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Investigation of Al–Cr alloy targets sintered by various powder metallurgy methods and their particle generation behaviors in sputtering process

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ABSTRACT

Al–Cr–N films for tribological application are commonly prepared by sputtering on Al–Cr alloy targets in an Ar + N_2 mixed atmosphere. Generally, a film is manufactured by co-sputtering on an Al and Cr target, which tends to produce an arbitrary composition. It is difficult to produce an alloy target with a high Al ratio by melting technology due to the formation of brittle intermetallic compound phases (IMCs). In this study, alloy targets were manufactured by various powder metallurgy methods, included hot pressing (HP), hot isostatic pressing (HIP), and low temperature novel forming (LTNF). The results showed that at higher temperature, HP targets were dense and developed a large amount of IMCs, giving the target poor mechanical properties. Cracking tended to occur on the target surface, and many particles were generated during the sputtering process. At a lower temperature, IMC formation was inhibited in these targets, but the density was poor. The HIP method produced similar results to those of HP. LTNF was developed to achieve a dense target free of IMCs. Furthermore, the sputtering performances of the alloy targets were verified. For the LTNF target, almost no arcing count was recorded, fewer particles were generated and better film uniformity was obtained. The target and sputtering characteristics of conventionally-made (HP and HIP) methods were less desirable.

1. Introduction

Transition metal nitride films have been widely used as protective hard coatings in the mechanical and automotive industries due to their high microhardness, excellent wear resistance, and superior chemical stability [1–3]. Recently, Al–Cr–N films have replaced titanium-based coatings because of their higher thermal stability and hardness, particularly in intermediate- and high-speed cutting applications [4]. It has been shown that the oxidation resistance of Al–Cr–N films is superior to that of Ti–Al–N [5]. Fox-Rabinovich et al. [6] revealed that the Al content in $Al_xCr_{(1-x)}N$ films is limited to the range of $x = 0.6–0.7$ due to the undesirable transformation from B1 (cubic) to B4 (hexagonal) phase in coatings with Al content beyond that range. Reiter et al. [7] studied the mechanical properties of $Al_xCr_{(1-x)}N$ in relation to the formation and the content of cubic B1 phase. They found that the hardness and oxidation resistance are optimal when the aluminum content in $Al_xCr_{(1-x)}N$ coatings is around 70 at%.

To develop metal nitride films of high quality, most researchers have focused on studying the sputtering parameters, including the power density, working pressure, annealing temperature, and N_2 flow rate [8–12]. Very few studies have attempted to investigate the influence of an Al–Cr target on the sputtering performance. A general method of producing Al-rich $Al_xCr_{(1-x)}N$ films is to co-sputter them on Al and Cr targets in an Ar + N_2 mixed gas atmosphere [13–15], which is easy to control the film composition for superior performance [16]. However, co-sputter technology is not popular and cost-effective for mass production in industry. Furthermore, the Al–Cr alloy target is difficult to produce by air or vacuum melting techniques because in the Al–Cr system, brittle intermetallic compound phases (IMCs) tend to form [17–19]. Being brittle, IMCs can degrade the shaping ability of the target, and surface cracks may appear on the target edge during computer

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numerical control (CNC) lathing. In addition, during the sputtering process, microcracks on the sputtered target surface could cause instability and arcing, which could greatly degrade the quality of the films [20]. In this study, Al–Cr alloy targets with an Al:Cr atomic ratio of 70:30 were manufactured by various powder metallurgy methods, and the microstructures and phases were then investigated. The Al–Cr alloy targets were also utilized to prepare Al–Cr–N film for observation of the stability during the sputtering process.

2. Experimental details

Elemental powders of Cr (purity of 99.9% and average size of 78 μm) and Al (purity of 99.9% and average size of 23 μm) were mixed in a stainless steel container with 100 rpm under an Ar protective atmosphere for 2 h. The Al–Cr alloy targets (Al/Cr = 70:30 at%) were manufactured by three different powder metallurgy methods. In the first, the hot pressing (HP) method, the mixed powders were poured into a graphite die and uniaxially pressed in the die at a pressure of 17 MPa at room temperature. The pressed powders in the die were then heated in a vacuum hot pressing furnace (Centorr HP-16X) to 500 °C under 31 MPa and held at that temperature for 1 h, after which the temperature was increased at 10 °C/min to 700 °C, 800 °C and 900 °C for 1 h, respectively. In the second method, hot isostatic pressing (HIP), the mixed powders were poured into a stainless steel container and compressed at 14 MPa to obtain a higher initial packing density. The compact in the container was then degassed at 200 °C for 1 h and sealed by welding. The container was placed inside the HIP furnace (AVURE QIH-21) and heated at 10 °C/min up to 500 °C and 600 °C at 173 MPa, respectively. The last method, low temperature novel forming (LTNF), employed a prototype machine designed by Solar Applied Materials Technology Corp. (Tainan, Taiwan, ROC). Before LTNF forming, the mixed powder was compacted into a green compact by cold isostatic pressing (CIP) (Kobelco CW1700) and then sintered in the LTNF machine at 500 °C in an Ar protective atmosphere. Because the LTNF machine is the prototype design, the limitation of max temperature is around 500 °C for the time being. The LTNF process features discontinuous pressing force (150 MPa) during the heating process to obtain the dense bulk through serious deformation, as illustrated in Fig. 1. The densities of the targets produced by different powder metallurgy methods were measured by Archimedes' method. The microstructures of the specimens were examined by SEM (Hitachi S4300–N). X-ray diffraction analysis (Rigaku Ultima IV) with Cu Kα1 radiation was employed to identify the crystal structures of the sintered targets. The hardness was measured with a Vickers hardness tester (SHIMADZU HMV-2) with a load of 200 gf. The oxygen content of the target was measured by using a LECO TC-300 analyzer which the samples dropped into the hot crucible fuse (melt) and release forms of oxygen. Oxygen species react with hot graphite to form carbon monoxide (CO) and carbon dioxide (CO_2), then the gases which are detected by a non-dispersive infrared (NDIR) cell. Finally, the target machinability was tested by computer numerical control (CNC) lathing machine.

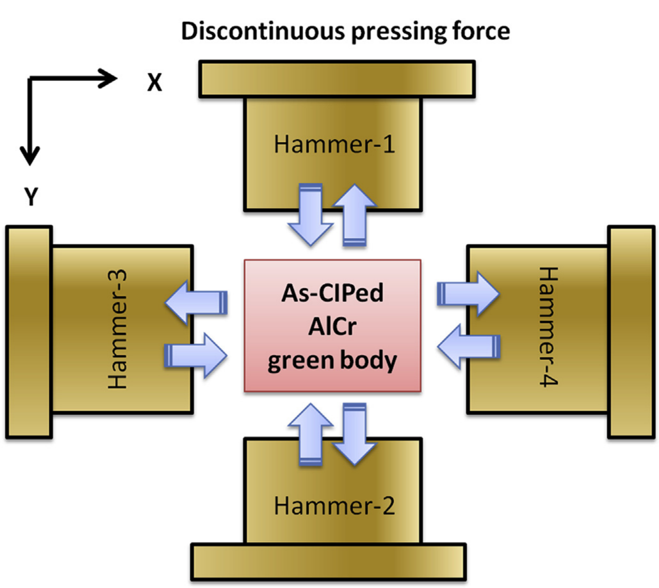

Fig. 1. Illustration of low temperature novel forming (LTNF) process.

Al–Cr–N films were deposited on a silicon substrate using 76 mm-diameter Al–Cr alloy targets produced by various powder metallurgy methods and the distance of target to substrate was set at 90 mm. The chamber was pumped down to a base pressure of 1.0×10^{-3} Pa. Before deposition, Ar gas was first introduced into the vacuum chamber for 30 min of pre-sputtering. The mixed atmosphere Ar + N_2 at the ratio 1:4 were introduced separately into the chamber and the pressure during deposition was 5 Pa. The substrate temperature was held at 300 °C during the whole deposition process. The power applied to the target was set at 300W, and deposition continued for 3 h. In order to objectively compare the performance of sputtering behavior, the chamber and shields were cleaned when changing the target. The accumulated arcing counts, which could reflect the stability of the target during the sputtering process, were recorded by a power supply recorder (HUTTINGER TruPlasma DC3002). Particles on the film surface were examined by SEM and also statistically measured by film surface analysis system with 488 nm laser beam (KLA-Tencor Surfscan 6420). The film compositions were analyzed by energy dispersive spectroscopy (EDS). The hardness of the films was measured by nano-indenter (Hystron T1900).

3. Results and discussion

3.1. Target density

The densities of the Al–Cr alloy targets sintered by hot pressing (HP), hot isostatic pressing (HIP), and low temperature novel forming (LTNF) are shown in Table 1. The theoretical density of an Al–Cr target with an Al:Cr atomic ratio of 70:30 is 3.763 g/cm^3, as calculated from the theoretical densities of Al and Cr. The density of the HP target increased when the process temperature was increased, and a fully-dense target could be obtained at 900 °C. Fully-dense targets could also be produced with the HIP and LTNF methods. In addition, the densities of the targets sintered by HIP and LTNF methods were higher than those of targets produced by HP at the same temperature. The actual densities of the targets sintered by HP-900 °C, HIP-600 °C, and HIP-500 °C were slightly higher than the theoretical density due to the formation of IMC phases during the sintering process. According to the study of Ayako Kimura et al., hot-pressed Al-based alloy targets for

Table 1
Target density and averaged arcing counts during sputtering.

Sample	HP-700 °C	HP-800 °C	HP-900 °C	HIP-600 °C	HIP-500 °C	LTNF-500 °C
Target density (g/cm^3)	3.345	3.491	3.872	3.842	3.788	3.759
Arcing counts (hr^{-1})	23	16	14	7	5	1