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Outline of the Thesis

Chapter 1 Introduction

Ti(C, N)-based cermets have attracted much attention for use in cutting tools because of their high wear resistance and absence of W element as compared with WC-Co cemented carbide. In order to increase the cutting performance of cutting tool inserts, α-Al_2O_3 film is widely used as protective coating due to its high hardness, oxidation resistance and high-temperature stability. However, α-Al_2O_3 coating on Ti(C, N)-based cermet has not been available by conventional preparation methods due to oxidation of the cermet substrate and serious outward diffusion of metal elements. A laser enhanced chemical vapor deposition method (LCVD) developed by our research group is proposed for the preparation of α-Al_2O_3 films. α-Al_2O_3 films with a well-controlled microstructure were obtained by LCVD at low deposition temperature. Adhesive α-Al_2O_3 film was prepared on a Ti(C, N)-based cermet substrate.

Chapter 2 Preliminary investigation

The research status of α-Al_2O_3 film preparation is reviewed in this chapter. The common issues in the preparation of α-Al_2O_3 film are an excessively high deposition temperature (above 1300 K), no controllability of orientation, as well as low adhesion between film and the Ti(C, N)-based cermet substrate. In order to solve these problems, research objectives are defined and the experimental methods are evaluated.

Chapter 3 Low-temperature deposition of α-Al_2O_3 films by laser CVD

Effects of deposition temperature (T_{dep}), laser power (P_L), pre-heating temperature (T_{pre}) and precursor vaporization temperature (T_{Al}) on the crystal phase, microstructure and deposition rate of α-Al_2O_3 film were investigated. Figure 1 shows the XRD patterns of Al_2O_3 films deposited on AlN substrate at T_{Al} = 443 K and T_{pre} = 293 K. At T_{dep} = 825 K (P_L = 100 W), the XRD peaks were indexed as α- and γ-Al_2O_3 (Fig. 1(a)). Single-phase α-Al_2O_3 film was obtained at T_{dep} = 918 K (P_L = 120 W) (Fig. 1(b)). (104)-oriented α-Al_2O_3 film was prepared at T_{dep} = 973 K (P_L = 150 W) (Fig. 1(c)). The lowest T_{dep} was 918 K for single-phase α-Al_2O_3, which is about 350 K lower than that of thermal CVD. These results indicate that diode laser CVD offers a significant advantage in preparation of α-Al_2O_3 coatings at low T_{dep}.

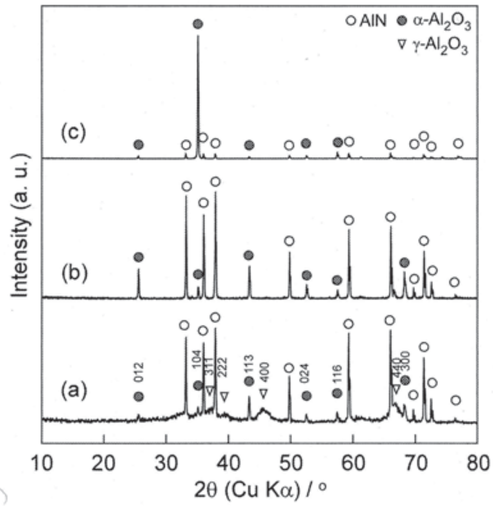

Fig. 1. XRD patterns of Al_2O_3 films prepared at T_{pre} = 293 K and P_{tot} = 0.2 kPa. The single-phase α-Al_2O_3 was prepared at a low temperature of 918 K, which is about 350 K lower than that of thermal CVD.

Chapter 4 Orientation control of α-Al_2O_3 films by laser CVD

Effects of T_{dep}, P_L, and T_{Al} on the crystal phase, orientation, and microstructure of α-Al_2O_3 film were investigated. Figure 2 summarizes the effects of P_L and T_{dep} on the phase and orientation of Al_2O_3 films prepared on AlN substrate. At P_L = 0, namely, without laser irradiation, no deposition was observed even at T_{dep} > 700 K. From T_{dep} = 623 to 881 K (P_L = 50 to 75 W), amorphous-like Al_2O_3 films were obtained. From T_{dep} = 931 to 1031 K (P_L = 110 to 140 W), single-phase α-Al_2O_3 films with the (006) orientation were

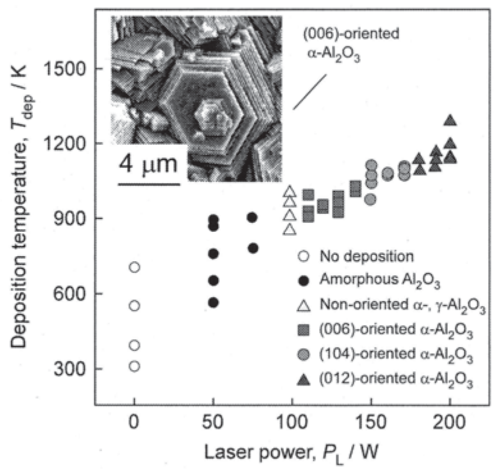

Fig. 2. Effect of P_L and T_{dep} on the phase and orientation of Al_2O_3 films at P_{tot} = 0.2 kPa and various T_{pre}. LCVD method shows good controllability in orientation of α-Al_2O_3 films.

obtained. From T_{dep} = 973 to 1173 K (P_L = 150 to 200 W), single-phase α-Al_2O_3 films with the (104) and (012) orientations were obtained. The orientation of α-Al_2O_3 films changed from (006) to (104) to (012) with increasing T_{dep} and P_L. The LCVD method shows good controllability in orientation of α-Al_2O_3 films.

Chapter 5 Preparation of α-Al_2O_3 films using a CO_2-H_2 mild oxidant by laser CVD

α-Al_2O_3 films were prepared in a CO_2-H_2 atmosphere. The effects of the CO_2 mole fraction (F_{CO_2}) and laser power (P_L) on the crystal phase, microstructure, and deposition rate (R_{dep}) were investigated. α- and γ-Al_2O_3 mixture films were prepared at T_{dep} = 818 K (P_L = 90 W), whereas (006)-oriented single-phase α-Al_2O_3 films were obtained at T_{dep} = 863 to 893 K (P_L = 110 W). Hexagonal grains were observed on the surface of (006)-oriented α-Al_2O_3 films prepared at T_{dep} = 873 K (F_{CO2} = 0.75) and T_{dep} = 883 K (F_{CO2} = 1) (Fig. 3). The texture coefficient and the R_{dep} of the (006)-oriented films increased with increasing F_{CO_2}. This indicates that (006)-oriented α-Al_2O_3 films can be prepared even in a mild oxidant of CO_2-H_2 atmosphere by using the LCVD method.

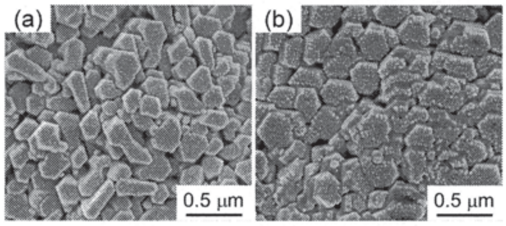

Fig. 3. Surface SEM images of (006)-oriented α-Al_2O_3 films prepared at: (a) F_{CO2} = 0.75 (T_{dep} = 873 K) and (b) F_{CO2} = 1 (T_{dep} = 883 K). By using LCVD method, (006)-oriented α-Al_2O_3 film can be deposited even in a mild oxidant atmosphere.

Chapter 6 Preparation of AlN, TiN and AlN/α-Al_2O_3, TiN/α-Al_2O_3 multilayers

AlN and TiN films were prepared using Al(acac)$_3$-NH_3 and Ti(OiPr)$_2$(dpm)$_2$-NH_3, respectively. The effects of P_L, T_{dep} and total pressure (P_{tot}) on the crystal phase, orientation, and microstructure of AlN and TiN films were investigated. Single phase AlN film was prepared at T_{dep} > 803 K. The microstructure of AlN film changed from aggregated grains to faceted ones, then to pyramidal ones with increasing T_{dep} and decreasing P_{tot}. Single phase TiN film was prepared at T_{dep} > 903 K (P_L > 100 W). The microstructure of TiN film changed from flower-shaped grains to pyramid-like ones, then to aggregated grains with increasing T_{dep}. AlN/α-Al_2O_3 and TiN/α-Al_2O_3 multilayers were also prepared by changing the precursor to Al(acac)$_3$-CO_2-H_2. AlN and TiN films can be prepared by LCVD even using an oxygen-containing precursor.

Chapter 7 Effect of cermet nitridation on the adhesion of α-Al_2O_3 coatings

The effect of nitridation on the properties of Ti(C, N)-based cermet and the adhesion of α-Al_2O_3 coating was investigated. The LCVD setup was used for nitriding the cermet substrate. Substrates were nitrided in NH_3 atmosphere with a total pressure of 0.8 kPa. A laser was used for heating the substrate. The adhesion between the α-Al_2O_3 coating and the substrate was qualitatively evaluated based on ISO 26443:2008 using a Rockwell-type hardness tester. α-Al_2O_3 film delaminated from the Ti(C, N)-based cermet substrate which was not nitridated (Fig. 4 (a). The adhesion of α-Al_2O_3 coating increased with increasing nitridation time (t_{Nit}) (Fig. 4 (b), (c) and (d)). α-Al_2O_3 coating prepared on Ti(C, N)-based cermet substrate nitrided for t_{Nit} = 40 min showed high adhesion (Fig. 4(d)).

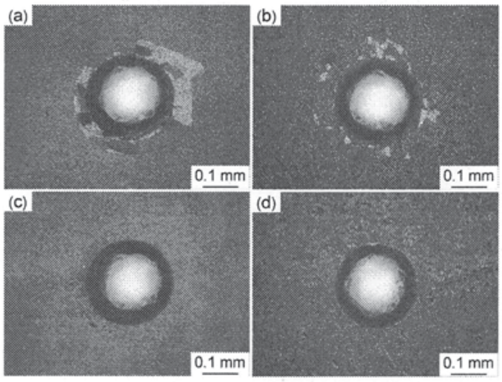

Fig. 4. The adhesion of α-Al_2O_3 films prepared on Ti(C, N)-based cermet substrate (a): without nitriding, and nitridated at T_{Nit} = 1100 K for a nitriding time of (b) 5 min, (c): 20 min and (d): 40 min.

Chapter 8 Conclusions

Chemical vapor deposition enhanced by laser irradiation facilitated low-temperature deposition of α-Al_2O_3 films. Highly oriented α-Al_2O_3 films with controlled microstructures were prepared in both O_2 and CO_2-H_2 atmosphere using an Al(acac)$_3$ precursor. Results proved laser CVD to be an effective method for the preparation of oriented α-Al_2O_3 coating for application in cutting tools. The interlayer, i.e., TiN, AlN, promoted a dense structure of α-Al_2O_3 film. Nitridation of Ti(C, N)-based cermet promoted the grain growth of adhesive α-Al_2O_3 films. These results are of great significance for the commercial application of α-Al_2O_3 films for coating Ti(C, N)-based cermet cutting tool inserts.

論文審査結果の要旨

本論文は、レーザー気相化学析出 (CVD: chemical vapor deposition) 法を用いて α-Al_2O_3 膜を合成し、合成条件が膜の結晶相、配向性および微細構造に与える影響について明らかにするとともに、Ti(C,N) 系サーメット上への優れた硬質コーティング法を開発するための指針を得ることを目的とした研究であり、全 8 章からなる。

第 1 章および第 2 章では、研究の背景を述べ、本論文の目的と構成を紹介した。

第 3 章では、Al_2O_3 膜を様々な条件で合成し、成膜条件が膜の結晶相、配向性および微細構造に与える影響について報告した。有機金属錯体 Al(acac)$_3$ (トリアセチルアセトナートアルミニウム) を原料とし、基板予熱温度を室温から 673 K, Nd:YAG レーザー出力を 0 から 238 W、原料気化温度を 413 から 443 K、炉内圧力を 0.5 から 2 kPa の範囲内で変化させた。レーザー出力の上昇に従い、膜の合成温度は上昇し、得られる膜の結晶相は、γ 相単相から γ 相と α 相の混相、そして α 相単相へと変化した。α 相単相膜が得られた温度はおよそ 900 K 程度であり、レーザーCVD 法を用いることで、従来の熱 CVD 法よりも 400 K 程度低い合成温度で α-Al_2O_3 膜を合成できることを示した。

第 4 章では、合成温度および炉内圧力が α-Al_2O_3 膜の結晶配向成長に与える影響を調べた。合成温度を変化させることで、α-Al_2O_3 膜の配向を (006), (104) および (012) と制御できた。(006) 配向 α-Al_2O_3 膜の表面微細構造を観察したところ、α-Al_2O_3 の六方晶コランダム構造を反映した、六角形のファセットが顕著に認められた。(104) 配向膜では、六角形のファセットが基板面に対してやや斜めに成長しており、これは (104) 面と (006) 面との面角度に対応したものと推察される。いずれの膜においても、結晶粒は柱状に成長していた。

第 5 章では、CO_2-H_2 雰囲気中で α-Al_2O_3 膜を合成した。レーザーCVD 法を用いることで、CO_2-H_2 雰囲気のような低酸素雰囲気であっても、α-Al_2O_3 膜を合成しその配向を制御できることを示した。CO_2-H_2 雰囲気で合成した (006) 配向 α-Al_2O_3 膜は、微細な六角形の結晶からなっていた。

第 6 章では、レーザーCVD 法を用いた窒化物膜の合成を行った。NH_3 雰囲気中で成膜を行うことで、Al 有機金属錯体 (Al(acac)$_3$) は酸素を含有しているにも関わらず、AlN 膜を合成することが出来た。一方、TiN 膜においても、NH_3 雰囲気で成膜を行うことで、酸素を含有した Ti 有機金属錯体 (Ti(O*i*P)$_2$(dpm)) を用いた場合であっても、TiN 膜を合成出来ることを実証した。また、これらの成膜プロセスを組みあせることで、TiN 膜と α-Al_2O_3 膜の多層膜を合成したり、AlN と α-Al_2O_3 の複合膜を合成したり出来ることも報告した。

第 7 章では、Ti(C,N) サーメット基材の表面予備処理について実験を行った。α-Al_2O_3 膜を Ti(C,N)サーメット基材上に直接合成する場合、基材表面の酸化により膜の密着性が低くなる問題があった。しかし、Ti(C,N) サーメット基材の表面窒化を行い膜／基材界面の構造制御を行うことで、基材表面の酸化を抑制し、基板との密着性が良好 (ISO 26443 試験で class 0 あるいは 1) な α-Al_2O_3 膜および TiN 膜が得られた。

第 8 章では、本論文を総括した。

本論文により、レーザーCVD 法を用いた α-Al_2O_3 膜の合成において、合成条件と膜の結晶相、配向性および微細構造の関係が明らかになった。これらの結果は、レーザーCVD 法を用いた高配向性 α-Al_2O_3 膜の低温合成法および Ti(C,N) 系サーメット上への優れた硬質コーティング法を開発するための指針となるものである。

よって、本論文は博士(工学)の学位論文として合格と認める。