

Journal of Korean Institute of surface Engineering
Vol. 32, No. 3, Jun., 1999

NEW PROGRESS IN TiN-BASED PROTECTIVE COATINGS DEPOSITED BY ARC ION PLATING*

R. F. Huang* and L. S. Wen**

*SES and City University of Hong Kong Hong Kong, China

**Institute of Metal Research, Academia Sinica, Shenyang, 110015, china

Abstract

Titanium nitride and related overlayers produced by arc ion plating (AIP) are applied as commercial coatings in world-wide scale since the middle of 80s. Due to the achievements of low temperature deposition (LTD), they begin now to be used as wear and corrosion-resistant coatings for machine parts, besides applications on cemented carbide and high speed steel cutting tools. On the other side, TiN can be now applied successfully to brass, Al-alloy, ZnAl alloy articles as decorative coating through LTD. Various nitrides, carbonitrides, borides and other refractory compounds, such as (Ti, Al)N, TiCN, CrN, are used as the coatings for special heavy-duty working conditions instead of TiN since 90s. More and more multilayer coatings are applied now substituting single layer ones. Duplex processes are under development.

Key words: Titanium nitride, arc ion plating, low temperature deposition, refractory compound, protective coating

1. INTRODUCTION

During the last decade, TiN overlayer prepared by ion plating has been applied successfully as a wear-resistant coating in industrial metal working practice and as the decorative coating for metallic products resulting in formation of a new industry of ion plated protective coating in all over the world. Since then, great progresses have been attained. Arc ion plating (AIP) becomes now the sole commercial process of hard coating production substi-

tuting all other types of ion plating. Then, a series of new coating materials emerge in catalog of commercial hard coatings. They are nitrides, carbonitrides, borides and other refractory compounds. To meet the requirements of application in different areas, the coating structure designing, coating process and equipment are innovated and improved evidently. This paper gives a review on the latest progresses in titanium nitride and related protective coatings deposited by AIP.

2. NEW COATING MATERIALS

TiN was the only material for commercial hard coating in 80s. It was shown already in 80s¹⁻⁹ that the performance of TiN coating could be evidently improved by alloying it with

other nitrides, carbides or borides, or substituting titanium in TiN partially or entirely with other metals. For example, addition of aluminum into TiN up to Ti : Al ratio of 50 : 50 leads to complex nitride (Ti, Al)N (50 : 50) formation and increase of oxidation-resistant temperature from 550°C for TiN to 700°C for (Ti, Al)N (50 : 50) Fig. 1⁴⁾ resulting in a twofold or more improvement of drilling performance of (Ti, Al)N (50 : 50) in comparison with that of TiN coating Fig. 2^{4, 11)}. Although the hardness of (Ti, Al)N remains at the same level of TiN^{4, 15)} and its rolling contact fatigue life is even slightly lower than that of TiN¹⁶⁾, it can be used, nevertheless, at significantly higher cutting speed than that of TiN¹²⁻¹⁴⁾. Factors influencing oxidation behavior of (Ti,Al)N, are up to now in the central point of (Ti, Al)N based high temperature resistant coating research and development^{4, 17-19)}. Contrary to the early results, it has been shown Fig. 3¹⁷⁾ that the best oxidation-resistance of (Ti, Al)N is attained in range of (Ti : Al) = (0.75 : 0.25) ((0.5 : 0.5). Addition of silicon to (Ti, Al)N increases its oxidation-resistance, while addition of zirconium to (Ti, Al)N hinders the growth of a dense protective alumina layer and lower the oxidation-resistance¹⁸⁾. (Ti, Al)N has been deposited by dc reactive

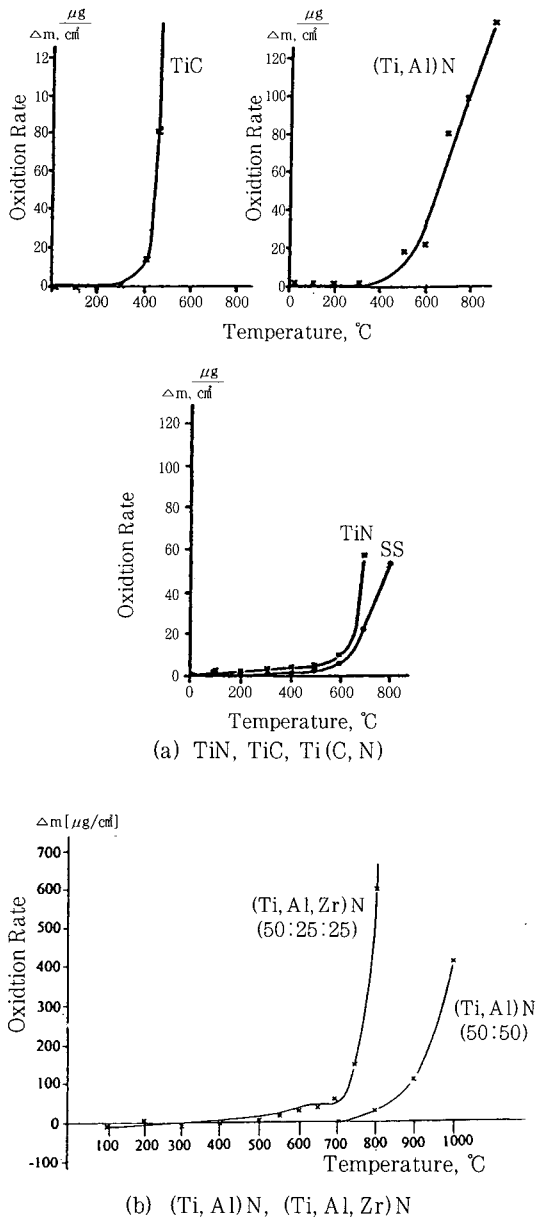


Fig. 1 Oxidation resistant temperature of coatings

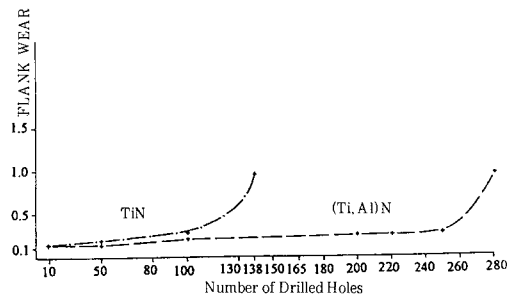


Fig. 2 Cutting performance of TiN and (Ti,Al)N

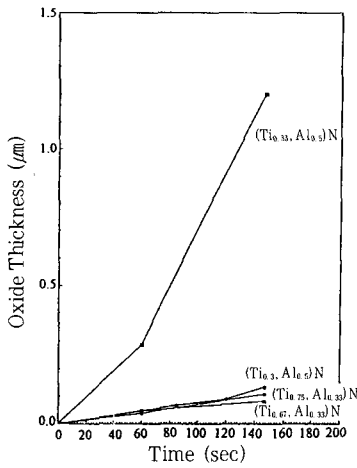


Fig. 3 Dependence of oxidation resistance on Ti Al ratio

magnetron sputtering^{1, 4)}, rf reactive magnetron sputtering^{4, 20)}, AIP^{5, 11, 21)}, electron beam ion plating²²⁾ and ion beam assisted deposition²³⁾. Process parameters²⁴⁾, underlayer²⁵⁾, microstructure, phase composition and properties^{23, 26-28)} of (Ti, Al)N were studied.

Addition of carbon into TiN leads to Ti(C, N) formation the phase composition of which is determined by its chemical composition according to the phase diagram of Ti-TiC-TiN system Fig. 4²⁹⁾. When the titanium level is lower than 58 at.%, δ -TiCN with NaCl structure is formed. When the titanium is above this level, the phases possibly formed are α -Ti, ϵ -Ti₂N and δ' -Ti₁₋₂N with dissolved carbon in them, and δ' -TiC_{0.5-0.6} with dissolved titanium in it. A smooth transition from one component to another without creation of hardness maximum or minimum is obtained in the hardness curves of the coating with T_s at 580°C and 630°C, while the curve with T_s=480°C gives a maximum in the medium carbon content range. (Fig. 5)⁷⁾

Ti(C, N) is deposited by dc reactive magne-

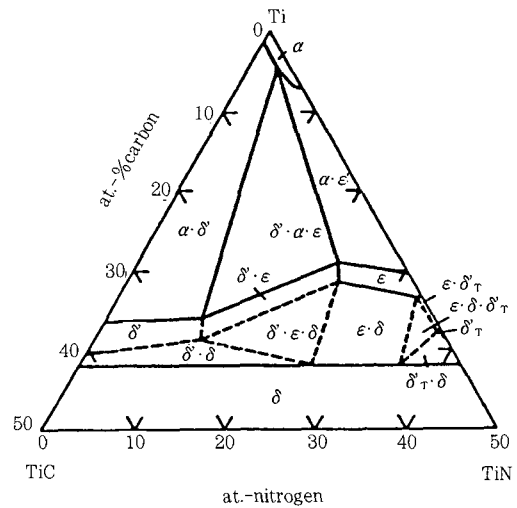


Fig. 4 Phase diagram of Ti-TiC-TiN system

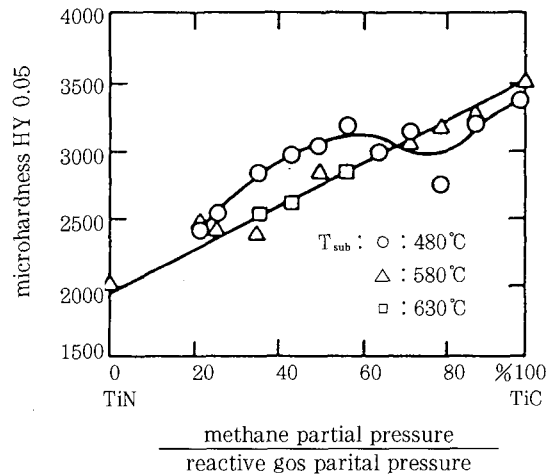


Fig. 5 Dependence of microhardness of Ti(C,N) coatings on methane partial pressure

tron sputtering^{7, 30-33)}, hollow cathode discharge ion plating (HCDIP)⁸⁾ and AIP³⁴⁻³⁷⁾. Knotek et al³¹⁾ has noted that chemically more stable carbon source gas, such as methane, permit unproblematic control of the process, but often fail to achieve adequate stoichiometric saturation of the hard material phases, resulting in unsatis-

factory coating performance. In contrast, the highly reactive acetylene produces extremely hard TiC films and extremely wear-resistant Ti (C, N) coatings. However, greater process control effort should be made in order to ensure reproducibility of the manufacture stability and product quality. In contrast with CH₄ and C₂H₂, ethan is sufficiently reactive to obtain good TiC and Ti(C, N) quality and has at the same time good process stability. Ti(C,N) coatings have been proved especially suitable for low cutting speed stresses. Their advantages over TiN and (Ti, Al)N stem from their superior friction behavior in contact with steel and high thermal conductivity³⁸. To these advantages may be added a soft chip flow, which relieves the coating edge, prevents cutting edge deformation on high speed steels and reduces the risk of cutting edge chipping on carbides³⁸.

To improve the wear- and corrosion-resistance, Ti-Al-C-N has been studied³⁹. It is a combination of high thermal stability of (Ti,Al)N with low friction coefficient and high hardness of Ti(C, N). It was shown that the formed metastable phase (Ti, Al) (C, N) has a phase stability superior to (Ti, Al)N. Its Al loss temperature is higher than that of (Ti,Al)N. It has a secondary hardness maximum at 1200°C which is caused by recrystallization effects and the Al loss.

Chromium nitride is one of the most promising alternative hard coating materials to TiN. It can be deposited by HCDIP^{40, 41}, magnetron sputtering^{1, 42}, reactive ion plating^{43, 44} and AIP⁴⁵⁻⁴⁷. Depending on stoichiometry, single-phase film of bcc Cr, hex β -Cr₂N, fcc CrN as well as mixed phase layers of Cr/ β -Cr₂N or (β -Cr₂N/CrN

could be obtained⁴⁸. Early results already shown¹ that extremely high deposition rate can be achieved in system Cr-N with easier controlling in comparison with TiN. Chromium nitride exhibits very high toughness. The bias causes a transformation to a nearly amorphous, very dense coating with a smooth surface. Chromium nitride has very good wear- and corrosion-resistance, especially in case of fretting wear. Its oxidation-resistant temperature is as high as 700°C⁴⁹. To increase thermal stability as well as corrosion- and wear-resistance, the effects of addition Ti⁴⁹⁻⁵¹, B⁵² and Ta⁵³ were studied.

(Ti, Al)N, Ti(C, N) and CrN are commercialized since the beginning of 90s⁵⁴. They have now around half volume of the total PVD hard coating market. The typical applications of CrN are wear-resistant coating for piston ring of internal combustion engines⁵⁵, coating for friction reduction and saving lubricant amount and corrosion-resistant coatings⁵⁴. Among the new hard coating systems other than TiN, (Ti, Al)N, Ti(C, N) and CrN, one of the most attractive new systems with great potential is Ti-B-N. TiB₂ and TiB₂-based coatings attract now great interest because of their superhigh hardness of 6700Hv^{56, 57}, good corrosion-resistance and high electrical conductivity⁵⁷. However, other compositions of Ti-B-N system are also studied⁵⁸⁻⁶⁰.

3. MULTILAYERS

In the early 70s, Koehler suggested a model of strong solid with multilayer structure of two components with widely different elastic constants⁶¹. The idea was based on retarding the generation and motion of dislocation in thin-lay-

ered metallic materials. Koehler's model together with Esaki and Tsu's theory and experiments on semiconductor superlattices set up the beginning of nanostructured materials and nano science and technology. Science then, great efforts have been made to reveal the multilayer structure induced mechanical enhancement of strength, hardness and toughness and the basic results are as follows⁶²⁻⁷². Multilayer structure is characterized by its chemical composition modulation wavelength Λ . It was shown that hardness H of multilayer increases with decreasing Λ in range of $\Lambda \sim \mu\text{m}$ according to Hall-Petch equation Fig. 6⁷¹). When correlating the enhancement with grain size refining with decreasing Λ (grain refining effect) in the same film system Fig. 7, it is obvious that the hardness enhancement of multilayer films in range of $\Lambda \sim \mu\text{m}$ stems from Hall-Petch effect. On the other side, in range of $\Lambda \sim 10\text{-}100\text{nm}$, a peak in curve $H(\Lambda)$ was observed Fig. 8⁷⁰), the mechanism of

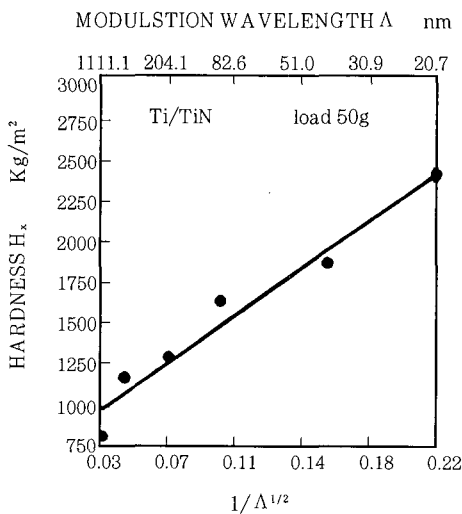


Fig. 6 Dependence of hardness of Ti/TiN multilayer on composition modulation wavelength Λ in range $\Lambda \sim \mu\text{m}$

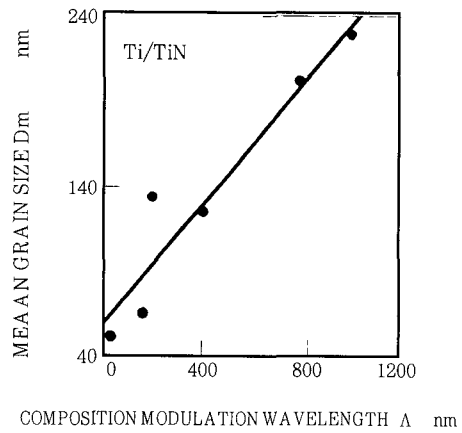


Fig. 7 Grain refining effect

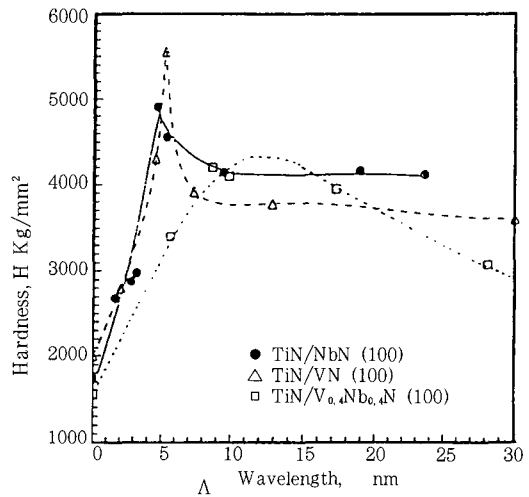


Fig. 8 Dependence of hardness of TiN/NbN, TiN/VN and TiN/Nb_{0.4}V_{0.6}N in range of $\Lambda \sim 0\text{-}30\text{nm}$

which remains not clear up to now. Besides, multilayered structure promotes toughening⁷², corrosion-resistance⁷³ and cracking-resistance⁷⁴ of the coating.

Recently, TiN has been used as spacing layer of multilayer film with (Ti, Al)N, Ti(C,N) and CrN in order to enhance the wear-and corrosion resistance of the coating. For example, TiN/CrN multilayer can give higher oxidation resi-

stance that both single layers TiN and CrN⁷³⁾. Following the successful CVD multilayer TiN/Al₂O₃, (Ti, Al)N/Al₂O₃ (ALOX) multilayer was prepared for metal cutting operation. (Fig. 9)⁷⁴⁾

Grain refining with decreasing Δ is caused by stopping the growth of the former layer and beginning the re-nucleation and growth of the next layer. This process is favorable not only for grain refining, but also for elimination of pinhole detrimental to the corrosion resistance of the coating.

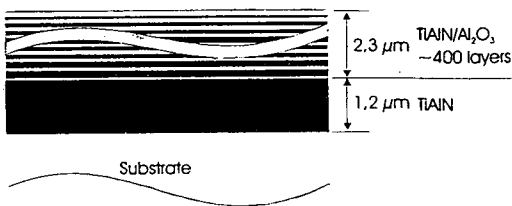


Fig. 9 Structure of (Ti,Al)N/Al₂O₃ (ALOX 400)

4. LOW TEMPERATURE DEPOSITION (LTD)

The key point of extension of application area of TiN-based coatings is deposition at lowered substrate temperature T_s , guaranteeing a dense microstructure and an enough high coating-to-substrate adhesion. At present time, LTD can be realized through modification of ion plating process with reduced energy balancing, pulsed bias and Hyper-Ion processes etc.^{75, 77)} Conventional ion plating process involve only stationary process, in which the negative bias voltage U_s is maintained constant in range of -50— -300v during the process and leads to an additional heating of the substrate as well. By using pulsed bias voltage U_p with low duty circle coefficient τ_{pd} Fig.10-12 suerimposed on a dc

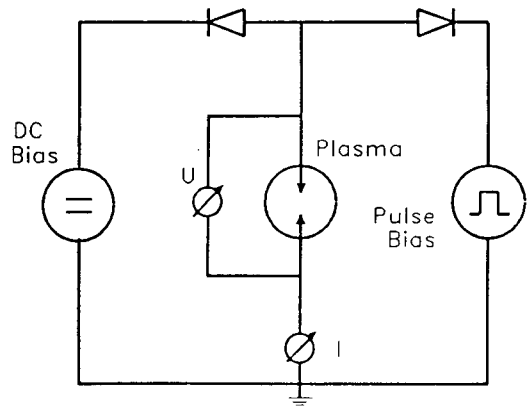


Fig. 10 Wiring diagram of a negative bias voltage superimposed by negative dc pulsed bias voltage

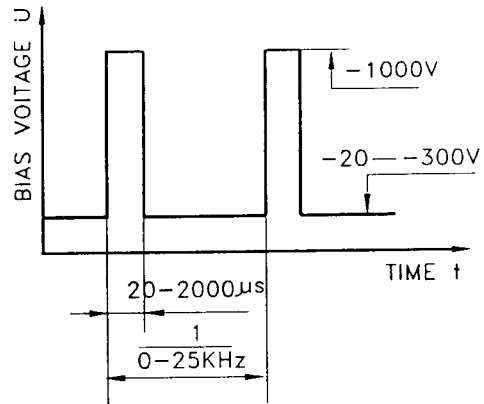


Fig. 11 Typical voltage-time diagram of superimposed dc pulsed bias voltage

ground voltage U_s , low T_s has been attained. Duty circle coefficient τ_{pd} is the ratio of the pulse duration τ_d to the pulse period τ_p . τ_{pd} and U_p can be regulated independently during the work. With LTD, commercial TiN-based protective and decorative coatings can be now applied at low alloyed steels, Cu-alloys, Al-alloys, Mg-alloys and even ZnAl alloys.

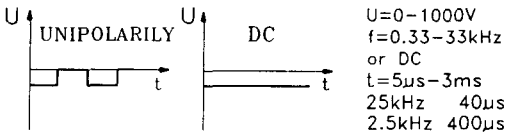
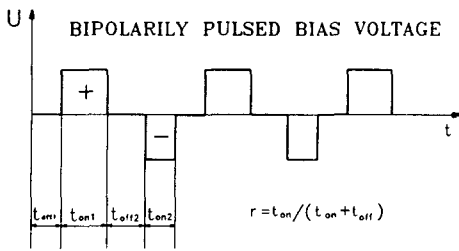
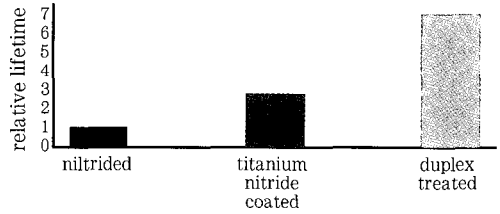


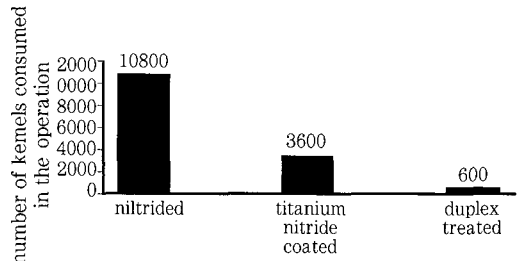
Fig. 12 Comparison of voltage-time diagram of bipolar pulsed bias with that of dc and unipolar bias.

5. DUPLEX PROCESSES

When applying ion plated TiN-based coatings on low alloyed steel substrate, their application will be limited by substrate hardness. Recently, duplex processes consisting of a nitriding and a succeeding ion plating with TiN or CrN coatings, are studied in order to provide a mechanical support for ion plated coatings⁷⁸⁻⁸⁰. The first results are attractive. For example, duplex treatment of metal (Al) injection molding dies increase the lifetime of central plug and decrease of its consumption evidently Fig. 13⁸¹. Duplex treatment of different substrates have shown good result for low alloyed steel⁸²⁻⁸⁴. Corrosion resistance of construction and hot working steel improved obviously in comparison with nitriding or PVD coating. However, for cold working and stainless steels, duplex treatment leads to a loss in corrosion resistance. The effects of residual stresses variation during the duplex treatment are also complex, not always positive: Besides, the nitrided surface needs to be



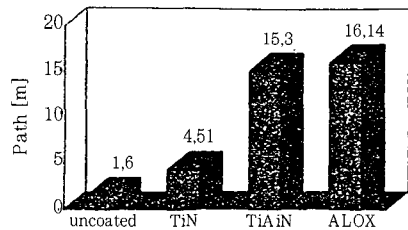
(a) Relative increase in lifetime of central plug



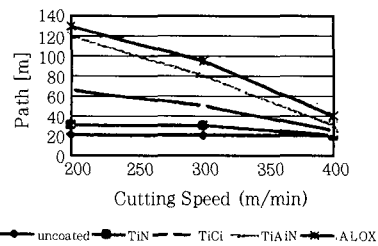
(b) Consumption of central plug

Fig. 13 Effect of duplex treatment of the central plug of metal injection die

- a) Relative increase in lifetime of central plug
- b) Consumption central plug



a) Drilling test



b) Milling test

Fig. 14 Performance of ALOX in comparison with other coatings

- a) Drilling test
- b) Milling test

ground after nitriding and before ion plating⁸⁴⁾ is also a problem influencing the stability of product quality. In-situ and continuous duplex process was set up with higher production efficiency^{85, 86)} in comparison with the first works using a discontinuous processes. Based on the above-mentioned results, it is obviously that additional study is still necessary in order to have a reliable production process of duplex treatment.

6. APPLICATION

Due to the progresses of LTD, TiN and related coatings can be applied now as wear- and corrosion-resistant coatings for machine parts, besides wear-resistant coatings for cemented carbide and high speed steel cutting tools and decorative coatings for stainless steel articles. For example, TiN is used as the erosion and salt corrosion-resistant coating for compressor blade of airplane engine^{87, 88)}. It is also used as high temperature sulphidation resistant coating of the parts in coal gasification equipment⁸⁹⁾.

Highly (111) oriented and nonstoichiometric TiN coating have been developed as erosion-protective coatings for turbomachinery⁹⁰⁾. Multilayered coatings exhibit their prevalence. TiN/Ti, TiN/Ti(C, N), TiN/CrN and (Ti, Al)N/Al₂O₃ are now commercialized in world-wide scale⁹¹⁾. Their performances can be demonstrated by data of (Ti, Al)N/Al₂O₃ (Fig. 14)⁷⁶⁾. TiN/C and CrN are proved to be the bearing coatings with high wear resistance at present time. It is shown Ti(C, N) behaves well in cavitation protection, while TiB₂ is good for particle erosion-resistant applications. For the further improve-

ment, both of them could be multilayered with TiN spacer.

References

1. O. Knotek, W. Bosch, T. Leyendecker, Proc. of The First Int. Conf. On Surface Engineering, Brighton, 25-28 June, 1985, P68-1—68-5.
2. Herman A. Jehn, S. Hofmann, V. E. Ruckborn, W. D. Munz, J. Vac. Sci. Technol, A 4(1986)2701.
3. Kontek, M. Bohmer, T. Leyendecker, J. Vac. Sci. Technol, A4(1986)2695.
4. W. D. Munz, J. Vac. Sci. Technol, A4(1986)2717.
5. H. Freller, H. Haessler, Thin Solid Films, 153(1987)67.
6. L. S. Wen, X. Jiang, S. L. Yang, Y. L. Cai, Chinese J. Mat. Protection, 20(1989)5
7. O. knotek, W. Bosch, Metal Powder Report, 39(1984)406.
8. B. H. Yu, L. S. Wen. Y. Z. Chuang, Proc. First. Chin. Symp on Solid State Films, Sept. 1988, Changchun, China.
9. L. S. Wen, X. Z. Chen, Q. Q. Yang, Y. Q. Zheng, Y. Z. Chuang, Chin. J. Vac. Sci. Technol, 7(1987)31.
10. H. Karner, J. Laimer, H. Stori, P. Rodhammer, Surface and Coatings Technology ,39/40(1989)293.
11. R. F. Huang, J. Gong, J. Wu, L. S. Wen, X. Gao, Proc. of C-MRS and MRS-K Joint Symp. 96, Nov. 17-21, 1996, Beijing, China, p582
12. W. Konig, R. Fritsch, D. Kammermeier, Surface and Coatings Technology, 49(1991)

- 316.
13. Oknotek, W. D. Munz, T. Leyendecker, J. Vac. Sci. Technol., A5(1987)2173.
 14. T. Leyendecker, O. Lemmer, S. Esser, J. Ebberink, Surface and Coatings Technology, 48(1991)175.
 15. C. T. Huang, J. G. Duh, Surface and Coatings Technology, 71(1995)259.
 16. R. Thom, L. Moore, W. D. Sproul, T.P. Chang, Surface and Coatings Technology, 62(1993)423.
 17. Joshi, H. S. Hu, Surface and Coatings Technology, 76-77(1995)499.
 18. L. Rebouta, F. Vaz. M. Andritschky M. F. da Silva, Surface and Coatings Technology, 76-77(1995)70
 19. C. T. Huang, J. G. Duh, Surface and Coatings Technology, 81(1996)164.
 20. S. Inoue, H. Uchida, A. Hioki, K. Koterazawa, R. P. Howson, Thin Solid Films, 271(1995)15.
 21. B. F. Coll, R. Fontana, A. Gates, P. Sathrum, Materials Science and Engineering, A140(1991)816.
 22. J. Palmers, M. Van Stappen, Surface and Coatings Technology, 76-77(1995)363.
 23. Y. Setsuhara, T. Suzuki, Y. Makino, S. Miyake, T. Sakata, H. Mori, Surface and Coatings Technology, 97(1997)254.
 24. B. Y. Shew, J. L. Huang, Surface and Coatings Technology, 71(1995)30.
 25. D. F. Lii, J. L. Huang, M. H. Lin, Surface and Coatings Technology, 99(1998)197.
 26. Y. K. Wang, X. Y. Cheng, W. M. Wang, X. H. Gu, L. F. Xia, T. C. Lei, W. H. Liu, Surface and Coatings Technology, 72(1995)71.
 27. Y. Tanaka, T. M. Gur, M. Kelly, S. B. Haggstrom, T. Ikeda, Thin Solid Films, 228(1993)238.
 28. U. Wahlstrom, L. Hultman, J. E. Sundgren, F. Adibi, I. Petrov, J. E. Greene, Thin Solid Films, 235(1993)62.
 29. M. P. Arbizov, et al., Inorganic Materials, 14(1970)9, 281.
 30. D. Muller, Y. R. Cho, S. Berg, E. Fromm, Surface and Coatings Technology, 60(1993)401.
 31. V. Poulek, C. Quaeys, G. Knuyt, L. Stals, V. Fagard, Surface and Coatings Technology, 60(1993)480.
 32. J. Musil, V. Poulek, V. Valvoda, R. Kuzel, Jr. H. A. Jehn, M. E. Baumgartner, Surface and Coatings Technology, 60(1993)484.
 33. I. Grimberg, B. Bouaifi, U. Draugelates, K. Soifer, B. Z. Weiss, Surface and Coatings Technology, 68/69(1994)166.
 34. J. Vetter, W. Burgmer, A. J. Perry, Surface and Coatings Technology, 59(1993)152.
 35. B. F. Coll, M. Chhowalla, Surface and Coatings Technology, 68/69(1994)131.
 36. G. H. Kang, H. Uchida, E. S. Koh, Surface and Coatings Technology, 68/69(1994)141.
 37. J. Walkowicz, J. Smolik, K. Miernik, J. Bujak, Surface and Coatings Technology, 81(1996)201.
 38. O. Knotek, F. Loffler, G. Kramer, Surface and Coatings Technology, 61(1993)320.
 39. O. Knotek, F. Loffler, L. Wolkers, Surface and Coatings Technology, 68/69(1994)176.
 40. S. Komiya, S. Ono, N. Umezu, T. Narusawa, Thin Solid Films, 45(1977)433.
 41. T. Sato, M. Tada, Y. C. Huang, Thin Solid Films, 54(1978)61.
 42. A. Aubert, Thin Solid Films, 126(1985)61.

43. D. D. Wang, T. Oki, *Thin Solid Films*, 185 (1990) 219.
44. S. J. Bull, D. S. Rikerby, *Surface and Coatings Technology*, 39/40 (1989) 435.
45. E. Erturk, H. J. Heuvel, H. G. Dederichs, *Surface and Coatings Technology*, 39/40 (1989) 435.
46. O. Knotek, F. Loffler, H. J. Scholl, *Surface and Coatings Technology*, 45 (1991) 53.
47. R. R. Ahazanov, B. F. Coll, R. P. Fontana, *Surface and Coatings Technology*, 61 (1993) 223.
48. A. Ehrlich, M. Kuhn, F. Richter, W. Hoyer, *Surface and Coatings Technology*, 76/77 (1995) 280.
49. Y. Otani, S. Hofmann, *Thin Solid Films*, 287 (1996) 188.
50. Y. Massiani, P. Gravier, L. Fedrizzi, F. Marchetti, *Thin Solid Films*, 261 (1995) 202.
51. J. Vetter, H. J. Scholl, O. Knotek, *Surface and Coatings Technology*, 74/75 (1995) 286.
52. B. Rother, H. Kappl, *Surface and Coatings Technology*, 73 (1995) 14.
53. R. Saha, R. B. Intuzi, J. A. Barnard, *Surface and Coatings Technology*, 82 (1996) 42.
54. M. Van Stappen, L. M. Stals, M. Kerkhofs, C. Quaeyhaegens, *Surface and Coatings Technology*, 74/75 (1995) 629.
55. C. Friedlich, G. Berg, E. Broszeit, F. Rick, J. Holland, *Surface and Coatings Technology*, 97 (1997) 661.
56. O. Knotek, F. Jungblut, K. Breidenbach, *Vacuum*, 789 (1990) 2184.
57. E. Kelesoglu, C. Mitterer, *Surface and Coatings Technology*, 98 (1998) 1483.
58. W. Gissler, *Surface and Coatings Technology*, 68/69 (1994) 556.
59. B. Rother, H. Kappl, G. Ebersbach, H. A. Jehn, *Surface and Coatings Technology*, 97 (1997) 564.
60. S. Heck, T. Emmerich, I. Munder, J. Steinerbrunner, *Surface and Coatings Technology*, 86/87 (1996) 467.
61. J. C Koehler, *Phys. Rev*, B2 (1970) 547.
62. R. W. Springer, D. C. Catlett, *Thin Solid Films*, 54 (1978) 197.
63. R. W. Springer, N. L. Ott, D. S. Catlett, *J. Vac. Sci. Technol*, 16 (1979) 878.
64. R. F. Bunshah, C. Deshpandey, H. J. Doerr, B. A. Movchan, A. V. Demchishin, G. F. Badilenko, *Thin Solid Films*, 96 (1982) 59.
65. R. W. Springer, C. D. Hosford, *J. Vac. Sci. Technol.*, 20 (1982) 3, 462.
66. L. S. Wen, J. Gong, B. H. Yu, R. F. Huang, L. P. Guo, *Proc. C-MRS 1990 Int.*, June 18-22, 1990, Beijing, V4, p. 219.
67. A. T. Alpas, J. D. Embury, D. A. Hardwick, R. W. Springer, *J. Mat. Sci.*, 25 (1990) 1603.
68. R. F. Huang, L. S. Wen, L. P. Guo, J. Gong, B. H. Yu, H. Bangert, *Surface and Coatings Technology*, 50 (1992) 97.
69. S. Menezes, D. P. Anderson, *J. Electrochem. Soc.*, 137 (1990) 2, 440.
70. M. Shinn, L. Hultman, S. A. Barnett, *J. Mat. Res.*, 7 (1992) 4, 901.
71. L. S. Wen, R. F. Huang, L. P. Guo, J. Gong, T. Y. Wei, Y. Z. Chuang, *J. Magnetism and Magnetic Materials*, 126 (1993) 200.
72. A. Wagendustel, R. F. Huang, H. Bangert, X. Yang, L. H. Wu, H. F. Wang, H. Pangratz, P. Skalicky, *Acta Metallurgica Sinica*, B6 (1993) 1, 29.
73. M. Herranen, U. Wilklund, J. O. Carlsson, S. Hogmark, *Surface and Coatings Technology*

- gy, 99 (1988) 191.
74. U. Wilklund, P. Hedenqvist, S. Hogmark, Surface and Coatings Technology, 97 (1997) 773.
75. P. Panjan, B. Navinsek, A. Cvelbar, A. Zalar, J. Vleck, Surface and Coatings Technology, 98 (1998) 1497.
76. T. Leyendecker, I. Rass, G. Erkens, M. Feldhege, Surface and Coatings Technology, 97 (1997) 790.
77. L. S. Wen, R. F. Huang, Chin. J. Mat. Sci. Technol., 14 (1998) 289.
78. W. Olbrich, Kampschalle, Surface and Coatings Technology, 61 (1993) 262.
79. A. J. Perry, J. R. Treglio, A. F. Tian, Surface and Coatings Technology, 76/77 (1995) 815.
80. S. C. Lee, W. Y. Ho, W. L. Pao, Surface and Coatings Technology, 73 (1995) 34.
81. K. T. Ric, E. Broszeit, Surface and Coatings Technology, 76/77 (1995) 425.
82. L. Wang, X. L. Xu, B. Xu, T. G. Wang, L. S. Wen, Pro. of C-MRS and MRS-K Joint Symp, 96, Nov. 17-21, 1996, Beijing, China, P.565.
83. N. Dingremont, E. Bergmann, P. Collignon, Surface and Coatings Technology, 72 (1995) 157.
84. N. Dingremont, E. Bergmann, M. Hans, P. Collignon, Surface and Coatings Technology, 76/77 (1995) 218.
85. J. Michalski, E. Lunarska, T. Wierzchon, S. AlGhanem, Surface and Coatings Technology, 72 (1995) 189.
86. M. Bader, H. J. Spies, K. Hock, E. Broszeit, H. J. Schroder, Surface and Coatings Technology, 98 (1998) 891.
87. N. Dingermont, E. Bergmann, P. Collignon, H. Michel, Surface and Coatings Technology, 72 (1995) 163.
88. K. Hock, G. Leonhardt, B. Bucken, H. J. Spies, B. Larisch, Surface and Coatings Technology, 74/75 (1995) 339.
89. V. R. Parameswaran, L. P. Immarigeon, D. Nagy, Surface and Coatings Technology, 52 (1992) 251.
90. H. J. Kolkman, Surface and Coatings Technology, 72 (1995) 30.
91. H. L. Du, P. K. Datta, J. S. Burnell-Gray, A. S. James, A. Matthews, Surface and Coatings Technology, 81 (1996) 151.
92. J. A. Sue, Surface and Coatings Technology, 61 (1993) 115.