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Scripta Materialia 52 (2005) 445–448

Scripta MATERIALIA

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Oxidation behaviors of TiAl(La)N coatings deposited by ion plating

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Received 9 August 2004; received in revised form 1 November 2004; accepted 15 November 2004

Abstract

The effect of Al and La on the oxidation rates of TiAl(La)N coatings were estimated. Addition of not only Al but also La effectively reduced the oxidation rate. In particular, La had acted to induce the preferential formation of dense α-Al_2O_3 on the outer surface oxide.

Keywords: Nitrides; Coatings; Oxidation; Rare earth; Lanthanum

1. Introduction

The hard coatings technology has been widely used as tools and mould for machining and forming metals. In particular, in machining, the hard coatings on high-speed steel and tungsten carbide have improved the life cycle and properties of tools. TiN is a typical wear resistant coating [1]. It was reported that TiN coating was available to 873 K [2]. TiAlN coatings have a higher oxidation resistance compared with TiN in high speed machining of metals [3]. Many studies reported that the good wear resistance was due to the formation of stable protective-Al_2O_3 film on TiAlN coatings [4–6]. Harris et al. suggested that the wear resistance of TiAlN is about four times higher than that of TiN [7]. Recent studies have focused on increasing the Al content in TiAlN coatings as an Al source [6,8,9], which resulted in the problems such as macro-particles, high residual stress and low adhesion [10]. To overcome these problems, a way to reduce oxidation rate without an addition of excessive Al should be found. The major concern of this work is to investigate the effect of Al and La on the oxidation rate and oxide films growth of TiAl(La)N coatings.

2. Experimental

TiN and TiAl(La)N coatings with different Al content were deposited by Ion Plating, equipped with pulsed-arcs. In $Ti_{1-x(-y)}Al_x(La_y)N$, Al content was changed from $x = 0.1$ to $x = 0.44$ and La content was varied as $y = 0$ and $y = 0.02$. Disk-shaped WC-9%Co with 2 mm thick and 20 mmϕ diameter was used for substrates. Before the deposition, the substrates were polished by using diamond-impregnated paste and cleaned in acetone solution. The coatings were deposited on one-side surface of the substrates with process conditions including substrate temperature of 723 K, nitrogen pressure of 1.5 Pa, deposition rate of about 300 nm/min., pulse frequency of 20 kHz and bias voltage of 100 V. The thickness of the coatings was about 2.5 μm. The compositions of the coatings were analyzed by auger electron spectrometry (AES) and the quantitative results were summarized, as shown in Table 1. The oxidation specimens with the coatings area of $0.5 \times 0.5\ cm^2$ were oxidized at 1273 K in vacuum of

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1359-6462/$ - see front matter
doi:10.1016/j.scriptamat.2004.11.013

Table 1
Compositions of TiAl(La)N coatings

Specimens	Compositions
1	$Ti_{0.9}Al_{0.1}N$
2	$Ti_{0.8}Al_{0.2}N$
3	$Ti_{0.56}Al_{0.44}N$
4	$Ti_{0.88}Al_{0.1}La_{0.02}N$
5	$Ti_{0.66}Al_{0.32}La_{0.02}N$

about 7 Pa to avoid a severe oxidation of the exposed WC–Co substrate, leading to the breakaway of TiAl(La)N coatings. The weight gains by the oxidation of the specimen were measured as a function of oxidation time by thermo gravimetry (TG). To calculate the weight gain of the coatings, the weight gain of the WC–Co substrate was subtracted from total weight gain of the specimen. The microstructures and oxide crystal structures of oxidation specimens were investigated by field-emission scanning electron microscope (FE-SEM) equipped with energy dispersive spectrometry (EDS) and X-ray diffraction (XRD) with a target of CuK_{α} respectively. The concentration depth profiles of the coatings oxidized were analyzed by AES.

3. Results and discussion

The purpose of the Al addition is to improve the oxidation and wear resistance. In particular, a small amount of La with Al was added by expectation for refinement of surface oxide and good oxide to the substrates adherence, considering the oxidation resistance effects of La in Fe–Cr–Al alloys [11] and Y in TiAlCrYN coatings [12].

The oxidation was carried out in vacuum of ~7 Pa to avoid the severe oxidation of WC–Co substrate causing a breakaway of the coatings. As shown in Fig. 1, the weight gain changes were similar to parabolic behavior as a function of oxidation time. These experimental data were mathematically curve-fitted to parabolic equation.

$$\Delta W/A = (k_p t)^{1/2}$$

where, ΔW(g), A(cm^2), k_p and t(s) are incremental weight gain, coating area, oxidation parabolic rate constant and oxidation time.

With increasing Al content, the weight gains tended to reduce. In particular, La addition with Al effectively reduced the weight gain. The oxidation results, as shown in Table 2, were expressed as a rate constant by an assumption of parabolic oxidation. The parabolic oxidation rate constant of $Ti_{0.66}Al_{0.32}La_{0.02}N$ was 2.09×10^{-9} (g^2/cm^4 s), which was about 10 times lower than that of TiN and 4.4 times lower than that of $Ti_{0.56}Al_{0.44}N$. According to previous reports, a good wear resistance was due to the formation of a stable protective α-Al_2O_3 film on TiAlN coatings [4–6] and the wear resistance of TiAlN coatings were about 4 times higher than that of TiN [7]. From these results, it was expected that a simultaneous addition of Al and La could be effective to improve a wear resistance.

Fig. 2 shows the parabolic oxidation rate constants with the variation of Al and La content. The oxidation

Table 2
Parabolic oxidation rate constants in TiAl(La)N coatings oxidized at 1273 K

Specimens	Parabolic rate constant (g^2/cm^4 s)
WC–Co(sub.)	3.07959×10^{-8}
TiN	2.16114×10^{-8}
$Ti_{0.9}Al_{0.1}N$	1.59853×10^{-8}
$Ti_{0.8}Al_{0.2}N$	1.12455×10^{-8}
$Ti_{0.56}Al_{0.44}N$	9.21404×10^{-9}
$Ti_{0.88}Al_{0.1}La_{0.02}N$	2.35121×10^{-9}
$Ti_{0.66}Al_{0.32}La_{0.02}N$	2.09377×10^{-9}

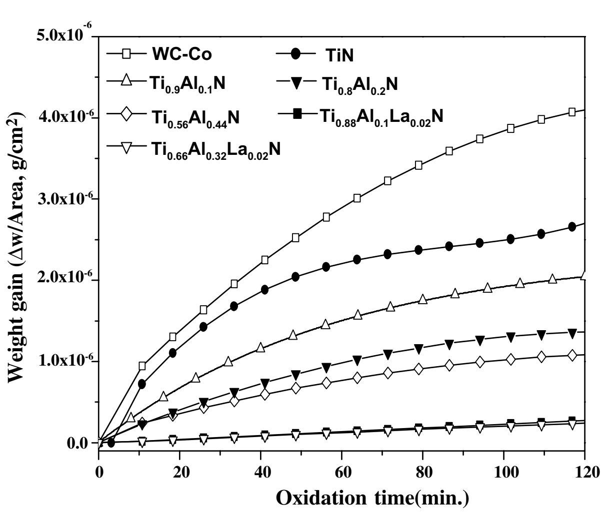

Fig. 1. Effect of oxidation times on the weight changes of TiAl(La)N coatings oxidized at 1273 K.

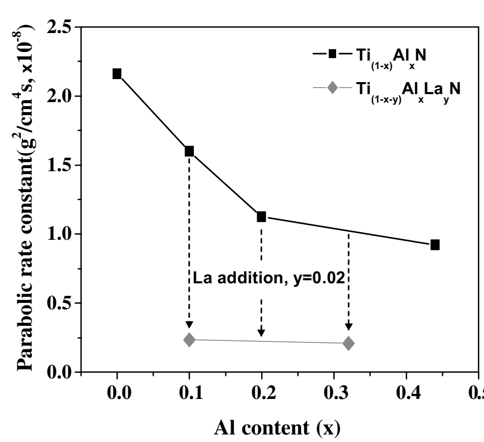

Fig. 2. Effect of Al and La addition on parabolic oxidation rate constants in $Ti_{1-x(-y)}Al_x(La_y)N$ coatings oxidized at 1273 K.