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Microstructure and properties of VN/Ag composite films with various silver content

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ABSTRACT

The VN/Ag composite films with various silver content were prepared by PLD technique, and the microstructures, mechanical and tribological properties at elevated temperature to 900 °C of films were investigated, respectively. The results show that the films were composed of the fcc VN and Ag nanocrystalline grains. With the increase of silver content from 8.2 to 56.1 at.%, the grain size increased and the surface morphology deteriorated gradually, the hardness and elastic modulus of the films decreased from 18.6 GPa, 226.3 GPa–8.1 GPa, 126.6 GPa, respectively. Only appropriate silver addition could improve the lubricity of the VN/Ag films. The film with 16.6 at.% Ag were found to be optimized for lubrication from RT to 900 °C. At low temperatures, the lubricant property of the film relied on the metal silver heavily. At elevated temperatures, a series of Magnéli phase (vanadium oxides) and the layered structure silver vanadates (such as Ag_3VO_4, $AgVO_3$) formed by tribochemical reactions in the contact area played a critical role in improving lubrication properties. A synergy of the lubricating Ag at low temperatures and the new lubrication phases generated at high temperatures could be responsible to the excellent lubricity of the VN/Ag films in wide temperature range.

1. Introduction

With the development of self-adaptive lubrication materials, the vanadium nitride in the form of thin films have been focused in protective and lubrication applications due to their outstanding hardness and anti-wear properties [1], especially the lubricious vanadium oxides generated by oxidation of VN influenced the tribological properties significantly during high-temperature friction process [2–5]. In addition, the noble metal silver has attracted great attention in various anti-wear and lubrication composite materials, where the silver [6–8], and the generation of silver molybdate [9–13], silver tantalate [14], silver niobate [15,16] and silver vanadate [17] can play a lubrication role in the contact area during friction process in a wide temperature range. However, the silver in above literature were mostly applied in the films deposited by magnetron sputtering and thermal spraying technique, or solid bulk material prepared by powder metallurgy and spark plasma sintering technique, but the researches on VN/Ag films fabricated individually by pulsed laser deposition (PLD) technique and in high-temperature lubrication application were really rare [18–20].

The goal of the present work was to fabricate the VN/Ag composite films with various silver content by PLD technique, and systematically compare the effect of silver content on microstructures, mechanical properties and tribological performance (from room temperature to 900 °C in ambient atmosphere) of the films. Moreover, the lubrication mechanism of VN/Ag films was revealed and analyzed comprehensively, so as to provide valuable technical reference for wide temperature range lubrication. It is also anticipated that the VN/Ag films with excellent mechanical and tribological performance could be applied to lubrication in a wide temperature range.

2. Experimental details

2.1. Films preparation

The VN/Ag composite films were fabricated on mechanically

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polished Inconel 718 (for the mechanical property tests) and Si wafer (for the microstructure characterize) substrates by PLD technique at the substrate temperature of 200 °C. The details of the deposition process have been reported in previous work [21]. Briefly, a KrF excimer laser (λ = 248 nm, pulse duration = 25 ns, ComPexPro 205) was used to irradiate the target with pulsed laser energy of 300 mJ at 10 Hz in frequency, the pulse number was set to 36000 for each sample and all the film thickness in the 2.0 ± 0.1 μm range. In order to alter the silver content, the individual VN and Ag targets with the same dimension (Φ60 mm × 5 mm, 99.99% purity) were cut to eight-equal sections, different sections of VN and Ag were set symmetrically in a target holder. The proportion of VN and Ag target number was fixed at seven to one, six to two, five to three, four to four, and then the films were denoted as F1, F2, F3, F4, respectively. The target holder was placed parallel to substrate and keeping the distance about 50 mm. Prior to deposition, the vacuum chamber was evacuated to 6.0×10^{-5} Pa and the high-purity N_2 at flow of 90 ml/min was introduced into the chamber, and the working gas pressure was fixed at 0.3 Pa.

2.2. Films characterization

The phase composition of the films before and after wear test were identified by X-ray diffraction (λ = 0.15 nm) diffractometer (X'Pert PRO, Panalytical company, Netherlands) with Cu Kα radiation which was running at scanning range of 15–80° and at the grazing incidence angle of 1°. The results were investigated based on standard ICSD patterns (89/54378) data files using Jade6.0 software. The grain size and microstrain of the films were calculated according to the Williamson–Hall plot of the $\beta \times \cos\theta_B/\lambda$ vs. $\sin\theta_B/\lambda$, where β was the full width at half maximum of the peak, which had been corrected for instrumental broadening, θ_B was the Bragg angle, and λ was the Cu Kα X-ray wavelength [22].

The surface morphologies of films and wear track were characterized by the SU-8020 scanning electron microscope equipped with energy dispersive X-ray detector, respectively. High resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) were performed using a FEI Tecnai F30 microscope operated at an acceleration voltage of 300 kV to study what state the silver existed in the film. The film sample for TEM observation was deposited on sodium chloride crystal. The deposition parameters were the same to other samples (Si and Inconel 718 substrates) except the deposition pulse number, which was set to 1000 for the TEM sample. Subsequently, we placed the specimen in deionized water and with copper net catching the film that floating in the water, then, put the specimen in the clean room and dried naturally.

The hardness (H) and elastic modulus (E) of the films were evaluated using Ti-950 insitu nanomechanical testing system with a cube-corner diamond tip and calculated following the model of Oliver and Pharr [23]. During the test, the loading and unloading speed were fixed at 12 nm/s, the holding time at maximum depth was 3 s. In order to reduce the error, the experiments were conducted at five indents for every sample in a controlled contact depth of 200 nm, and averaging the five hardness and elastic modulus values respectively as the final results.

The tribological properties of the composite films at different temperatures were investigated using UMT-3 tribometer and carried out three times for each sample to reduce the error. The test parameters were as follows: normal load = 10 N, test time = 20 min, test temperatures = room temperature (RT), 300 °C, 500 °C, 700 °C, 900 °C, a 10 mm diameter alumina ball as counterpart, rotated velocity = 200 rpm, radius of circular track = 3 mm, in ambient atmosphere with a relative humidity of 40 ± 5%, respectively. The tribochemical reactions and the structure changes of wear products during the tests were detected by Raman spectroscopy (He-Ne laser, λ = 532 nm).

3. Results and discussion

3.1. Microstructures

Fig. 1 shows the grazing incidence X-ray diffraction (GIXRD) patterns of VN/Ag composite films with various silver content. The results indicate that all the films are consist of polycrystalline face-centered cubic (fcc) structured vanadium nitride (PDF card No. 73–2038) and silver (PDF card No. 87–0717), which is in good agreement with the unbalanced magnetron sputtering VN/Ag film [17]. The peak-differentation-imitating operation was performed on the XRD pattern of F1 film at the range of 42–46° (for example). The results show that the peaks correspond to VN (200) and Ag (200) well (as shown in the insert in Fig. 1), which can confirm that the peaks of VN and Ag are overlapped. The obtained F1, F2 and F3 films growth oriented highly in (200) orientation of vanadium nitride, suggesting that the VN retains the largest volume fraction in the film. With a further increase of Ag target number, the F4 film exhibits preferred orientation growth in (111) of silver, indicating that the film composition is mainly of silver. In addition, all the peaks position of F2, F3 films shift to lower diffraction angles than that of F1 film, which might be the result of increased metal Ag atom flux during deposition and mean larger lattice parameter, and in accordance with results reported by other authors for ion-assisted growth of YSZ-Ag films [24]. Concerning the peaks variation, a further investigation is carried out by Jade 6.0 software based on the Williamson–Hall plot, the structural parameters are calculated and tabulated in Table 1. With the increase of Ag target number, the more silver ablated and distributed in VN matrix during deposition process could be the reason for increased lattice parameters and grain size, and result in higher micro-strain of the F3 and F4 films.

Fig. 2 illustrates the surface morphologies of VN/Ag films with various silver content. The EDX results revealed that the content of silver was 8.2 at.%, 16.6 at.%, 40.2 at.%, 56.1 at.% corresponding to the F1, F2, F3, F4 film, respectively. It can be seen clearly that the Ag particles (bright) in different sizes embedded in VN matrix (dark grey), microstructure and morphology of the films change along with the variation of silver content obviously. The F1 and F2 films exhibited much flatter and denser structure compared to the F3 and

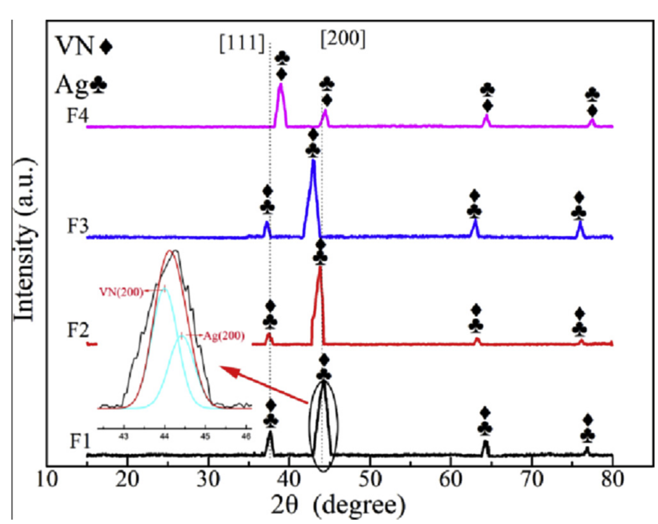

Fig. 1. GIXRD patterns of the VN/Ag films.