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Residual stresses in thermally cycled CrN coatings on steel

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Abstract

CrN coatings were deposited on polycrystalline ferritic steel substrates at 350°C by magnetron sputtering using Cr targets in Ar + N_2 atmosphere. In order to simulate the thermal fatigue, the samples were repeatedly irradiated using a laser beam of 6mm in diameter. The thermal cycling was performed in the range of 50–650°C with up to 100 000cycles. Subsequently, the structures were characterized using high-energy synchrotron and high-temperature laboratory X-ray diffraction. The structures exhibit complex changes in the morphology and in residual stress state in the heated spot. The annealing results in the relaxation of compressive stresses in the coating and in the formation of high tensile stresses in the steel substrate. This effect decisively depends on the number of applied cycles. The reduction of compressive stress in the coating is caused by the annealing of point defects and by dimensional changes of the substrate due to its plastic deformation in the center of the irradiated spot. The plastic deformation of the substrate is also the probable reason for the ripples observed for samples cycled more than 3000 times. The presented approach allows a complex characterization of thermo-mechanical processes in coating-substrate composites and opens the possibility to understand phenomena related to the thermal fatigue of coated tools.

Keywords: XRD; High temperature; Coating; Thermal fatigue; CrN

1. Introduction

Hard coatings are routinely used to protect working tools from abrasion and corrosion [1,2]. The friction between the coating and the work piece however results in local thermal and mechanical stresses which can negatively influence the tool performance and the lifetime [3]. During services, local temperature gradients with the peak temperatures up to 1000°C were observed in the contact region between the working tool and the work piece [3].

The extreme conditions induce significant changes in intrinsic coating/substrate properties like an annealing of point defects in the coating, a relaxation of residual stresses in the substrate, a formation of high thermal stresses and a plastic deformation in the substrate [4]. For the relaxation of intrinsic stresses in the coatings, the length of the temperature pulses is important since the diffusion controlling the relaxation of point defects is a time-dependent process [5]. The stresses in the thermo-mechanically loaded region are influenced also by the actual thermal stresses depending on the mismatch of substrate and coating coefficients of thermal expansion (CTE) [6].

In the case of interrupted services, temperature pulses in millisecond range can cause cyclic thermo-mechanical loads on the coating/substrate composite resulting in phenomena like coating cracking, delamination, spalling or even vertical cracking across the whole composite [5,7]. Thermal fatigue occurring in cyclically loaded tools can be simulated in laboratory conditions by pulsed laser radiation [5,7]. Laser thermal shock experiments enable to locally heat coated surfaces and simultaneously tune the temperature, pulse shape, pulse duration as well as the number of pulses. Using that approach, degradation effects in (Ti,Al)N coatings prepared using plasma assisted chemical vapour deposition were studied extensively [5,7]. It was observed that cyclic thermal loading results in the annealing of coating point defects, relaxation of

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compressive stresses and subsequent formation of high tensile stresses inducing cracks in the coating. Similarly, formation of cracks and spalling was observed in ZrO_2 thermal barrier coatings after laser cycling [8]. Studies of thermal fatigue were performed also for other types of layers like CrN, CrC and TiAlN whereby especially the conditions connected with the formation of cracks, spalling and buckling were analysed [9]. In all cases, cyclic thermo-mechanical loads induce changes in the residual stresses. The magnitude of those stresses influences decisively morphological changes in the coated samples.

The aim of this paper is to determine *simultaneously* residual stresses in hard coatings and in the underlying steel substrates thermally cycled using pulsed laser radiation. As a model system, CrN deposited on steel was selected and analysed using advanced X-ray diffraction techniques. Residual stresses are characterized (i) *ex-situ* after the thermal treatment as a function of the distance from the spot center and (ii) *in-situ* during independent temperature cycling in a high-temperature chamber. Finally, the results provide a possible explanation for the formation of ripples on the sample surface.

2. Experimental

2.1. Sample preparation

As a substrate for the specimen preparation, sheets of ferritic steel W300 (AISI H11 type) with the thickness of 3mm obtained from the commercial partner Böhler Edelstahl (Kapfenberg, Austria) were used. The substrates were mechanically and electrochemically polished and then coated using magnetron sputtering (Oerlikon Balzers RCS coating system) with a 3µm CrN layer in an Ar + N_2 atmosphere at 350°C using a bias voltage of −80V. According to the technical information provided by the producer, the substrate flow stress was about 700MPa at room temperature and about 450MPa at 650°C.

2.2. Thermal cycling experiments

Thermal cycling of the samples was performed using a diode laser system DL 028Q (provided by the company Rofin, Hamburg, Germany) operating with the wavelength of 940nm and a maximal power of 2800W. The beam diameter was adjusted to 6mm. The sample temperature was monitored using a calibrated pyrometer. The samples were cycled in the temperature range of 50–650°C applying up to 100 000 cycles with the frequency of 1Hz. An example of the temperature changes observed in the irradiated spot is presented in Fig. 1.

For the experiments, two different types of laser treatments differing by the duration of the laser pulse (with the length of 50 and 250ms) in Fig. 1 were used.

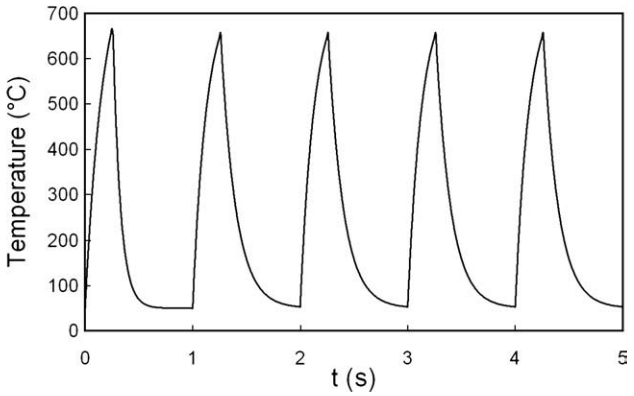

Fig. 1. A time dependence of temperature pulses on the sample surface produced by the laser beam. The duration of the laser pulse is about 250 ms and the frequency is 1 Hz.

2.3. Diffraction measurements

Residual stress characterization was performed at Energy Dispersive Diffraction (EDDI) beamline of BESSY in Berlin, Germany [10,11]. The measurements were carried out with a X-ray white beam of the energy range of 20–100keV. For the data acquisition, a N_2 cooled LEGe detector system from Canberry with a resolution of 160eV at 10keV and 420eV at 100keV was used. The acquisition was performed at a constant 2θ angle of 14° in symmetric $\theta/2\theta$ configuration with a counting time of 60s per one recorded spectrum. The high penetration depth of the synchrotron radiation enabled to obtain a diffraction signal from the coating and also from the substrate in one diffraction spectrum. In this way, it was possible to characterize stresses in both materials *simultaneously* by evaluating CrN (111) and Fe (110) reflections. The correlation between the lattice spacing $d^{T}_{\psi}(hkl)$ and the recorder diffraction line $E(hkl)$ is given by

$$d^{\mathrm{T}}_{\psi}(hkl) = \frac{hc}{2sin\,\theta}\frac{1}{E(hkl)} = \mathrm{const}\frac{1}{E(hkl)} \qquad (1)$$

whereby h is the Planck's constant and c is the velocity of light. From the measured lattice spacing $d^{T}_{\psi}(hkl)$, in-plane isotropic residual stresses in the CrN coating and in the substrate surface region were evaluated using $\sin^2\psi$ method according to

$$d_{\psi}(hkl) = d_0(hkl)\left(1 + \sigma\left[2s_1(hkl) + \frac{1}{2}s_2(hkl)sin^2\psi\right]\right) \qquad (2)$$

whereby $s^{T}_1(hkl)$ and $\frac{1}{2}s^{\mathrm{T}}_2(hkl)$ are the X-ray elastic constants (XECs) of the material. It was supposed that the stresses are in-plane isotropic with $\sigma^{\mathrm{T}} = \sigma^{\mathrm{T}}_{11} = \sigma^{\mathrm{T}}_{22}$. XECs for CrN and ferritic iron were calculated from the single-crystal elastic constants assuming Hill grain-interaction model and using the software ElastiX [12].

Since the beam size was about 500µm, it was possible to characterize the residual stresses across the irradiated spot and to evaluate the stress dependence in the substrate and in the coating as a function of the distance from the spot center.

Additionally, one sample was characterized in laboratory conditions using Seifert PTS 3000 diffractometer. The sample was thermally cycled in the range of 25–650°C using an Anton Paar heating chamber DHS 1100 at constant heating and cooling rates of 0.3°C per second [13,14] in order to monitor the development of stresses in CrN coating as a function of temperature. The measurement was performed on a sample which was not irradiated by laser. In this case the beam size was 6mm in diameter.

3. Results and discussion

In Figs. 2 and 3, a representative optical image of a sample surface after thermal treatment and a scanning electron microscopy (SEM) image in the center of the fatigued spot are presented. The sample was thermally cycled 10 000 times and the procedure resulted in a formation of relatively large surface ripples. This type of behaviour was observed for all samples which were cycled more than 3000 times. There could be two reasons for the formation of ripples namely a buckling of the coating due to high compressive stresses or morphological changes of the substrate induced by its plastic deformation.

In Fig. 4, the distribution of the stresses in the coating and in the substrate across the irradiated spot is presented for a sample thermally loaded 10 000 times. In the virgin region, the coating possesses a stress of about −4GPa, whereby in the center of the spot the stress was reduced to about − 1GPa. However, it is not clear if that reduction was induced by the annealing of point defects in the coating or if there were also dimensional changes in the plastically deformed substrate which contributed to the reduction of thermal stress. In the case of the substrate, the stresses were about − 300MPa in the virgin region and switched to about 300MPa in the irradiated spot.

The changes in the substrate stresses in the irradiated spot can be easily explained as follows. Due to the irradiation, the sample surface is locally heated and the heated material tends to expand. The expansion of the steel in the irradiated spot is however hindered by the surrounding material. Based on this hindrance, compressive residual stresses arise and lead finally to a plastic deformation in the center of the heated spot. When cooling down starts the plastically deformed region contracts. This contraction is however blocked by the surrounding material and tensile stresses arise in the spot (Fig. 4). In addition, different CTE of CrN (6×10^{-6} K^{-1}) and steel (11×10^{-6} K^{-1}) are leading to another thermal stress component. Both the stresses due to the local heat treatment and due to the thermal expansion are contributing to a complex stress distribution in the laser spot. The effects described above are however dependent on the number of cycles as documented in Figs. 5 and 6.

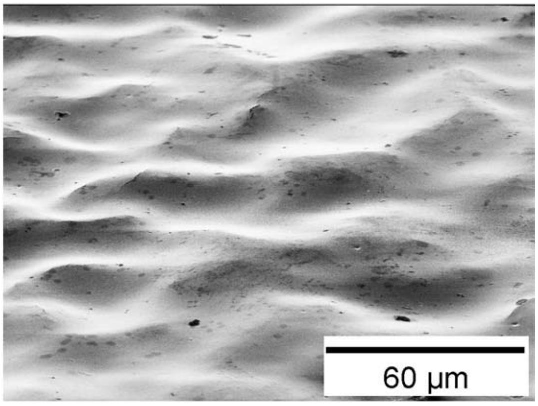

Fig. 3. A SEM image of a sample surface is presented. The sample was 30 000 times thermally cycled in the temperature range of 50–650 °C using a laser beam. The ripples on the surface indicate a plastic deformation in the substrate.

With the increasing number of cycles, the high compressive stresses in the coating decreased continually whereby the duration of the pulse played a very important role. According to Fig. 5, the stress in the coating changed from − 4.0GPa to − 1.8GPa after 100 000 cycles applying pulses with the duration of 250ms. For the samples cycled using pulses of 50ms, the stress reduction was significantly smaller.

In the case of the substrate (Fig. 6), the cyclic thermal loading resulted in a decrease of compressive stresses and a formation of relatively high tensile stresses caused by the plastic deformation at high temperatures. After a certain number of cycles, a maximum of the residual tensile stress can be observed and the tensile stress in the spot center starts to decrease with the increasing number of cycles (Fig. 6). This effect can be

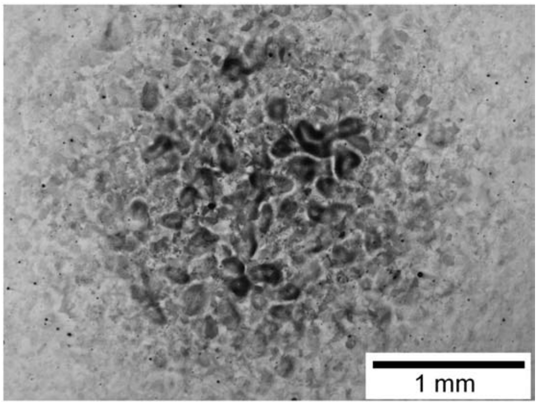

Fig. 2. An optical photograph of a sample surface is presented. The sample was 10 000 times thermally cycled in the temperature range of 50–650 °C using a laser beam. The ripples on the surface indicate a plastic deformation in the substrate.

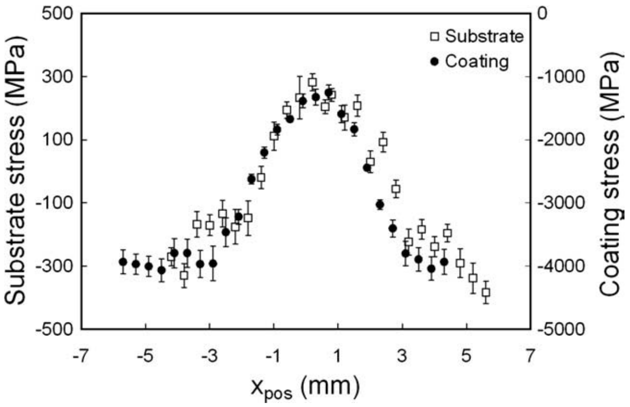

Fig. 4. Results from a position resolved characterization of residual stresses in CrN coating and in the underlying substrate across the irradiated spot. The sample was 10 000 times thermally cycled. The results indicate a relaxation of compressive stresses in the coating and a formation of tensile stresses in the substrate.

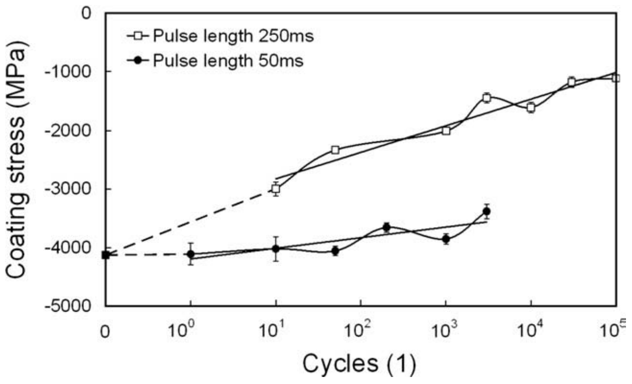

Fig. 5. Residual stress in CrN measured in the center of the irradiated spot. The compressive stress decreases with the increasing number of thermal cycles.

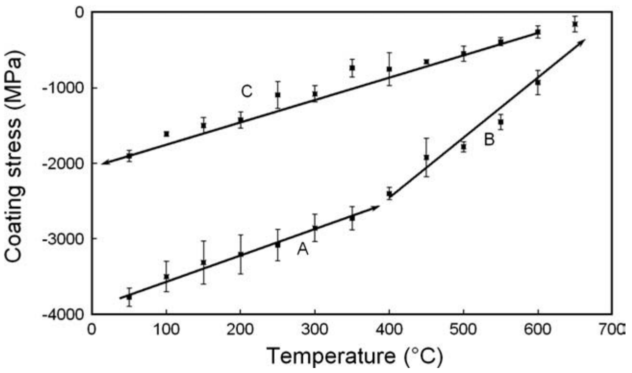

Fig. 7. A temperature dependence of residual stress in CrN coating on steel during one temperature cycle measured *in-situ* in laboratory conditions. The cyclic diffraction experiment took 8 h. Behaviour related to A–C regions is discussed in the text.

explained by a continuous degradation of material properties due to cyclic thermal degradation.

The decrease of the compressive stress in the coating (Fig. 5) can be caused by (i) an annealing of point defects and (ii) by changes in surface morphology of the plastically deformed substrate. Longer pulses of course enhance the annealing of the point defects compared to shorter ones, but annealing of the defects should be finished after reaching a certain cycle number. In order to understand the influence of (i) the point defect annealing and (ii) the changes in the surface morphology on the final stress in the coating, a virgin CrN coating was characterized by *in-situ* high-temperature X-ray diffraction technique in laboratory conditions (Fig. 7).

In the temperature dependence of residual stresses in CrN on steel, one can identify three segments. In the region denoted as A, a compressive stress in CrN decreases thermo-elastically since CTE of CrN is smaller than that of steel [15]. In region B above the deposition temperature of 350°, an annealing of intrinsic stresses caused by the presence of point defects starts. When cooling down, a compressive stress is formed in the coating as a result of CTE mismatch with a final stress relaxation of 2.0 GPa at room temperature. During the second temperature cycle, there was no stress relaxation observed. In other words, there was no stress-temperature hysteresis detected and one can suppose that there were no point defects annealed during the second temperature cycle (Fig. 7).

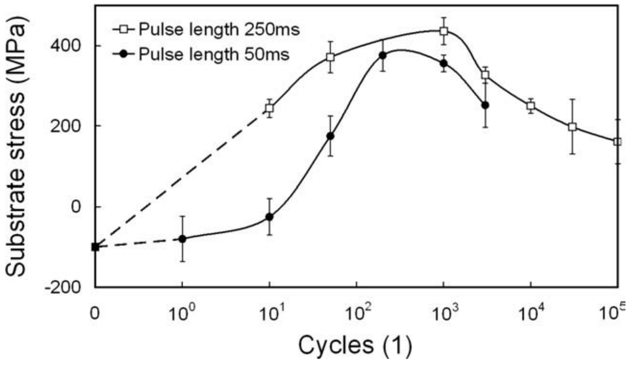

Fig. 6. Residual stress in steel substrates measured in the center of the irradiated spot. The compressive stress switched to tensile and saturated. The results indicate a plastic deformation in the substrate.

It is evident that the experiment in Fig. 7 differs from those performed using laser heating. The main difference resides in the fact that the whole sample is heated and there is no plastic deformation in the substrate due the dimensional constrains. Moreover, since the experiment took a few hours, the diffusion in the coating can take place and contribute to the annealing of point defects with a more extensive reduction of compressive stress. The data in Fig. 7 however document that, even at 650 °C, there is no tensile stress in the ceramic coating on this type of substrate. This demonstrates that in the case of thermal cycling performed in the range of 50–650 °C, the stress in the coating was always compressive.

The stress relaxation mechanism caused by the annealing of point defects cannot be therefore responsible for the whole reduction of the compressive stresses of 3 GPa observed in the coating after 100 000 cycles (Fig. 5). Since the magnitude of the compressive stress decreased with the number of cycles, it cannot be expected that a buckling of the coating causes the formation of the ripples in Fig. 2. One can suppose that the plastic deformation accompanied by the formation of slip bands in the irradiated substrate causes the surface morphological changes (Figs. 2 and 3). Those changes are also contributing to the relaxation of the compressive stresses in the CrN coating. This statement is supported by the fact, that the adhesion of the coating to the substrate was not changed and no spalling was observed after the cyclic experiments.

4. Conclusions

Energy-dispersive XRD was used to characterize temperature dependence of stresses in the CrN coatings on steel. The presented approach demonstrates a unique possibility to characterize simultaneously complex residual stress states in the coating and in the underlying substrate and opens a possibility to understand phenomena related to the thermal fatigue of coated tools. The results reveal complex thermo-mechanical behaviour like annealing of intrinsic stresses in the coatings and plastic deformation in the underlying substrate.

The irreversible changes in the substrate contribute very probably to the formation of ripples observed on the surface and also to the reduction of compressive stresses in the coating.

In the future, it is expected that a detailed analysis of the stresses in the coating and in the substrate will be performed simultaneously at high temperature in order to characterize phenomena contributing primarily to the stress changes in the coating/substrate composite and identify origins of the thermal fatigue in this specific system.

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