

## Editorial

The current issue of *Revue de Métallurgie* publishes articles based on the works presented during the C13 Symposium “Metallic glasses and related composites: new routes for functional and strong materials”. This symposium belongs to the series of the European Congress and Exhibition on Advanced Materials and Processes (EUROMAT). EUROMAT meetings have been held every two years since 1989. These conferences, which are organized under the auspices of the Federation of European Materials Societies (FEMS), have become prime events in Europe for a major gathering of academics and industrialists active in Materials Science and Technology. The 2011 meeting took place in Montpellier between 12 and 15 September and was jointly organized by two FEMS member societies: AIM (Associazione Italiana di Metallurgia – Italian Association of Metallurgy) and SF2M (Société Française de Métallurgie et de Matériaux – French Society for Metallurgy and Materials). The EUROMAT conferences are managed by individual member societies of FEMS, while the Scientific Committee is drawn from across Europe, and coordinated by FEMS.

The C13 symposium aimed to promote international scientific and technological exchanges on the recent progress in synthesis, processing, properties and applications of metallic glasses. Stimulated by the high demand for new materials with enhanced mechanical, chemical and physical properties, metallic glasses and composites containing glassy or metastable phases are currently at the cutting edge of metal research. These materials exhibit unique technological properties which often surpass those of conventional functional and structural materials and are therefore attractive for “high-end” applications. Today, improvement in the processing of such materials is essential to promote their widespread application.

The C13 symposium consisted in 5 separate oral sessions and one poster session. The topics covered were: thermodynamic of the glass formation, modelling and simulations, mechanical, magnetic and electrochemical properties of metallic glasses and related composites, phase transformation and devitrification, processing, industrial and bio-medical applications. The symposium attracted a total of 60 abstracts submitted by scientists working not only within Europe, but also in Asia and North America. During the Symposium 2 keynote and 2 highlighted talks, as well as 23 regular oral contributions and 17 posters were presented.

Nowadays several groups all over the world are working on metallic glasses and their related composites. It was our pleasure and great honour to have the two keynote talks delivered by leading scientists working in Japan and, respectively, USA, coming from research centres which are among the pioneers regarding the preparation and properties of metallic glasses, as well as their possible use in applications. Prof. Dr. Dmitri Louzguine from the World Premier Institute (WPI) – Advanced Institute for Materials Research, Tohoku University, Sendai, Japan, presented in his key-note lecture some aspects regarding the atomic structural changes in the supercooled liquid regime by X-ray diffraction measurements during in-situ vitrification of the  $\text{Pd}_{42.5}\text{Cu}_{30}\text{Ni}_{7.5}\text{P}_{20}$  liquid alloy. In-situ vitrification in a synchrotron beam during cooling allows continuous acquisition of X-ray diffraction spectra in the supercooled liquid region and below the glass transition temperature with subsequent creation of real space-distribution functions. In this temperature range, a reversible expansion of the nearest neighbour distances in the first coordination shell is observed. The nearest neighbour distance in the first coordination shell have a low distance peak (pre-peak) that appears and grows on cooling from above the liquidus temperature to the glass transition

in the supercooled liquid region. It was found that atomic clusters with P at the centre and Ni and Cu at the nearest neighbour bonded to P covalently form during undercooling of the melt. The slope of the expansion changes discontinuously at the glass transition. Below the glass-transition temperature the metallic glassy solid contracts/expands in a usual way according to thermal vibrations. The results were discussed based on present theories of glass-formation and structure of liquids.

Dr. Sundeep Mukherjee from Yale University, New Haven, USA, presented very interesting results regarding the thermoplastic forming of bulk metallic glasses. The metastable nature of these materials has imposed a barrier to broad commercial adoption, especially where the processing requirements conflict with conventional metal processing methods. Fabrication processes based on thermoplastic forming decouple the rapid cooling required to form a glass from the forming step, mitigate the effects of heterogeneities on crystallization, and overcome geometrical limitations associated with casting. The talk introduced such techniques that are unique among metals. For example, through blow moulding of bulk metallic glasses, geometries can be achieved that were preciously unachievable with any other metal processing method. Due to the absence of an intrinsic size limitation and a first order phase transition during solidification, the amorphous alloys can be precision net-shaped on the micro, nano and even atomic length scale. Furthermore, these length scales can be combined even on complex surfaces. The bulk metallic glasses can be considered high strength material that can be processed like (thermo)plastics, whereby previously mutually exclusive attributes of materials – processibility and performance – can be combined.

In his highlighted talk, Dr. David Klaumünzer from the Swiss Federal Institute of Technology (ETH) Zürich, Switzerland, spoke about the progress in the understanding of shear banding in metallic glasses. It was shown that by using high acquisition rates when recording stress and strain during compression testing of a glassy Zr-based alloy, new insights can be gained into the temperature-dependent dynamics of shear-band propagation. The results conduct toward the conclusion that non-serrated flow, as achieved by lowering the temperature, cannot be viewed as a shear-band nucleation dominated process.

The other highlighted talk was given by Dr. Nele Van Steenberge from OCAS N.V. Zelzate, Belgium. OCAS is an advanced, market-oriented research centre for steel applications. Based in Belgium, it is a joint venture between the Flemish Region and ArcelorMittal, the world's largest steel group. Dr. Van Steenberge discussed about the industrial upgrade of bulk metallic glasses- challenges to overcome. Although the bulk metallic glasses possess a remarkable range of interesting properties for mechanical and electrochemical applications, their industrial development has not been successfully realized yet. For example, Zr-based alloys have been the most widely studied glass forming alloy family at academic level. However, their implementation on an industrial scale suffers mainly from a high cost. In turn, Fe-based bulk metallic glass alloys could be a suitable alternative due to their reduced cost. Furthermore, they offer the possibility for electromagnetic applications, not present in Zr-based alloys. OCAS N.V. is actively trying to overcome the former bottlenecks, which are actually limiting the industrial upgrade of bulk metallic glass.

The EUROMAT meetings cover many topics and bring together established scientists together with their young scientists. In addition and depending on the location and the organisation, many other scientists young and old, are attracted to specific symposia. The EUROMAT meetings have also become an excellent venue for young scientists to exchange knowledge with senior scientists and industry delegates. This time, the "Metallic glasses and related composites: new routes for functional and strong materials" symposium attracted more than 110 people in the audience during every oral session. Finally, 7 papers were accepted to be included in the actual issue of *Revue de Métallurgie*. The papers cover topics such as processing, thermodynamic aspects and atomic structure related to metallic glasses and nanostructured materials. In the following we would like to present briefly the works, in order to familiarize non-specialists readers with these new materials.

The collection of selected papers starts with the work of Loïc Perrière, Minh-Thanh Thai, Sandrine Tusseau-Nenez, Patrick Ochin, Marc Blétry and Yannick Champion: “*Spark plasma sintering for metallic glasses processing*”. This paper deals with the analysis of spark plasma sintering – named short SPS – densification of a  $Zr_{57}Cu_{20}Al_{10}Ni_8Ti_5$  metallic glass prepared by gas atomization. Several studies have already performed on this alloy, and is thus the relevant reference for comparison with sintered parts. Development of metallic glasses is hindered by the difficulties in manufacturing bulk parts. The SPS technique is very promising assuring the synthesis of metallic glass parts with increased dimensions and complicated geometries. In their work, the authors study the effect of powder particles size and sintering time through structural and thermal analyses. Local and partial devitrification of the amorphous alloy was detected, resulting from local temperature overshoots. From these analyses, an approach of the spark plasma sintering mechanism of metallic glasses is proposed.

The next presented paper: “*Synthesis of functional porous metallic material from metallic glass composites precursor by powder metallurgy route*” by Ji Su Kim, Min Ha Lee, Do Hyang Kim, Uta Kühn and Jürgen Eckert, shows how porous metallic glass with uniformly distributed micro-scale porosity can be fabricated. Bulk metallic glasses foams are under consideration as highly functional material, such as energy absorbers or ultra-light weight structures, due to their porous structure combined with desirable strengths at relatively low densities. Also, the characteristics of high surface area of foams synthesized from metallic glasses make them viable candidates as emerging materials for high-sensitivity sensors, catalysts or hydrogen storage media. In the current study, bulk metallic glass foams were fabricated by extruding powder mixtures comprised of metallic glasses blended with various kinds of fugitive phases (such as Ni, brass ( $Cu_{80}Zn_{20}$  wt%) and Cu) followed by dissolution of the fugitive phases in an aqueous chemical solution, to yield the final porous structure. The effect of the different fugitive phase on the formability of metallic glass composite and porous metallic glass foam is discussed in detail.

The processing-dedicated papers continue with “*New chalcogenide glasses in the  $GeSe_2-Sb_2Te_3-CdTe$  system*” by Temenuga Hristova-Vasileva, Venceslav Vassilev and Lilia Aljihmani. The chalcogenide glasses are a new perspective class of semiconductor materials, which are relatively easy to obtain and are characterized by a great variety of properties. Binary and multicomponent chalcogenide glasses are promising materials for different optical and photonic applications in the spectral area from 0.5 to 16  $\mu m$ . Nowadays both passive (lenses, fibers, windows) and active devices (laser fibre amplifiers, non-linear components, etc.) are developed on their basis. Their electrical and optical properties are very interesting and useful in the practice because of the possibility for their usage as threshold switches and cheap solar cells. The aim of the present work was to determine the region of glass formation within the  $GeSe_2-Sb_2Te_3-CdTe$  system.

In the same field of chalcogenide glasses, Lilia Aljihmani, Venceslav Vassilev and Temenuga Hristova-Vasileva investigated the “*Cooling rate and situation of the glass forming border in the  $GeSe_2-Sb_2Te_3-PbSb_2Te_4$  system*”. The glass forming ability of this system was investigated at different cooling rates. The samples were synthesized by direct synthesis in evacuated quartz ampoules from the initial compounds and quenched in air, water, water+ice+NaCl and liquid nitrogen at different cooling rates. The obtained bulks were characterized by visual and X-ray diffraction analyses. It was found that the critical cooling rate for obtaining chalcogenide glasses from the investigated system is 34 K/s. It is interesting that above this rate the border between the glassy and crystalline phases shows a tendency towards narrowing of the glass forming region.

Robert F. Tournier is discussing the “*Thermodynamics of the vitreous transition*” from a particular point of view. The present work follows the ideas previously published by the same author. The vitreous transition is seen as a thermodynamic transition without latent heat. A new model is used in the paper to describe this phenomenon. The author added to the classical Gibbs free energy change for a crystal formation in a melt a volume energy

saving term equivalent to a complementary Laplace pressure. There is a change of the Vogel–Fulcher–Tammann (VFT) temperature at the glass transition corresponding to a decrease of the free volume disappearance temperature. Scaling laws linking the homogeneous crystal nucleation temperatures to the glass transition temperature were used to predict the two VFT temperatures, the thermodynamic vitreous transition induced by vitreous (super)-clusters and the frozen enthalpy and entropy at the glass transition.

Further in the present issue follows the paper “*Short range order around Sc atoms in Fe<sub>90</sub>Sc<sub>10</sub> nanoglasses using fluorescence X-ray absorption spectroscopy*” by Aline Léon, Jörg Rothe, Horst Hahn and Herbert Gleiter. Nanoglasses or compacted amorphous nanostructured materials consist of nanometer-sized glassy regions which are connected by glass-glass interfaces. These materials combine the structural features of nanocrystalline materials with those of metallic glasses. They are generated by introducing interfaces into metallic glasses on a nanometer scale. For the first time, the synthesis of a Pd<sub>70</sub><sup>57</sup>Fe<sub>3</sub>Si<sub>27</sub> nanoglass was carried out in 1989. Fe<sub>25</sub>Sc<sub>75</sub> and Fe<sub>90</sub>Sc<sub>10</sub> nanoglasses exhibit different mechanical and magnetic properties compared to the amorphous bulk alloy. The authors applied in their work X-ray absorption spectroscopy – which is a local structural probe – in order to clarify the local structure of the Fe<sub>90</sub>Sc<sub>10</sub> nanoglass around Sc and Fe.

The collection of the selected papers finishes with a very interesting structural analysis at the atomistic level of the glassy alloys in the supercooled state: “*Icosahedral symmetry, fragility and stability of supercooled liquid state of metallic glasses*” by Masato Shimono and Hidehiro Onodera. The fragility of materials should be related to the local structure formed in the supercooled liquid state. Especially, in the case of metallic glasses, the icosahedral order formation is considered to play an important role. To clarify the relation between the local structure formation and the relaxation behavior (or fragility) in the supercooled liquid state of metallic glasses, molecular dynamics simulations were performed for a simple model of binary alloys, in which one can change the atomic size ratio. From the simulation results, it was found that icosahedral clusters exist in the supercooled liquid and form a medium-range network structure in the strongly supercooled regime near the glass transition as well as in the glassy state. It was also found that the number density of the clusters increases as the atomic size difference increases. Consequently, the calculated fragility parameter takes a lower value in a system with larger atomic size difference due to the richness of the icosahedral clusters. The results are very helpful to estimate the glass-forming ability of such metallic alloys systems.

Altogether these papers perfectly match the profile of the *Revue de Métallurgie*. The present papers were reviewed by two independent reviewers. We would like to express our sincere thanks to all the referees for their efficient and prompt efforts. We acknowledge the support from the Scientific Committee, particularly from Prof. Jean-Marc Chaix and Prof. Livio Battezzati, as well as from Prof. Michel Rappaz, the Topic Coordinator. Finally, we are grateful for all the support which we received from Prof. Jürgen Eckert (IFW Dresden) and Prof. Alain Reza Yavari (INP Grenoble).

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