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Editorial

Engineered materials: micro-nanostructure, properties and applications

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Abstract This special issue presents scientific results related to recent developments on the link between functionality and structure in micro- and nano-structured 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 trans-disciplinary discussion on the multi-scaled properties of 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 and 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 nanostructures. The main idea of this collection is to open the debate on possible reliable strategies for characterizing the microstructures and link them to the performance 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 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 performance) 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 scale and their interactions. Their domain ranges from the nanoscale 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 physicochemical and mechanical properties of rock masses compared to conventional grain materials. Indeed, the chemical natures of surfaces in nanostructures are straightforwardly correlated with 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 microstructures and identify the role of the different parameters allowing the reproducibility of size, morphology, chemical composition, structural and physical functionality. The main strategy for characterizing these nano-architectures is based on the combination of diffraction techniques, microscopies, magnetic and dielectric measurements, and local probe techniques to afford a non-invasive means of obtaining 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) with local atomic structures including interfaces and grain boundaries and thus engineering them for new applications.

2 Elaboration methods

The nano- and microstructure 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 consist in transforming, by thermomechanical treatment, grains of conventional sizes of an initially dense material into nanometric grains by disintegration of the initial structure. The

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second route, called the bottom-up strategy, enables the production of nanostructures 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 vapour deposition or PVD for physical vapour 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 at the consolidation of these powders by unconventional sintering processes such as hot isostatic compaction (HIC) or flash sintering (spark plasma sintering, SPS).

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

3 Relevant scales and functionalities

The specific physical properties of the nanomaterials (specifically magnetic and mechanical) are linked to the multi-scale microstructure organization in these systems. The crystallite 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 in the 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 Fig. 1 (left side) we show that the competition between grain size (D) and the characteristic length of the physical phenomenon (δ) breaks down conventional size behaviour. The range where these two parameters overlap is of particular interest, because a reversal of the conventional laws can be observed (see Fig. 1).

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 reverses when D starts to be comparable to δ, and for smaller grain sizes, an effect of hardening is observed as a function of D. Thus, the nanostructured system is observed to go from soft to hard to soft again as a function of the grain size. Surprisingly enough, this inversion of properties is also observed 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 display an interesting analogy with the previous mechanical properties. This magnetic field characterizes the magnetic strength of the ferromagnetic material: the higher the value, the harder it is to demagnetize and reverse the magnetization of the system. In this case, the physical phenomena concern the competition between the magnetic domain wall size (δ) linked to the magnetic characteristic of the media and the grain one (D). Again, maximum magnetic strength is obtained at $\delta = D$, and the hardening behaviour is reversed at this point as a function of increasing grain size. It is important to underline that for $\delta < < D$, the peculiar non-conventional behaviour is called the superparamagnetism effect [5].

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

4 Discussion and outlook

Size effects are abundant in the materials world, and in the previous paragraph we focus only on the mechanical and magnetic properties, but such effects can be studied and evidenced in many other functionalities. In fact, a question of considerable technological importance concerns the dimensional effects in nanoscale engineered devices based on these nanostructured materials. In addition, the physical reason for 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 makes it possible to envisage the development of compounds with optimized properties requiring less active material than 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 nanopowders, 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 nano- and microstructuring can affect the functionalities of different materials (metals and oxides) and how those different effects can be identified, detected and modelled. We summarize 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 have been reported as the origin of several anomalies in conventional physical behaviour. We report here that the

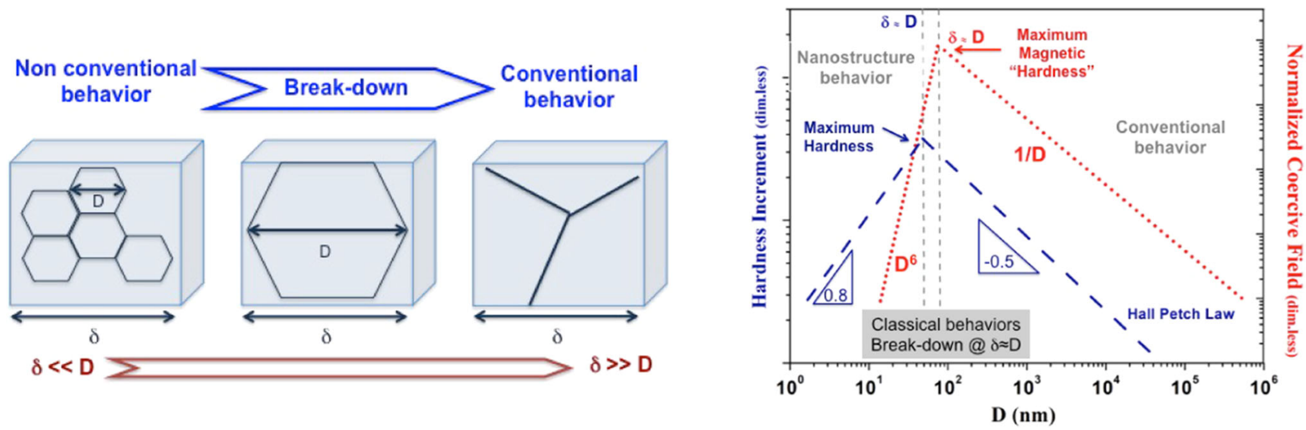

Fig. 1 (Left side) Schematic diagram showing the characteristic length and the possible size effect for the mechanical functionalities of the microstructured materials; (right side) mechanical hardness (Hall–Petch law) and coercive field behaviour as a function of the grain size in micro- and nanostructures

lattice defect structure, such as the amount, type and arrangement of dislocations, planar faults and grain boundary effects on the crystal and mechanical properties, can be studied by X-ray line profile analysis. An overview of the applicability of X-ray diffraction line profile analysis (XLPA) for the characterization of the microstructure in nanostructured materials is provided. It is also demonstrated that XLPA reveals that bottom-up processing methods can produce high defect density in nanostructured materials in the same way as severe plastic deformation (SPD). This latter effect can influence the transparency and microwave response as reported on fine-grained $MgAl_2O_4$ 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 Ag_3Sn-based materials, when the grain size approaches the crystallite size, the thermal and electrical conductivity undergo an inversion of the expected behaviour at room temperature. Also, the microstructure can influence the recycling efficiency of the 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 performance of the SPS magnets can 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 of the recycled magnet. If, on one hand, a bottom-up process such as SPS elaboration can produce high defect density, then on the other hand it can also be beneficial. Two of the articles in the collection show how SPS makes it possible to obtain dense and efficient $SrTiO_3$-based thermoelectric ceramics and optimized piezoelectric lead-free $K_{0.5}Na_{0.5}NbO_3$ 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 techniques.

4.2 Modelling the microstructural confinements on devices performance

In the frame of wireless sensor networks (WSN), the energy power supply constitutes a major constraint. Battery durability and support is a major cost. Thus, harvesting mechanical energy from the surrounding vibrations of the environment could represent a solution, and so it is necessary to optimize this route. The use of finite element simulation is reported here for optimizing a new microelectromechanical systems (MEMS) electromagnetic energy harvester based on an 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 the efficient conversion of the mechanical energy into magnetoelectric energy. 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 clearly demonstrated that micro- and nanostructure have a tremendous impact on the physical properties of ceramics, the next question is how to control them in order to control the functionalities. A few articles in the collection report on the 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, 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 contribute substantially to future constructive discussions on the multi-scale properties of micro and nanostructured materials. We also hope that a transdisciplinary debate will take place in the near future to identify the parameters that govern the macroscopic physical properties in these systems. This debate is necessary to be able to predict whether the size of the grains, the interaction between them, and the influence and the nature of the size of the crystallites constituting these grains are in competition or operate collectively to give rise to the micro- and nanostructured functionalities and performance.

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Data availability The datasets analysed during the current study are available from the corresponding author on reasonable request and can be partially be extracted and analysed from reported references.

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