学校编码：10384　　　　分类号________密级________
学号：20620081151603　　　　UDC_______

厦门大学

硕　士　学　位　论　文

PVD-TiAlN 硬质涂层的高温摩擦学行为研究

Research on High-temperature Tribological Behaviors of TiAlN Hard Coatings by Physical Vapor Deposition

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论文提交日期：2011 年　月
论文答辩时间：2011 年　月
学位授予日期：2011 年　月

答辩委员会主席：________
评　　阅　　人：________

2011 年 5 月

Research on High-temperature Tribological Behaviors of

TiAlN Hard Coatings by Physical Vapor Deposition

A Thesis

Submitted to the Graduates School in Partial Fulfillment of the

Requirements for the Degree of

Master of Engineering

By

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26. 5. 2011

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摘 要

TiAlN 是一种生产工艺成熟、加工性能优异，且极具代表性的硬质耐磨涂层，在切削刀具表面的应用非常广泛。相对于传统的 TiN 等金属氮化物涂层，TiAlN 涂层最突出的特点是其在高速切削和高温氧化条件下表现出来的优异摩擦学性能，国内、外研究者们对此特别关注，并做了大量的相关研究，但其中的机理性研究尚不充分，且结论的可重复性不高。弄清 TiAlN 涂层在高温氧化、负载条件下的磨损机理，不仅可以给 TiAlN 涂层生产工艺优化和涂层产品质量提高提供指导，而且对深化涂层摩擦学理论基础也具有重要意义。

本文运用多弧离子镀（MAIP）沉积工艺，在商业化设备中分别制备了中、高 Al 含量的两种 TiAlN 涂层（即 $Ti_{0.46}Al_{0.54}N$ 和 $Ti_{0.34}Al_{0.66}N$）。通过 CSM 纳米力学和涂层高温摩擦学测试系统，针对上述涂层在室温~1000℃区间内的摩擦学行为进行了系统的测试。采用场发射扫描电子显微镜（FE-SEM）、电子能谱仪（EDS）、电子探针显微分析仪（EPMA）、X 射线衍射仪（XRD）、俄歇电子能谱仪（AES）、X 射线光电子能谱仪（XPS）等多种先进表征手段对测试结果展开深入分析。从结构、成分、力学性能、摩擦性能、磨损机理等多个角度全面地讨论了测试温度对涂层的影响；找出了这两种 TiAlN 涂层在高温条件下的氧化行为和磨损行为的内在机制及相互联系。最后，在上述研究的基础上对高 Al 系列 TiAlN 涂层进行了尝试性的退火改性处理，并对相应的涂层刀具进行了实际切削加工测试。主要研究结论如下：

1. 中铝涂层（$Ti_{0.46}Al_{0.54}N$）为 B1-NaCl 结构，在（200）方向择优生长，晶粒尺寸约 26nm，截面为柱状结构；测试范围内，温度升高会引发涂层轻微的应力释放，但不会导致晶粒长大。温度升高引起涂层氧化加剧，Al 原子外扩散导致涂层表面形成双层结构的氧化膜。应力释放和氧化膜增厚共同导致涂层表面硬度和弹性模量的降低；涂层与基体的结合强度受高温影响不大，划痕测试失效模式主要表现为塑性磨损破坏。由于氧化膜的隔离和润滑作用，涂层的高温摩擦系数低于常温摩擦系数。中铝涂层常温磨损机制主要为磨粒磨损，磨损率很高；200℃~800℃，涂层表面生成了以非晶态 Al_2O_3 为主要成分的氧化膜，起到了防护与润滑的作用，主要磨损机制转变氧化层的轻微塑性磨损，涂层磨损率降低近

一个数量级；1000℃时，TiO_2等 Ti 系氧化物的大量生成导致氧化膜失去保护作用，磨损机制变为重度氧化磨损，磨损率增大。

2.高铝涂层（$Ti_{0.34}Al_{0.66}N$）也为 B1-NaCl 结构，只有（200）单一取向，晶粒尺寸仅有 6~7nm，截面平滑、无柱状结构；测试范围内，温度升高对其结构几乎没有任何影响。涂层表面氧化膜的厚度、连续性、致密性均随测试温度的升高而不同程度地增大；更高的 Al 含量有利于形成更致密的非晶 Al_2O_3层，故防护性更好。高铝涂层表面纳米硬度随测试温度升高而降低，主要原因是氧化膜的生成和增厚；受“反 Hall-Petch”效应影响，高铝涂层晶粒虽小，但硬度更低；涂层弹性模量随测试温度的升高，先减小后增大；高铝涂层结合强度受测试温度的影响不大，临界载荷低于中铝涂层，划痕测试失效模式也以塑性磨损破坏为主。高铝涂层常温摩擦系数与中铝涂层接近，主要磨损机制也为磨粒磨损，磨损率约是中铝涂层的 2 倍；高铝涂层的高温摩擦系数很高，这主要是硬度和弹性模量减小导致的粘着机制强化，其高温磨损机制为轻度粘着磨损，磨损率很低；800℃时，高铝涂层磨损机制向塑性变形磨损过渡，磨损率逐渐增大；1000℃时，高铝涂层表面氧化膜仍以 Al_2O_3为主，推测在更高温度下，高铝涂层的抗氧化磨损性能优于中铝涂层。

3. 700℃退火 2h，高铝涂层开始发生调幅分解，析出的亚稳相 c-AlN/c-TiN 与母相 c-TiAlN 形成了纳米复合结构，时效硬化机制引起涂层硬度的增大；900℃退火的高铝涂层，其硬度达到最大值~30.58GPa；退火温度达到 1100℃以上，稳定态 h-AlN 大量生成，涂层晶粒迅速长大，导致涂层硬度急剧降低。随退火温度的升高，热应力增大，涂层与基体的结合强度下降，划痕失效模式变为为结合力破坏。涂层常温摩擦系数受退火温度影响很小，主要磨损机制仍为磨粒磨损，结果表明，适当的退火温度能降低涂层的磨损率。从实际切削测试结果看，退火处理可以提高高铝涂层铣刀的加工性能，但需合理选择退火温度，其它处理参数也有待进一步优化和调整。

关键词：TiAlN；涂层摩擦学；高温；氧化行为；磨损机制

Abstract

TiAlN coating has been widely applied on cutting tools because of its highly developed production technology and excellent machining performance，as one of the most representative protective coatings. Compared to the traditional TiN and other metal nitride coatings，TiAlN coating shows remarkable tribological properties, especially in high-speed cutting condition or high-temperature oxidation environment, which has drawn much attention from the researchers at home and abroad. Lots of work has been carried out in order to find out the mechanism in the serving process, but it is still necessary to make studies on the wear mechanism of TiAlN coatings under high temperature and oxidative atmosphere，which can be taken as useful references for optimizing the coating process or increasing the product qualities. It is also important to develop and make full use of the coating tribology theory.

In this study, two series of TiAlN coatings with moderate and high Al content ($Ti_{0.46}Al_{0.54}N$ and $Ti_{0.34}Al_{0.66}N$) were fabricated by multi-arc ion plating (MAIP) process on ceramic carbide substrates in a commercial coating system, respectively. The tribological tests were carried out by using CSM ball-on-disc tribo-meter under different temperatures from 25℃ to 1000℃ in air. After the high-temperature testing, the coating samples were investigated through multiplicate advanced characterization methods, including X-ray diffraction (XRD), electron probe microscopy analysis (EPMA), Auger electron spectroscope (AES), X-ray photo-electron spectroscope (XPS), field emission scanning electron microscope (FE-SEM), as well as CSM nanoindentation tester. The influences of testing temperature on the microstructure, composition, mechanical properties, friction behaviors and wear mechanism were discussed in details, and the relationship between the oxidation behavior and wear behavior of the coatings with different Al content were found out. At last, a tentative annealing treatment was implemented on the TiAlN coatings with high Al content and the coated milling cutters, the machining performances of which were tested and evaluated. The main conclusions of this paper are summarized as follows:

1. The as-deposited TiAlN coatings with moderate Al content ($Ti_{0.46}Al_{0.54}N$) showed B1-NaCl phase and (200) orientation, from the cross-section of which columnar structure was observed. Within the testing range, elevated temperature resulted in slight stress relaxation, while the coating grain size did not increase with the temperature rising up. Oxidation proceeded by outward diffusion of Al atoms to form atmosphere Al-rich oxide layer at topmost surface of the coating, which got thicker with temperature increasing. The hardness and elastic modulus of the coating decreased by the stress relaxation and oxidation effects. The high temperature hardly affected the adhesion strength between the coating and the substrate. The high-temperature friction coefficient was lower than that of room temperature due to the isolation and lubrication of the Al-rich oxide layer. The abrasive wear was responsible for the high wear rate of as-deposited TiAlN coating. In the range from 200℃ to 800℃, the atmosphere Al_2O_3 layer protected the coating from severe wear, and the wear mechanism was transformed into slight plastic deformation with a much lower wear rate. At 1000℃, TiO_2 and other titanium oxides grew faster than Al_2O_3, which weakened the surface strength and accelerated the inner oxidation, causing severe oxidation wear and increasing the coating wear rate.

2. In the case of the TiAlN coating with high Al content ($Ti_{0.34}Al_{0.66}N$), similar XRD patterns were observed for the coatings tested at different temperatures, indicating good thermal stabilities. The coating grain size was extremely small (6~7nm), and the columnar structure could not be observed anymore. The oxide top layer got thicker and denser with the testing temperature increasing, in which more Al_2O_3 was formed for the high Al content of the as-deposited coating. The decrease of hardness and significant improvements on wear resistance were obtained at high temperature condition, which were highly connected to the oxidation behaviors on the coating surface. The inverse Hall-Petch was responsible for lower hardness of the high-Al% coating with smaller grain size than that of moderate-Al% coating. The coating elastic modulus increased firstly, and decreased afterwards, with the testing temperature going up. The adhesion strength kept stable and the failure mode of scratching remained plastic deformation at different testing temperatures. The

room-temperature tribological behaviors of the high-Al% coatings were quite similar to the moderate-Al% coating, but with nearly a doubled wear rate. The friction coefficients of the high-Al% coatings were very high in the high temperature conditions, for the decay of hardness and elastic modulus based on adhesive mechanism, and at the same time, the coating wear rare were remarkably decreased. The plastic deformation started to be the dominant wear mechanism at 800℃ with the wear rate increasing. At 1000℃, the content of Al_2O_3 in the oxide layer were sufficient to protect the inner coating, indicating a better wear resistance than that of the moderate-Al% coating at higher temperatures.

3. For high-Al% TiAlN coatings, the spinodal decomposition into the metastable c-AlN and c-TiN phase formed a nano-composite structure with the base phase of c-TiAlN, which resulted in the age-hardening of the coatings annealed over 700℃ for 2h. The coating hardness reached the maximum of ~30.58GPa at 900℃. At 1100℃, the phase transformation to stable h-AlN from the c-AlN, as an intermediate step, occurred, and the coating grain size increased rapidly, both of which weakened the coating hardness. The high temperature treatment reduced the adhesive strength between the coating and substrate caused by thermal induced stress. The friction coefficients of the coatings hardly changed with annealing temperature increasing, while the abrasive wear was greatly restrained by the age-hardening effect. The application of the coatings on milling cutters showed that the annealing of TiAlN coatings could improve the machining performance of coated tools by proper annealing temperature, however, the other treating parameters also needed further optimization.

Keyword: TiAlN; Coating tribology; High temperature; Oxidation behaviors; Wear mechanism

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