

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

孙 鹏

指导教师姓名: 王周成 教授

专业名称: 化学工艺

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

Peng SUN

Directed by Prof. ZhouCheng Wang

Department of Chemical Engineering and Biochemical
Engineering
Xiamen University

26. 5. 2011

厦门大学学位论文原创性声明

本人呈交的学位论文是本人在导师指导下,独立完成的研究成果。本人在论文写作中参考其他个人或集体已经发表的研究成果,均在文中以适当方式明确标明,并符合法律规范和《厦门大学研究生学术活动规范(试行)》。

另外,该学位论文为()课题(组)的研究成果,获得()课题(组)经费或实验室的资助,在()实验室完成。(请在以上括号内填写课题或课题组负责人或实验室名称,未有此项声明内容的,可以不作特别声明。)

声明人(签名):

年 月 日

厦门大学学位论文著作权使用声明

本人同意厦门大学根据《中华人民共和国学位条例暂行实施办法》等规定保留和使用此学位论文，并向主管部门或其指定机构送交学位论文（包括纸质版和电子版），允许学位论文进入厦门大学图书馆及其数据库被查阅、借阅。本人同意厦门大学将学位论文加入全国博士、硕士学位论文共建单位数据库进行检索，将学位论文的标题和摘要汇编出版，采用影印、缩印或者其它方式合理复制学位论文。

本学位论文属于：

1.经厦门大学保密委员会审查核定的保密学位论文，
于 年 月 日解密，解密后适用上述授权。

2.不保密，适用上述授权。

（请在以上相应括号内打“√”或填上相应内容。保密学位论文应是已经厦门大学保密委员会审定过的学位论文，未经厦门大学保密委员会审定的学位论文均为公开学位论文。此声明栏不填写的，默认为公开学位论文，均适用上述授权。）

声明人（签名）：

年 月 日

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，TiO₂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Al₂O₃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Al₂O₃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 ($\text{Ti}_{0.46}\text{Al}_{0.54}\text{N}$ and $\text{Ti}_{0.34}\text{Al}_{0.66}\text{N}$) 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°C to 1000°C 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 ($\text{Ti}_{0.46}\text{Al}_{0.54}\text{N}$) 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°C to 800°C, 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°C, 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 ($\text{Ti}_{0.34}\text{Al}_{0.66}\text{N}$), 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 rate were remarkably decreased. The plastic deformation started to be the dominant wear mechanism at 800°C with the wear rate increasing. At 1000°C, the content of Al₂O₃ 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°C for 2h. The coating hardness reached the maximum of ~30.58GPa at 900°C. At 1100°C, 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

目 录

摘 要	I
Abstract	III
第一章 绪 论	1
1.1 引 言	1
1.2 物理气相沉积 (PVD) 技术	2
1.2.1 PVD 技术的基本原理	3
1.2.2 PVD 技术的特点和优势	3
1.2.3 PVD 技术的分类与应用	4
1.2.4 PVD 刀具涂层的发展现状及未来趋势	7
1.2.5 PVD 技术之多弧离子镀 (MAIP) 简介	9
1.3 摩擦学理论与涂层摩擦学	11
1.3.1 摩擦学的基本理论及其发展历程	12
1.3.2 涂层摩擦学理论及应用	17
1.3.3 硬质涂层的高温氧化与摩擦磨损	21
1.4 TiAlN 涂层的研究与应用	22
1.4.1 TiAlN 涂层的生产制备	23
1.4.2 TiAlN 涂层的特性及应用	24
1.4.3 TiAlN 涂层的摩擦学研究进展和趋势	28
1.5 本文的选题背景与研究内容	29
第二章 实验方法与材料	32
2.1 整体实验研究思路	32
2.2 TiAlN 涂层的制备	33
2.2.1 制备工艺与设备	33
2.2.2 制备参数	34
2.3 高温处理及摩擦学测试	34
2.3.1 摩擦学测试设备与方法	34

2.3.2 高温摩擦磨损实验.....	36
2.3.3 涂层的真空退火.....	36
2.4 TiAlN 涂层刀具的切削试验.....	37
2.4.1 刀具试样的选择与处理.....	37
2.4.2 实施方法和参数.....	38
2.5 样品表征方法.....	39
2.5.1 涂层的力学性能测试.....	39
2.5.2 结构分析.....	41
2.5.3 形貌分析.....	42
2.5.4 成分分析.....	42
2.5.5 磨损率测算.....	42
第三章 中铝系列 TiAlN 涂层的高温摩擦学行为.....	44
3.1 温度对中铝系列 TiAlN 涂层相结构的影响.....	44
3.2 温度对中铝系列 TiAlN 涂层成分的影响.....	46
3.3 温度对中铝系列 TiAlN 涂层力学性能的影响.....	49
3.3.1 涂层的硬度.....	49
3.3.2 涂层与基体的结合力.....	51
3.4 温度对中铝系列 TiAlN 涂层摩擦特性的影响.....	54
3.5 温度对中铝系列 TiAlN 涂层磨损机制的影响.....	57
3.5.1 温度对涂层磨损率的影响.....	57
3.5.2 磨损机制及其与表面高温氧化行为的关系.....	59
3.6 本章小结.....	65
第四章 高铝系列 TiAlN 涂层的高温摩擦学行为.....	67
4.1 温度对高铝系列 TiAlN 涂层相结构的影响.....	67
4.2 温度对高铝系列 TiAlN 涂层成分的影响.....	69
4.3 温度对高铝 TiAlN 涂层力学性能的影响.....	72
4.3.1 涂层的硬度.....	72
4.3.2 涂层与基体的结合力.....	74
4.4 温度对高铝系列 TiAlN 涂层摩擦特性的影响.....	76

4.5 温度对高铝系列 TiAlN 涂层磨损机制的影响.....	79
4.5.1 温度对涂层磨损率的影响.....	79
4.5.2 磨损机制及其与表面高温氧化行为的关系.....	81
4.6 本章小结.....	85
第五章 高铝系列 TiAlN 涂层高温退火改性及其应用	87
5.1 退火温度对高铝系列 TiAlN 涂层相结构的影响.....	87
5.2 退火温度对高铝系列 TiAlN 涂层成分的影响.....	90
5.3 退火温度对高铝系列 TiAlN 涂层力学性能的影响.....	92
5.3.1 涂层的硬度.....	92
5.3.2 涂层与基体的结合力.....	93
5.4 退火温度对高铝系列 TiAlN 涂层摩擦学行为的影响.....	94
5.5 退火改性高铝 TiAlN 涂层的应用——切削性能分析.....	96
5.6 本章小结.....	100
第六章 结 论	102
附 录.....	104
参考文献.....	105
攻读硕士学位期间发表的论文和公开的专利	115
致 谢	118

Contents

Abstract in Chinese	I
Abstract in English	III
CHAPTER 1 Introduction	1
1.1 Introduction	1
1.2 Physical Vapor Deposition	2
1.2.1 The principal of PVD	3
1.2.2 The characteristics and advantages of PVD	3
1.2.3 The classification and application of PVD	4
1.2.4 The development and trend of PVD cutting tools	7
1.2.5 Brief introduction of Multi-Arc Ion Plating.....	9
1.3 Tribology principal and coating tribology	11
1.3.1 The fundamental theory and the development of tribology	12
1.3.2 The application of tribology principal	17
1.3.3 The high-temperature oxidation and the friction and wear of hard coatings	21
1.4 Studies and applications on TiAlN coatings	22
1.4.1 The preparation of TiAlN coatings	23
1.4.2 The characteristics and applications of TiAlN coatings	24
1.4.3 The development and trend of TiAlN coating tribology.....	28
1.5 The backgrounds and major contents of this paper	29
CHAPTER 2 The experimental methods and materials	32
2.1 The integral route of research	32
2.2 The preparation of TiAlN coatings	33
2.2.1 The preparation process and equipment	33
2.2.2 The preparation parameters.....	34
2.3 The high-temperature treatments and tribological tests	34

2.3.1 The equipment and methods of tribological tests	34
2.3.2 The high-temperature tribological tests	36
2.3.3 The high-temperature tribological tests	36
2.4 The cutting tests of TiAlN coated cutting tools.....	37
2.4.1 The option and treatments of the cutting tool samples	37
2.4.2 The implementation and parameters	38
2.5 Characterization methods	39
2.5.1 The mechanical properties of the coatings.....	39
2.5.2 The microstructures analysis.....	41
2.5.3 The morphology analysis.....	42
2.5.4 The composition analysis.....	42
2.5.5 The calculation of wear rate.....	42
CHAPTER 3 High-temperature tribological behaviors of the TiAlN coatings with moderate Al content.....	44
3.1 Influence of testing temperature on the microstructure of the TiAlN coatings with moderate Al content	44
3.2 Influence of testing temperature on the composition of the TiAlN coatings with moderate Al content	46
3.3 Influence of testing temperature on the mechanical properties of the TiAlN coatings with moderate Al content.....	49
3.3.1 Coating hardness.....	49
3.3.2 Adhesion between coating and substrate	51
3.4 Influence of testing temperature on the frictional properties of the TiAlN coatings with moderate Al content	54
3.5 Influence of testing temperature on the wear mechanism of the TiAlN coatings with moderate Al content	57
3.5.1 Influence of testing temperature on wear rate.....	57
3.5.2 Relationship between wear mechanism and oxidation behaviors on coating surfaces.....	59

3.6 Conclusions	65
CHAPTER 4 High-temperature tribological behaviors of the TiAlN coatings with high Al content.....	67
4.1 Influence of testing temperature on the microstructure of the TiAlN coatings with high Al content	67
4.2 Influence of testing temperature on the composition of the TiAlN coatings with high Al content	69
4.3 Influence of testing temperature on the mechanical properties of the TiAlN coatings with high Al content	72
4.3.1 Coating hardness	72
4.3.2 Adhesion between coating and substrate	74
4.4 Influence of testing temperature on the frictional properties of the TiAlN coatings with high Al content	76
4.5 Influence of testing temperature on the wear mechanism of the TiAlN coatings with high Al content	79
4.5.1 Influence of testing temperature on wear rate.....	79
4.5.2 Relationship between wear mechanism and oxidation behaviors on coating surfaces.....	81
4.6 Conclusions	85
CHAPTER 5 High-temperature annealing and applications of the TiAlN coatings with high Al content	87
5.1 Influence of annealing temperature on the microstructure of the TiAlN coatings with high Al content	87
5.2 Influence of annealing temperature on the composition of the TiAlN coatings with high Al content	90
5.3 Influence of annealing temperature on the mechanical properties of the TiAlN coatings with high Al content	92
5.3.1 Coating hardness	92

5.3.2 Adhesion between coating and substrate	93
5.4 Influence of annealing temperature on the tribological behaviors of the TiAlN coatings with high Al content	94
5.5 Applications of the annealed TiAlN coatings with high Al content — analysis on the milling performance of coated tools	96
5.6 Conclusions	100
CHAPTER 6 Summary	102
Appendix	104
References	105
Publications	115
Acknowledgements	118

Degree papers are in the "[Xiamen University Electronic Theses and Dissertations Database](#)". Full texts are available in the following ways:

1. If your library is a CALIS member libraries, please log on <http://etd.calis.edu.cn/> and submit requests online, or consult the interlibrary loan department in your library.
2. For users of non-CALIS member libraries, please mail to etd@xmu.edu.cn for delivery details.

厦门大学博硕士论文摘要库