

Films as Nanostructured Materials with Characteristic Mechanical Properties

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Preparation methods of nanostructured materials are discussed and the main attention is given to the film/coating technique. Short history is also reported on mechanical properties of the thin films. The most interesting result is application of structure and properties of nanostructured films.

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1. Introduction

In recent 15–20 years, the development of nanostructured (or nanocrystalline, nanosize, nanophase) materials (NMs) has emerged as an important step in creating a new generation of materials. Because of their very fine microstructure (a grain size is usually below 100 nm) NMs potentially revolutionize the traditional material design in many applications via atomic-level structural tailoring of the mechanical, physical, chemical and other properties. A great interest in NMs was stimulated in the mid-1980s when Gleiter and coworkers first paid attention to the increasing role of interfaces and particularly grain-boundary regions with decreasing a grain size.^{1,2)} However, generally speaking the topic of NMs has long history based on colloid chemistry, catalysis, ultrafine powders and films/coatings (*e.g.*^{3,4)}).

Now the consolidated NM preparation methods may be classified into four main groups including powder methods, severe plastic deformation, controlled crystallization from the amorphous state, and film/coating technique (Table 1).^{4,5)} Certainly, this classification is arbitrary and the boundaries between the various processing methods are often very diffuse. Nevertheless, each method has its own advantages and shortcomings. For example, the powder technology is not always successful in providing poreless NMs but it is more universal in terms of size and chemical composition. In turn, the controlled crystallization from amorphous state produces poreless materials but it is obviously limited to compositions that provide the amorphous state. The methods listed in Table 1 are complementary rather than competing, thus substantially widening the variety of structures, properties, and practical applications.

The general analysis of properties and structure of all types of NMs seems to be very interesting for understanding of NMs' nature. In this connection it is important to keep in mind that films/coatings are the characteristic types of NMs. This is evident from the following reasons such as the universal composition, the possibility to obtain poreless samples with very wide interval of crystallite size including amorphous state and multilayer structures (superlattices), leading to wide application of films in tool and electronic industry. Practically the thickness of films/coatings is limited and so NMs in a bulk form can not be prepared. However, this disadvantage is not so important for model considerations.

It should be also recorded that high value of plasticity of nanocrystalline Ni and Cu was observed only in the case of thin poreless samples obtained by electroplating.^{6–8)} Some new results as applied to structure and properties of nanostructured films will be considered below.

2. History and New Results on the Mechanical Properties of Nanostructured Films

First of all, we emphasize that the scientific study of films started more than one hundred years ago. Moser and Stone investigated electrical resistance (ρ) of films and pointed the high value of ρ for films as compared with conventional samples.^{9–11)} Tompson pioneered in the theory of size effects and proposed the relationship between ρ_0/ρ and δ/l (where ρ_0 is electrical resistance of conventional sample, δ is the thickness of film, and l is the free pass of electron).¹²⁾ Quantum size effects in films and other low-dimensional subjects were being considered since the middle of XX century.¹³⁾ Mechanical properties of metal films are intensively investigated about 40 years (*e.g.*¹⁴⁾). It should be also noted that Vekshinsky¹⁵⁾ is likely one of the pioneer investigator of this problem. He pointed more than 60 years early that the strength of Al films is more than four times higher than that of Al foils with the same thickness. This historical excursus is very short and does not pretend to the completeness. It should like only to emphasize the long standing of these investigations as compared with those for NMs. At the present time the thin film topic is also very popular and is deeply discussed on many international events such as the MRS Meeting, the International Conference of Metallurgical Coatings and Thin Films, the International Conference on Plasma Surface Engineering and so on. However, it should be also recorded that consideration of films/coatings deals not only with surface engineering aspect, but it is strongly interlinked with development of NMs. Unfortunately, the scientific change between these two directions is sporadic and not regular. This situation probably arises from the fact that scientists engaged in films and NMs are often in isolated communities without contacts.

In addition to above-mentioned interesting results on plasticity of electrodeposited NMs,^{6–8)} some another new results in the field of nanostructured films can be outlined shortly:

1. In the case of the boride/nitride films with the grain size of 5–15 nm, the majority of grain boundaries is to great

Table 1 General methods of preparation of consolidated NMs.

Group	Version	Object
Powder methods	Gleiter's method (vapor-phase deposition and compacting); conventional pressing and sintering; electric-discharge sintering; hot working (hot pressing, forging, extrusion, etc.); high static and dynamic pressures at ambient temperatures	Elements, alloys, compounds
Severe plastic deformation	Equal-channel pressing; torsion under high pressure; transformation-induced hardening.	Metals and alloys
Controlled crystallization from amorphous state	Ordinary and high pressures	Amorphous solids
Film/coating technique	CVD, PVD, electrodeposition, sol-gel technology	Elements, alloys, compounds

extent crystalline in nature and has a typical clear fringe contrast.^{16,17} Essentially amorphous phases and layers do not reveal in the grain boundaries.

2. Edge dislocations have been observed inside some nitride and boride crystallites.^{16–18} The availability of dislocations in structure is also approved by calculations of the characteristic length of dislocation stability in nanocrystals $\Lambda = 0.04Gb/\sigma_{PN}$, where G is shear modulus, b is the Burgers vector and σ_{PN} is the Peierls-Nabarro stress.¹⁹ When the crystallite size is lower than Λ the dislocation existence is unlikely. With using for TiN the value of $\sigma_{PN} \sim 3.7$ GPa,²⁰ it is possible to estimate the Λ value as of about 0.1 nm. So our dislocation observations in nitride films with the grain size of about 10 nm seem to be very realistic. In addition, the availability of residual plastic deformation of the TiN nanocolumns under indentation has been also fixed.^{16,17,21}
3. There are two types of deformation of the nanostructured films such as homogeneous and inhomogeneous deformations.^{16,17,22} The first is connected with the presence of the clearly defined columnar structure. In this case homogeneous deformation by slip on the boundary columns is dominant. The best known example for this type is the TiN film deformation. Localized inhomogeneous deformation is accompanied by the formation of shear bands and observed in the case of the TiB₂ and AlN films with partly columnar or stonelike structure.
4. The record-breaking values of hardness about of that for diamond have been observed in the case of nitride and boride films with mono- and multilayer nanocrystalline structures (*e.g.*^{23–26}). These results seem to be very important in the development of new types of superhard materials based on the nanostructured high-melting point compounds.
5. The proper caution must be exercised in interpretation of the nanoindentation tests because of topography and composition features of surface layer films.^{27,28} The reliability of strain parameters obtained from the nanoindentation data is rather conventional and the contribution of possible effects should be considered in detail in each particular case.
6. The significant level of high-temperature oxidation resistance has been observed in the case of AlN-SiC-TiB₂ films during the air oxidation up to 1500°C.²⁹ The formation of a self-reinforced structure has been also fixed

in these films.

7. Finally, the very small crystallites with size about of 1–2 nm and lower have been observed in the HREM studies of boride, nitride and other films (*e.g.*^{16,18,30–33}). Although the interpretation of the HREM images of such very small crystallites is not so simple and is ambiguous, the availability of these small grains in structure is likely and such subjects could be named as cluster-consolidated NMs. In this connection it seems to be very interesting to study the availability of quantum size effects in these films. It is well known that such effects take place when crystallite size is of the same scale as de Broglie's wave for carriers. Such situation is observed for many semimetals and semiconductors. It is commonly known that many of high-melting point compounds especially with oxygen contamination are close to semimetals which are characterized by quantum size effects. A manifestation of these effects may be revealed in the transport properties of nanocrystalline high-melting point compounds. This phenomenon seems to be interesting and important for many application areas of NMs such as sensors, thermal/diffusion barriers and so on.

Undoubtedly, this enumeration can be extended but the paper size is limited and some additional interesting information in this field could be found in recent books.^{34,35}

3. Conclusions

It is evident from the number of examples, which have appeared in this short review that there is considerable scientific interest in results obtained in nanostructured film studies. The wide range of different metals, alloys, and compounds as well as the ability to obtain them in the wide interval of crystallite size suggests that many possibilities remain to be explored. One might expect that many outstanding problems in NMs science, such as a selection of optimal crystallite size, thermal stability nanocrystalline structure and so on, could be resolved with using films as subjects.

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