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Surface Engineering with Light Alloys—Hard Coatings, Thin Films, and Plasma Nitriding

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Light alloys have been attracting increasing attention over the past decade, since they can be used to reduce weight and save energy. For many years, light metals such as titanium and aluminum have also been used to synthesize hard compound coatings such as physically vapor deposited (PVD) TiN, (Ti,Al)N, and chemically vapor deposited (CVD) Al_2O_3. The coatings field is developing rapidly. Combining plasma-aided coating and diffusion processes has led to the development of so-called "duplex treatment," consisting of plasma nitriding and subsequent hard coating. Another interesting development is TiN coating of aluminum vacuum parts, such as pumps, to reduce degassing and make the cleaning of the surfaces easier. Despite the many advantageous properties of light alloys, their surface properties sometimes cause problems. For example, galling may be a severe problem with titanium parts, and plasma nitriding has been applied successfully to combat it. However, due to adherent oxide scale, plasma nitriding of aluminum has proven to be more difficult. In this paper, we discuss some recent trends in the application of plasma-aided coating, thin film deposition, and diffusion processes, and give practical examples of industrial applications.

Keywords hard coatings, thin films, plasma nitriding, titanium, aluminum

1. Introduction

Light alloys have been attracting increasing attention in various applications due to the trend toward lighter constructions. Obvious advantages, *e.g.*, in transportation equipment, are the reduced energy consumption and improved performance. The performance of aluminum and titanium is often improved by the presence of a thin oxide skin on their surface. However, additional surface treatments are also needed, for example, when good wear resistance is required. In addition to the traditional chemical and electrolytic processes,[1] newer plasma-aided surface engineering processes have attracted increasing attention, in particular, to improve the wear resistance. In the following discussion a few examples of the application of plasma-aided coatings and diffusion treatments will be presented, and their limitations and problems will be discussed.

2. Hard Coatings and Thin Films

There has been considerable research activity in the development of hard coatings and thin films for various applications. Physically vapor deposited (PVD) TiN coatings became commonly available in the early 1980s from various sources.

2.1 Development of PVD Hard Coatings

There has been a considerable amount of research carried out to develop hard thin film coatings that can be deposited at low temperatures. The commercial breakthrough of the chemically vapor deposited (CVD) titanium carbide coatings took place in the late 1960s. In 1972, Bunshah and Raghuram[2] published a paper in which they had studied the deposition of TiC coatings by evaporating titanium in a hydrocarbon atmosphere. It appeared, however, to be difficult to deposit TiC at low temperatures with consistent properties. There were also differing opinions about the correct deposition parameters, such as the need and magnitude of substrate bias. Therefore, Bunshah's group preferred to call their process "activated reactive evaporation" instead of using the term "ion plating," which had been coined by Mattox[3] in 1964. Later the term "biased activated reactive evaporation (BARE)" was used as a synonym for ion plating. The breakthrough in PVD hard thin film coatings, however, did not come until the late 1970s. In 1976, Komiya and Tsuruoka[4] of the ULVAC Corporation (Japan) published their work on ion plating with a hollow cathode electron beam gun, which was subsequently used to deposit TiN coatings as well. Experiments on the deposition of TiN on forming tools were carried out also at Balzers in Liechtenstein using another type of electron beam gun.[5] In the early 1980s, gold-colored Tin-coated cutting tools became available from several sources. The processes competing with ion plating with an electron beam gun were sputtering[6] and arc evaporation.[7]

After the successful introduction of TiN coatings, attempts were made to develop new and better coatings, for example, by using other elements in addition to titanium. This kind of approach was especially well suited to sputtering. Knotek proposed the addition of aluminum to TiN, and improved wear resistance due to improved oxidation resistance was subsequently reported.[8] Early applications of (Ti,Al)N coatings included twist drills. In electron beam evaporation, Ti(C,N) coatings were introduced by Balzers, and they were found to outperform (Ti,Al)N coatings in interrupted cutting applications,[9] such as gear hobbing or milling. CrN became the fourth

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common coating.[10] It is often applied when additional corrosion resistance is required. According to some reports, CrN coatings could be advantageous in the forming of aluminum.

2.2 Superhard Coatings

Intensive research has been carried out to develop new superhard coatings such as cubic BN and diamond and diamond-like films. Despite progress, however, problems have also been encountered. The deposition of PVD cubic BN appears tricky and it is not yet commonly available commercially. Diamond and other carbon films do not apply to the cutting of steel, since carbon reacts with steel and the tools wear out rapidly. They have, however, been successfully used in the cutting of hard aluminum alloys. Another problem with hard carbon coatings is adhesion. Before the recent upsurge of interest in diamond coatings, work done at Philips laboratories had already showed that adhesion to metals could be improved by adding a metal alloyed interfacial layer between the hard carbon coating and the metal substrate. It has been proposed[11] that there exists a compound called carbon nitride C_3N_4 and that it is even harder than diamond. Despite the theoretical calculations, it has not yet been possible to synthesize it to confirm the predicted properties.

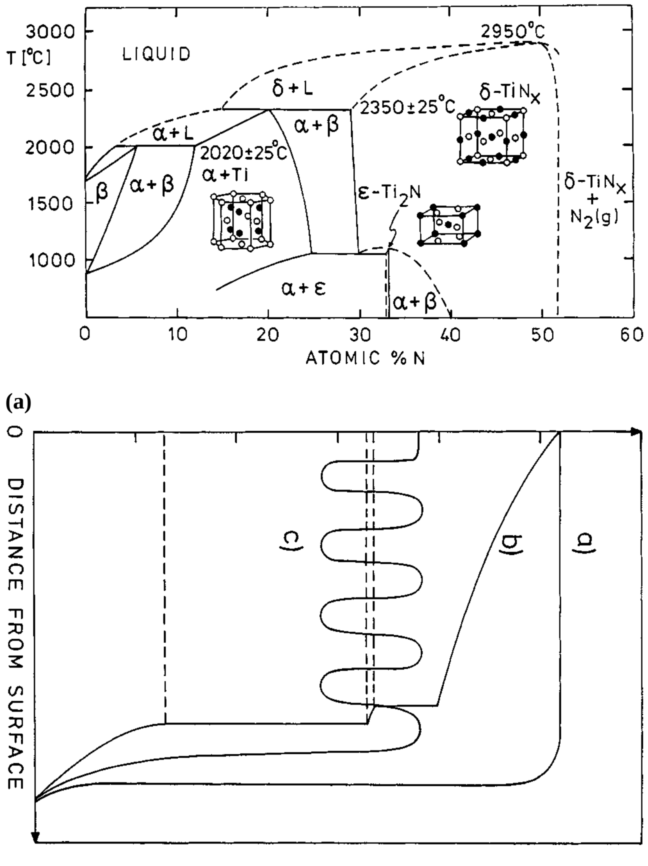
The development of CVD coatings for cemented carbides has generally followed the multilayer path. More and more layers have been added on top of the first TiC coating next to the substrate. Other coating layers have included oxidation-resistant Al_2O_3 or a thin top layer of TiN. Yet, the structure and properties of the CVD and PVD coatings are distinctly different due to the greatly differing deposition temperatures and different chemical composition of the deposition sources.[12] In PVD coatings, a different concept for multilayers has been proposed. It consists of the deposition of successive very thin nanometer-thick layers of different nitrides.[13] Provided that the lattice spacings of the successive nitride layers are close enough, a superlattice structure is formed. If the layers are appropriately thin, greatly increased hardness has been observed. Chu *et al.*[14] have subsequently applied the technique.

2.3 Other Alternative Coatings and Treatments

Although TiN coatings still seem to dominate in industrial applications, four common coatings, *i.e.*, TiN, (Ti,Al)N, Ti(C,N), and CrN, cover most of the applications.[9] There has been some work to introduce alternative coatings and treatments. Instead of trying to develop hard coatings, the idea of using soft lubricating coatings such as MoS_2 in tools has been proposed.[15] Historically, the first tribological applications of MoS_2 coatings were in bearings, which were needed in spaces where no conventional lubricants could be used. Much of the early development was done in Switzerland by Hintermann and his group. The problem with MoS_2 appeared to be its sensitivity to humidity under normal atmospheric conditions. The present sputtered MoS_2 coatings appear, however, not to suffer from this problem and some positive results have been obtained both in forming[16] and cutting tools.

Ti_2N coatings received a lot of attention during the early development of PVD TiN coatings. It was sometimes reported that they could show even higher hardness than TiN. However, due to the narrow range of stability of the Ti_2N phase, they have been difficult to produce in uniform composition. It has been claimed that they could be used, *e.g.*, in the machining of stainless steel.

Another approach in the development of coatings has been the combination of different layers produced by various techniques. This has been used in the production of multilayer coatings. One variation is the so-called duplex treatment, which usually refers to combining nitriding heat treatment with the subsequent TiN coating. Korhonen and Sirvio[17] showed that plasma nitriding at a low pressure in an ion plating unit was possible. Later, Korhonen *et al.*[18] showed that subsequent TiN coating could be used to improve the wear resistance. Although the duplex treatment consisting of plasma nitriding and subsequent coating was originally proposed for steel, titanium has also been successfully plasma nitrided.[19,20] The nitriding of aluminum turns out to be more difficult, as discussed in detail in a subsequent section dealing with the nitriding of light metals. Further work to develop and apply the method for steel has been done by many authors. It has been demonstrated, *e.g.*, by Sun and Bell[21] and Dingremont *et al.*,[22] that the development of a nitrogen deficient black layer on the interface between the nitrided steel and the TiN coating can be avoided if nitrogen



(a)

(b)

Fig. 1 Various possibilities for producing coatings and surface layers in the Ti-N system. (**a**) Uniform TiN coating, (**b**) diffusion layer, and (**c**) a coating produced by pulsing the nitrogen flow during the deposition

Fig. 2 PVD TiN-coated flanges for vacuum systems (courtesy of C, Hayashi, ULVAC Corporation)

Fig. 3 A valve with PVD TiN-coated inside surfaces (courtesy of C. Hayashi, ULVAC Corporation)

is added in a sputter precleaning atmosphere before the deposition of the TiN coating. Figure 1 illustrates schematically various possibilities for producing coatings and surface layers in the Ti-N system.

2.4 Thin Films

Various metallization layers are being used in electronics. However, these layers may react during annealing after, *e.g.*, ion implantation. To prevent the intermixing of incompatible metal layers, *e.g.*, aluminum and gold, diffusion barrier layers are needed. Sputtered TiN has become a very popular diffusion barrier layer.[23,24] It may be noted that the deposition of good quality golden yellow TiN coatings was first accomplished for tools. In the early 1980s, the corresponding TiN barrier layers tended to look brownish and the role of the deposition parameters, most notably correct biasing of the substrates, was not generally understood in microelectronic applications. Now TiN has become almost the universal standard as a barrier layer in the metallization schemes and, despite the great amount of research done to develop other and better barriers, TiN is what the industry usually prefers.

2.5 Coatings for Aluminum and Titanium

The light weight of aluminum alloys makes them an interesting material in applications where ease of handling is an important factor. Examples include large tools such as molds.[25] Another application of aluminum is in the manufacturing of vacuum equipment. According to a recent estimate of one manufacturer,[26] the annual consumption of aluminum in 1996 to 1997 for structural members was 310 tons, while the corresponding figure for steel was 1700 tons. Cast alloys accounted for more than half of this amount (180 tons), with forged alloys making up the remainder. The total worldwide consumption of east alloys for structural vacuum components is estimated to be over 18,000 tons, while the consumption of wrought alloys is from 2000 to 2500 tons. Coating of the inside surface of vacuum components such as pumps has been introduced to improve their performance. Hard, wear-resistant PVD TiN coatings have been used. Figure 2 and 3 show examples of such components.

3. Plasma Nitriding

Plasma nitriding of steel has been studied for a long time and many industrial furnaces have been produced. Plasma nitriding of light alloys is, however, a much less developed art; *e.g.*, plasma nitriding of titanium cannot usually be carried out in existing commercial furnaces.

3.1 Plasma Nitriding of Titanium

Plasma nitriding of titanium was studied by Molarius *et al.*[19] It was found that plasma nitriding was possible at low pressure triode discharge, when the substrate temperature was sufficiently high. The required relatively high substrate temperature has so far prevented nitriding in most commercially available plasma nitriding furnaces, which have been designed primarily for nitriding of steel. However, it was also found that the substrate temperature should not be too high. If the alpha-to-beta transformation temperature is exceeded, bad surface quality results from nitriding in the two-phase region. Typical applications of plasma-nitrided titanium components include ball valves for process industries, where good corrosion resistance is required. Plasma nitriding provides a deeper case, although the surface quality is not comparable to PVD TiN coating.

3.2 Plasma Nitriding of Aluminum

Nitriding of aluminum is possible at lower temperatures and ordinary plasma nitriding units designed for steel may be used. The difficulty in plasma nitriding of aluminum is the dense natural oxide skin. This transparent glassy layer consists of an extremely thin and compact-base layer and a hydrated upper layer whose thickness from 0.005 to 0.01 μm.[27] Removing this oxide layer is a prerequisite for successful nitriding. It was

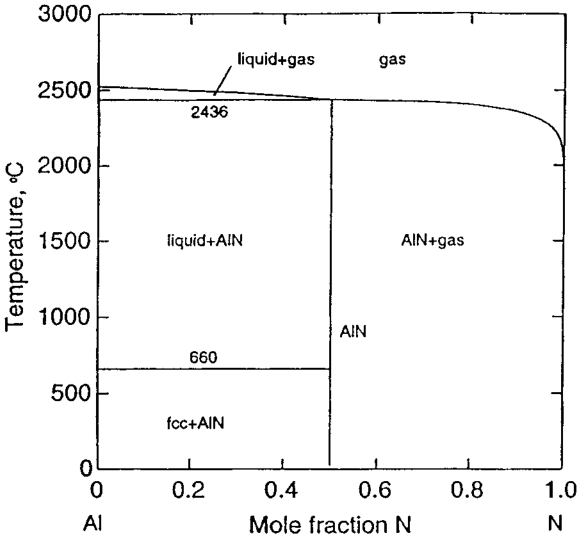


Fig. 4 A calculated Al-N phase diagram[32]

first shown by Arai *et al.*[28] that ordinary sputter precleaning can be used for this purpose. However, the relatively high substrate temperature required causes some problems and various techniques have been studied for nitriding.[29,30]

The sputtering yield of Al_2O_3 is relatively low compared with the sputtering yield of aluminum,[31] which easily results in strong etching of the aluminum substrate in spots where the aluminum oxide has been sputtered away. To avoid the increasing roughness of the substrate material, the cleaning parameters and the sputtering time should be selected carefully.

Regarding the phases in the Al-N system, conflicting information exists. According to Chen *et al.*[30] the existence of only one hexagonal nitride compound, AlN, has been confirmed, although fcc aluminum nitride also has been reported by Meletis and Yan.[32] Figure 4 shows a calculated Al-N phase diagram.[33]

4. Summary and Conclusions

There has been considerable progress in surface engineering with light alloys over the past 2 decades. The most intensive development has taken place in the field of hard thin film coatings, where coatings such as TiN and (Ti,Al)N have found many applications. Alternative coatings ranging from other nitrides and carbides to thin multilayer coatings have also been introduced. Since about the mid-1980s, an intensive research effort has been directed at the development of hard carbon-based coatings, although these coatings still seem to be limited to some special applications such as the cutting of hard aluminum alloys. Plasma diffusion treatments have been successfully combined with PVD hard coating. Although plasma nitriding of titanium cannot usually be carried out in conventional plasma nitriding furnaces designed for the treatment of steel parts, it seems that nitriding of titanium has reached a more advanced stage than nitriding of aluminum, where problems are often still being encountered due to the protective hard oxide skin.

References

1. *ASM Handbook*, ASM International, Materials Parts, OH, 1994, vol. 5.
2. R.F. Bunshah and A.C. Raghuram: *J. Vac. Sci. Technol.*, 1972, vol. 9, p. 1385.
3. D.M. Mattox: *Electrochem. Technol.*, 1964, vol. 2, p. 295.
4. S. Komiya and K. Tsuruoka: *J. Vac. Sci. Technol.*, 1976, vol. 13, p. 520.
5. R. Buhl, H.K. Pulker, and E. Moll: *Thin Solid Films*, 1980, vol. 80, p. 265.
6. W.-D. Münz and G. Hessberger: *Ind. Res. Development*, 1981, vol. 23 (9), p. 130.
7. P.C. Johnson: in *Thin Films and Processes II*, J.L. Vossen and W. Kern, eds., Academic Press, New York, NY, 1991, pp. 209-80.
8. W.-D. Münz: *J. Vac. Sci. Technol.*, 1986, vol. A4, p. 2717.
9. W. König, R. Fritsch, and D. Kammermeier: *Surf. Coating Technol.*, 1991, vol. 49, p. 316.
10. M. Van Stappen, L.M. Stals, M. Kerkhofs, and C. Quaeyhaegens: *Surf. Coating Technol.*, 1995, vol. 74-75, p. 629.
11. A.Y. Liu and M. Cohen: *Science*, 1989, vol. 245, p. 841.
12. D.T. Quinto, G.J. Wolfe, and P.C. Jindal: *Thin Solid Films*, 1987, vol. 153, p. 19.
13. U. Helmersson: Ph.D. Thesis, Linköping Studies in Science and Technology, 1986, Dissertation No. 153, Linköping University of Technology.
14. X. Chu, M.S. Wong, W.D. Sproul, and S.A. Barnett: *Surf. Coating Technol.*, 1993. vol. 61, p. 251.
15. J. Rechberger, P. Brunner, and R. Dubach: *Surf. Coating Technol.*, 1993, vol. 62, p. 393.
16. L. Helle: Suomen Rahapaja Oy - The Finnish Mint, private communication, 1993.
17. A.S. Korhonen and E. Sirvio: *Thin Solid Films*, 1982, vol. 96, p. 103.
18. A.S. Korhonen, E. Sirvio, and M. Sulonen: *Thin Solid Films*, 1983, vol. 107, p. 387.
19. J.M. Molarius, K.U. Salmenoja, A.S. Korhonen, M.S. Sulonen, and E.O. Ristolainen: *Härterei-Technische Mitteilungen*, 1986, vol. 4 (6), p. 391.
20. A.S. Korhonen, J.M. Molarius, and M.S. Sulonen: *Surf. Eng.*, 1988. vol. 4, p. 1, 44.
21. Y. Sun and T. Bell: *Mater. Sci. Eng.*, 1991, vol. A140, p. 419.
22. N. Dingremont, E. Bergmann, M. Hans, and P. Collignon: *Surf. Coating Technol.*, 1995, vol. 76-77, p. 218.
23. I. Suni, M. Mäenpää, M.-A. Nicolet, and M. Luomajärvi: *J. Electrochem. Soc.*, 1993, vol. 130, p. 1215.
24. M. Wittmer: *J. Vac. Sci. Technol.*, 1985, vol. A3, p. 1797.
25. D. Altenpohl: Aluminum Viewed from Within, 1st Edition, Aluminum-Verlag, Dusseldorf, 1982.
26. C. Hayashi: ULVAC Corporation, private communication, 1998.
27. D.G. Altenpohl: *Aluminum: Technology, Applications and Environment*, The Aluminum Association, Inc., Washington, D.C., and TMS, Warrendale, PA, 1998.
28. T. Arai, H. Fujita, and H. Tachikawa: *Proc. 1st Int. Conf. on Ion Nitriding*, T. Spalvins and W.L. Kovacs, eds., Cleveland, OH, 1986, pp. 37-41.
29. N. Renevier, T. Czerwiec, A. Billard, J. von Stebut, and H. Michel: *6th Int. Conf. on Plasma Surface Engineering*, Garemisch-Partenkirchen, Germany, Sept. 14–18, 1998.
30. H.-Y. Chen, H.-R. Stock, and P. Mayer: *Surf. Coatings Technol.*, 1994, vol. 64, p. 139.
31. *Handbook of Thin Film Technology*, L.I. Maissel and R. Gang, eds., McGraw-Hill, Inc., New York, NY, 1970.
32. E.I. Meletis and S. Yan: *J. Vac. Sci. Technol.*, 1991, vol. 9A, p. 2279.
33. Yong Du, R. Wenzel, and R. Scmid-Fetzer: CALPHAD, 1998, vol. 22 (1), p. 43.