Fundamental study of coatings produced by sputtering methods for high temperature applications(スパッタ法により作製した超高温材料用被膜に関する基礎的研究)

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論文内容要旨

1. Introduction

In high temperature environments carbon structural materials (CSM) have excellent physical properties (high strength and creep resistance up to 3000℃ and excellent thermal shock resistance). However, when they are exposed to oxidizing atmospheres they does not form solid oxides that could provide protection against further attack. Thus, the problem of protecting carbon structural materials against oxidation in air above 773 K has not yet been solved satisfactorily.

The current state of the art in coatings for oxidation protection of CSM's uses silicon based ceramics silicon carbide and silicon nitride as the primary oxygen barrier, coupled with internal glass forming inhibitors and sealants to seal thermal stress cracks and defects in outer coating. However, these coating materials are limited to about 1873 K by thermochemical reactions.

This fundamental research is concerned to develop the new coating materials for CSM to use at more higher temperature ($>$ 1873 K) and for long time. Furthermore, their deposition parameters, microstructural studies, adhesion, interfacial reaction and microcracking on carbonaceous material before and after high temperature annealing in Ar gas atmosphere. The proposed coating was designed to be chemically and mechanically stable to carbonaceous substrate.

As no single coating can prevent the diffusion of both oxygen and carbon, binary or multilayered coating system may be a possible solution. This coating system is composed basically of two layers: first an inner layer of iridium and second, an overlayer of alumina. The first layer of iridium deposited onto carbonaceous substrate acts as a diffusion barrier for carbon. Iridium coatings may be most promising as a barrier layer material because it melts at 2713 K, has a very low oxygen permeability up to 2373 K, and is non reactive with carbon below 2573 K. The second layer alumina can behaves as an oxygen retention material. Compared with other ceramics, alumina have many attractive properties such as low vapor pressure, low oxygen diffusion coefficient, excellent high-temperature strength, good corrosion resistance and oxygen stability.

2. Sputtering and analysis techniques

Chapter 2 describes the coatings preparation, analysis and testing techniques. The method by which the coatings are applied to the substrate is as important as the coating material itself in order to obtained the high purity excellently bonded coating without damaging the substrate. The sputtering techniques were selected to deposit the coatings. Nevertheless, the process chosen was found to avoid reactions that could occur between the coating components and carbonaceous substrate.

3. Iridium coating on CSM by DC sputtering

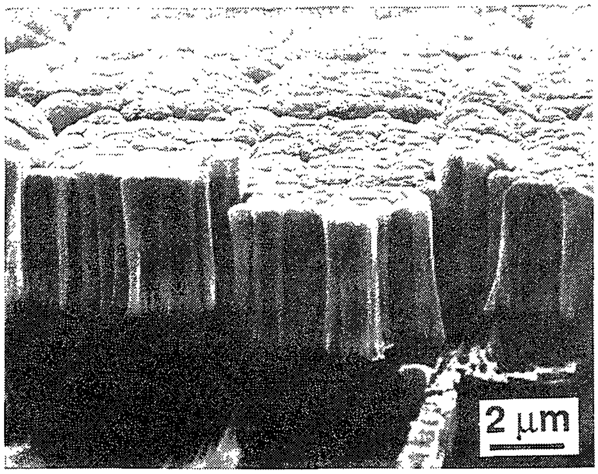

Fig. 1 DC sputtered iridium coating on polished surface of C-C composite.

High melting point iridium coatings were deposited by DC sputtering on different surfaces of C-C composite substrate. On the as-received surface of the C-C composite iridium coating was found to be discontinuous with uncovered surface in some places. The polished surface of C-C composite allowed the iridium coating to be deposited homogeneously. The dislocation free iridium coating with average grain size of about 450 nm was formed on polished surface of C-C composite. Figure 1 shows that iridium coating had tapered crystal with domed tops which were seperated by voided intergrain boundaries.

This type of microstructure may be due to the DC sputtering which uses low discharge current, high discharge voltage, high argon gas pressure and also deposition at low substrate temperature resulted in insufficient adatom diffusion to overcome the effects of shadowing. Condensing an iridium coating from a vapor arriving from one direction.

After high temperature annealing iridium coating broke into interconnected islands with grain growth. The initially as-deposited porous columnar structure, voided boundaries and sputtered iridium atoms bonded to the substrate with low strength were the probable reasons for the formation of interconnected islands and surface uncoverage after high temperature annealing. Some penetration effect and no interfacial reaction of iridium with the C-C composite were observed.

4. Iridium coating on CSM by RF magnetron sputtering

RF magnetron sputtering was used to produce iridium coatings on C-C composite and isotropic graphites with different coefficient of thermal expansion at room temperature and 1073 K.

Extremely fine grained columnar structures of iridium were observed when deposited at room temperature. Compared with room temperature deposition, substrate heating at 1073 K produced denser coatings with less strain and larger grain (Fig. 2).

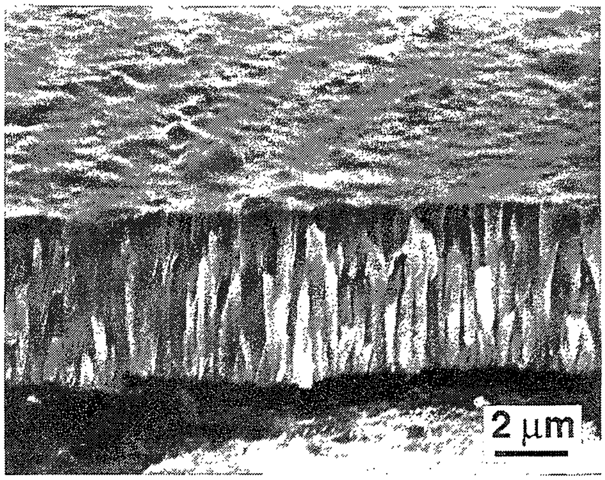

Fig. 2 RF magnetron sputtered iridium coating on isotropic graphite deposited at 1073 K.

RF magnetron sputtering allows a uniform and through coverage of iridium coatings on C-C composites and IG substrate.

Microcracking was observed on the coating deposited at 1073 K in the case of C-C composite and IG with a thermal expansion coefficient of approximately (0.92-4.8) $\times 10^{-6}K^{-1}$. Result shows that the increase in coating thickness on the IG substrate with coefficient of thermal expansion $4.8\times10^{-6}K^{-1}$ resulted in no microcracking.

Calculations of the thermal stress during cooling of iridium coatings on carbonaceous substrate from high deposition temperature reveal that thermal stresses were induced in the coatings. These thermal stresses (tensile or compressive) are due to expansion or contraction mismatch of the coating and the substrate.

For iridium coatings deposited onto isotropic graphite (CTE $7.6\times10^{-6}K^{-1}$) at 1073 K and degased before deposition, after annealing at high temperatures in N_2 there was no cracking, no outward diffusion of carbon, no dislocation, and pores were reduced or eliminated.

5. Thermalstability of iridium coatings

Thermal cycling between 300 K and 1873 K shows that columnar grains structure were remained within the coating. However, crystallized granular grains embedded in the grooves of IG at coating-substrate interface were well defined. The coating thickness had increased slightly after thermal cycling due to the outward diffusion of gases entrapped in porous substrate accompanied with iridium diffusion. The columnar grain structure of iridium coating on IG was replaced by dense equiaxed grains and grain size increases with time and temperature after thermal cycling between 300 K and 1973-2173 K. All thermal cycled and annealed specimens showed no microcracking and good adherence with the substrate retained.

6. Al_2O_3 coatings on iridium coated IG substrate by RF magnetron sputtering

Al_2O_3 coatings were deposited on iridium coated IG substrate at substrate temperature of (RT-1073 K), RF power (200-600 W) in Ar or Ar+1-10% O_2 sputtering gas atmosphere by RF magnetron sputtering. Room temperature deposited Al_2O_3 coatings were amorphous even at high RF power.

Al_2O_3 coatings which were deposited at high substrate temperature, high RF power in Ar or Ar+O_2 sputtering gas atmosphere resulted in dense crystalline γ-Al_2O_3 coatings with fine columnar structure. Furthermore, HRTEM micrograph Figure 3 shows epitaxial growth in γ-Al_2O_3 coatings. The micrograph also shows that there is a direct correspondence between the edges of iridium crystallites and the γ-Al_2O_3 and iridium (111) surface succeed to γ-Al_2O_3 (111).

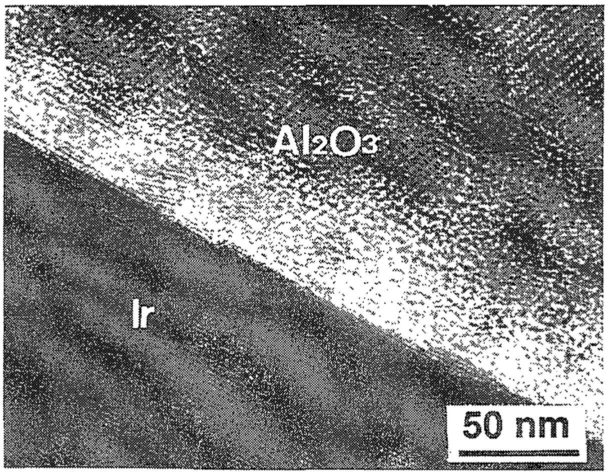

Fig. 3 HRTEM micrograph of Al_2O_3/Ir coatings.

The misfit strain between iridium and γ-Al_2O_3 phases with the orientation relationship of (hkl)//(hkl) was about 2.69 %, which is very small and this may be the reason for (hkl)//(hkl) growth of γ-Al_2O_3. XPS and AES analysis revealed that O/Al ratio was about to stoichiometric value of 1.5 when Al_2O_3 coatings were deposited at high temperature in $Ar+O_2$ sputtering gas atmosphere. The crystallinity and grain size in Al_2O_3 coatings were increased and argon content was decreased with the increase in % O_2 in the sputtering gas mixture. All as-deposited thick and thin Al_2O_3 coatings exhibited good adherence with the iridium coated IG substrate and with no microcracking.

Numerical calculation shows that compressive stresses were developed in Al_2O_3 coatings after cooling from high deposition temperature which may inhibited the microcracking. Results also revealed no formation of interfacial compound between Al_2O_3 and iridium coatings. Hardness values of 840 Hv for amorphous Al_2O_3 coatings and 1050 Hv for crystalline γ-Al_2O_3 coatings were obtained.

7. Annealing of Al_2O_3/Ir coatings on IG substrate

After annealing at 2073 K for 7.2 ks in Ar gas atmosphere very fine grains of as-deposited γ-Al_2O_3 coating on iridium coated IG was converted into large flake like α-Al_2O_3 coatings as shown in Figure 4. However, amorphous Al_2O_3 coatings after high temperature annealing showed microcracking with sub-micrometer size round pores. The volume changes involved in phase transition from amorphous to α-Al_2O_3 and rapid evolution of entrapped argon may be the reason of microcracking. Result shows that the Al_2O_3 coating thickness was decreased after annealing. The columnar structure of iridium coating was retained but the width of the columns were increased.

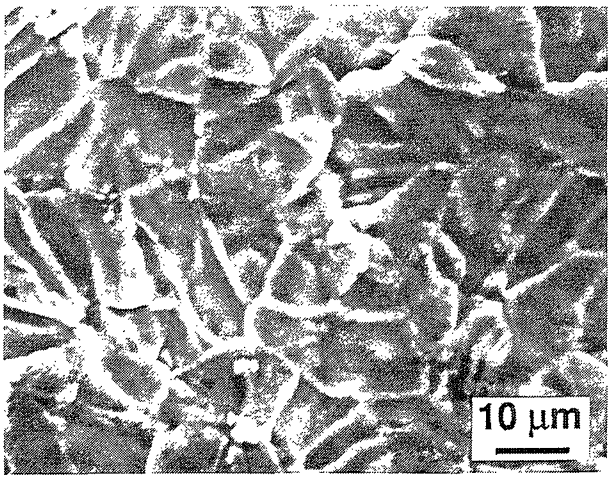

Fig. 4 Al_2O_3/Ir coatings after annealing at 2073 K for 7.2 ks in argon atmosphere.

An interfacial layer of AlIr compound was formed between Al_2O_3 and iridium coatings. It seems that evolving CO gas from the substrate resulted in the reduction of Al_2O_3 at the Al_2O_3/Ir interface at high temperature annealing in Ar atmosphere. The solubility of Al_2O_3 in iridium is known to be negligibly small. Therefore, AlIr compound formation seems to be the phenomena under the inert atmosphere on carbonaceous substrate. On the otherhand, Al_2O_3/Ir coatings on α-Al_2O_3 substrate after annealing at 1973 K for 7.2 ks in air showed dense α-Al_2O_3 grains coating, good thermal stability, no microcracking or decohesion. Furthermore, no interfacial compound formation between Al_2O_3 and iridium was observed after annealing in oxidizing atmosphere.

8. Conclusions

Chapter 8 presents the conclusions from this study.

審査結果の要旨

近年，宇宙開発などの分野で，軽量高強度，耐酸化性および耐熱衝撃性をかね備えた材料が望まれている。本論文は，炭素系材料の表面被膜による超高温耐熱材料の開発のための基礎研究として，スパッタ法を用い，グラファイトおよびC／C複合材上にイリジウムおよびアルミナを成膜し，そのプロセスと成長組織・熱的安定性との相関関係の解明を試みた結果をまとめたもので，全編7章よりなる。

第1章は序論であり，従来の研究を総括し本論文の目的を述べている。

第2章はdcスパッタ法によるイリジウムのC／C複合材およびグラファイト上への成膜とその成長組織，その後の熱処理組織を調べ，dcスパッタ法では一様な成膜は可能だが，熱処理によりイリジウムの島構造が起こることを明らかにしている。

第3章は第2章を基に導入ガスが少なくてすむrfスパッタ法を用いてC／C複合材およびグラファイト上へイリジウムを成膜し，ミクロ組織，結晶配向度，界面組織を調べ，その相互関係を明らかにしている。また，基板／被膜間の熱膨張係数の差による熱応力を算定し，クラックのない被膜の成長条件を見いだしている。

第4章はrfスパッタ法を用いて成膜したグラファイト上のイリジウム膜を1800℃まで加熱したときの組織変化を材料組織学の立場から明らかにしている。

第5章はグラファイト／イリジウム上にアルミナをrfスパッタ法を用いて成膜し，その成膜条件と結晶構造，微細組織，界面組織との関係を明らかにし，これからrfスパッタ法を用いたアルミナの最適成膜条件を明らかにしている。

第6章はグラファイト／イリジウム上に成膜したアルミナを1900℃まで加熱したときの組織を調べ，熱的にも安定で，かつ剥離，クラックのない積層膜が得られることを明らかにし，この複合被膜を施した炭素系材料が将来有望な高温材料として期待されていることを示している。

第7章は総括である。

以上要するに本論文は，スパッタ法によるイリジウム／アルミナの成膜と組織・熱安定性について系統的な研究を行ない，高融点金属の成膜プロセスの点で重要な知見を与えたと同時に，積層被膜を用いた超高温耐熱材料の開発のための基礎的指針を与えたもので，材料加工学に寄与するところが少なくない。

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。