MEETING REPORT

# Rapidly quenched and metastable materials*

The 12th International Conference on 'Rapidly Quenched and Metastable Materials' (RQ 12) brought together scientists from all over the world to discuss the latest developments in the field of physics and metallurgy, processing and applications of a variety of materials such as metastable, nanostructured, amorphous and quasi-crystalline materials. The conference was attended by more than 350 scientists from 22 countries. There were 8 participants from India. 'RQ Distinguished Fellowship' for pioneering and landmark contribution in the field of RQ was awarded to R. W. Cahn (University of Cambridge, UK), T. Masumoto (Tohoku University, Japan) and D. Turnbull (Harvard University, USA).

There were 224 papers scheduled for oral presentation and the remaining 233 were for poster presentation. There were four parallel sessions for the oral presentation totalling 48 sessions, including 13 plenary lectures and 35 invited lectures. The conference covered all fundamental aspects as well as original technical contributions on synthesis and processing, phase transformations, structural characterization, physical and mechanical properties, theoretical modelling and computer simulation, near and long-term applications, etc. Details of the programme and abstract titles are available in the website: http://suny.yonsei.ac.kr/~rq12/. Most of the papers and discussions were on (i) metallic glasses and bulk metallic glasses (BMGs), (ii) nanomaterials, (iii) quasi-crystals (QCs) and complex crystalline materials, and (iv) rapidly solidified metastable materials. Here we highlight some of the interesting features of the conference. The technical papers, after a paper review, will be selected for publication in a special issue of *Materials Science and Engineering A*.

The most extensively discussed topic in this conference was BMGs, with special emphasis on glass formability, stability and deformation characteristics. After the inauguration, the first plenary lecture was delivered by A. Inoue (Japan) on fabrication, properties and applications of bulk glassy alloys in late transition metal base system. A great majority of studies on BMGs was focused on early transition base alloys in Zr-, Ti-, and Hf-based systems, lanthanide (Ln) metal base alloys, simple metal base alloys in Mg- and Ca- and noble metal base alloys in Pd- and Pt-based systems. Based on three empirical component rules for stabilization of supercooled metallic liquid, Inoue's group synthesized late transition metal BMGs such as Fe-(Al, Ga)-(P, C, B, Si), Fe-(Cr, Mo)-(C, B), Fe-(Zr, Hf, Nb, Ta)-B, Fe-Ln-B, Fe-B-Si-Nb, Fe-Nd-Al for Fe-based alloys, Co-(Ta, Mo)-B, Co-B-Si-Nb for Co-based alloys, Ni-Nb-(Ti-Zr)-(Co) for Ni-based alloys, and Cu-(Zr-Hf)-Ti, Cu-(Zr, Hf)-Al and Cu-(Zr, Hf)-Ti-(Ni, Co) for Cu-based alloys. These BMGs were shown to exhibit useful properties of high mechanical strength, high corrosion resistance, etc. The soft magnetic properties of Fe- and Co-based BMGs exceeded largely those of conventionally amorphous-type alloys. It can be pointed out that Fe- and Ni-based BMGs were already used in some fields of application. Thus these LTM-based BMGs are quite promising as new metallic engineering materials. K. Hono (Japan) discussed the issue of phase separation prior to crystallization in BMGs, which was linked to the formation of nanocrystals. Through careful studies by TEM and three-dimensional atom probe analysis, it was shown that the phase separation did not occur in Pd–Si–Au, Cu–Zr–Ti, Zr–Ti–Be, Al–Gd–Er–Ni, Zr–Cu–Ni–Al–Ti, Zr–Ti–Cu–Ni–Be metallic glasses contrary to earlier reports. However, phase separation in La–Zr–Al–Cu–Ni and Cu–Al–Ni–Ag was shown in the present study. Phase separation in nanoscale appeared to be directly related to the formation of nanocrystals. The phenomena of phase separation were attributed to the existence of large positive heat of mixing among the pairs of elements present in the BMGs. Correlation with clusters and glass-forming ability were proposed by C. Dong (China). It was demonstrated that cluster-based criteria could predict the range of glass formability and stability. This approach was demonstrated in Cu-based and RE-based BMGs. B. S. Murty (India) synthesized BMG by mechanical alloying and showed that the glass-forming ability could be better understood based on thermodynamic and topological models. The milling energy was correlated with thermodynamic and glass-forming criteria and the relative importance of these criteria in multicomponent systems was emphasized. J. H. Perepezko (USA) presented work on amorphization and devitrification in metallic glasses. It was shown that though crystallization kinetics initiated and proceeded via heterogeneous modes, it was not a steady state process since both nucleation and growth decreased with time. However, the initial nucleation appeared to have been derived from quenched-in clusters to yield high nucleation number density. It was suggested that these issues are important for controlling the nanoscale microstructures, which could be important for many applications.

F. Spaepen (USA) elegantly demonstrated the atomic scale mechanism for plastic flow of amorphous metals through a physical modelling and simulation. Though the plastic flow is known to occur by the superposition of shear events on atomic scale, the nature of these events (i.e. number of atoms, local shear strain and jump rate) is still not clear. The formation of shear bands was shown to be due to the creation of a free volume within the material ranging from 10 to 15 nm length scales. It is well known that BMGs exhibit a high degree of elastic deformation and less or no ductility. In fact, this is one of the challenges in the field of BMGs – how to make BMGs more ductile and tougher so that they can be used in many applications. On this aspect, A. L. Greer (UK) discussed how to reduce the brittleness of metallic glasses. It was shown that the ratio of shear to bulk modulus ($G/B$; which is greater than 0.41–0.43) is an important parameter for deciding about the brittleness. Thus by careful choice of alloying elements, the ratio can be modified so that the glassy alloy is less likely to be brittle in as-cast as well as annealed condition. It is also known that BMGs showing local plasticity tend to appear macroscopically brittle because of the lozalized plastic flow into shear bands. Intense activities are on in many labora-

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tories to control the mechanisms of shear banding and thereby making plastic deformation more diffuse. Some of these efforts were understood as introducing fine scale voids or crystalline phases in BMGs, which are effective in controlling the proliferation of shear bands. The mechanisms of shear band formation and their propagations were discussed by many authors. Nanocrystallization during mechanical deformation was also reported. However, the issue of nanocrystallization has not yet been settled. There were two schools of thought – one group believes that nanocrystallization of BMG during deformation is due to heat generated during shear band formation causing nanocrystallization. The other group suggests that the activation energy for nanocrystallization can be reduced during deformation and hence nanocrsytallization is a natural consequence subsequent to shear band formation without the further need of thermal energy. It appears from this conference that this controversy of nanocrystallization during deformation would take some time to be resolved, after more developments in controlled experiments and theoretical work. T. G. Neigh (USA) studied the shear banding in BMG using high temperature nanoindentation of Pd–Ni–P and Mg–Cu–Gd. At low rates and temperatures, inhomogeneous or serrated flow was observed. It was shown that even at temperatures below the glass transition temperature, homogeneous flow was observed. The critical radius of shear band as it converted from nucleation to propagation, was estimated to be in the submicron range. In case of BMGs, the plastic flow exhibited strain softening unlike crystalline materials and abrupt failure occurred with shear localization. It was demonstrated in the literature earlier that some Cu-based metallic glasses containing a dispersion of embedded nanocrystals could sustain room-temperature compressive plastic strain up to 50%. A. Yavari (France) critically studied this behaviour and found direct evidence of systematic shear delocalization in Cu-based BMGs with 3–8 nm crystallite particle dispersions. Shear delocalization occurred in the form of shear band thickening as well as crack blunting (which eventually strain hardens) and increased the fracture toughness without compromising with the ductility in metallic glass-based nanocomposites. N. K. Mukhopadhyay (India) showed serrated flow in the indentation load-displacement data in Cu-based BMG and correlated with the elastic–plastic transition in the form of shear band formation and propagation. The upper bound estimate of the energy required for such transition, i.e. a single serration (also known as displacement bursts) was calculated. It was interesting to note that the nanocrystalline precipitates beneath the indent were observed through careful TEM. This nanocrystallization was attributed to deformation-induced enhanced diffusion ($10^{-17}$ $m^2/s$), which is very high compared to that at room temperature ($10^{-30}$ $m^2/s$), required for the formation of nanocrystals of 20–30 nm size. Thus nanocrystallization appeared to be a distinct possibility during the loading period (~ 10 s) of nanoindentation.

There were many interesting papers on nanostructured materials and nanocomposites in the conference. The usefulness of nanomaterials is now well understood. Jurgen Eckert (Germany) dealt with the preparation of bulk nanostructured materials in Zr- and Ti-based multicomponent alloys through solidification routes. The strength of such materials was generally higher than that of conventional alloys. Large elastic strains were also exhibited. The bulk nanocrystalline materials were developed by primary-dendrite/nano eutectic composites, where a high-strength nanostructured matrix was combined with a ductile dendrite bcc-type solid solution as the toughening phase. Besides, fully nanostructured eutectic morphologies could be tuned. Using severe plastic deformation such as Equal Channel Angular Pressing, bulk nanostructured materials (ultra fine grains) were reported which exhibited high strength as well as superplasticity. G. Wilde (Germany) discussed the possibility of porosity-free bulk nanocrystals by straining BMGs. The ultra fine-grained (~ 200 nm) austenitic alloys were fabricated by a repetitive thermomechanical processing consisting of cold rolling and annealing. A Singh (Japan) discussed the melting behaviour of Pb and Bi nanoparticles in Al–Cu–Fe quasicrystalline matrix and emphasized the role of interfaces and showed the contrasting behaviour of melting in the presence and absence of crystalline matrix. Mechanical properties and wear resistance of carbon nanotube reinforced Cu nanocomposites were reported by K. T. Kim *et al.* (Korea). It was found that the strength and wear resistance improved significantly compared to that in monolithic Cu samples. Explosive compactions of nanocomposites were suggested while consolidating the nanopowder to form the compact. By controlling the nanocarbide precipitations in conventional tool steels by deep cold treatment, the wear resistance of tool steel was enhanced. Surface modification by the formation of nanophases in surfaces by mechanical attrition was presented. Nano-precipitates in various shapes and sizes in amorphous matrix leading to improved magnetic properties were discussed by many workers. Some papers also dealt with the development of magnetic anisotropy, thereby improving the hard magnetic properties in addition to the increased mechanical properties.

There were some interesting papers dealing with QCs and complex crystalline metallic materials. S. Ranganathan (India) described gamma-brass in Al–Cr–Cu and Al–Cr–Fe systems, which also exhibited the existence of QC phases. It was shown that by manipulating with the motifis such as icosahedral clusters, the disordered $\gamma$-brass, ordered $\gamma$-brass and Fcc $\gamma$-brass structures could be linked. Through this the orientation relationship was predicted. Using a bigger cluster such as Mackay clusters, the orientation relationship between the QC and crystalline phases was explained in Al–Fe–Si and Al–Mn–Si alloys. The usefulness of Pettifor maps was brought out in the context of the synthesis and stability of glasses, crystals and QCs. J. M. Dubois (France) discussed the QC structure and its importance for analysing the complexities in the crystals in many unexplored ternary, quaternary and other multicomponent systems. By studying the structures and their characteristics, the application of many such unknown phases could be realized in future. The Complex Metallic Alloy (CMA) Project is being pursued in a systematic manner throughout Europe under the sponsorship of the European Union. H. J. Chang (Korea) reported the precipitation of two-dimensionally aperiodic H-phase in Al–Mn–Be during heat treatment. This phase maintained an orientation relationship with the Al-phase and transformed to hexagonal phase by subsequent heat treatment. P. A. Theil (USA) presented the relationship between friction and quasicrystallinity and the frictional anisotropy of Al–Co–Ni decagonal surfaces. Detailed analysis of AFM and STM studies indicated that these low frictional coefficients of QC surface could be attributed to the atomic structures of QC. E. Belin Ferre (France) studied the role of hybridization in wetting and friction of Al-based complex metallic compounds and QCs. Performing pin-on-disk experiments, it was shown that the surface energy of QCs is in the range 0.5–0.8 J/m$^2$, where it increased to 2 J/m$^2$ in metallic compounds. These parameters were correlated with hybridization mechanism between Al-*p* and TM-*d* states in the bulk, and this mechanism is ultimately responsible for the stabilization of QC and approximant phases.

A. P. Tsai (Japan) showed the high activity of QC in some catalytic reaction. It was demonstrated that in contrast to industrial Cu-based catalysts, where the sintering of Cu particles generally occurred around 300°C, QC-supported Cu catalysts showed high activity and no sintering of Cu particles. The detailed mechanism for this behaviour was discussed. K. B. Kim *et al.* (coworker of B. Cantor) presented the evolution of nanoscale icosahedral phase in a new type of BMGs with high degree of supercooling (56 K). The alloy $(Ti_{33.3}Zr_{33.3}Hf_{33.3})_{70}(Ni_{50}Cu_{50})_{20}Al_{10}$ was designed by equiatomic substitution of chemically similar elements starting from ZrCuNiAl alloy. They studied the stability of the nano QC phases in details. M. Kubota (Japan) showed the precipitation of QC phases in rhombohedral shape in Al-10Mg-0.5Ag alloy, while aging at 240°C was found to be the main strengthening phase in this alloy system. The orientation relationship was also reported as expected from the structure. T. P. Yadav (India) presented the evolution and stability of decagonal QCs in Al–Cu–Co–Ni quaternary alloying, substituting Ni by Cu. It was shownthat depending on *e*/*a* ratio, the decagonal (*D*) phase or vacancy ordered ($\tau_3$) or superstructure of $\tau_3$ phases could be formed. K. S. Shin (Korea) reported significant improvement in mechanical properties of QC (Al–Fe–Cu) strengthened aluminium composites compared with Al-based conventional composite materials. J. Y. Lee also reported better performance of QC reinforced Mg–Zn–Y alloys at high temperature formability (300°C) and correlated with the stability, morphology and distribution of the QC phases in Mg matrix.

There were several interesting papers dealing with the rapid solidification and solidification techniques with high undercoolings in order to develop a variety of metastable microstructures and crystalline structures, including modelling of the solidification process. B. Cantor (UK), in a plenary lecture, presented some recent studies of squeeze casting and semi-solid deformation of aluminium alloys and dealt with the investigations of grain size, microsegregation, macrosegregation, and mechanical properties as a function of solidification and deformation condition such as applied pressure, melt temperature and alloy composition. D. M. Heralach *et al.* (Germany) presented *in situ* diagnostics and theoretical modeling on rapid solidification. They reported direct experimental observation of non-equilibrium crystallization in undercooled melts. Containerless processing was applied for undercooling and was utilized to critically assess physical models for rapid solidification. Depending on undercooling prior to solidification, the effects of solute diffusion, convective flow, solute trapping and microstructure evolution were demonstrated. R. Trivedi (USA) showed how the eutectic growth could be modelled with accuracy when rapid solidification was conducted. K. Chattopadhyay (India) used the model proposed by Trivedi *et al.* for understanding the evolution of microstructure during laser solidification. The role of undercooling was also emphasized to control the solidified microstructures. Y. Kawamura (Japan) showed some applications of rapidly solidified Mg–Zn–RE alloys containing precipitates having long-period stacking order. It was shown that by adopting the RSP technique, grain refinement, reduction of segregation, and increase of solid solubility could be achieved. Thus high strength Mg-based alloys are being developed for application as aircraft structural materials. There were several papers dealing with development of Mg-based alloy for commercial applications as lightweight structural materials.

The maximum number of papers in the conference was on BMGs. It indicates the direction of RQ field due to its potential for commercial applications. In fact, papers on the mechanical properties and deformation of BMGs were more than any other single topic.

There is considerable interest these days in the metrics of performance of Indian science. In the field of rapid quenching, India had an early start. As early as 1965, just five years after the epoch-making discovery by Pol Duwez, T. R. Anantharaman established a school of research in this field at the Banaras Hindu University, Varanasi. This theme took firm roots and then spread to other university centres and laboratories over the past four decades. Indian scientists have to their credit many original publications covering rapidly quenched crystalline, QC and non-crystalline phases. It is to be hoped that Indian science will be strongly represented in the next conference at Dresden, Germany in 2008.

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