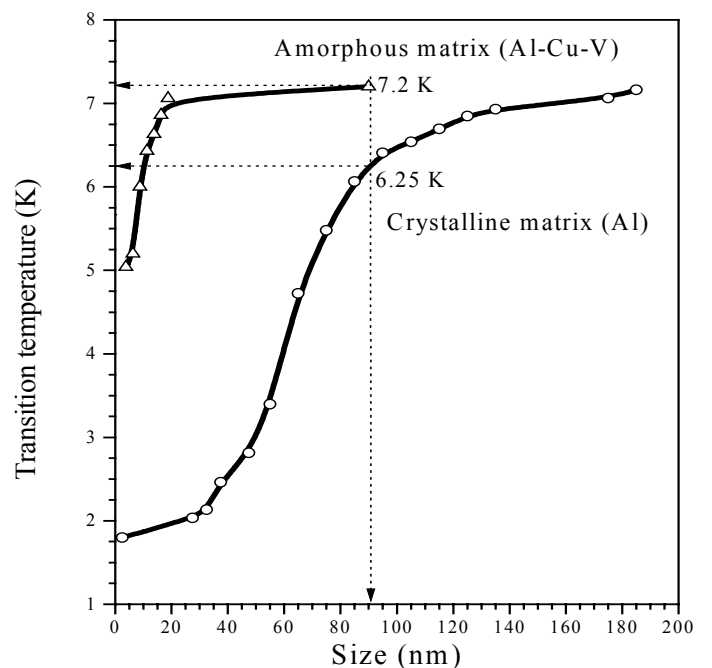


Figure 12 Comparative transition temperature vs size plot for Pb dispersed in Al and Al-Cu-V glassy matrix (Chattopadhyay et al, 2002) [31]