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Engineered Materials: Micro-Nanostructure, Properties and Applications

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Abstract. The special issue presents a series of 12 contributions related to recent developments on the link between functionalities and structure in micro and nanostructured materials. The main singularity of our collection is that we proposed to bring together the know-how of several disciplines (physics, mechanics and chemistry) for a transdisciplinary discussion on the multi-scaled properties on nanostructured systems. We put together different communities for a better understanding of the relations between elaboration-structure-and-properties in bulk nanostructured materials. Particular attention has been paid to the parameters which seem to govern the macroscopic physical properties of these structures: the size of the grains, the interaction between these grains but also the influence and the nature of the size of the crystallites constituting these grains as well as their confinement by different designed nanostructuration. The main idea of this collection is to open the debate on the possible reliable strategies able to characterize the microstructure and link them to the performances of the nanostructured materials. As reported in the contributions presented in this collection, this latter point is essential for improving the physical functionalities of new nanostructures.

1. Introduction

Over the past three decades, much attention has been paid to the development of nano-architectures, particularly their elaboration, using either direct chemical synthesis routes or/and post-treatments using different processes. Nanostructured bulk materials are in the forefront of materials science due to their unique properties (e.g., improved mechanical and magnetic performances) and they consist of grains whose size is less than one micron. In this frame, to a large extent, nanomaterial properties are couched in terms of scales and their interactions. Their domain ranges from the nano-scale to the macroscopic aspects giving rise to a zoology of physical properties tuneable by changing the microstructure, the crystallite size, the amount, type and arrangement of dislocations and planar or stacking faults. The various works initiated by Gleiter in 1995 [1] show that nanostructuring generates a significant modification of the physico-chemical and mechanical properties of rock masses compared to conventional grain materials. Indeed, the chemical natures of surfaces in nano-structures are straightforwardly correlated to their physical properties and the role of interfaces still needs to be fully and deeply understood. Many new characterization techniques have been developed to study well-defined nano- and micro-structures and identify the role of the different parameters allowing the reproducibility of size, morphology, chemical composition, structural and physical functionalities. The main strategy to characterize these nano-architectures is based on the combination of diffraction techniques, microscopies, magnetic and dielectric measurements and local probe techniques to get a non-destructive detailed insight at different scales. The goal is to correlate the physical behaviours (magnetic energies, exchange bias effect, deformation, electromechanical coupling, dielectric and piezoelectric properties...) to local atomic structures including that of interfaces and/or grain boundaries and thus engineering them for new applications.

2. Elaboration Methods

The nano- and micro-structure of a material is controlled by the processing steps chosen for their elaboration. There are two ways to elaborate nanostructures. The first so-called "top-down" methods consists in transforming, by thermo-mechanical treatment, grains of conventional sizes of an initially dense material into nanometric grains by disintegration of the initial structure. The second route, called the "Bottom-up" strategy, allow producing nano-structures driving a successive arrangement of atoms or layers of atoms relative to each other. This route includes many processes such as Electrodeposition (ED), gas phase deposition (CVD for Chemical Vapor Deposition or PVD for Physical Vapor Deposition), or even techniques related to powder metallurgy. These latter usually decompose the elaboration process in two steps: a first step related to the synthesis of powders at the nanometric scale and a second step aiming the consolidation of these powders by unconventional sintering processes such as Hot Isostatic Compaction (HIC) or flash sintering (Spark Plasma Sintering-SPS).

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The proposed collection will be devoted to bulk nano-structured magnetic materials mainly developed by the bottom-up way (by experimental or numerical methods).

3. Relevant scales and functionalities

The specific physical properties of the nanomaterials (specially magnetic and mechanical) are linked to the multi-scale microstructure organization in these systems. The crystallites arrangement inside the grain and their mutual sizes as well as their organization inside the macroscopic structure exerts a strong influence on the material properties. For the sake of comparison we consider here two classical cases reported into literature: strengthening a metallic matrix by particles or grain boundaries and the analogous magnetic strengthening in ferromagnets. In the first case lattice dislocations are forced by the microstructural constraints to bow out and in the second case magnetic domain wall motion similarly forces the magnetic behaviour in the material. In figure 1 (left side) we show that the competition between grain size (D) and the characteristic length of the physical phenomenon involved (δ) are in competition and breaks down conventional size behaviour. The range where these two parameters overlap is of particular interest, because a reversing of the conventional laws can be observed (see Figure 1).



Fig. 1. (left side) Schematic diagram showing the characteristics length and the possible size effect for the mechanical functionalities of the microstructured materials; (right side) Mechanical Hardness (Hall Petch law) and Coercive field behaviour as function of the grain size in micro- and nanostructures.

In fact, previous works from Scattergood and Koch [2-4] have shown that Hall Petch behaviour correctly explains the softening behaviour of mechanical properties in nanocrystalline metals in the case of $D >> \delta$. Thus in this range, metal behaves conventionally. This softening revers when D stars to be comparable to δ and for smaller grain sizes an effect of hardening is observed as function of D. Thus the nanostructured system is observed to go from soft to hard to soft again as function of the grain size. Surprisingly enough, this inversion of properties is observed also in the coercive field behaviour of the magnetic properties in nanostructures. In ferromagnetic material, the magnetic field values needed to reverse the magnetization and the system displays an interesting analogy with the previous mechanical properties. This magnetic field, characterize the magnetic strength of the ferromagnetic material: the higher is the value the hardest is to demagnetize and revers the magnetic domain wall size (δ) link to the magnetic characteristic of the media and the grain one (D). Again, a maximum of the magnetic strength is obtained at δ =D and the hardening behaviour is inversed at this point as function of increasing size of the grains. It is important to underline that for $\delta \ll D$ the peculiar non-conventional behaviour is called superparamagnetisme effect [5].

These two examples show how size effect and their competition with physical phenomenon characteristic lengths govern the material functionalities.

4 Discussions and Outlook

Size effect are abundant in the materials world, in the previous paragraph we just focus on the mechanical and magnetic properties but such effect could be studied and evidenced in many other functionalities. In fact, a question of considerable technological importance concerns the dimensional effects in nano-scaled engineered devices based on these nanostructured materials. Besides, the physical reason of the drastic inversion of functionalities observed is of the utmost fundamental interest. The use of nanoparticles as inclusions within composite materials or the control of their organization during the shaping step, make it possible to envisage the development of compounds with optimized properties requiring less active material than the conventional systems for an equivalent level of performance. However, the development of these nanostructures still requires

the removal of many obstacles both scientifically and technologically: the control of the processes of synthesis and consolidation of nano-powders, the compatibility of the latter with a secure industrial production respecting the environmental challenges, the control of the structuring of composites and in particular of the repair or organization of inclusions within the matrix in order to limit their possible interactions, the problems related to the nature of the interfaces inclusion - matrix (hybrid interfaces) and finally the understanding and mastery of the fundamental physical mechanisms at the nanometric scale giving rise to the remarkable properties of these materials. We therefore report some recent examples of studies, illustrating in particular how the nano- and micro-structuration can affect the functionalities of different materials (metals and oxides) and how those different effects can be identified, detected and modelled. We summarize here below the reported results presented in the collection.

4.1 Effect of microstructure on the physical properties of nanostructured material

It is well known that crystal defects and stacking faults are frequently observed in many compounds and are usual referred as the origin of several anomalies in conventional physical behaviour. We report here that the lattice defect structure, such as the amount, type and arrangement of dislocations, planar faults and grain boundaries effects on the crystal and mechanical properties can be studied by X-Ray line profile analysis. The applicability of X-ray diffraction line profile analysis (XLPA) for the characterization of the microstructure in nanostructured materials is overviewed. It is also demonstrated that XLPA allows revealing that bottom-up processing methods can produce high defect density in nanostructured materials as the same as a severe plastic deformation (SPD). This latter effect can influence the transparency and microwave response as reported on fine-grained MgAl₂O₄ sintered ceramics. In this case, the thermal treatment of the obtained ceramics can rearrange structural defects and induce the loss of transparency as well as the degradation of the high frequency signal. In intermetallic Ag₃Sn-based materials, when the grain size starts to be comparable to the crystallite size, the thermal and electrical conductivities go under an inversion of the expected behaviour at room temperature. Also, microstructure can influence the recycling efficiency of NdFeB permanent magnet. Although the coercive field is similar to the non-recycled magnet, it is reported that the field generated by the magnets made by SPS after recycling, is lower than that of a similar off the shelf one. In order to countervail this effect, the performances of the SPS magnets could be enhanced by orientating the grains of the precursors before or during the sintering process in an easy magnetization direction as it is shown that the magnetization of the NdFeB grains is anisotropic in the case if the recycled magnet. If on one hand, bottom-up process as the SPS elaboration one, can produce high defect density, on the other hand it can also be beneficial. Two of the articles in the collection show how SPS allow obtaining dense and efficient SrTiO₃-based thermoelectric ceramics and optimized piezoelectric lead-free K_{0.5}Na_{0.5}NbO₃ microstructured materials.

Last but not least a review of the magnetic characteristics of nanostructured materials (saturation magnetization, coercive field, exchange bias, dipolar interactions) and their correlation with the local atomic structures including interfaces and/or grain boundaries is analysed by static susceptibility and Mössbauer technique.

4.2 Modelling the microstructure confinements on devices performances

In the frame of wireless sensor networks (WSN), a major constraint concerns the energy power supply. Batteries durability and support is a major coast. Thus harvesting mechanical energy from surrounding vibrations of the environment can be a solution and thus it is mandatory to optimize this route. It is reported here, by finite element simulation how to optimize new MEMS electromagnetic energy harvester based on array of micromagnets. The micro-dimensioning of the magnet array and the specific design of the coil are addressed in order to enhance the electromechanical coupling that allows to efficiently converting the mechanical energy into magnetoelectric one. In addition, a theoretical model is reported to accurately describe the relationship between an impedance matching and different structure.

4.3 How to control the microstructure

As it is highly demonstrated that micro and nanostructures have tremendous impact on the physical properties of the ceramics, the consecutive question is how to control them in order to control the functionalities. Few articles in the collection, report on high pressure effect on the chemical structural properties of nanocrystalline electride compounds as well as the effect of the metal ions and synthesis pathway on Co, Fe and CoFe oxide nanoparticle assemblies within an ordered silica matrix. Finally a viscosity control of the morphology and structure is presented for the elaboration of metallic perovskite oxides into 3D microstructured substrates.

5. Conclusions

We hope that the richness of the selected articles in this collection can really contribute to future constructive discussions on the multi-scaled properties of micro and nanostructured materials. We also hope that a transdisciplinary debate will be process in the next future in order to identify the parameters that govern the macroscopic physical properties in these systems. This debate is mandatory in order to be able to predict if the size of the grains, the interaction between them, the influence and the nature of the size of the crystallites constituting these grains, are in competition or collectively operate to give rise to the micro and nanostructured functionalities and performances.

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