Thermal cycling of AlTiN- and AlTiON-coated hot work tool steels at elevated temperatures

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ABSTRACT

The principle failure mechanism in thixoforming dies is thermal fatigue as the mechanical loading on the tooling is modest owing to a mushy feedstock. X32CrMoV33 hot work tool steel samples coated with AlTiN and AlTiON via Cathodic Arc Physical Vapour Deposition were submitted to thermal cycling under conditions which mimic thixoforming of steels. While the AlTiN and AlTiON coatings provide adequate protection against oxidation of the hot work tool samples, identified to be their major shortcoming in steel thixoforming together with temper softening, they fail to avoid thermal fatigue cracking. This is attributed to the extensive softening of the tool steel substrate and to the thermal expansion mismatch between the hot work tool steel and the nitride and oxy-nitride coatings. An ultra hard coating on a much softer substrate lacks proper substrate support. Thermal stresses, whether tensile or compressive, are detrimental to the stability and the integrity of thin coatings. The situation is aggravated further when the tool steel substrate undergoes plastic deformation encouraged by temper softening with increasing number of thermal cycles. This produces a plastic strain component in addition to the thermal strain imposed on the thin coating generated by the thermal expansion mismatch.

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1. Introduction

While forming in the semi-solid state is a well established near-net shape manufacturing route for magnesium and aluminium alloys [1], it is still the focus of fundamental research for steels [2,3]. The evolution of steel thixoforming into a commercial success depends on the quality of the tools to be used [4]. Cyclic thermal loads in steel thixoforming are substantial [5]. Thermal fatigue, combined with the erosive wear due to abrasion and impact of the solid α-Fe particles in slurries and high temperature oxidation, render the conventional hot work tool steels entirely inadequate [6]. Several replacements with superior performance have been identified in recent years [5,7–12,13]. However, cost considerations favour coating hot work tool steels over employing high temperature alloys for tooling applications. Such coatings must offer thermal and chemical stability as well as adequate resistance to thermal fatigue, oxidation and abrasion by the slurries. Thin hard coatings, employed to reduce friction and wear of tools for cutting, hot- and cold-working and die casting processes could offer a solution [14–16].

Of the several modern thin film coating technologies widely used in tooling industries [17], Physical Vapour Deposition (PVD) is capable of depositing ceramics below the temper softening temperature of tool steels providing superior wear and high temperature resistance and is thus the most attractive [18–20]. Hence, it has received a great deal of attention as the method of choice for surface engineering of forming and cutting tools in recent years [21,22]. However, there have been very few attempts to explore the potential of PVD coatings in thixoforming tools for high temperature alloys [23–27]. The present work was undertaken to investigate the potential of AlTiN and AlTiON coatings deposited on X32CrMoV33 hot work tool steel via Cathodic Arc Physical Vapour Deposition (CAPVD) process under steel thixoforming conditions.

2. Experimental

The substrate was X32CrMoV33 hot work tool steel (Table 1) widely employed in the hot forging of steel parts. X32CrMoV33 samples were machined from the as-received block and were subsequently austenized at 1025 °C for 30 min, quenched in circulating air and finally tempered twice at 625 °C for 2 h yielding a hardness of 47 ± 2 HRC.

A Novatech Model NVT 12 unit was employed for the CAPVD process. CAPVD offers high ionization levels in the plasma and thus leads to a dense coating structure [28]. 99.99 at.% purity Cr and

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Table 1
Chemical composition of the X32CrMoV33 hot work tool steel used in the present work.

C	Si	Mn	Cr	Mo	Ni	Al	Cu	Nb	V	Fe
0.281	0.190	0.200	3.005	2.788	0.221	0.025	0.1651	0.0015	0.413	92.63

67/33 at.% Al–Ti cathodes were used for the deposition of AlTiN and AlTiON coatings on a CrN bond coat on heat-treated and polished tool steel samples. The chamber was evacuated to approximately 10^{-3} Pa before the deposition step. Substrates were heated and ion-etched with chromium ion bombardment by applying bias voltage up to −1000 V for 5 min. The temperature of the substrate samples increased to approximately 500 °C due to IR and plasma heating. Pure chromium was deposited on the substrate first at a bias voltage of −150 V for 1 min to improve the adhesion of hard films. The cathode current was 75 A. High purity (99.999%) nitrogen and oxygen were used for AlTiN and AlTiON coatings, for deposition times of 10 and 50 min at a N_2 pressure of 1 Pa, respectively. AlTiN coating was oxidized for 15 min to transform it into an AlTiON coating.

The coating thickness was measured by a Wirtz-Buehler Calotest ball cratering test unit. Elemental depth profiles of the coatings were checked with a Horiba JobinYvon model Glow Discharge Optical Emission Spectrometer (GD-OES). A Jeol 7000F FEG-SEM scanning electron microscope, equipped with an energy dispersive spectroscopy (EDS) unit, was employed to analyze the chemistry of the coatings. A PANalytical X'pert Pro model glancing angle X-ray diffractometer, with a high resolution ψ goniometer and Cu Kα radiation at an incidence angle of 2°, was employed to identify the phases in the coatings. A Fischerscope H100 model Ultra micro hardness tester was used to measure their hardness. 20 mN was applied in 120 steps every 0.5 s with load and depth sensitivities of 0.2 mN and 0.01 nm, respectively. The average of 20 measurements was reported.

The thermal fatigue test has been previously described [29]. This test involves cyclic heating and cooling of coated prismatic tool steel samples (25 mm × 25 mm × 20 mm) between 450 °C and 750 °C (Fig. 1) [29]. These temperatures were measured to be the minimum and maximum temperatures, the die cavity surface had to endure in steel thixoforming experiments. Only the front face of the samples, which was heated by an oxyacetylene flame, was coated with AlTiN and AlTiON to establish the thermal gradients that prevail across the section of the die during steel thixoforming.

3. Results and discussion

The composition of the AlTiN coating was estimated by EDS to be 53.14 at.% Al, 24.74 at.% N, and 22.11 at.% Ti while that of the AlTiON coating was 39.31 at.% Al, 13.09 at.% Ti, 40.89 at.% O and 6.69 at.% N, giving coatings of the type $Al_{0.53}Ti_{0.22}N_{0.24}$ and $Al_{0.39}Ti_{0.13}O_{0.41}N_{0.07}$, respectively. The Al/(Al+Ti) atomic ratio of 0.67 in the $Ti_{33}Al_{67}$ cathode material was thus increased to 0.71 and to 0.75 in the AlTiN and AlTiON coatings, respectively. The thickness and hardness of the former were measured to be 6.3 μm and 2080 HV while those of the latter were 7.8 μm and 1976 HV. Oxygen in the AlTiON coating evidently played a softening role as reported for other transition metal oxynitride coatings [30–32]. The inner CrN layer in this multi-layer structure serves to improve adhesion of the coatings to the substrate.

The glancing angle X-ray diffraction spectra from the coatings are shown in Fig. 2. The structure of the AlTiN coating is based on the structure of NaCl–TiN with a fraction of the titanium atoms substituted by aluminium atoms [33]. The incorporation of aluminium in the fcc TiN structure effectively enhances the coating thermal stability and hardness [34]. Multiple orientations, mainly of (1 1 1), (2 0 0) and (2 2 0), are revealed. These reflections fall between those of B1 TiN (ICDD Card No.00-038-1420) and B1 AlN

(ICDD Card No.00-025-1495) [35,36]. No evidence for the softer hcp-AlTiN phase is available in the XRD spectra [37]. While the AlTiON coating was shown by the GD-OES depth profile spectra and SEM-EDS data to contain oxygen [32], there is no evidence for titanium oxide and aluminium oxide in the respective XRD pattern. This could be due to the amorphous structure of any oxides that might have formed on the surface as the background deflection at low 2θ values implies. AlTiON coatings are known to maintain the same NaCl structure as the AlTiN coating [35]. The similarity between the XRD patterns of the film deposited under oxygen pressure (AlTiON) and the coating produced without oxygen pressure (AlTiN) is thus not surprising.

Typical thermal cycles at the AlTiN-coated front and the uncoated rear faces of the tool steel samples are illustrated in Fig. 3. The temperature vs time profiles for the AlTiON-coated sample are nearly identical. The coated front face continuously warms up to 750 °C during the heating step and starts to cool as soon as the sample is elevated to the cooling position. The rear face is still warming up as it has to accommodate the heat transfer. After about 15–20 s, the temperatures of the front and rear faces are equalized when the former is cooling in contrast to the rear face which is still warming up. The latter also starts to cool soon after. Both surfaces keep cooling during the rest of the cycle, with temperatures running higher this time at the rear face. It takes only a few seconds for the front face to become warmer than the rear face once the next heating cycle is underway.

The temperature vs time profiles for the coated hot work tool steel show features typical of uncoated tool steel samples [29]. However, the rear face temperature in the coated sample seems to have been slightly displaced in the coated samples implying a barrier effect of the AlTiN and AlTiON coatings on heat transfer. This effect, consistently observed in the coated samples, is believed to be due to the relatively lower thermal conductivity of the PVD coatings. Yet, it is very small as both AlTiN and AlTiON coatings are very thin and becomes apparent only after several hundred cycles. Hence, it might be linked with the formation of Al_2O_3 on the coating with increasing thermal exposure. Several additional reflections in the XRD spectrum of the AlTiN coating after thermal cycling, which could be assigned to the Al_2O_3 phase, seem to support this account.

The magnitude of thermal stresses generated in the coating is dictated by the thermal expansion mismatch between the coating and the substrate, $\Delta\alpha$, and the difference between their temperatures, ΔT. Assuming a balanced biaxial stress state, these stresses can be estimated from [38]:

$$\sigma = \frac{\Delta\alpha\Delta TE}{1-\upsilon} \tag{1}$$

where E and υ are the Young's Modulus and Poisson Ratio of the AlTiN coating, respectively. The Young's Modulus of an AlTiN coating, relatively richer in N ($Al_{0.35}Ti_{0.22}N_{0.43}$) was reported to be 560 ± 40 GPa [39]. That of the present AlTiN coating was thus assumed to be 550 GPa. Poisson Ratio, υ, was taken as 0.25 [40]. The thermal expansion coefficient of the tool steel substrate is reported to be approximately 13×10^{-6} °C^{-1} in the temperature range of interest [29] while that of the AlTiN coating is 9×10^{-6} °C^{-1}. Finally, the ΔT vs t data recorded during thermal cycling (Fig. 4a) was used to estimate the change in thermal stresses generated in the AlTiN coating during a typical thermal cycle (Fig. 4b). The maximum compressive and tensile stresses are approximately 400 MPa in compression and 80 MPa in tension and are nearly identical to