CLSI PROPOSAL SUBMISSION
GENERAL USER

Proposal #14-3648
11ID-2 (PGM)

Date Submitted: 2011-03-01
Cycle 14 (July 2011 - December 2011)

Title of Proposal:	Boron K-edge XANES of TiBC/a-C nanocomposites in high temperature tribology
Type of Proposal:	General User
Proposal Duration:	3 cycles (18 months)
Subject of Research	Material and Chemical Sciences
Industrial Partners Involved?	No
Five Key Words	tribology, thin films, hard coatings, sefl-lubrication, absorption
Funding Sources	NSERC, CSIC, NSRC

RESEARCH TEAM

First Name	Last Name	Institute/Affil.	Email	Department	Classification	Status
Spokesperson						
Jose	Endrino	Instituto de Ciencias de Materiales de Madrid	jlendrino@ icmm.csic.es	Surface Engineering	Scientist	Coming to CLS
Other Research Team Members						
Manuel	Abad	McMaster University	abadmd@ mcmaster.ca	Mechanical Engineering	Post Doctoral Fellow	Coming to CLS
Juan Carlos	Sanchez-Lopez	Instituto de Ciencia de Materiales de Sevilla (CSIC-US)	jcslopez@ icmse.csic.es	Tailored Nanomaterials and Microstructure	Scientist	Coming to CLS

INVOICING DETAILS

Name	Address	City	State / Province	Postal / Zip Code	Country
Jose Luis Endrino - ICMM CSIC	C Sor Juana Ines de La Cruz 3	Campus Cantoblanco Madrid	Madrid	28049	Spain

BRIEF DESCRIPTION

This proposal builds up from our previous beamtime at VLS-PGM that resulted already in one accepted article in Plasma Processes and Polymers Journal (I.F. = 5.0). In this research, we have synthesized two series of TiBC/a-C nanocomposite coatings with different chemical compositions by sputtering of a graphite target and a second one composed of either TiB2:TiC (40:60) (mixed) or pure TiB2 (single) by the co-sputtering deposition technique using a ceramic multiphase TiB2:TiC (40:60) and a pure graphite targets. Due to the quasi-amorphous character and possible multiphase formation of Ti-B-C compounds, XANES studies of the B K-edge are appropriate for better understanding of their electronic structure and its correlation with tribo-mechanical properties.

SCIENTIFIC MERIT

TiBC/a-C nanocomposite are promising materials as protective coatings for machine and tool elements due to the appropriate combination of crystalline hard phases (borides, carbides) and amorphous carbon as phase boundary. This nanoscaled heterostructure allows to combine hardness with other interesting properties for engineering applications as low friction coefficient, wear resistance and toughness [1-3]. In particular, the presence of carbon and boron may be suitable to further improve the tribological performance by forming self-lubricious compounds that can work both at room and at high temperatures since the boron at the surface can react with the atmospheric moisture at high temperatures and form lubricant transfer films. In this sense, further insight concerning the correlation between the phase composition, chemical bonding and tribomechanical properties by comparing the two series of Ti-B-C coatings prepared by different routes could be useful to determine the formation of ternary TIBxCy compounds and its influence on the tribological response. Currently, self-lubricant composite coatings are under intense

investigation for its application as a protective wear resistant coating in both Canadian and European manufacturing industries [4]. A number of different questions will be addressed in this program dealing with TiBC and the boron electronic and bonding structure. Specifically, we will try to resolve the following questions that were not fully answered in our previous beamtime:
1) what is the local environment of boron after friction tests at room or high temperature (300C-700C)?
2) Does the presence of carbon influence the formation of sub-oxide boron compounds?
Based on previously obtained data on BN content cermets two types of tribo-films could be formed: TiBO and BO oxide phases. First one is amorphous-like oxide and the BO oxide is lubricating oxide that presents on the surface in liquid state at elevated temperatures of cutting and serves as liquid lubricant [5].
REFERENCES

[1] C. Mitterer, P.H. Mayrhofer, M. Beschliesser, P. Losbichler, P. Warbichler, F. Hofer, P.N. Gibson, W. Gissler, H. Hruby, J. Musil, J. Vlek, Surf. Coat. Technol. 120-121 (1999) 405.
[2] J.-T. Ok, I.-W. Park, J.J. Moore, M.C. Kang, K.H. Kim, Surf. Coat. Technol. 200 (2005) 1418.
[3] R. Gilmore, M.A. Baker, P.N. Gibson, W. Gissler, Surf. Coat. Technol. 105 (1998) 45.
[4] C.G. Gureluz, J.E. Krzanowski, S.C. Veldhuis, G.S. Fox-Rabinovich. Surf. Coat. Technol. 203 (2009) 3370-3376.
[5] M.D. Abad, D. Cceres, Y.S. Pogozhev, D.V. Shtansky, J.C. Snchez-Lopez. Plasma Process. Polymers. 2009 (in press).

EXPERIMENT PROCEDURE

In our initial characterization tests, we are applying X-ray diffraction (XRD), surface and cross-sectional scanning electron microscopy (SEM), X-ray photoelectron Spectroscopy (XPS), and energy electron loss spectroscopy (EELS), which will be followed by XANES measurements at VLS-PGM.
In order to carry out the proposed program, it is necessary to have 1 shift for optimization of the experimental set-up. We will need 2 shifts for standards (such as TiB2, B4C, h-BN, BxOy, etc.). It is plan to run a minimum of three scans for each of them and we estimate the sample transfer time to be around 20 minutes. Then, we will need 3 shifts for measurements of the B K-edge in TiBC sputtered and annealed films and another 4 shifts of measurements of the B K-edge in transfer tribofilms in sample disks and cutting inserts. Consequently, a total of 10 shifts are requested for this proposal.
This proposal involves the collection of XANES measurements from the boron K shells in:
(1) standard boron compounds (TiB2, B4C, h-BN, BxOy, etc).
(2) Eight as-deposited TiBC films produced with co-sputtering technique.
(3) Six TiBC films annealed at three different temperatures (18 samples).
(4) The wear track of 6 TiBC fims after high temperature tribological tests (24 samples).

All these samples have been prepared ex-situ. And we will simply bring them to the beamline in order to carry out the proposed X-ray absorption experiments.Experimental details regarding the use of the absorption chamber and estimation of beamtime needed to carry out the proposed experiments have been discussed with beamline scientist Dr. Lucia Zuin.

SUITABILITY

The energy scans used in powerful spectroscopic techniques such as X-ray absorption require synchrotron radiation because of the need of tunable light. Therefore, beam time at a third-generation synchrotron radiation facility such as CLS is essential in order to carry out the proposed XANES experiments
We consider the VLS-PGM beamline at the CLS the most suitable for the proposed program due to the following reasons:
i. The energy range (5.5-250eV) and high resolution (>10,000 E/E) of the Variable Line Spacing Plane Grating Monochromator (VLS PGM) beamline are ideal to carry out the proposed absorption experiments at B 1s (188 eV).
ii. Several Boron K-edge XANES studies have been carried out at VLS-PGM as reported in the CLS 2007 Activity Report: (1) The Chemical Structure of Boron Oxide Species at Melt-Derived Glass Fibre Surfaces by R. A. Schaut et. al. (2) Borosilicate Glasses Proposed as Nuclear Waste Encapsulation Materials and (3) The dependence of the BO3/BO4ratio on iron redox in iron rich sodium borosilicate glasses by G.S. Henderson et. al.
iii. The VLS-PGM beamline has been employed with great success in the characterization of other tribological thin film systems (Pereira, G et. al. Tribology Materials, Surfaces & Interfaces, Vol. 1, p. 105 ; Anuradha, Set. Al. Tribology Transactions, Vol. 52, Issue 4, pp. 511-525).

PAST PRODUCTIVITY - Shifts received in the past two years:

Access Mechanism	Cycle 11	Cycle 12	Cycle 13	Cycle 14
General User	21	0	0	17
Total Shifts	21	0	0	17

a) Recently, we have investigated the chemical bonding of the series prepared by using the TiB2:TiC mixed target including XANES results measured in this beamline. See proposal attachment, and published in
"Identification of ternary phases in TiBC/a-C nanocomposite thin films: influence on the electrical and optical properties. M.D. Abad, R. Sanjins, J.L. Endrino, R. Gago, J. Andersson, J.C. Sanchez-Lopez
Plasma Process and Polymers, (accepted with minor revisions).

Also closely related:
Extended X-ray absorption fine structure (EXAFS) investigations of Ti bonding environment in sputter-deposited nanocomposite TiBC/a-C thin films.
J. L. Endrino, M. D. Abad, R. Gago, D. Horwat, I. Jimenez, J. C. Sanchez-Lopez
IOP Conf. Ser.: Mater. Sci. Eng. 12, 012012 (2010).

b) n/a

BEAMLINE REQUIREMENTS	
Beamline:	11ID-2 (PGM)
CLS Staff Contacted:	Lucia Zuin
Endstation:	Absorption Chamber
Technique:	X-ray Absorption Spectroscopy (XAS)
Wavelength / Energy Range:	188 eV
Spotsize on Sample:	8
Energy Resolution:	5000

SCHEDULING REQUIREMENTS	
Total # shifts for entire proposal:	13
	Anticipated Timeline
Cycle	**# of 8-hour shifts requested**
Cycle 14 - July - December, 2011	8
Cycle 15 - January - June, 2012	0
Cycle 16 - July - December, 2012	5
Specific scheduling requirements:	
Preferred dates (current cycle)	
Unacceptable dates (current cycle)	

SAFETY AND MATERIALS

LOW RISK

Chemical Information

Are you bringing any hazardous chemical materials to the CLS?	No

Biological Information

Are you bringing any biological materials to the CLS?	No
Does this research involve human tissue and/or biological fluids?	No
Does this research involve the study of aboriginal people's culture?	No

Does this research involve:

Live animals?	No
Animal tissue and/or biological fluids from live animals?	No
Does your work involve Genetically Modified Organisms, Genetically Modified Microorganisms or Transgenic Organisms?	No

Radioactive Material Information

Are you bringing anything radioactive?	No

Nano Material Information

Are you bringing any nanomaterials to the CLS?	No

Pesticide Information

Are you bringing pesticides to the CLS?	No

Non-Hazardous Material Information

Name	Quantity	Units	State
Ti-B-C thin films on Steel	1cm diameter disks 3mm thick	33	solid
B4C standard on Silicon	1cm2 x 1mm	1	solid
BN standard on Silicon	1cm2 x 1mm	1	solid

You have indicated that you will not be bringing any heavy atom solutions or other hazardous/biohazardous substances to CLS.

EQUIPMENT

Are you bringing any equipment to the CLS to assist you with this experiment?	No

ANCILLARY FACILITIES REQUESTED

Dry Lab

Wet Lab

Person(s) Preparing Samples

Jose Endrino - Wet Lab, Dry Lab

Juan Carlos Sanchez-Lopez - Wet Lab, Dry Lab