Recent Developments in the Processing and Applications of Structural Metals and Alloys

Edited by

Marcello Cabibbo
Stefano Spigarelli

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Recent Developments in the Processing and Applications of Structural Metals and Alloys

Selected, peer reviewed papers from the international conference
on Recent Developments in the processing
and applications of structural metals and alloys,
Conference organized to celebrate
the 70th birthday of Prof. Enrico Evangelista,
Dept. of Mechanical Engineering, Marche Polytechnic University, Italy, COMO (Italy) from
22nd to 25th June 2008

Edited by:

Marcello Cabibbo and Stefano Spigarelli

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Recent Developments in the Processing and Applications of Structural Metals and Alloys

Forehead

Dear participant, dear colleague,

The organizing committee welcomes all of you for taking part in the International conference dedicated to Prof. Enrico Evangelista on the occasion of his 70^{th} birthday.

In particular,
Prof. Stefano Spigarelli and Prof. Marcello Cabibbo
express all their gratitude for the Enrico's invaluable guidance in their scientific and professional endeavours.

This Conference is intended to be the proper opportunity for wishing Enrico Evangelista to be as successful in his future activities as he has been in his academic and scientific career.

Introduction

The conference honors Prof. Enrico Evangelista on the occasion of his 70th birthday.
Prof. Evangelista has been working in the field of materials science for more than 30 years and has served on the faculty of the *Marche Polyitechnic University* of Ancona since 1982. He has been very active in a range of research programs and has published over 300 papers to date, collaborating with several highly regarded scientists in Europe, Asia, Australia and the US.
He is a fellow of ASM International and has particularly wide collaborations in the US and Europe.

The conference was intended to serve as a forum for the exchange of ideas between international and, especially, European researchers on the latest developments of severe plastic deformation techniques and thermo-mechanical processing of materials for both structural and functional applications. Areas of interest include both conventional hot and cold deformation of metals as well as recently developed severe plastic deformation processes for the production of ultra-fine and nanostructured materials. Top experts on this field will gather with the mission of enunciating the state of the art and of identifying areas for further research. The total number of attendees and oral presentations was 60 from several different countries: USA, Canada, UK, Spain, Germany, Italy, Hungary, Austria, Norway, Russia, Ukraine, Israel, Korea, Japan. Of these 60 contributions 40 left a manuscript to be published in Mater Sci Forum (Trans Tech Pub, Switzerland).

In particular, the following specific topics were covered:

i. Multifunctional nanostructured coatings
ii. Modelling and recrystallization
iii. Nano-structured materials and Severe plastic deformation
iv. Hot plastic deformation
v. Process Mechanics and Microstructure

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Editors, Editorial and Advisory Board

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Scope

Materials Science Forum specializes in the rapid publication of international conference proceedings in every area of Materials Science, Solid State Physics and Chemistry. This permits such proceedings to be conveniently referenced, abstracted and read.

Materials Science Forum also publishes, on a regular basis, collections of research and review papers on topics of current interest. Abstracted in all of the major abstract media, and available in practically all of the major libraries which service materials research communities, *Materials Science Forum* offers both very rapid publication and high visibility.

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Chapter 1:

Multifunctional Nanostructured Coatings

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Fabrication and Characterisation of Nanostructured Coatings by Magnetron Sputtering for Wear Resistant Applications

This paper is dedicated to Prof. Enrico Evangelista in the occasion of his 70th birthday

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Abstract. Magnetron sputtering is a powerful process for the production of thin films and coatings employed for the surface modification of tools and engineering components in various industrial sectors. Nanostructured coatings for multifunctional applications were deposited by means of magnetron sputtering by adjusting the experimental parameters in order to tailor the chemistry, the microstructure and the morphology of the coatings. Among the several systems that were investigated, $TiC–TiB_2$ for wear applications were successfully tested. $TiC–TiB_2$ coatings were deposited on a hardmetal WC–Co substrate in an unbalanced DC magnetron sputtering system starting from composite targets fabricated by the Self-propagating High-temperature Synthesis (SHS) consolidation method, involving the material synthesis and densification in one step. The results, showing the achievement of nanostructured films with thickness ranging between 1 and 2 µm, are here presented. The properties evaluated on the developed films (hardness, adhesion, friction coefficient and volumetric wear) are promising for the improvement of wear-resistant applications.

Introduction

The production of composite thin films is becoming more important in the engineering of surfaces to meet specific property requirements and applications. This is particularly the case of wear- and corrosion-resistant applications.

Nanocomposite coatings have recently attracted growing interest due to the possibility of synthesising materials with unique properties, e.g. super-hardness [1–4], combined high hardness and toughness [5, 6], or hardness and low friction [7–9]. This led to an increasing number of papers dealing with different nanocomposite wear-resistant coating materials, even if in many cases the origins of the attractive properties of these materials are not completely understood. It is the aim of this paper to consider possible approaches for an optimized 'nanostructural' design of coatings for anti-wear applications. Within the background results obtained on fabrication, microstructural and mechanical characterization of sputtered nanocomposite films, coatings pertaining to the Ti–B–C system are here presented.

Regarding nanocomposite materials, it is assumed that multiple mechanisms are responsible for hardness and toughness optimization [10] and that the key role in this framework is played by the synergism between these mechanisms. However, it has to be emphasised that not only the nanoscale grain size, but also the interfacial arrangement and strength are crucial in determining the coating properties. To avoid unstable crack propagation, a well-defined interface of high cohesive strength is needed. Inferred from thermodynamics, this may be obtained for those compounds showing a wide miscibility gap in the solid state but a certain chemical affinity to each other to form high-strength grain boundaries. This may be fulfilled, e.g. for the quasi-binary system $TiC–TiB_2$, showing an eutectic point, as well as for other similar transition metal nitride/boride [11] or carbide/boride films.

Composite targets for sputtering can be produced by a number of techniques such as for instance sintering, hot pressing or hot isostatic pressing, or by plasma spraying of the component materials. However, each of these techniques can result in various defects in the targets, such as non-uniform microstructure, porosity, high impurities or oxygen content. Besides, each one of the aforementioned technologies require multi-stage processing with a number of time- and resource-consuming steps like e.g. powder production, powder blending and mixing of additives, cold shaping, densification, machining, grinding and finishing. Self-propagating High-temperature Synthesis (SHS) [12] offers a simple and efficient alternative route for the production of composite targets to be employed in sputtering of composite thin films. Carbides and borides of transition metals are refractory materials that can be easily synthesised by SHS [13] and offer considerable potentials for the fabrication of both thermally and chemically stable coatings [14]. Composite materials with accurately controlled compositions suitable as targets for sputtering can be produced by SHS. This work explores the potential of applying SHS to fabricate TiC/TiB_2 composite targets to be used for the realisation by sputtering of Ultra High Temperature Ceramic (UHTC) thin coatings with controlled microstructure to improve the behaviour of metallic materials in view of wear-resistant applications. The performance of the developed coatings in terms of resistance to wear and oxidation is also tested.

Self-propagating High-temperature Synthesis (SHS) is a well known technique using an exothermic reaction to provide the energy needed to synthesise ceramic, intermetallic or composite materials. Self-propagating high-temperature synthesis (SHS) is based on highly exothermic reactions, which upon initiation, become self-propagating. Among various materials, TiC and TiB_2 can be synthesized by means of SHS [15]. However, the products of the process are porous and therefore have to be compacted and sintered to produce bulk components suitable for engineering applications [16]. In this framework, the pressure-assisted SHS is an attractive technique for the preparation of dense composites [17]. If the SHS process is assisted by the application of pressure, it is possible to achieve synthesis and densification simultaneously [18, 19].

Magnetron sputtering (Fig.1) is a technique by which a target of the material to be deposited is introduced into a vacuum chamber [20]. When power is supplied to a magnetron, a negative voltage of typically –300V or more is applied to the target. This negative voltage attracts positive ions to the target surface. By colliding with the atoms of the surface an energy transfer occurs. Surface atoms become sputtered if the energy transferred is larger than the surface binding energy. An unbalanced magnetron possesses stronger magnets on the outside, resulting in the expansion of the plasma away from the surface of the target towards the substrate. The effect of the unbalanced magnetic field is to trap fast moving secondary electrons that escape from the target surface. These electrons undergo ionizing collisions with neutral gas atoms and produce a greater number of ions and further electrons increasing the substrate ion bombardment, while a secondary plasma is formed in the region of the substrate.

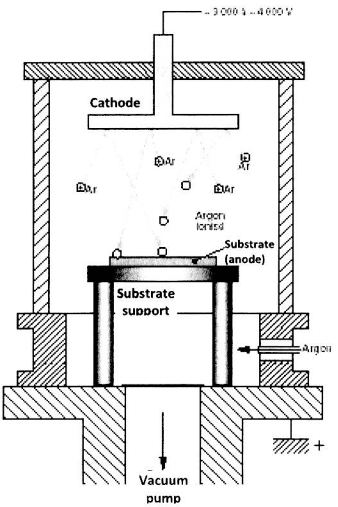

Fig.1. Magnetron sputtering process used for the realisation of the coatings.

Experimental activity

Composite TiC-TiB_2 targets were produced using the pressure-assisted SHS technology above described. Titanium powders (diameter < 45 μm), carbon black (< 1 μm) and amorphous boron (< 1 μm) were used as reactants for the synthesis of the TiC-TiB_2 targets according to the following self-sustaining reaction:

$$3Ti + 2B + 2C \rightarrow 2TiC + TiB_2. \quad (1)$$

The reactant powders were blended in the stoichiometry required to yield composites with a composition approximately equal to the eutectic (i.e. 60%wt TiC – 40%wt TiB_2). Green samples with square shape and dimensions 70 x 70 mm were produced by cold compaction in a steel die using an uniaxial press.

The reacting sample was placed into a steel die and was covered by sand used as a porous thermal insulator to reduce the cooling rate of the SHS products and to protect the inner wall of the die from the effect of the high combustion temperatures reached during the process. The sand also acts as a porous medium for evacuating impurity gases from SHS products and producing a macroscopic pseudo-isostatic load on the compact. Before ignition the sample was loaded with a mechanical pressure equal to 100 atmospheres, which was maintained constant during the overall process. The ignition was achieved by means of an electrical resistance wire. The SHS reaction was completed in a wave propagation form in few seconds, and the mechanical load was removed after 30 seconds. Reacted samples with a thickness of about 8 mm were obtained after the pressure-assisted SHS. The samples were ground and polished using diamond wheels to achieve a flat geometry and remove surface contaminations. The thickness of the polished samples was reduced to 6 mm. Fig.2 shows the products of the pressure-assisted SHS, as reacted and after polishing.

After polishing, the square plates were cut by electro-discharge machining (EDM) and assembled on a copper plate support in order to produce targets of dimension 500 x 88 mm as shown in Fig. 3.

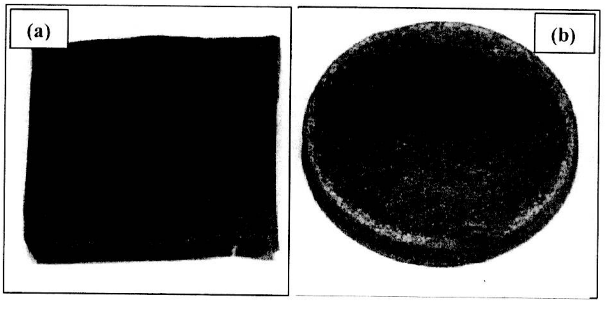

Fig.2. Products of pressure-assisted SHS, as reacted (a) and after polishing (b).

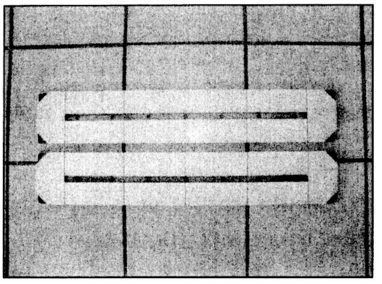

Fig.3. Composite targets fabricated by assembling the plates produced by SHS. The substrate is a copper plate support.

Finally the coatings were produced using Unbalanced DC Magnetron Sputtering (PVD) technique from targets designed from the SHS-fabricated materials. Commercial tungsten carbide hardmetal substrates (WC-Co 94/6 at.%) were used for the deposition of the coatings. The substrate was mirror-polished with diamond wheels and 3 μm diamond paste. The conditions used for the magnetron sputtering are reported in Table 1. The sputtering was carried out in vacuum within the pressure range of 0.5 to 0.8 Pa under a direct current discharge. Argon served as the working ion-producing gas.

DC power density	14 W·cm^{-2}
Total gas pressure	0.8 Pa
Substrate temperature	365°C

Table 1. Sputter parameters applied for the deposition process.

The coatings deposited by DC magnetron sputtering were characterised in terms of chemical and structural composition by EPMA (electron probe micro analyser) analysis and XRD respectively. The microstructure of the deposited coatings was observed by scanning electron microscopy in a LEO SUPRA 35 Field–Emission Scanning Electron Microscope (FESEM). The mechanical characterisation regarded the micro hardness and the Young modulus evaluation, using a 100 mN force and a Fisherscope H100 tester according to PrENV 1071-7, and the critical load of failure by scratch test (Fig.4). The scratch tester moves a Rockwell diamond tip with a radius of 200 μm across the coated surface of the substrate at a constant velocity while a normal force is applied with a constantly increasing loading rate. Acoustic emission and coefficient of friction were also recorded during the experiments.

Velocity of diamond tip	10 mm/min
Maximum load	70 N
Load rate	100 N/min

Table3. Conditions for the scratch tests.

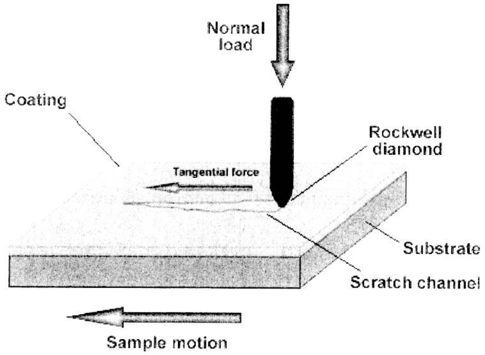

Fig.4. Scratch test for the evaluation of the critical load of failure of the magnetron sputtered films.

The wear behaviour of the coated materials was evaluated by ball-on-disk wear tests. According to this method, the sliding contact is brought by pushing a ball specimen onto a rotating disc specimen under a constant load. The disk was made of WC-Co substrate coated with $TiC–TiB_2$ layer. Square disks with dimension 15x15 mm and height 7 mm were used. The friction coefficient μ and volumetric wear rate, both of the coating and of the ball counterparts, were measured in the tests against a ceramic (silicon nitride, Si_3N_4) counterpart ball. During the wear tests the temperature in the ball–disk contact zone was also determined. In addition, the wear tracks were analysed by SEM. The ball-on-disk tests were carried out without lubricant according to the ISO 20808:2004(E). The parameters used in the wear tests are shown in Table 3.
The starting oxidation temperature of the coating was evaluated by thermogravimetric analysis (TGA) with 30°C/min heating rate and 1100°C maximum temperature.

Counterpart material (ball)	Si_3N_4
Ball diameter	1 mm
Normal load	1 N
Sliding velocity	0.1 m/s
Sliding track radius	5 mm
Linear length	100 m

Table3. Conditions for the ball-on-disk tests.

Results and discussion

The results of the characterisation carried out on the sputtered coatings are summarised in Table 4. By thermogravimetric analysis it was observed that the oxidation started at 680°C. A mass gain of 0.078 mg/cm^2 was measured on the sample heated to 700°C for one hour.