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过渡金属氮化物纳米结构硬质涂层的性能优化及其 塑性变形机制研究

Performance enhancing and plastic deformation mechanism of nanocrystalline transition metal nitride hard coatings

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**Performance enhancing and plastic deformation mechanism
of nanocrystalline transition metal nitride hard coatings**



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摘要

针对高速干式切屑加工的苛刻服役环境,本文研究工作主要集中于优化提升 Zr 基及 Cr 基氮化物硬质涂层的力学及抗氧化性能;探讨氮化物硬质涂层的塑性变形机制;并建立硬质涂层组织结构与性能演变之间的关联。本文从涂层成分设计及结构设计角度出发,阐述了优化提升 Zr 基及 Cr 基氮化物硬质涂层力学及抗氧化性能的方法;同时也提出研究二维薄膜材料塑性变形行为的实验方法,并归纳出硬质涂层塑性变形机制的研究内容。本文所取得的主要结论如下:

(1)、掺杂元素的离子半径决定了涂层晶胞参数的变化规律;同时掺杂元素离子的价态对于涂层氧化层中的相结构、氧空位浓度以及离子扩散速率有着重要影响,从而对直接影响到涂层的抗氧化性能。适量掺杂活性元 Y、Hf 及 Nb 均能提高 Zr 基及 Cr 基氮化物硬质涂层力学及抗氧化性能。Zr 基及 Cr 基氮化物硬质涂层其高温氧化动力学进程分别受氧阴离子内扩散以及金属阳离子外扩散控制。 Y^{3+} 、 Hf^{4+} 及 Nb^{5+} 离子的带电电荷数分别低于、等于、高于 Zr^{4+} 离子,因而当 Zr-X-N (X= Y, Hf, Nb)涂层发生高温氧化后, Y^{3+} 、 Hf^{4+} 及 Nb^{5+} 离子掺杂将导致氧化产物 ZrO_2 中的氧空位浓度分别产生增加、维持不变、减少的变化;此外由于 Y^{3+} 及 Nb^{5+} 离子与 Zr^{4+} 离子存在电荷及半径差异,能增强 t- ZrO_2 的相稳定性。氧化层缺陷浓度的降低以及 t- ZrO_2 相稳定性的增强将提升氧化层的保护性,从而增强涂层的抗氧化性能。而活性元素离子 Y^{3+} 、 Hf^{4+} 及 Nb^{5+} 均难溶于 Cr 基涂层的氧化产物 Cr_2O_3 中,将以第二相形式偏析于 Cr_2O_3 的晶界上。掺杂活性元素增强及破坏 Cr 基涂层抗氧化性能的作用机制具有相似性,活性元素其优先外扩散特性抑制了金属 Cr^{3+} 离子的外扩散行为及活性元素的溶质拖拽效应共同导致了涂层抗氧化性能的增强;而过量掺杂则将导致偏析于 Cr_2O_3 晶界上的第二相含量增加,从而加速氧的内扩散进程,并最终引起涂层抗氧化性能下降。

(2)、引入非晶态或结晶态复合相均有利于细化氮化物涂层的组织结构,从而实现涂层力学性能的强化,但非晶态复合相相比于结晶态复合相其无定型结构更有利于实现对基体相的完全包覆。如若非晶复合相具有高热稳定性并能抑制氧的内扩散或金属阳离子的外扩散行为,增加复合相含量则将持续增强涂层抗氧化

性能，甚至避免氧化的发生。而对结晶态复合相，其与基体相均为微柱结构，无法实现复合相对基体相的完全包覆。氧化过程中氧的内扩散或金属阳离子的外扩散行为仍将继续进行，即使复合相热稳定性再高也无法避免氧化反应的发生。因此，设计制备纳米复合结构涂层，复合相材料的选择对于涂层力学及抗氧化性能的影响极为关键。

(3)、位错滑移以及微裂纹的萌生与扩展机制共同导致了二元 ZrN 涂层塑性变形的发生。在 ZrN 涂层纳米压痕下方塑性变形区域内，压头塑性功消散于涂层内部并诱发缺陷结构萌生与运动，导致塑性变形区域内位错密度上升。塑性变形区域内微裂纹萌生位置与扩展路径均位于 ZrN 柱状晶的晶界处，表明涂层界面强度低于晶内强度，界面的低结合强度成为增强 ZrN 涂层硬度的主要限制因素。加载基体偏压以及掺杂活性元素导致 ZrN 晶粒发生细化后，ZrN 涂层其塑性变形仍由位错滑移以及微裂纹萌生与扩展驱动，且微裂纹扩展路径仍为 ZrN 柱状晶的晶界，但塑性变形区域内位错密度下降。表明细化晶粒有利于强化晶粒，但未对晶界产生强化作用。对于 nc-ZrN/a-Si₃N₄ 纳米复合涂层而言，当 Si 含量为 1.9 at.% 时，nc-ZrN/a-Si₃N₄ 纳米复合涂层其塑性变形机制仍由位错滑移机制以及微裂纹萌生及扩展机制共同主导。相比于 ZrN 涂层，微裂纹数量减少且增殖扩展不再沿着晶界或界面处发生，而是出现了裂纹偏转，涂层界面强度得到了增强。而当 Si 含量增大至 20.9 at.% 时，ZrN 晶粒内部无可动位错存在，此时微裂纹萌生与扩展导致纳米复合涂层塑性变形的发生。

关键词：硬质涂层；力学性能；抗氧化性能；活性元素；纳米复合；塑性变形

Abstract

This work aims to improve the mechanical properties and oxidation resistance of the Zr- and Cr-based nitride hard coatings used for high speed, yet dry machining. In addition, the plastic deformation mechanisms of the coatings have been investigated. This thesis presents the strategies for improving the mechanical properties and oxidation resistance of the nitride hard coatings with the viewpoints of compositional optimization and structural design. The experimental method for investigating the plastic deformation behaviors of the coatings was provided as well. The mechanisms behind the plastic deformation of the nitride hard coatings were discussed. The major conclusions were outlined as follows.

(1). The ionic radius of doped reactive elements dominates on the cell parameters of the Zr- and Cr-based nitride hard coatings. Additionally, the charge valence of the dopants illustrates impacts on the phase structure, oxygen vacancy concentration and ionic diffusion rate of the oxide scales of the coatings. Incorporating a moderate amount of reactive elements improves both the mechanical properties and the oxidation resistance of the coatings. The high-temperature oxidation kinetics of the Zr- and the Cr-based nitride coatings are dominated by oxygen inward diffusion and metallic Cr^{3+} ions outward diffusion, respectively. The oxygen vacancies in the oxidation product ZrO_2 will be increased, unchanged and reduced after adding Y^{3+} , Hf^{4+} and Nb^{5+} ions, respectively. In addition, both incorporation of Y^{3+} and Nb^{5+} improves the phase stability of the t- ZrO_2 . The reduction of oxygen vacancy concentration and improved stability of the t- ZrO_2 result in the increase of the oxidation resistance of the ZrN coating. However, the Y^{3+} , Hf^{4+} and Nb^{5+} ions reveal extremely low solid solubility in the oxidation product Cr_2O_3 of the CrN coating. The reactive elements preferentially segregate to the grain boundaries of the Cr_2O_3 , forming the second phase oxides. Both the preferential outward diffusion of the reactive elements and the solute drag effect inhibit the fast growth of the oxide scale,

resulting in the promoted oxidation resistance. However, an excessive addition of the reactive elements deteriorates the oxidation resistance. Instead, the over added reactive elements form a larger amount of the second phase oxides in the oxide scales. They allow a fast oxygen inner transport, producing the loss of the resistance.

(2). Both introducing amorphous and crystallized nanocomposite phases into the Zr- and Cr-based nitride coatings provide a favorable condition for the grain size refinement, producing an enhanced mechanical properties of the coatings. The ZrN or CrN crystals are much easier be completely coated by the amorphous nanocomposite phase compared to the crystallized one. The amorphous interfacial phase provides a better protection for the crystalline/amorphous-type nanocomposite coatings against the high-temperature oxidation. However, for the crystalline/crystalline-type nanocomposite coatings, the oxygen inward diffusion or the metallic ions outward diffusion still occurs during the oxidation. Therefore, the crystalline state of the composite phase reveals an important role in improving both the mechanical properties and the oxidation resistance of the Zr- and Cr-based nitride coatings.

(3). The dislocation glides together with the initiation and propagation of the microcracks contribute to the plastic deformation of the nanocrystalline ZrN coating. The plastic work provides the necessary energy for the formation and growth of defects (such as microcracks and dislocations) in the deformed zone underneath the nanoindentation of the ZrN coating. The microcracks preferentially initiate just underneath the contact surface and then propagate along the columnar yet weak bonded grain boundaries. The microcrack propagation is found to be the primary factor deteriorating the coating hardness. Both applying substrate bias and adding reactive elements result in the grain size refinement of the ZrN coating. The fine-grained ZrN coating still reveals the dislocation- and microcrack-related plastic deformation. The microcracks preferentially propagate along the columnar grain boundaries as well. However, the dislocation density in the deformed zone decreases. This indicates that the grain size refinement produces the strengthening of the ZrN grains. However, the grain boundaries still possess a weak bonding strength. Adding 1.9 at.% Si, the plastic deformation of the nc-ZrN/a-Si₃N₄ nanocomposite coating still

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