Advanced Materials and Processes

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YUCOMAT II

Proceedings of the Second Yugoslav Conference on Advanced Materials,
held at Herceg - Novi, Yugoslavia, September 15-19, 1997

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TRANS TECH PUBLICATIONS LTD
Switzerland • Germany • UK • USA

ISBN 0-87849-812-5

Volumes 282-283 of
Materials Science Forum
ISSN 0255-5476

***Distributed** in the Americas by*

Trans Tech Publications Inc
PO Box 699, May Street
Enfield, New Hampshire 03748
USA

Phone: (603) 632-7377
Fax: (603) 632-5611
e-mail: ttp@ttp.net
Web: http://www.ttp.net

and worldwide by

Trans Tech Publications Ltd
Brandrain 6
CH-8707 Uetikon-Zuerich
Switzerland

Fax: +41 (1) 922 10 33
e-mail: ttp@ttp.ch
Web: http://www.ttp.ch

Printed in the United Kingdom
by Hobbs the Printers Ltd,
Totton, Hampshire SO40 3WX

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PREFACE

The Proceedings ADVANCED MATERIALS AND PROCESSES includes 49 papers presented at the Second Yugoslav Conference on Advanced Materials (Yu-MRS Meeting) held in Herceg Novi, Yugoslavia, September 15-19, 1997.

One hundred seventy scientists from Yugoslavia and abroad participated in the conference. From 143 papers 50 were presented orally and 93 as posters. All the submitted papers were reviewed by at least one of the members of the Scientific Committee and the accessory review team. The papers accepted for publication have been considered to be sufficiently original and to contain new data that deserve to be published in the Proceedings. Authors from 12 countries, except Yugoslavia, are included in the Proceedings, proving our international orientation.

Forty-nine papers selected by the Editors for inclusion in this volume are thematically pressented in nine sections: (1) Nanophase and Amorphous Materials; (2) Nonequilibrium Processing; (3) Fullerenes and Nanotubes; (4) Thin Films; (5) Ceramics; (6) Particulate Composites; (7) Carbon Materials and Polymer Composites; (8) Polymers; and (9) Physical Metallurgy.

The Editors wish to thank heartily to all members of the Scientific and Organising Committees for their efforts to organize the conference successfully, and to perform their duties as Session Chairmen and reviewers. Special thanks to Prof. F.E. Karasz (University of Massachusetts at Amherst, MA, USA), Dr. C. Loos-Neskovic, (C.E.N. Saclay Gif-sur-Yvette, France), Prof. P. Zannela (Institute of Chemistry, Inorganic Technologies and Advanced Materials, Padua, Italy), Prof. R.A. Andrievski (Institute of New Chemical Problems, Chernogolovka, Russia), Prof. V.D. Krstic (Queen's University, Kingston Ontario, Canada) as well as to domestic scientists for delivered plenary lectures which were very timely and informative.

Unfailing help and enthusiasm of Mr. Predrag Živanović, secretary of the conference is gratefully acknowledged. The Editors wish to thank Predrag for his technical editing of the materials before, during and after the conference and for preparing Table of Contents, Author Index, Keyword Index, and other details for the Proceedings. Special thanks to Mrs. Verica Roglić-Korica for her text language revisions.

Our gratitude to the Ministry of Development, Science and Environment of the Federal Republic of Yugoslavia, Ministry of Science and Technology of the Republic of Serbia, Ministry of Science and Education of the Republic of Montenegro, and other sponsors without whose support the Proceedings and the conference could never have been mounted.

Dragan P. Uskoković
Slobodan K. Milonjić
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Belgrade, December, 1997

YUGOSLAV MATERIALS RESEARCH SOCIETY
YU – MRS OFFICERS (1997-1999)

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Yugoslav Materials Research Society (Yu-MRS), a non profit scientific association founded in 1997, promotes multidisciplinary goal-oriented research on materials science and engineering. Its primary purpose is to hold symposia on materials research. Through these symposia Yu-MRS promotes interactions between chemists, physicists, ceramists, metallurgists, polymerists, engineers, etc., who are studying different aspects of a particular materials topic. Membership is open to anyone who has an interest in materials synthesis, processing, characterization and development.

Technical Editor of Proceedings: **Predrag Živanović**

Welcome Address by Dragan Uskoković,
President of the Yugoslav Materials Research Society,
at the 2nd Yugoslav Conference on Advanced Materials
YUCOMAT II

Herceg Novi, Sept. 15, 1997

Ladies and Gentlemen, dear Friends,

I have the honour and great pleasure to address to you as the President of the Yugoslav Materials Research Society, probably the youngest society of the kind in the world, founded only a hundred days ago. Nevertheless, knowing that the oldest MR societies (American and E-MRS) are barely 15 years of age we may, with a good reason, say to have joined the MRS family relatively quickly. Although young, our society has already accounted a few notable achievements. First is the previous conference held two years ago when a decision was made to articulate all our activities through a society. The Conference Proceedings was published by Transtec Publications, Switzerland (ADVANCE MATERIALS FOR HIGH TECHNOLOGY APPLICATIONS, Mater. Sci. Forum, Vol. 214 (1996) 276) and is available in numerous libraries worldwide. About thirty papers therein represent worthily our research programs. It was a good starting point so that this second conference was included in the World MRS Conferences Calendar (MRS Bulletin, Vol. 22, May, 1997, No.5), proving our good orientation.

Let me take the opportunity to express some of the remarks of mine on the current situation in the field of materials science and engineering in general and in our country in particular as well as on the tasks and objectives of our Society. Last decade of this century, marked by clear orientation of industry towards high technologies, is a very difficult time for science, research and development. There are no visible indications on whether the great changes, occurred recently, are the signs of improvements, meaning a prelude to the coming century and controlled modeling of future, or a sign of a shift of significance from science to other fields of human activities. Science will remain, as it is, unstable until the mankind, taking into consideration real challenges, finds appropriate new ways out or adequate place for it. Industrial, therefore, rich countries although experiencing the crisis, which is practically global, have relatively easily maintained their stability.

Free market introduced into the East European countries contributed significantly to the confusion of political, economic and social changes. Countries of the former Soviet Union, artificially balanced owing to the military technology in the period of East-West bloc countries rivalry, had to face almost overnight the newly created situation and serious problems including a great number of scientists without programs and financial support and impossible reorientation of the very military technology.

The most difficult situation is, to our regret, here on this territory. The country which according to economic statistics belonged to the Central European countries in the beginning of the 1980s and at the door of the European Union, today is among the least developed ones, far beyond the former East European countries, which only a couple of years ago were a few times backward. Exhaustion as a consequence of war, drastic national income drop, "inner" and "outer" sanctions caused collapse of science and economy. As estimated, it will take us at least 20 years to return to our previous positions, a tragic fact for us all and especially for new generations, that creative young people, whose dream to be professionally engaged in science will hardly come true.

It would have been ideal if the science had never been dependent on a financier. Of course, this is impossible and our intellectual and material discoveries are inevitably dependent on various sources. If these sources become limited, the scientific work will begin to stagnate, which means that the scientific programs must be financially supported but the global interests have to be considered closely and the moral integrity preserved.

The role of the materials science is to set new boarders, to extend within the discipline the region of the known. It is certainly a field of great intellectual challenge. Just remember the race for high-temperature superconductors of some ten years ago and recent fullerenes rush, crowned by Nobel prizes. Today, especially attractive fields are direct breakthrough into the world of atoms and their arrangements via high resolution methods and nanostructure designs; models applications and computer simulation at a large scale to predict the structure and properties of materials; and use of principles of self-organization of living organisms for synthesis and tailoring of materials structure at the molecular level (biomimicric materials).

All the time we have to be aware that the results of our activities achieved at institutes and universities are to speed up the application of high technologies in industry and that their validity has to be tested on the market. It is believed that, in the beginning of the century to come, only those industries, which are able to incorporate, quickly and successfully, new materials into their production processes will become competitive. Materials science, today, meets different but similarly important challenges such as:

- preserving of its basic mission in the range of fundamental science, i.e., shortening of the boundaries of the unknown,
- independent organization which is to make the science work efficient in defining aims to bridge the gap to industry,
- offering of innovations, competitive on the world market, to industry.

Answers to how to achieve all this, at least some of them, I hope will be found at three symposia and three round tables, the Society planned for this meeting. Within this frame we expect to come to the solutions of a series of problems of special interest to our country. Among them are the answers to:

- how to channel the scientific creativity of talented and successful scientists in order to develop fully their potentials,
- how to define the mechanisms to promote the highest quality programs and encourage the scientists; a suggestion is formation of centers of excellence where our top-level scientists may achieve the ultimate goals,
- how to overcome the interests of some small but powerful groups for whom their own interests are of primary importance,
- how to provide and direct financial support to be truly fruitful.

These are, certainly, the main objectives and tasks of the Yugoslav Materials Research Society we will focus on in the period to come.

I hope that deeply absorbed in the problems with high aims pursuing us to solve them, we will spend these five days in constructive and fruitful discussions, which are to result in new ideas, suggestions, and maybe new tasks for our Society.

I wish all the attendees a successful work. Pleasant stay in Herceg Novi is something that is understood, for this town always, due to its beauty, fascinating surroundings and our perfect hosts, creates an ideal atmosphere for spiritual rise and relaxation which we all need in a difficult time as this.

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State-of-the-Art and Perspectives in Particulate Nanostructured Materials

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Keywords: Nanostructured Materials, Structure, Processing, Consolidation

ABSTRACT

Nanostructured materials (NM) are characterized by a typical structural size below 100 nm. The possibility of realization of some unique physico-mechanical and physico-chemical properties in the nanocrystalline state is attractive for many specialists of material science, physics and chemistry of solid state, and high technology. The understanding of relationship between different properties and structure is so found to be not trivial. Methods of NM preparation particulate and film NM are generalized in this review. A "soft" crystallization from amorphous state and plastic deformation are also considered. Special attention is given to high-energy consolidation methods. Properties of NM are discussed in connection with possible application.

1. INTRODUCTION

Nanostructured materials (NM) are normally characterized by a crystallite size below 100 nm. This limit is very conditional and defined rather by convenience than some rigid physico-chemical parameters. Great attention to NM, increasing in the last 10-15 years everywhere, is connected with two reasons at least. First, it is a hope to realize unique mechanical, physical and chemical properties (and therefore performance ones) in nanocrystalline state. Second, it is a lack in not only our understanding of the features of nanocrystalline state, but its technology realization as well. So all above-mentioned has encouraged many investigations. Since 1992, the journal Nanostructured Materials has been published in the USA. Three specialized conferences were held (the fourth one will be held in Sweden in 1998) and the total number of meetings is about 20-25 for a period of 5-7 years.

Undoubtedly, the results of Gleiter and coworkers [1, 2] were an important impact on this problem. In the eighties the NM basic idea has been formulated and the gas-condensation synthesis of ultrafine powders (UFP) in combinations with vacuum compaction (pressure up to 3-5 GPa) realized for the preparations of small nanostructured specimens (10-15mm diameter and 0.2-0.5mm thickness). This has assisted in preparation of many NM without contact with air and revealed many new interesting results on the nature of nanocrystalline state. The scientific groups of Siegel (ANL) and some USA Universities have actively settled down in this area [3, 4]. The state-of-the-the-art in this problem has recently been reflected in reviews [5-8] and discussed at the 3-rd International Conference on Nanostructured Materials (USA, Hawaii, July 8-12, 1996) [9].

However, the NM topic has been brought significantly earlier and dated from the UFP investigations, colloidal materials and catalysis. Gleiter [5] mentions that strengthening of metals by small particles has been studied from the beginning of our century. At the same time it is known that Bercellius and Faraday investigated colloidal-dispersed metals in the middle of the previous century and some colloidal formulae had been realized way back in ancient Egypt. At this point it is appropriate to remind us on some collections and books (for example) [10-39]; the quantity of our and especially foreign sources may be enlarged in this list) not to say on separate publications and comprehensive literature on colloids and catalysis. The investigations performed in the fiftieseighties [10-39] have been of great importance for NM science and engineering. Special attention has been paid to traditional topics of gas-condensation and plasma chemistry methods of UFP preparation and their characterization and sintering. Unfortunately, investigations [1-6] and [10-39] have been developed, to a great extent, separately as we can observe from literature. Only from the nineties some consolidation of efforts and approaches can be seen as a result of frequent contacts, meetings and conferences, and so on.

We will focus on the NM classification. Leaving aside the structure features (see classifications of Gleiter and Siegel [5, 6], let us consider the main preparation methods of NM only (Table 1 [40]).

Table 1. Main Preparation Methods of NM

Method	Materials Type
Compaction and sintering Hot pressing including HIP Hot forming by pressure (hot forging, etc) Technique of high pressures and high temperatures Electrodischarge compaction	Particulate NM
Crystallization from amorphous state Plastic deformation and dynamic recrystalization	Particulate and film NM
CVD PVD Electroplating Sol-gel technique	Film and multilayer NM

Of course, this classification is very conditional because, for example, it does include any of the features of metalpolymers and membranes [41]. Nevertheless, a variety of NM preparation methods are obvious. This is one of the advantages of these materials, which enlarges their technical possibilities. Foregoing methods are complementary but competitive to some extent. This should be accounted in their selection including economic and other information. It is worth noting that the NM problem had clearly defined interdisciplinary character in developing of which specialists in powder technology as well as those whose interest is focused on the clusters, films and amorphous materials preparation and investigations have taken part. Below, only particulate NM will be discussed. Powder technology seems to be more universal in comparison with other technologies.

2. PREPARATION AND CONSOLIDATION OF UFP

Preparation of UFP is one of the long-explored areas. Production of UFP has been realized not only on a laboratory scale, but also on a large scale as well for many metals, alloys, intermetallics, and high-melting compounds. Table 2 shows the main methods of UFP preparation.

As in the case of previous Table, we emphasize that there are various, complementary and competitive methods, among them the most popular ones are reduction, plasma synthesis, gas condensation technique, thermal decomposition and mechanosynthesis. High-energy ball milling seems to be very attractive (the ratio ball/powder sometimes is equal to 30:1), but problems of admixture contamination, oxidation, and behavior of powders at compaction and sintering remain to be solved. The accumulation of technical-economical results, including transport and storage problems and final performance, continues and at the moment it is difficult to give the impartial assessment of UFP prepared by different methods.

Table 2. Main Methods of UFP Preparation (particles-crystallites size below 100 nm)

Method	Metal, Alloy, and Compound
Reduction and synthesis	
reduction of oxides [7, 8, 11, 12, 16, 19, 21, 34, 37]	Co, Ni, Fe, Mo, W, Ni-Fe, Ni-Cu, Mo-W, WC-Co
plasma-chemical synthesis [18, 35, 39]	TiN, Ti (C, N), Si_3N_4, AlN, BN, Al_2O_3
laser synthesis [7, 39]	SiC, TiB_2, Si_3N_4, MgO, SiO_2
reduction and synthesis in solutions [7, 9, 41]	Cu-Co, Ni-Cu, Fe-Cu, Mo_2C, TiB_2
mechanosynthesis [7, 8]	TiAl, $NbAl_3$, NiAl, Fe-Cu, TiN, TiC, TiB_2
Electrolysis [7, 10, 13]	Fe, Ni, Zn, Cd, Pb, WC, ZrO_2
Thermal decomposition	
condense precursors [7]	Si_3N_4, SiC, TiO_2, BN, AlN, ZrO_2, Al_2O_3
gaseous precursors [7]	TiB_2, ZrB_2, BN
Gas-condensation	
in inert gas or vacuum [1-8, 17, 27, 31, 39]	Pd, Ag, Cu, Zn, Pb, Al, Au, Ni, TiO_2, TiAl, MgO, Al_2O_3, ZrO_2
in reactive gas [7, 39]	TiN, ZrN, NbN, AlN, VN, ZrO_2, Y_2O_3
Electrical explosion of conductors [27, 36]	Al, Pt, Au, W, Al_2O_3
High-energy ball milling [7, 8, 38]	Practically all metals and compounds

We show only the data of two USA companies which have realized the R&D of ANL and the Rutgers University on a commercial scale (Table 3) [6-9].

Table 3. Output of Some UFP in USA [8]

UFP	Company	US$/kg
TiO_2, Y_2O_3, CeO_2, Cr_2O_3, Fe_2O_3, MnO_2 Al_2O_3, Fe, Co, Ni, Cu, Pd, Ag, Au, Al, Si	Nanophase Technologies Corp., Darien, IL	110 (TiO_2, d ~ 30 nm)
WC-Co (WC particles of 20-40 nm)	Nanodyne Inc., New Brunswick, NJ	77 (output of 90 000 kg/year)

It should be noticed that already in the seventies-eighties the R&D regarding UFPs of W, Mo, TiN, ZrN, TiC, Ti (C, N), AlN, BN, SiC, Si_3N_4, etc. at the Institute of Metallurgy of USSR AS (Tsvetkov), Institute for New Chemical Problems of USSR AS (Troitskiy), and the Institute of Inorganic Chemistry of LatvSSR AS (Millers) have been realized on a pilot and industrial level. Some Japanese Companies (Ube Ind., Toshiba Cer., Denka and others) as well as the H.C. Starck Company (Germany) have been specialized in production of some high-melting compounds UFP (see about Si_3N_4 UFP in review [42]).

Some UFP's properties and their consolidation will be discussed (see also [7, 34, 35, 37, 38]). The features of these powders such as the high level of adsorbed gases, low compressibility, and shrinkage localization at sintering has been pointed in our works [7, 38, 40, 42]). All these features are connected with the high level of specific surface area and interparticle friction as well as agglomeration. Skorokhod has analysed the evolution of microstructure and densification of UFP at sintering in detail [37]). Interesting observation on the role of agglomerates at sintering of ZrO_2 and TiO_2 UFP have been carried out by Mayo [43]. In particular, it was demonstrated that the difference in densification of agglomerated and nonagglomerated powders with similar crystallite sizes could be varying significant at low-temperature sintering. This can be connected with the formation of non-