CrAlSiN 박막의 대기중 고온산화

High temperature air-oxidation of CrAlSiN thin films

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초 록: Nano-multilayered CrAlSiN films consisting of crystalline CrN nanolayers and amorphous AlSiN nanolayers were deposited by cathodic arc plasma deposition. Their oxidation characteristics were studied between 600 and 1000°C for up to 70 h in air. During their oxidation, the amorphous AlSiN nanolayers crystallized. The formed oxides consisted primarily of Cr_2O_3, α-Al_2O_3, SiO_2. The outer Al_2O_3 layer formed by outward diffusion of Al ions. Simultaneously, an inner (Al_2O_3, Cr_2O_3)-mixed layer formed by the inward diffusion of oxygen ions. SiO_2 was present mainly in the lower part of the oxide layer due to its immobility. The CrAlSiN films displayed good oxidation resistance, owing to the formation of oxide crystallites of Cr_2O_3, α-Al_2O_3, and amorphous SiO_2.

1. 서론

Transition metal nitride films such as CrN and AlSiN are widely used for cutting tools or die molds because of their high hardness and superior resistance to wear and corrosion, however they are inevitably degraded by oxidation during service at high temperatures. CrN oxidizes rapidly to Cr_2O_3 above 700°C. The oxidation of nitrides is always accompanied by the liberation of nitrogen. To further increase the oxidation resistance and mechanical properties, CrN, CrSiN, CrAlN, CrAlSiN films were developed. CrAlSiN films are a recent development for enhanced high temperature performances, and their microhardness, microstructures, and cutting properties were previously studied. Their thermal stability was examined by annealing in a vacuum for 2 h between 800 and 1100°C, or oxidizing in air for 0.5-2 h between 800 and 1000°C. The thermal stability of the films depends sensitively on the deposition method and parameters that affect their crystallinity, composition, stoichiometry, thickness, surface roughness, grain size and orientation. Hence, it is necessary to study the high-temperature oxidation behavior of the CrAlSiN films under diverse oxidizing conditions for wide applications.

In this study, CrAlSiN film consisting of alternating CrN/AlSiN nano-multilayers were deposited on a steel substrate by cathodic arc plasma process. It is important to note that nano-multilayered films are of increasing interest due to their superior mechanical and lubrication properties in advanced tribological applications where single layer films are insufficient. The purpose of this study is to investigate the oxidation behavior of nano-multilayered CrAlSiN thin films, which was not yet studied. In this study, the oxidation conditions were expanded to a temperature range between 600 and 1000°C for up to 70 h in air. The oxidation kinetics was studied using a thermogravimetric analyzer (TGA) and compared to other films. The oxidation mechanism was proposed by performing Au-marker tests. Transmission electron microscopic (TEM) analyses were performed to investigate the scale morphology in detail.

2. 본론

CrAlSiN films were deposited on SKD11 tool steel (1.5%C, 11.5%Cr, 0.8%Mo, 0.9%V) with dimensions of 10x5x2 mm^2 by cathodic arc plasma deposition. A 70 at.%Ti-30 at.%Cr alloy and 88 at.% Al-12 at.% Si alloy were used for cathodes. The films were deposited on both sides of the steel substrate at a nitrogen pressure of 4 Pa, a temperature of 300 °C, a bias voltage of -100 V, Ti-Cr cathode arc current of 55 A, and Al-Si cathode arc current of 50 A. The substrate holder was rotated at 4.55 rpm during deposition. By rotating the substrate between two opposing cathodes of pure chromium and Al-Si alloys, nano-multi layered CrAlSiN films were deposited.

The CrAlSiN films deposited on the steel substrates were oxidized between 600 and 1000°C for up to 70 h in air using a TGA. Each sample was suspended by a platinum wire in an alumina reaction tube within the hot zone of the

$MoSi_2$furnace. The CrAlSiN films were characterized by an X-ray diffractometer, X-ray photoelectron spectrometer, Auger electron spectrometer, electron probe microanalyzer, and TEM equipped with an energy dispersive spectrometer. When exposed to hot air, the amprphous AlSiN layer became crystalline, as shown in the high-resolution TEM image (Fig. 1a). The selected area electron diffraction patterns of the white and dark layers consisted of Debye rings superimposed with spots, as is usually the case for polycrystalline materials (Fig. 1b). The TEM analyeses indicated that the white layer were crystalline B1(NaCl) type *fcc*-CrN and the dark layers were *hcp*-AlN. Even After oxidation at 800°C for 5h, the film was only slightly oxidized, indicating its good oxidation resistance (Fig. 1c). In Fig. 1b, the outermost CrN/AlSiN layers were in the process of being destroyed. It was noted that the initially deposited CrN layers had dissolved Al and Si ions, whereas the AlSiN layers had dissolved Cr ions from the beginning (Fig. 1d).

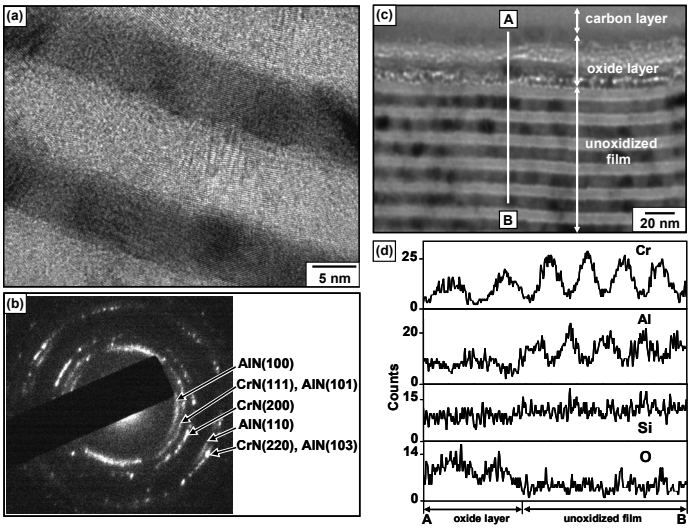

Fig. 1. TEM analyses of the CrAlSiN film

3. 결론

CrAlSiN films were deposited on tool steel substrates by the cathodic arc plasma deposition method, and their high-temperature oxidation behavior was investigated in order to understand the oxidation kinetics, mechanism and oxide scales formed. The following observations were made:

(1) The films consisted of alternating layers of nanometer-size, polycrystalline CrN and AlSiN. These phases oxidized into extremely protective Cr_2O_3, α-Al_2O_3, SiO_2. The oxidation modified the original nano-multilayers into submicron oxide grains. The overall oxidation rate of the CrAlSiN film was approximately comparable to the Cr_2O_3- and SiO_2-forming kinetics.

(2) The films displayed good oxidation resistance due to the formation of Cr_2O_3, α-Al_2O_3, and SiO_2. For example, the thickness of the scales formed on the unoxidized films was approximately 0.7 and 1 μm when the films were oxidized for 70 h in air at 900 and 1000 °C, respectively. The oxidation of the CrAlSiN films occurred via complex routes such as the outward diffusion of Al, Cr, Si, nitrogen, and the inward transport of oxygen.

(3) The formed oxide scales were divided into three oxide layers. The outer layer was Al_2O_3 containing a small amount of Cr ions that was formed primarily by outward diffusion of Al and a small amount of Cr ions. The inner layer was a (Al_2O_3+Cr_2O_3)-mixture containing a small amount of Si ions. The inner and innermost layers formed by the inward diffusion of oxygen ions.

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