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Ion beam assisted deposition of Ti–Si–C thin films

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ABSTRACT

Purpose: Deposition of hard thin multilayer coatings is a common practice in improving the performance of tools for many different applications. From this aspect Ti_3SiC_2, due to its lamellar structure and unique combination of properties is a potential interlayer material candidate for thermo-mechanical application.
Design/methodology/approach: Multiphase Ti–Si–C thin films were deposited by the ion beam assisted deposition (IBAD) technique from a single Ti_3SiC_2 compound target on an AISI 316L steel substrate. To optimize the deposition process, Monte Carlo simulations were performed; the range of the deposition parameters was determined and then experimentally verified. Scanning and transmission electron microscopies were used to examine the microstructure and quality of the deposited films. Mechanical properties were determined by nanoindentation tests.
Findings: The deposited film was flat, smooth and dense with small crystalline particles. The hardness H_{IT} of coated substrates was in the range 2.7 to 5.3 GPa. The average calculated value reduced elastic modulus E_{IT} for coated substrates was 160 GPa. The hardness and reduced elastic modulus for uncoated substrates were H_{IT} = 4.4 GPa and E_{IT} = 250 GPa, respectively.
Practical implications: PVD techniques enable low substrate temperature deposition, preferred due to the thermal limitations of the metallic substrates commonly used in industrial applications. The aim of this work is low temperature deposition of Ti-Si-C film, from a single Ti_3SiC_2 compound target, on 316L steel substrate, using the IBAD technique, known for excellent film connection to the substrate.
Originality/value: Ion beam assisted deposition parameters were calculated and experimentally verified.
Keywords: Ti–Si–C system; IBAD; Thin films; Nanoindentation

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1. Introduction

Deposition of hard thin multilayer coatings is a common practice in improving the performance of tools for many different applications. From this aspect Ti_3SiC_2, due to its lamellar structure and unique combination of properties [1], [2] is a potential candidate as interlayer material or binding phase for thermo-mechanical applications [3]. Different deposition methods, both chemical vapour deposition (CVD) and physical vapour deposition (PVD) methods, were used to form Ti-Si-C thin films: magnetron sputtering [4], [5] and pulsed laser deposition [6], [7]. Each of these methods displayed difficulties in Ti_3SiC_2 deposition: the presence of TiCx, $Ti_5Si_3C_x$, $TiSi_2$ and SiC phases as impurities, high deposition temperature - exceeding 300ºC [8], the requirement for sputtering from several sources [8] and unsatisfactory film adhesion to the substrate.

PVD techniques enable low substrate temperature deposition, which is the preferred condition due to the temperature limitations imposed by the metallic substrates commonly employed in industrial applications [10]. Multi-target, direct ion implantation of elements into metal substrates usually results in precipitate formation, rarely in a continuous compound surface layer. The aim of this work is low temperature deposition of Ti-Si-C film, from a single Ti_3SiC_2 compound target, on 316L steel, using the IBAD technique, known for excellent film connection to the substrate.

2. Experimental procedure

For calculation of the initial concentration of Ti, Si and C in the sputtered target, the SRIM 2008 code [11] - based on the Monte Carlo technique - was applied. The SRIM 2008 code was also applied for determination of the sputtering coefficients of the Ti, Si and C elements in various materials bombarded with a beam of Ar^+ ions at the energy of 15 keV. For all calculations, the beam impact angle was fixed at 67^0. For experimental verification of process parameters, Ti-Si-C thin films were grown on AISI 316L substrate by the IBAD technique. The description of the Dual Beam IBAD technique and adaptation of the 75 kV ion implanter to DB IBAD can be found in earlier papers [12]. The deposition process was performed at room temperature in vacuum (~10^{-6} mbar), using Ar+ ions (ion energy ~15 keV) and sputtering angle 65º. A single Ti_3SiC_2 compound target was used, produced from stoichiometric mixtures of Ti, Si and C powders by the SHS method at the Department of Advanced Ceramics, AGH, (Cracow, Poland). Steel substrates were prepared by cutting from 12.5 mm diameter rod or 3 mm thick plate samples (Goodfellow, UK) using a Struers Minitom cut-off wheel and CBN cutting disc,
then mechanically ground and polished using Struers MD system and diamond grinding and polishing suspensions. Microstructure, chemical and phase composition of samples were studied by scanning (SEM, SEI, EDS) and transmission (TEM, SAED) electron microscopy methods using a JEOL JSM-6460LV working with IXRF EDS 500 and Tecnai F20 (200kV). The hardness and reduced elastic modulus of coated and uncoated substrates were determined by nanoindentation using CSM with OM imaging system. Indentations were made under a load of 10 mN using a Berkovich-type diamond indenter. Five indentations were made in three areas for each sample. Load displacement curves were recorded, and hardness H_{IT} and reduced elastic modulus E_{IT} were calculated using the Oliver & Pharr method.

Table 1.
Sputtering coefficient(s) [atom/ion] calculated for a beam of Ar+ ions. Calculation parameters: impact angle: 670; impact energy: 15 keV

	Sputtering coefficient(s) [atom/ion]		
	Ti	Si	C
TiSiC target	3.74	3.52	2.01
Ti_3SiC_2 target	5.71	1.52	2.03
Ti	8.28	-	-
Si	-	13.10	-
C	-	-	8.77

3. Results and discussion

The sputter deposition method is frequently used for the formation of thin coating layers. The IBSD - Ion Beam Sputter Deposition technique is used especially for the formation of complex coatings with good adhesion tothe substrate. Unfortunately, the final elemental composition of the layer thus formed is different from that of the sputtered material (commonly known as the “sputtered target”). In this work, the initial elemental composition of the sputtered target was optimized for the formation of Ti_3SiC_2 coatings. The sputtering coefficients (e.g. ratio of the total number of sputtered atoms and ions to a number of sputtering ions) were calculated for titanium, silicon and carbon in the targets: TiSiC, Ti_3SiC_2 as well as in pure titanium, silicon and graphite. All calculated sputtering coefficients are given in Table 1. The sputtering target was formed on the basis of these values. In addition, the SRIM 2008 code was used to determine the energy distribution of the sputtered atoms and ions.

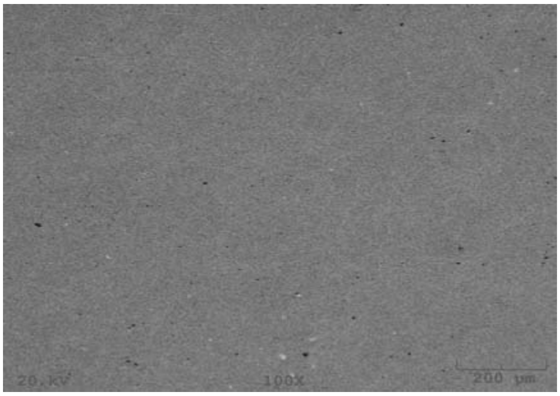


Fig. 1. BEC image of Ti-Si-C film grown on AISI 316L steel substrate by the IBAD technique

SEM methods used for examination of the Ti-Si-C coatings obtained by dual-beam ion assisted deposition on AISI 316L substrates showed that the films produced were dense and smooth. Planar view showing the morphology of as-deposited Ti-Si-C film surface is presented in Figs. 1-3.

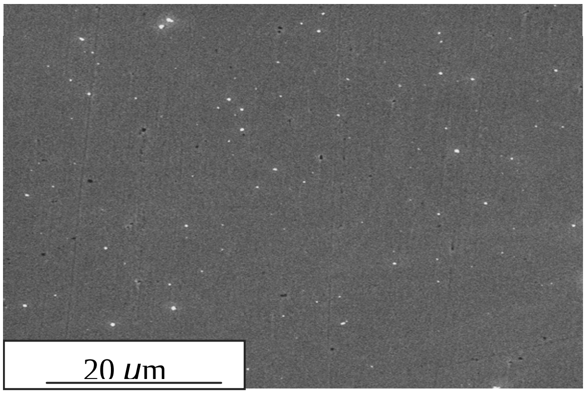
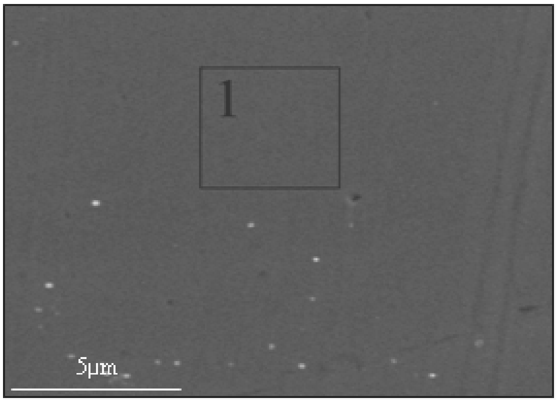


Fig. 2. SEM micrograph of as-deposited Ti-Si-C coating' surface

a)



b)

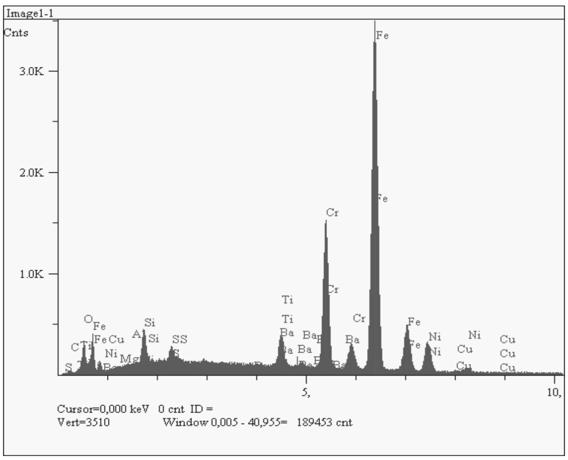


Fig. 3. Magnified SEM image of deposited film a) with EDS analysis results taken from marked area b)

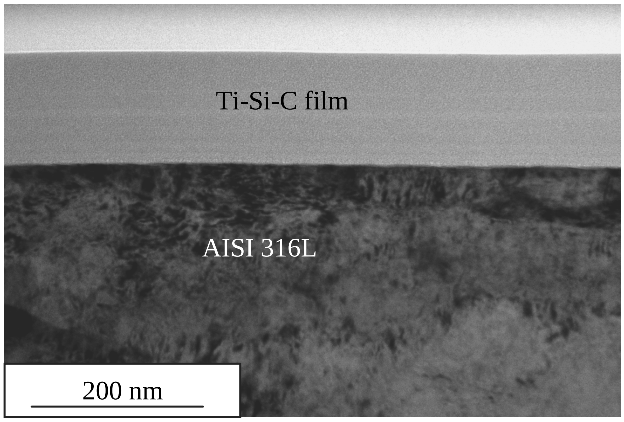
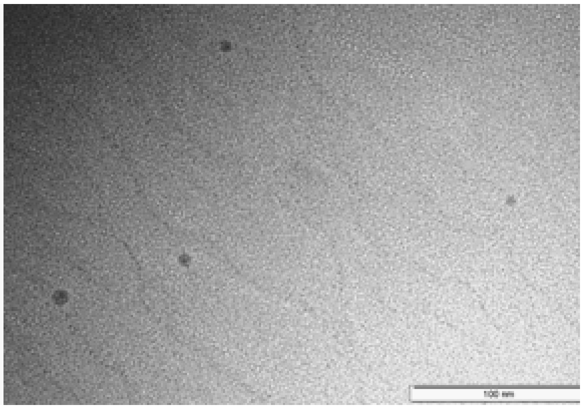


Fig. 4. TEM image of Ti-Si-C coating on AISI 316L substrate (cross-section), produced by IBAD technique

a)



b)

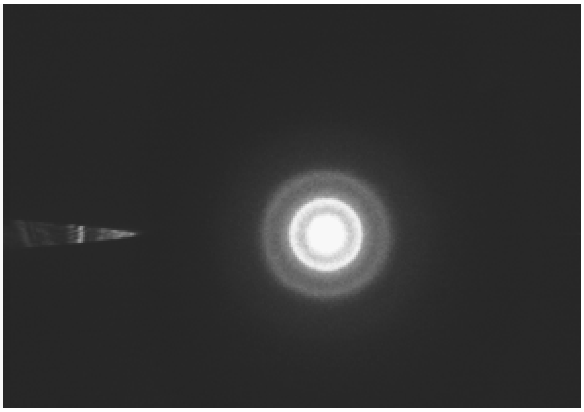


Fig. 5. TEM planar view image a); and selected area electron diffraction pattern, b) for Ti-Si-C film

The thickness of the film was low enough to indicate, in chemical analysis performed by EDS/WDS, the presence of Cr, Fe and Mo, i.e. the elements from the 316L steel substrates' composition. EDS spectrum taken from Ti-Si-C coating is presented in Fig.3b. Oxygen contents found in the films, ranging from 5 to 8 wt.%.

TEM investigations of coated substrates' cross-sections revealed that produced films' thickness was less than 100 nm, as shown in Fig. 4. The interface between AISI 316L substrate and deposited film was flat. Selected area electron diffraction, which accompanied TEM observations, indicated that deposited films were amorphous, as shown in Fig.5.

The hardness H_{IT} of coated substrates were in the range 2.7 to 5.3 GPa, values which are relatively low in comparison to data referred to in the literature for nanocrystalline Ti-Si-C coatings: 7.5-9.0 GPa [4], 16 GPa [8], but in good agreement with data referred to for Ti_3SiC_2 bulk material [1,2,13,14,15]. The average value of calculated reduced elastic modulus E_{IT} for coated substrates was 160 GPa. The hardness and reduced elastic modulus for uncoated substrates were 4.4 GPa and 250 GPa respectively.

4. Conclusions

Monte Carlo simulation is a very useful tool for optimizing the parameters of thin film deposition. The initial elemental composition of the sputtered target was optimized for the formation of Ti_3SiC_2 coatings and experimentally verified.

Ti-Si-C film obtained by dual-beam ion assisted deposition on AISI 316L substrates at room temperature are smooth, thin and amorphous.

The hardness H_{IT} of coated substrates were in the range 2.7 to 5.3 GPa, and the average calculated value reduced elastic modulus E_{IT} for coated substrates was 160 GPa, while the hardness and reduced elastic modulus for uncoated substrates were 4.4 GPa and 250 GPa respectively.

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References

[1] M.W. Barsoum, T. El-Raghy, C.J. Rawn, W.D. Porter, H. Wang, E.A. Payzant, C.R. Hubbard, Thermal properties of Ti_3SiC_2, Journal of Physics and Chemistry of Solids 60/4 (1999) 429-439.

[2] M.W. Barsoum, The MN+1AXN Phases: A New Class of Solids, Thermodynamically Stable Nanolaminates, Progress in Solid State Chemistry 28 (2000) 201.

[3] L. Jaworska, L. Stobierski, A. Twardowska, D. Królicka, Preparation of materials based on Ti-Si-C system using high temperature-high pressure method, Journal of Materials Processing Technology 162-163 (2005) 184-189.

[4] P. Eklund, T. Joelsson, H. Ljungcrantz, O. Wilhelmsson, Zs. Czigány, H. Högberg, L. Hultman, Microstructure and electrical properties of Ti-Si-C-Ag nano-composite thin films, Surface and Coatings Technology 201 (2007) 6465-6469.

[5] T. Zehnder, J. Matthey, P. Schwaller, A. Klein, P.A. Steinmann, J. Patscheider, Wear protective coatings consisting of TiC–SiC–a-C:H deposited by magnetron sputtering, Surface and Coating Technology 163-164 (2003) 238.

[6] A.R. Phani, J.E. Krzanowski, Structure and mechanical properties of Ti-Si-C coatings deposited by magnetron sputtering, Journal of Vacuum Science and Technology A 19 (2001) 2252.

[7] J.J. Hu, J.E. Bultman, S. Patton, J.S. Zabinski, Pulsed Laser Deposition and Properties of Mn+1AXn Phase Formulated Ti3SiC2, Thin Films, Tribology Letters 16 (2004) 113.

[8] W. Gulbinski, T. Suszko, A. Gilewicz, B. Warcholinski, Z. Kuklinski, Structure and high-temperature tribological behaviour of Ti-Si-C nanocomposite thin films, Surface and Coatings Technology 200 (2006) 4179-4184.

[9] J. Alami, P. Eklund, J. Emmerlich, O. Wilhelmsson, U. Jansson, H. Hogberg, L. Hultman, U. Helmersson, High-power impulse magnetron sputtering of Ti-Si-C thin films from a Ti3SiC2 compound target, Thin Solid Films 515 (2006) 1731-1736.

[10] P.H. Mayrhofer, C. Mitterer, L. Hultman, H. Clemens, Microstructural design of hard coatings, Progress in Materials Science 51 (2006) 1032–1114.

[11] J. F. Ziegler: www.srim.org.

[12] B. Rajchel, M. Drwięga, E. Lipińska, M. Wierba, Adaptation of the 70 kV INP ion implanter to the IBAD technique, Nuclear Instruments and Methods in Physics Research B89 (1994) 342-345.

[13] T.Y. Huang, C.C Chen, Synthesis of nano-laminated Ti3SiC2 from Ti-Ti_5Si_3 and CNTs, Materials Science and Engineering A 466 (2007) 148-155.

[14] T. El-Raghy, N.W. Barsoum, A. Zavaliangos, S. Kalidindi, Processing and mechanical properties of Ti3SiC2 II. Effect o grain size and deformation temperature, Journal of American Ceramic Society 82 (1999) 2855.

[15] R. Pampuch, J. Lis, L. Sobierski, M. Tymkiewicz, Solid combustion synthesis of Ti3SiC2, Journal European Ceramic Society 5 (1989) 283.