ZrO_2/Al_2O_3 박막의 고온산화

High-temperature Oxidation of ZrO_2/Al_2O_3 Thin Films

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Abstract. Thin ZrO_2/Al_2O_3 films were deposited on a tool steel substrate using Zr and Al cathodes in a cathodic arc plasma deposition system (CAPD), and then oxidized at 600-900°C in air for up to 50 h. They effectively suppressed the oxidation of the substrate up to 800°C by acting as a barrier layer against the outward diffusion of the substrate elements and inward diffusion of oxygen. However, rapid oxidation occurred at 900°C due mainly to the increased diffusion and subsequent oxidation of steel as well as the crystallization of amorphous Al_2O_3.

1. Introduction

ZrO_2/Al_2O_3 is an attractive coating candidate for high temperature applications due to its immunity to oxidation, while maintaining high hardness and excellent high temperature stability. Many features of deposition methods and the resulting physical, chemical and mechanical properties of thin and thick ZrO_2/Al_2O_3 coatings have been studied. The aim of this study is to deposit a nano-multilayered ZrO_2/Al_2O_3 thin film on a tool steel by CAPD, and investigate the kinetics and mechanism of oxidation in the temperature range of 600-900°C.

2. Experimental Results

Thin ZrO_2/Al_2O_3 films were deposited on SKD11 tool steel substrates (1.5%C, 11.5%Cr, 0.8%Mo, 0.9%V, Fe=balance) by CAPD. Substrates with dimensions of 10x5x2 mm^3 were ground and polished with 1 μm Al_2O_3 powders. Two cathodes (Zr and Al) were located at opposite ends of the deposition chamber so that the substrates alternatively faced each cathode to form multilayered films. The distance between the substrate and the cathode was 28 cm. ZrO_2 is known to exist in three distinct crystalline forms, i.e., cubic, tetragonal, and monoclinic. These three polymorphs are non-metal deficient and n-type semiconductors. So, oxygen transports via oxygen vacancies in ZrO_{2-x}, but cationic diffusion is difficult. Hence, ZrO_2 in the film acts as a diffusion barrier against the outward diffusion of substrate elements to suppress oxidation. On the other hand, Al_2O_3 is a highly stoichiometric compound where ionic diffusion is extremely slow. The $ZrO_2/Al2O_3$ film effectively protects the steel substrate at $T \leq 800$°C. However, it is too thin to protect the steel substrate at 900°C, where crystallization of amorphous Al_2O_3 occurred.

3. Conclusion

Thin ZrO_2/Al_2O_3 films were deposited on SKD11 tool steel substrates by CAPD. The amorphous Al_2O_3 crystallized to $Al_{0.01}Zr_{0.99}O_{1.995}$ at 900°C. At $T \leq 800$°C, the $ZrO_2/Al2O_3$ film effectively suppressed the oxidation of the substrate by acting as a diffusion barrier. At 900°C, the thin $ZrO_2/Al2O_3$ film failed owing to the increased outward diffusion of the iron and inward diffusion of oxygen, together with the crystallization of Al_2O_3. During heating, Fe continuously diffused out to become Fe_3O_4 and Fe_2O_3.

Acknowledgement

본 연구는 2014년도 산업통상자원부의 재원으로 한국에너지 기술평가원(KEPTEP)의 지원을 받아 수행한 연구 과제입니다. (No.20143030050070)