Nano Science and Technology in Pakistan

N. M. Butt*, F. A. Khalid**, S. K. Hasanain***, M. Mehmood****, A. Rauf****, and Shakeel Akbar****.

(Correspondening Author: N. M. Butt, e-mail: nmbutt36@yahoo.com)

*Scientist Emeritus, PINSTECH, P. O. Nilore, Islamabad, Pakistan

**Faculty of Metallurgy and Materials Engineering, GIK Institute of Engineering Sciences and Technology, Topi, NWFP, Pakistan.

***Physics Department, Quaid-i-Azam University Islamabad, Pakistan.

**** National Centre For Nanotechnology, Pakistan Institute of Engineering and Applied Sciences, Nilore, Islamabad 45650, Pakistan

*****National Commission on Nano Science & Technology (NCNST), 1-Constitution Ave. Islamabad. Pakistan.

ABSTRACT

Nano Science and Technology is newly growing and fast emerging field with unlimited industrial opportunities and helping solve many problems of human welfare, may it be consumer goods or health care. All countries the world over, particularly the industrially advanced countries, are trying to reap benefits from Nano-technology. Several developing countries are also actively and keenly pursuing to establish laboratories in this field.

Pakistan has been newly concentrating on establishing the Nano-technology laboratories with priority in Nano-biotechnology and establishing the synthesis and

characterization techniques on the Nano-scale. The attempt is not to miss entering to this fast emerging technology of great public welfare potential. The Government of Pakistan is allocating funds to projects which show promise of relevant human resource and success of good results. The Government has established a National Commission on Nano-Science and Technology (NCNST) to show its serious support to this area of research and technology. In this paper some programs and progress of NCNST has been briefly described.

The preliminary unpublished results of some of the laboratories working in the area of Nano-technology in Pakistan has been described. These areas include studies on synthesis and measurement of magnetization of Nano particles of CoFe₂O₄ and ZnFe₂O₄. Some recent results of these experiments will be given in this paper. Further, some recent experiments on Nano composites of Aluminum-Diamond have yielded interesting results which will also be described in this paper. In other laboratories in Pakistan the Nanoscience research on polymeric materials as well as carbon Nano-clusters is being carried. More areas of LED's development and other areas of Nano-technology are in process of planning. The National Commission on Nano-Science and Technology has extended programme of helping various universities in Pakistan to strengthening the research and technology in this area.

INTRODUCTION

Since the visionary paper of Feynmann in 1959 [1], precursor of the word Nanotechnology by the Japanese, Taniguchi in 1974, the field remaining dormant for many years a revolution has occurred in this area during the past 10 years. The pace of this development is exponentially developing in the recent years. The advanced countries have heavily invested in Nano-technology, both the Public and the Private Sectors in areas where commercial interests are important. Particular in the health care sector, the pharmaceutical companies and those in Nano-medicine are in abundance. Over 2000 companies world over are involved in the Nano-business with projection to 3-4x10¹²\$ (3-4 trillion dollars) business involvement by 2012.

The developing countries being conscious of the economic aspects of Nanotechnology covering industries of all kinds such as Biotechnology products, auto industry, pharmaceuticals & drugs, Agriculture and Energy Sector etc. feel the necessity of benefiting from this technology in the best possible way.

Realizing the importance of nano technology, Pakistan has embarked on a programme of encouraging university laboratories and other research centres to work in the area of nano-technology relevant to their expertise. Some laboratories have already hands on experience of research in nano-composites, nano-magnetics, nano-polymers and the techniques involved in the synthesis and characerisation of nano-materials thus produced. These laboratories have published their research [2,3] the results of which will be briefly given later.

To give a more serious attention to the establishment of work on nano science and technology, the Government of Pakistan has established recently a National Commission on Nano-Science and Technology (NCNST) whose mandate is to help all universities and research centres in the country in the establishment of such laboratories. Its mandate is also to monitor the quality of research and the work done in such laboratories. Already

the Public funding of about Rs 1.0 billion has been allocated by the Government of Pakistan in the past one year.

Over Rs 3.2 billion allocation has also been made for future research projects for the next four years. If however more successful results are obtained in the next few years, the increase in funding will be done.

The NCNST is now planning for medium term and long term projects in the nanotechnology whereby National Centres in this field will be planned for integrated work which will involve much heavier funds allocation to such National Centres. This funding will of course be in addition to the financial support to projects of the universities and research centres mentioned above.

The local industry will be greatly involved in the use of this technology and the business community will be encouraged to invest in industry which will generate jobs and will help reduce the poverty and will help the economic standards of Pakistan. It is important to mention that the NCNST has already held three conferences on Nanotechnology (including one international) in Pakistan in the year 2005 to help the Nano-technology community in Pakistan for possible interaction between various workers and enhancing the scope of future work in this field. More international conferences and cooperative research is envisaged. One such conference on Nano-Chemistry is planed for January 2006. With this brief general plans on the development of Nano-technology it is now appropriate to mention briefly the research being done in some areas of Nano technology.

RESULTS AND DISCUSSIONS

1- Production and investigation of aluminum-diamond nanocomposites

Nanostructured Al-diamond composites can be classified as a new kind of materials that have the potential for applications in electronic, microelectronic and thermal management packaging and engineering industries. The main benefits of such materials include: high thermal conductivity, low coefficient of thermal expansion (CTE), reduced weight, wear resistance, high strength and stiffness [4-8]. The continuing increase in the packaging density has caused significant requirements for materials with high thermal conductivities and closer matching of their coefficient of thermal expansion (CTE). Possible methods for achieving this objective by use of a substrate or chip carrier with higher thermal conductivity have been suggested to draw the heat away from the chip and dissipate into the surroundings.

This work deals with the Al-diamond nanocomposites produced by liquid metal infiltration process. These composites may exhibit thermal conductivity up to 500-600 W/mK. Furthermore, the problems associated with the interfacial reaction have been circumvented by optimizing the process parameters which may not be possible to avoid in other production methods. Therefore it became imperative to fully characterize the nanocomposites produced by the liquid metal infiltration process.

A number of investigations on the Al-SiC composites and other alloys have been carried out previously which had revealed the occurrence of Al₄C₃ precipitates at the interfacial regions [5-8]. The microstructure, phases and interfacial reaction were studied to optimize parameters of the infiltration process in order to achieve the production advantages.

Figure 1 illustrates different phases determined by using Calphad programme for the Al-C system. The formation and stability of Al₄C₃ precipitates was found at different temperatures. Figure 2 shows an example of nanosized diamond particles dispersed in the Al matrix. Evidence for the uniform distribution of the particles was found. This also demonstrated stability of nanosized diamond particles in the Al matrix. Faceting can be seen in the diamond particle without any reaction products formed at the interface. The reinforced nanozised particles can also significantly enhance the strength of the alloys by impeding the mobility of dislocations. Figure 3 illustrates the presence of Al₄C₃ particles formed in the Al-diamond specimen. The carbides grew along (011) Al with semicoherent interface. The carbides were very small and found occasionally indicating a negligible influence on the properties of the composite materials. The results are in confirmation with previous work on Al-C₆₀ composite materials [6].

It can be stated that stable structure can be achieved in the nanocomposites produced by liquid infiltration process with greater prospects for thermal management applications.

2- Size dependent magnetic characterization of Zinc Ferrite Nanoparticles

The Nanoparticles of Zinc Ferrite have been prepared by using Sol-Gel method in two different medium i.e. acidic and basic. For acidic medium we use Citric acid and whereas for the basic medium we used Urea. Those also played the role of catalyst in the preparation of ZnFe₂O₄. By the XRD analysis we found that the average sizes of the particles lie in the range of 18 to 51nm.

The field dependent magnetization of $ZnFe_2O_4$ samples prepared in Citric acid behaves as a paramagnetic at 300K as shown in Fig 6, whereas the samples prepared in Urea shows hysteresis loop even at 300K (Fig 7).

The remarkable difference in the magnetization of ZnFe₂O₄ samples prepared in Citric acid and Urea may be explained by considering a high degree of inversion in sample prepared in Urea as compared to Citric acid. Therefore from the magnetic studies one can conclude that ZnFe₂O₄ prepared in Urea, which is basic medium, has more ferromagnetic nature than those samples which has been prepared using Citric acid. From the M(H) loops, ZnFe₂O₄ nanoparticles prepared in both mediums are found to be far from magnetic saturation even at a field of 15kOe due to significant paramagnetic contribution.

Effect of size of the particles on the magnetization of $ZnFe_2O_4$ (Fig 9) shows that magnetization decreases with the increase in the size of the particles. The decrease in the magnetization indicates that inversion parameter decreases with the increase in the size of the particles.

3- Electrolytic Synthesis of Nanomaterials

Attempts for preparing thin sheet of nano-porous alumina have been made by anodic oxidation of aluminum sheet in oxalic acid at $0\sim1$ °C. Figure 10 shows photograph of a sample which has been partly transformed to nano-porous alumina through whole of its thickness, as clearly evident from transparent nature of this part. Thickness of this region is approximately 250 μ m.

Figure 11 shows a typical SEM image of the nano-porous alumina obtained by anodic oxidation of aluminum. The sample was subject to pore widening in this case after preparation. The pore diameter and inter-pore distance have been shown in Fig. 12. Well-arranged array of uniform-diameter pores is evident from these figures.

Alumina template was prepared by several steps (i) First anodizing, (ii) Chemical dissolution of alumina from aluminum, (iii) Second anodizing, (iii) Chemical pore widening and (iv) Multi-stage current-limited anodizing. Figure 13 shows changes in electrochemical potential during these stages indicating the thinning of the barrier layer. In this way alumina template was backed by aluminum. Nickel nanowires were grown through vertical pores in alumina by pulse deposition in aqueous medium. Figure 14 shows results of vibrating sample magnetometery. Effects of shape anisotropy are evident. Attempts are being made to grow nanowires by pulse deposition in non-aqueous media. This appears to facilitate nano-wire synthesis of a variety of metals and semiconductors using aluminum backed nano-porous alumina.

Figure 15 and 16 show XRD patterns of two typical electrodeposited nanostructured Ni-Zn and Ni-W alloys, respectively. The estimated particle size was ~20 nm and <10 nm, respectively. Nanostructured Ni-W alloy was subject to carburizing treatment and a nanocomposite was formed containing tungsten carbide particles of ~40 nm in the Ni-W metallic matrix, as revealed by XRD pattern given in Fig. 17.

CONCLUSION

The Government of Pakistan has laid emphasis on developing the field of Nano-science and Technology in Pakistan and provided encouragement for future through the efforts of the National Commission on Nano-Science and Technology (NCNST). Further the quality of research already being conducted on nanoparticles of different nano-composites and inorganic nano-particles, described above gives assurance of future useful investment in this fast emerging field.

Acknowledgements

We are grateful to the Rectors of our Universities to support this research work and to the Ministry of Science and Technology (MoST) for support through the National Commission on Nano Science and Technology (NCNST) for extending full cooperation and funding these activities.

REFERENCES

- [1] R.P. Feynmann; "There is a plenty of room at the bottom," lecture delivered at the annual American Physical Society Meeting, 29th December, 1959, California Inst. of Tech., (Caltech).
- [2] S. K. Hasanain (2005) Private Communications.
- [3] F. A. Khalid (2005) Private Communications.
- [4] C. Zweben, (2002) ASM Handbook on Composites, 21, 1078.
- [5] F. A. Khalid, et al., (2004) Diamond and Related Materials, 13, 393.
- [6] O. Beffort, S. Vousher and F. A. Khalid, (2004) Diamond and Related Materials, **13** 1834.
- [7] F. A. Khalid, et al., (2003) Acta Mat., **51**, 4575.
- [8] P. Gasser, et al., (2004) Microscopy and Microanalysis, **10**, 311.

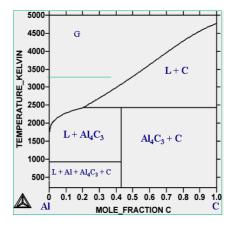


Fig. 1

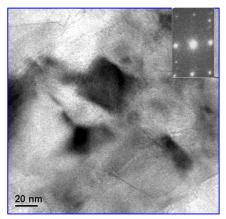


Fig. 2

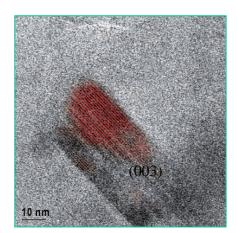


Fig. 3

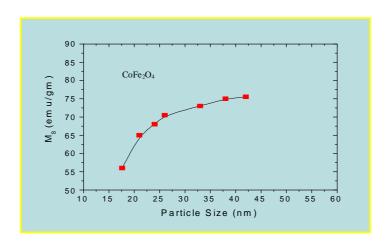


Fig. 4

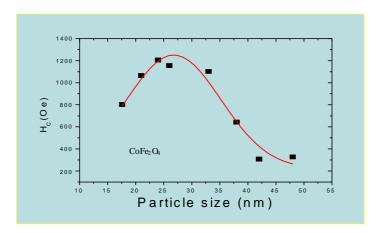


Fig. 5

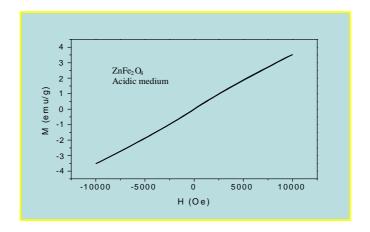


Fig. 6

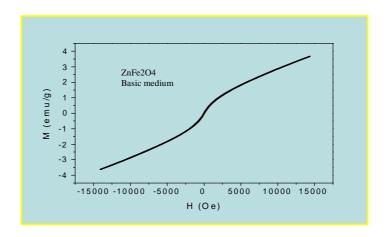


Fig. 7

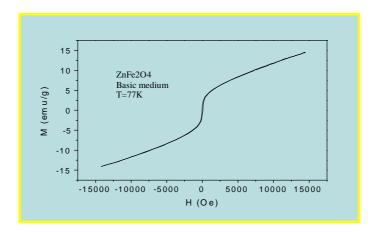


Fig. 8

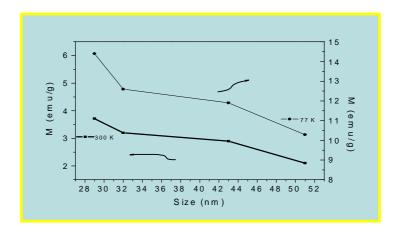


Fig. 9

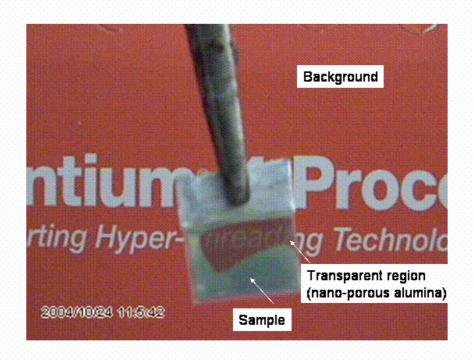


Fig. 10

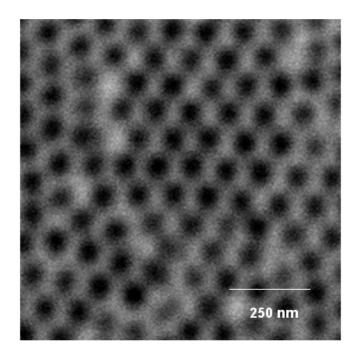


Fig. 11

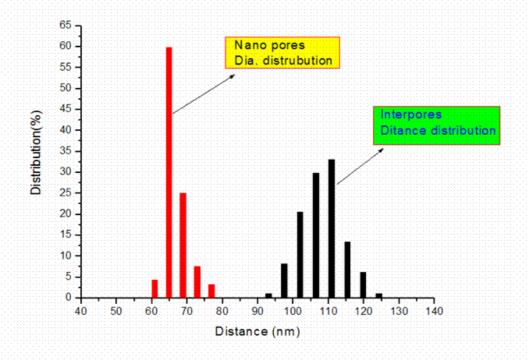


Fig. 12

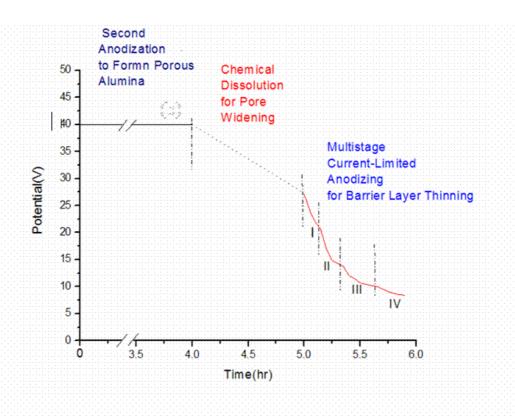


Fig. 13

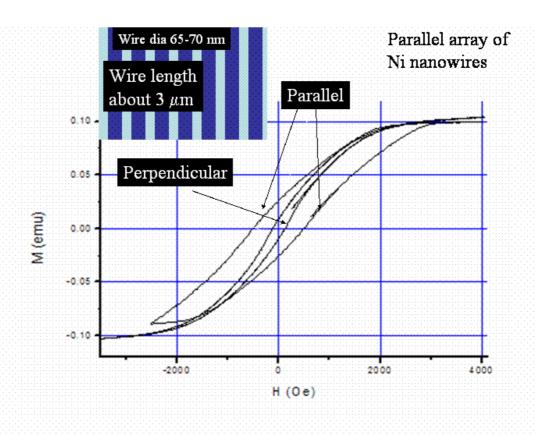


Fig. 14

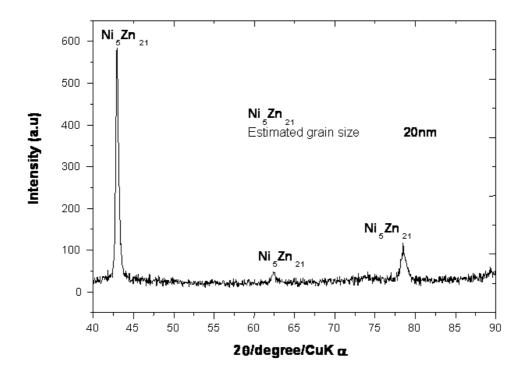


Fig. 15

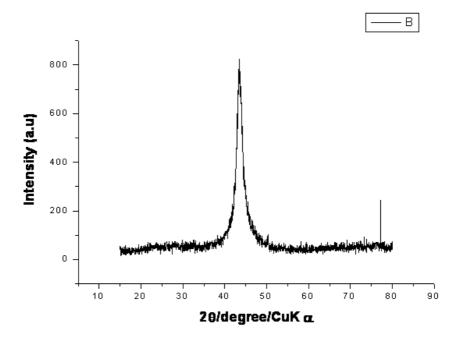


Fig. 16

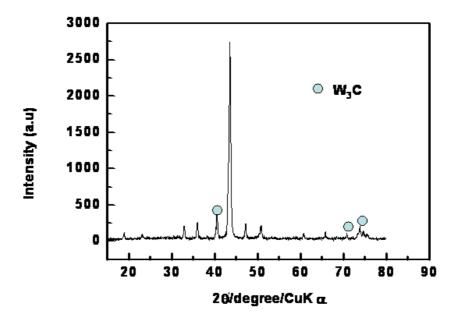


Fig. 17

Figure 1: Phase diagram of Al-C system determined by Calphad modeling.

Figure 2: Micrograph showing morphology of nanosized diamond particles in the Al matrix nanocomposite specimen, inset SADP, Z = [123] Diamond.

Figure 3: High resolution TEM image showing presence of rod-shaped Al_4C_3 precipitates in the nanocomposite sample.

- **Figure 4:** Effect of average particle size on the saturation magnetization (M_s) of Cobalt ferrite nanoparticles (CoFe₂O₄).
- **Figure 5:** Effect of the average particle size on the coericivity (H_c) of Cobalt ferrite nanoparticles (CoFe₂O₄).
- **Figure 6:** Magnetic behavior of the Zinc ferrite nanoparticles (ZnFe₂O₄) under the application of external magnetic field (H) prepared by sol-gel method in acidic medium.
- **Figure 7:** Magnetic behavior of the Zinc ferrite nanoparticles (ZnFe₂O₄) under the application of external magnetic field (H) prepared by sol-gel method in the basic medium at 300K.
- **Figure 8:** Effect of the average particle size on the coericivity of Zinc ferrite nanoparticles (ZnFe₂O₄) prepared by sol-gel method in the basic medium at 77K.
- **Figure 9:** Effect of the average particle size on the saturation magnetization (M_s) (at 300 and 77K) of Zinc ferrite nanoparticles prepared by sol-gel method.
- **Figure 10**: Photograph of a sample showing a region where aluminum sheet has been completely consumed to form transparent nano-porous alumina (alumite)
- **Figure 11**: Top view of the alumite showing the well-ordered hexagonal array of pores.
- Figure 12: Distribution of pore size and inter-pore distance.
- **Figure 13**: Potential vs. time response during 2nd anodizing, pore widening and current-limited anodizing. The changes in potential indicate decrease in barrier layer thickness necessary for subsequent nano-wire growth by pulse deposition.
- **Figure 14**: Magnetic hysteresis loops of nickel parralel array of nickel nanowires prepared in alumite. Shape anisotropy is evident.

Figure 15: XRD of a nanocrystalline Ni-Zn alloy prepared by electrodeposition. The estimated grain size is 20 nm.

Figure 16: XRD pattern of a Ni-W alloy prepared by electrodeposition. Large FWHM indicates extremely small particle / grain size.

Figure 17: XRD pattern of nanocomposites of W_3C (~ 40 nm) embedded in metallic matrix of NiW. The alloy was prepared by electrodeposition followed by carburizing in diluted alcohol atmosphere at $700^{\circ}C$.
