Oxidation resistance of TiN, CrN, TiAlN and CrAlN coatings deposited by lateral rotating cathode arc

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ABSTRACT

In this paper, four kinds of hard coatings, TiN, CrN, TiAlN and CrAlN (with Al/Ti or Al/Cr atomic ratio around 1:1), were deposited on stainless steel substrates by a lateral rotating cathode arc technique. The as-deposited coatings were annealed in ambient atmosphere at different temperatures (500–1000 °C) for 1 h. The evolution of chemical composition, microstructure, and microhardness of these coatings after annealing at different temperatures was systematically analyzed by energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) and nanoindentation experiments. The oxidation behaviour and its influence on overall hardness of these four coatings were compared. It was found that the ternary TiAlN and CrAlN coatings have better oxidation resistance than their binary counterparts, TiN and CrN coatings. The Cr-based coatings (CrN and CrAlN) exhibited evidently better oxidation resistance than the Ti-based coatings (TiN and TiAlN). TiN coating started to oxidize at 500 °C. After annealing at 700 °C no N could be detected by EDX, indicating that the coating was almost fully oxidized. After annealed at 800 °C, the coating completely delaminated from the substrate. TiAlN started to oxidize at 600 °C. It was nearly fully oxidized (with little residual nitrogen detected in the coating by EDX) and partially delaminated at 1000 °C. Both CrN and CrAlN started to oxidize at 700 °C. CrN was almost fully oxidized (with little residual nitrogen detected in the coating by EDX) and partially delaminated at 900 °C. The oxidation rate of the CrAlN coating is quite slow. After annealing at 1000 °C, only about 19 at.% oxygen was detected and the coating showed no delamination. The Ti-based (TiN and TiAlN) coatings were not able to retain their hardness at higher temperatures (≥700 °C). On the other hand, the hardness of CrAlN was stable at a high level between 33 and 35 GPa up to an annealing temperature of 800 °C and still kept at a comparative high value of 18.7 GPa even after annealed at 1000 °C, indicating a very promising applicability of this coating for high speed dry machining and other applications under high temperature environments.

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1. Introduction

Nowadays, thin wear-resistant hard coatings are widely applied on cutting and forming tools to improve their lifetime and performance, enhance productivity, and enable some new engineering applications as well. Hard coating deposition has now become a routing processing step in tools industry. Currently, a wide range of PVD hard coatings are available for a variety of applications. TiN is the first generation of PVD hard coating and is now still being widely used as protective hard coating and is now still being widely used as protective hard coating for bearings, gears, and cutting and forming tools [1–3]. However, the fracture toughness and oxidation resistance of the TiN coatings are not satisfactory for many advanced engineering applications. As one of the major milestones in the advances of hard coating development, TiAlN has been successfully commercialized particularly for high speed machining applications because of its significantly improved oxidation resistance and hardness over TiN [4–8].

Currently, Ti-based coatings, such as TiN and TiAlN, represent state-of-the-art of commercial PVD hard coatings used in tools industry. However, these Ti-based coatings are generally characterized with a high friction coefficient. The oxidation resistance at elevated temperatures of the Ti-based coatings is limited although it has been improved with aluminium incorporation. These drawbacks of the Ti-based coatings have strongly limited their practical applications. For instance, under some high speed dry machining conditions, the temperature at the cutting tool edge may reach well above 800 °C [9]. This fact results in a critical challenge for the Ti-based hard coatings. Most high temperature coatings rely on the formation of a protective oxide scale by interaction with the environment. This scale must fulfil several conditions: be stable, slow growing, dense and adherent. It is well known that in an oxidation or corrosive environment Ti element often forms a porous non-protective oxide scale [10], and therefore the oxidation and corrosion resistance of titanium-based coatings are limited. Nevertheless, it has been demonstrated that the presence of Ti, even out-diffused from the substrate, would perturb the formation of the protective Al2O3 scale at high temperature (>1000 °C) and
consequently affect the coating oxidation resistance. Recently, the new formula of Ti-free PVD coatings have been explored by various research groups worldwide [11–15]. CrN-based multicomponent nitride is a typical example. Particularly, AlCrN is a new generation of tribological hard coating. Similar to TiN, chromium nitride (CrN) has been successfully applied to the metal forming and plastic molding dies and wear components. CrN is known to be superior to TiN in corrosion and wear resistances, friction behavior, and toughness [16–19]. Similar to the TiAlN coating system, the incorporation of Al into the cubic CrN crystalline structure greatly enhances the hardness of the CrAlN coating system [15]. A better abrasive wear resistance, which is believed to be the major wear mechanism in machining and forming applications, of the CrAlN coatings (particularly with higher Al-content) was also reported than the TiAlN machining and forming applications, of the CrAlN coatings (particu-
larly with higher Al-content) was also reported than the TiAlN coatings [20]. Our previous results [15] showed that the tribological properties of CrAlN coatings are much better (with both lower wear rate and friction coefficient) than those of the TiAlN coatings in the sliding wear test. It was also demonstrated that the CrAlN coatings exhibited an evident higher corrosion resistance in a sodium chloride solution [21] and a better cutting performance under high speed machining conditions [15] than the TiAlN coatings. In this work, four kinds of hard coatings, TiN, CrN, TiAlN, and CrAlN (with Al/Ti or Al/Cr atomic ratio around 1:1), were deposited on stainless steel substrates by a lateral rotating cathode arc technique. The oxidation behaviour and its influence on overall hardness of these four coatings were investigated and compared to each other.

2. Experimental

TiN, CrN, TiAlN, and CrAlN coatings, with a thickness of about 3 µm, were deposited by a Platis π60 lateral rotating cathode arc system which has been described in detail previously [15,21]. This system consists of two lateral rotating elemental cathodes, Ti (or Cr) and Al, and a rotating carrousel sample holder. This system has two major advantages over the conventional planar vacuum arc deposition systems. The first advantage comes from the unique lateral cathode rotation, which results in a maximum effective cathode surface and longer cathode lifetime. The second advantage comes from the Virtual Shutter function, which makes it possible for in situ cathode cleaning before coating deposition without plasma interruption. This feature results in superior adhesion strength and smooth surface of the as-deposited coatings.

Coating deposition was carried out in a flowing pure nitrogen atmosphere under a working pressure of 1.5 Pa. A 1:1 atomic ratio of Cr/Al and Ti/Al was achieved for the CrAlN and TiAlN coatings respectively by properly controlling the ratio of the direct current (DC) power applied to the two cathodes. For deposition of the CrN and TiN coatings, only single cathode, Cr or Ti, was employed. Mirror finished stainless steel disks of 50 mm in diameter were used as substrates. Before loading into the deposition chamber, these substrates were ultrasonically cleaned in a series of alkaline solutions. Next, they were washed with deionized water, blown dry by nitrogen gas and further dried in an oven at 100 °C. The pre-cleaned substrates were then mounted on the carrousel substrate holder that rotates at a speed of 12 rpm during deposition. Prior to deposition, the substrates were bombarded by high energy ions to remove any traces of surface contamination and the native oxide layer. During deposition, a negative DC bias of −70 V was applied to the substrates and the deposition temperature was controlled at around 480 °C.

In order to investigate the oxidation resistance of the as-deposited hard coatings, the coating samples were first cut into small pieces with a dimension of about 15×15 mm². The small pieces of samples were annealed at different temperatures (500 °C, 600 °C, 700 °C, 800 °C, 900 °C and 1000 °C) for 1 h in ambient atmosphere using a Vulcan Furnace. The coating samples were naturally cooled down to room temperature in the furnace before moving out for different analysis. After the annealing treatments, the variation of the coatings’ composition, microstructure and microhardness as a function of the annealing temperature was systematically analyzed.

The composition of the as-deposited and annealed coatings was analyzed by energy dispersive X-ray spectroscopy (EDX) that is attached to a scanning electron microscopy (SEM) by using an INCA quantitative analysis software. The EDX analyses were carried out at 20 kV. Titanium, chromium, aluminium, Si₃N₄, and SiO₂ were selected as reference materials for quantitative analyses. 5 points were analyzed for every specimen and the average result was taken. The hardness of the coatings was measured by the Nanotest 550 nanoindenter with a Berkovich diamond indenter (a three-sided pyramid). The hardness of the coatings was calculated from the load-penetration depth curve using the Oliver and Pharr method [22]. The maximum indentation depth was set at 250 nm, which is less than one tenth of the coating thickness, to avoid the influence from the substrates. Eight points were analyzed for each sample and the average hardness and standard deviation were calculated. The coatings’ crystalline structure was analyzed by X-ray diffraction (XRD) using CuKα radiation (with a wavelength of 1.54 Å) in a 2θ/2θ scan mode. The scanning step size and counting time at each step were set at 0.05° and 10 s respectively. The 2θ angle scan range was set from 20° to 60°.

3. Results and discussion

Fig. 1 shows the variation of nitrogen and oxygen content, as determined by the EDX analysis, in the four coatings after annealing at different temperatures. It is evident that the nitrogen content decreases, meanwhile the oxygen content increases, with the increase of annealing temperature for all the four coatings. TiN has the least resistance to oxidation. It started to oxidize even at 500 °C with about 22 at.% oxygen detected. After annealed at 700 °C, no nitrogen could be detected. In our EDX analyses, the penetration depth of the electron beam, operated at an accelerating voltage of 20 kV, into the coating material is estimated to be 2.0–2.5 µm. Therefore, the experimental result indicated that the TiN coating, at least the top layer (>2 µm), was almost fully oxidized at 700 °C. The oxidized coating completely delaminated from the stainless steel substrate at 800 °C. Fig. 2 shows a typical SEM image and the corresponding EDX spectrum of the TiN coating.
coating sample after annealed at 800 °C. The EDX analysis result is Cr\textsubscript{18.8 ± 1.3}Fe\textsubscript{26.7 ± 1.0}Ni\textsubscript{5.4 ± 0.9}O\textsubscript{49.1 ± 2.8}. No Ti and N elements were detected anymore, with only oxygen and some elements from the substrate were detected. TiAlN has an evident better oxidation resistance than TiN. It started to oxidize at 600 °C. The oxygen content in the coating reached about 59 at.% after annealing at 900 °C. It, at least the top layer (>2 μm), was almost fully oxidized (with little residual nitrogen detected in the coating by EDX) and partially delaminated at 1000 °C. The enhancement of oxidation resistance of the TiAlN coating, compared to TiN, is attributed to the incorporation of Al, which forms a dense alumina scale on the coating surface and retards the further oxidation process down to the underneath coating material. Both the CrN and CrAlN coatings started to oxidize at 700 °C. The CrN coating, at least the top layer (>2 μm), was almost fully oxidized (with little residual nitrogen detected in the coating by EDX) and partially delaminated at 900 °C. The CrAlN coating, however, exhibited a much better oxidation resistance. The oxygen content in the CrAlN coating increased very slowly with the increase of annealing temperature. After annealing at 1000 °C, only about 19 at.% oxygen was detected in the coating.

Fig. 3 shows the XRD patterns of the TiN coating after annealed at different temperatures. The as-deposited TiN is well crystallized in a cubic structure with a strong TiN (111) preferential orientation. After annealed at 500 °C, the rutile structure TiO\textsubscript{2} phase could already be detected. After annealing at 800 °C, no any Ti-related phases were detected as the coating has completely delaminated from the substrate. Fig. 4 shows the XRD patterns of the CrN coating after annealed at different temperatures. The as-deposited CrN is also well crystallized in a cubic structure. Chromium oxide phase appeared after annealing at 600 °C. Cr\textsubscript{2}O\textsubscript{3} phase could be detected from 700 °C onwards and became more clear with the increase of annealing temperature. The evolution of the XRD pattern of the TiAlN coating after annealed at different temperatures is shown in Fig. 5. The as-deposited TiAlN coating is also well crystallized in the cubic structure with a significant (111) preferential orientation. A weak Al\textsubscript{2}O\textsubscript{3} (202) peak could be observed after annealing at 600 °C. No other evident oxide peaks could be detected even the annealing temperature was increased up to 900 °C. After annealing at 1000 °C, however, the coating was almost fully oxidized. Apart from the two peaks (at around 2θ = 43.8° and 51.0°) originated from the stainless steel substrate, all the other evident peaks could be assigned to various oxide phases, such as TiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, and AlTiO. Fig. 6 shows the XRD patterns of the CrAlN coating after annealing at different temperatures. Similar to the other three hard coatings, the as-deposited CrAlN is also well crystallized in the cubic structure. From 700 °C onwards, a peak of Cr\textsubscript{2}O (111) could be observed. Only after annealing at 1000 °C, some new oxide (Cr\textsubscript{2}O\textsubscript{3} and CrAlO) peaks appeared. It is important to note that the CrAlN peaks were still very strong, indicating only a small fraction of the CrAlN coating was oxidized, after annealing at 1000 °C. Now, it can be concluded that, among these four hard coatings, TiN has the worst oxidation resistance while CrAlN has the best oxidation resistance.

Fig. 7 shows the variation of hardness of the four hard coatings after annealing at different temperatures. The hardness of the as-deposited TiN coating was about 26.8 GPa. After annealing at 500 °C
and 600 °C, the coating hardness dropped to 23.5 GPa and 14.5 GPa, respectively. Although the oxygen content was over 20 at.% at 500 °C, the hardness did not drop significantly. This shows that the hardness is not greatly affected by the initial amount of oxygen content. It only became substantial when the oxygen content was above 40 at.%, i.e., the annealing temperature was ≥ 600 °C. After annealing at 800 °C, the coating was completely delaminated and the very low hardness was fully contributed from the oxidized substrate surface.

The hardness of the as-deposited CrN coating is about 19.4 GPa which is evidently softer than that of the TiN coating. After annealing at 500 °C, no obvious change in hardness was measured. After annealing at 600 °C and 700 °C, with the intervention of oxidation, the coating hardness decreased significantly. However, with increasing the annealing temperature further from 700 °C to 1000 °C, with the evident emergence of the Cr$_2$O$_3$ phase, the coating hardness recovered gradually. The underline mechanism of this abnormal hardness variation behavior of the CrN coating is still not clear yet. A high hardness up to 30 GPa of PVD Cr$_2$O$_3$ coatings has been reported [23,24]. The increase of the coating hardness after annealing at a temperature of ≥ 800 °C might be attributed to the formation of dense structure Cr$_2$O$_3$ phase.

The hardness of the TiAlN coating remained stable at a high level, similar to its as-deposited state of about 35 GPa, up to 600 °C. However, with further increase of the annealing temperature, this coating softened significantly. After annealing at 700 °C and 800 °C, the hardness dropped to about 22 GPa. As the annealing temperature was increased to 900 °C, the hardness dropped further to 12 GPa. This could be due to the high oxygen content (over 55 at.%) in the coating. The hardness of TiAlN dropped to about 4.34 GPa at 1000 °C which makes it have little use. Hörling et al. [25] once investigated the thermal stability of high Al-content cubic-phase Ti$_{1-x}$Al$_x$N coatings by annealing the coatings in a protective Ar atmosphere. It was reported that the high hardness (~37 GPa) of the as-deposited Ti$_{1-x}$Al$_x$N coatings are retained for annealing temperatures up to 950 °C. These facts indicate that oxidation detrimentally affect the high temperature mechanical properties of the nitride coatings.

It was interesting to note that the CrAlN coating is much more stable than all the other three coatings studied in this work. The high hardness of about 33–35 GPa of the CrAlN coating was maintained up to an annealing temperature of 800 °C. When the annealing temperature was increased to 900 °C, the coating hardness dropped slightly to 27 GPa. After annealing at 1000 °C, the hardness dropped further to 18.7 GPa. Although CrAlN could only maintain about 50% of its original hardness, it was much higher than that of the TiAlN coating after annealing at 1000 °C. The similar high hardness between the Cr-based coatings (CrN and CrAlN) after annealed at 1000 °C might be related to the formation of the dense structure Cr$_2$O$_3$ phase. Up to now, it can be concluded that the CrAlN coating possesses the best oxidation resistance and ability for retaining its high mechanical strength among the four hard coatings studied. These excellent properties might be responsible, at least partially, for the evident better performance of the CrAlN coating over the TiAlN coating for cutting a hardened steel material under high speed dry machining conditions, as observed in our previous work [15]. Recently, Fox-Rabinovich et al. [26] in situ measured the hardness of TiAIN and
CrAlN coatings at different temperatures up to 500 °C by using a nanoindentater with a high temperature stage. They found that the hardness of the CrAlN coating was about 18% lower than that of the TiAlN coating at room temperature, but the CrAlN coating exhibited about 30% higher hardness than the TiAlN coating at 500 °C. This excellent hot hardness had a significant effect on CrAlN coating and TiAlN coating. The CrAlN coating showed a better performance of the AlCrN coating over the TiAlN coating in end-milling the AISI 1040 steel.

From the above experimental results, it was also noted that the oxygen content in the CrN coating after annealing at 500 °C is similar to that in the CrAlN coating after annealing at 1000 °C, i.e., ~20 at.%. After annealing at 500 °C, the hardness of the TiN coating only decreased slightly (~12%) in comparison with its as-deposited state. However, the hardness of the CrAlN coating significantly dropped (~46%) after annealing at 1000 °C. The underline mechanism of this great difference of oxidation effect on the hardness of these two coatings is still not very clear. One possible explanation might be as follows. It is well known that TiN coatings deposited by PVD processes usually grow in a columnar structure [2,6,27]. In the annealing process, oxygen atoms could easily diffuse deep into the coating through the loose-structured grain boundaries which are perpendicular to the coating surface. Initially, the oxidation process would preferentially take place in these vertical grain boundary regions, while the grain parts were only slightly affected. As a consequence, the overall coating hardness was not significantly decreased. In our previous work [28], it was found that a small amount of oxygen incorporation (with the atomic ratio O/N≤0.72) into the TiN nanocomposite coatings does not reduce the hardness of these coatings, which can be ascribed to the formation of a new kind of nanocomposite coatings: C-TiON/a-Si3N4. Similarly, partial of the oxygen atoms in the initial oxidized TiN coating might also exist in a state of solid solution TiON1-X, which would not significantly affect the overall coating hardness. The CrN and CrAlN coatings, however, usually grow in a random oriented non-columnar dense structure [21,27]. The oxidation process on the CrAlN coating might take place much more uniformly over the whole surface area of the coating and gradually progress towards the substrate direction. Therefore, this uniform oxidation behaviour of the CrAlN coating, with the evident formation of oxide phases after annealing at 1000 °C, would be responsible for the significant reduction of the coating hardness.

4. Conclusion

Oxidation behaviour and its influence on overall hardness of four PVD coatings, TiN, CrN, TiAlN and CrAlN were investigated and compared by annealing these coatings up to 1000 °C in ambient atmosphere. With the incorporation of Al, TiAlN and CrAlN coatings showed better oxidation resistance as compared to TiN and CrN. Particularly, the TiN coating was evidently oxidized and soften at 500 °C, and completely delaminated from the substrate at 800 °C. TiAlN coating started to oxidize at 600 °C and its hardness decreased significantly at 700 °C. Its hardness was stable (between 33 and 35 GPa) up to an annealing temperature of 800 °C and still kept at a comparative high value of 18.7 GPa after annealing at 1000 °C. Therefore, CrAlN coating is very promising for high speed dry machine and other high temperature applications.

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