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Investigations of rheological properties of nitrided steels using thermodilatometric method with temperature modulation

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Abstract In this work were developed issues concerning the use of thermodilatometric methods for the evaluation of rheological properties of nitrided and non-nitrided steel substrates and systems composed of steel substrate and physical vapour deposition (PVD) coating. Analysis of the rheological properties of these systems (e.g. viscosity, ability to dissipate the energy of deformation or stress relaxation) is essential from the point of view of designing nitrided substrates to the so-called duplex processes: nitriding + PVD, since the viscosity of the substrate affects the fracture toughness of the deposited coatings and their adhesion state. Analysed samples were made of 42CrMo4 steel and had shapes of a cylinder, and the nitrided layer consisted only of diffusion zone and had a thickness of 350 μm. The scope of research included analysis of the effect of thermal loads on rheological properties of the systems using created diagnostic curves (sequences of annealing at 290 °C lasting for 26 h). Experimental measurements of elongation and temperature of the systems were made using thermodilatometric method with temperature modulation. In particular, were analysed the changes in the time shift between the temperature of the sample and its elongation τ—corresponding to viscoelastic properties of the system. Was also determined the relationship between the changes of the introduced equivalent thermal expansion coefficient (corresponding to the thermomechanical interactions in the system) for the tested systems, and the stages of annealing cycles. Basing on obtained results, it was shown that the nitriding of steel substrates significantly enhances their thermal stability as compared to non-nitrided substrates. It was also shown that the nitrided substrate is less susceptible to heat-induced deformations. In addition, the used method enabled the identification of the influence of gas atmosphere in which annealing sequences were carried out, on rheological properties of substrates. In particular, for nitrided and non-nitrided substrates different discontinuity of changes in the α_{AC} and τ parameters as a function of annealing time at the moment of change the gas atmosphere from argon to air was observed.

Keywords Thermodilatometry with temperature modulation · Nitriding · Antiwear PVD coatings

Introduction

Standard practice in the designing of safe aircraft constructions is the assumption that the construction should be resistant to damage at a certain level (damage tolerant design) as well as have a degree of redundancy that will prevent the catastrophe in the case of total dysfunction of any part (fail-safe design) [1–4]. In particular, in cases in which must be considered resistance on the changing impacts, accidental or resulting from the essence of functioning of the specific mechanisms, generally are produced composite surface layers on components exposed to such actions. It is also important to have knowledge about the service life of parts, on which were deposited composite layers, operating additionally at high temperatures [5–11].

The most commonly known and widely used technology of surface treatment which enables manufacturing of composite layers is combination of gas or plasma nitriding process with deposition of hard antiwear coatings via physical vapour deposition (PVD) methods—duplex

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technology [12–15]. The result of such configured technology is a possibility of production composite layer, consisting of nitrided layer and PVD coating formed directly on its surface. The main cause for combination of these processes is to increase load-bearing capacity of a substrate by applying nitriding before deposition of thin (in a range of few microns) hard coating.

Apart from increase of load-bearing capacity of a substrate, one of the possible ways for durability enhancement of discussed composite layers is the formation of a specific state of internal stress. It is well known that practically in all PVD coatings after deposition process, compressive residual stresses are formed [16]. The compressive residual stresses are also formed in the nitrided layers [17]. Thus, it is expected that compressive stresses in the composite layer will be a counterbalance to the formation of tensile stresses in the layer, as in the case of impact tests. However, the residual stresses in the nitrided layer might have also negative effect on the properties of the substrate–coating system. In the study described in [18], was observed the delamination of the single-layer coatings, which was probably caused by the occurrence of residual stresses in nitrided substrate. One can be assumed that in the case of multilayer coatings stresses are reduced because of the presence of the interlayer between the substrate and the coating.

Regardless of the enhancement of load-bearing capacity of the substrate and development of the particular stress state as a result of nitriding process, a question also raises, whether produced nitrided layer will be characterized by further specific viscoelastic (rheological) properties [19]. This is particularly important in cases where the dissipation of deformation energy and relaxation of accompanying stresses is desirable (high ability of crack accommodation). Research shown in this paper was focused on obtaining answer to this question. The only difference is that tests consist in measurement of differences in dilatometric responses of nitrided substrate under sinusoidally changing, non-mechanical, but thermal loads.

In the studies was used a method which is based on the idea of the thermomechanical analysis (TMA) and dynamic mechanical analysis (DMA) methods, i.e. a simultaneous influence on the examined sample of two impacts: temperature and mechanical forces. As a result of a programmed influence of these impacts on the sample, a dilatometric response is obtained [20–22].

Tests were carried out on samples of 42CrMo4 steel, quenched and tempered and gas-nitrided. A present study confirmed that the nitrided steel sample actually shows different rheological properties as a function of temperature and time compared to non-nitrided samples. In addition, studies of nitrided (non-nitrided) substrate–PVD coating systems clearly show that a nitrided substrate–PVD coating system is characterized by improved thermal stability.

Experimental

The studies were made using a dilatometer [22] that allows simultaneous measurement of elongation of the substrate and its temperature as a function of time, for given thermal loads. Tests were carried out on samples made of 42CrMo4 steel (nitrided and non-nitrided) of cylindrical shape with diameter and length 3 and 30 mm, respectively. Measurement of changes in linear elongation of the sample was performed using inductive linear displacement sensor (linear variable differential transformer). This sensor manufactured by TESA is characterized by high resolution of measurements equal to 0.01 μm. To avoid the negative effects of heat on sensors operational conditions, they are placed outside the measuring head. Elongation of the sample is transferred to the tip of the sensor through the quartz pushrod staying in contact with the front of the sample. Measurements of the samples temperatures were performed using a Pt–Pt/Rh thermocouple sensor with resolution 0.1 °C. Disc of this sensor is placed between the face of the sample and the tip of the pushrod. For the evaluation of the dilatometric responses of substrates under sinusoidally changing thermal loads (correlated with rheological properties), curve (Fig. 1) was postulated, according to which isothermal annealing processes were carried out.

Each heating cycle consisted of four identical sequences (Fig. 1). For each sequence was carried out annealing processes of specimens at 290 °C lasting 26 h. Identification of changes in the rheological properties of the sample during isothermal annealing was carried out through the use of simultaneous sinusoidal temperature changes of the heating device with amplitude $A_{Ts} = 10$ °C and 9 min of period. The amplitude A_{Ts} was determined on the basis of calibration tests in which the influence of the A_{Ts} on the dilatometric response of the system was investigated. The value of A_{Ts} was chosen to be 10 °C because for this amplitude the dilatometric response of the sample was still linear and the samples were homogenously heated in their

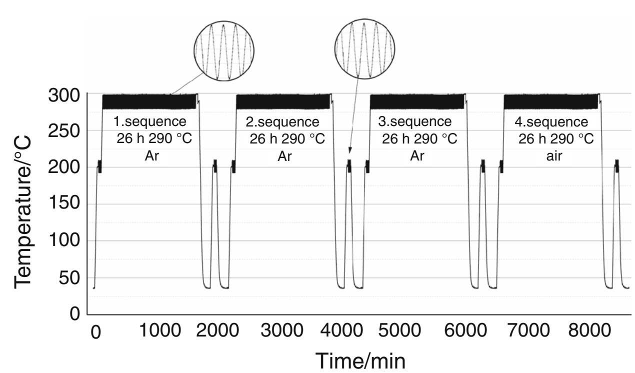

Fig. 1 Diagnostic curve

volume. Moreover, the value of period of temperature changes was chosen on the basis of extensive laboratory tests described in detail in [22]. The aim of the measurements was to determine with the use of the measuring method of "lock-in" type, the time evolution of the amplitude of the sample temperature A_T and its dilatometric response A_L and to determine the time delay τ between these signals (Fig. 2).

For quantitative characterization of changes in the rheological properties of the tested substrates, measurements of equivalent thermal expansion coefficient $\alpha(f)_{AC}$ (value of phasor) were carried out with modulation frequency f. The value of $\alpha(f)_{AC}$ was calculated using formula [22–25]:

$$\alpha(f)_{AC} = \frac{1}{L_{0T}} \cdot \frac{\langle A_L \rangle}{\langle A_T \rangle} \quad (1)$$

where $\langle A_T \rangle$ *i* $\langle A_L \rangle$ are the average values of the amplitudes, respectively, of sinusoidal temperature changes of the samples and their dilatometric responses (elongation), and L_{0T} is the initial length of the sample at the measurement temperature T_{mea}. Further, in the article it will be used instead of $\alpha(f)_{AC}$ simply α_{AC}. The second indicator used in the assessment of changes in rheological properties is ΔL_S, whose value corresponds to the difference in length of the substrate after annealing in each sequence relative to the length prior to annealing.

Nitrided layer have different thermomechanical properties in comparison with steel core. Cyclic thermal loads induce, for example, changes in residual stresses evoked by change in the nitrogen concentration profile and the change in distribution on nitrides of alloying elements. The annealing process in each sequence preceded and closed the measurement of α_{AC} coefficients at 200 °C. Relative changes in values of α_{AC}, as a result of the annealing, are a measure of the thermal stability of the sample [22].

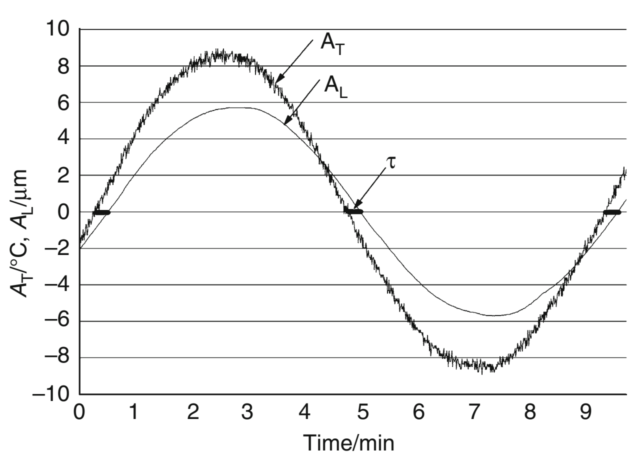

Fig. 2 Sample time courses of amplitudes of elongation A_L and temperature of the sample A_T with marked time delay τ

$$\Delta\alpha_{AC} = \frac{\Delta\alpha_{AC_{aa}} - \Delta\alpha_{AC_{ac}}}{\Delta\alpha_{AC_{ac}}} \cdot 100\% \quad (2)$$

where $\Delta\alpha_{AC_{aa}} = \alpha_{AC_{aa}} - \alpha_{AC_S}$, $\Delta\alpha_{AC_{ac}} = \alpha_{AC_{ac}} - \alpha_{AC_S}$, and α_{AC_S} is value of coefficient for substrate of 42CrMo4 steel after quenching and tempering, $\alpha_{AC_{ac}}$ value of coefficient for substrate of 42CrMo4 steel after nitriding and/or deposition of coating, $\alpha_{AC_{aa}}$ value of coefficient for substrate after given annealing sequence. In a quantitative way the thermal stability is determined on the basis of changes in the equivalent coefficient of thermal expansion after subsequent annealing stages. Namely, the high value of $\Delta\alpha_{AC}$ indicates changes in the energy state of the substrate and coating (e.g. stress relaxation, defects migration, cracks evolution), which leads to changes in the thermomechanical properties of system. Therefore, high thermal stability corresponds to low values of $\Delta\alpha_{AC}$; in particular, for $\Delta\alpha_{AC}$ close to 0 one can observe no change in thermomechanical properties. This publication presents the results of measurements of two types of samples: 42CrMo4 steel after quenching and tempering and samples identically prepared and then subjected to gas nitriding process. Nitriding of specimens was performed in a laboratory vertical quartz tube furnace, with an attached water tank (for quenching). The nitriding temperature of 540 °C was controlled within ±1 °C at the position of the samples. The nitriding atmosphere was composed of ammonia (99.9 vol.% pure) and hydrogen gas (99.999 vol.% pure). Nitriding process parameters were selected so as to obtain a nitrided layer consisting only of the diffusion zone. Effective thickness g_{400} (the distance from the surface to a place with a hardness of 400 HV) of nitrided layer was 350 µm (Fig. 3). More details concerning nitriding process are presented in [26, 27].

In order to obtain information about the influence of type of gas atmosphere on activation of the processes occurring in the nitrided layer as a function of temperature, first three sequences of measurements were performed by

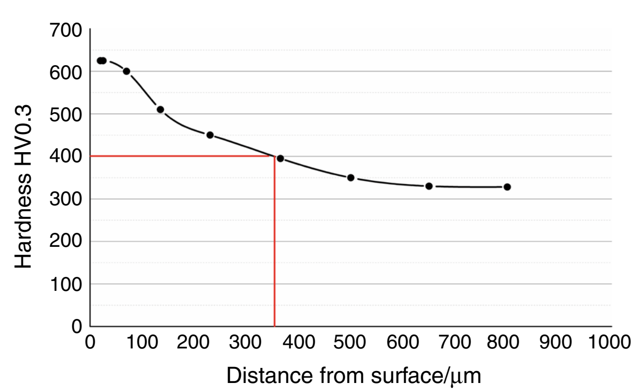

Fig. 3 Microhardness profile in diffusion zone of nitrided layer. Steel: 42CrMo4 [20]

placing the sample in an atmosphere of argon, and the fourth sequence was carried out when the sample was placed in an air atmosphere.

Results and discussion

In Figs. 4 and 5 is shown an example summary of courses of values of α_{AC} coefficients and time delays τ, respectively, that document the differences in rheological properties between the nitrided and non-nitrided sample as a function of time of isothermal annealing, at a temperature $T_{mea} = 290$ °C.

Basing on the presented time courses of α_{AC} and τ (Figs. 4 and 5), a direct coincidence between a character of changes of these variables, i.e. with increasing α_{AC}, and a decrement of the value of τ is observed. This fact is consistent with the more general statement that there is a correlation between the value of τ and the value α_{AC}. Namely, change of the time shift τ affects the value α_{AC}, because τ is related to the angle formed by the phasor α_{AC} with a vector component for a system without time shift τ (a system having purely elastic properties). It should also be noted that there are significant differences in values of α_{AC} and τ depending on the gas atmosphere, in which annealing was performed. In both cases of the samples, discontinuous changes in the value of these parameters are present, and the nitrided sample has a significantly lower step change of these parameters with respect to non-nitrided sample (Figs. 4 and 5). The summary results confirm that the nitrided sample is characterized by a significantly higher thermal stability as compared to the non-nitrided sample.

Figure 6 shows, in turn, results of registration at ambient temperature, a relative change of the ΔL_s indicator, after subsequent sequences of annealing of nitrided and non-nitrided samples. The results prove that the nitrided sample, which has a higher elasticity as compared to the non-nitrided sample, exhibits significantly higher thermal stability. Given the fact that these substrates will be used in the processes of duplex type (nitriding + PVD coating deposition), a key aspect is also to investigate the influence of substrate nitriding for thermal stability of substrate–PVD coating systems. Changes in the value of $\Delta\alpha_{AC}$ after subsequent annealing sequences on the example of the system substrate–CrCN coating with a thickness of 4 μm (Figs. 7 and 8) confirm the beneficial effect of substrate nitriding on thermal stability of a substrate–coating system.

Taking as a criterion for assessment of thermal stability, relative values of increments of α_{AC} coefficients designated at 200 °C after subsequent annealing sequences [21, 28, 29] show that the coatings deposited on the nitrided steel substrates had significantly higher thermal stability compared to coatings deposited on a non-nitrided substrate.

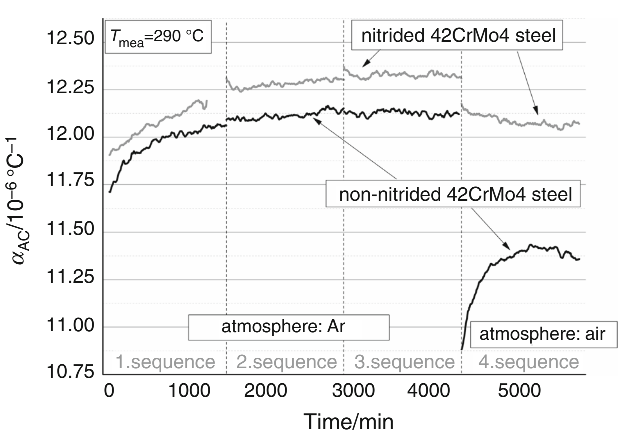

Fig. 4 Time courses of values of α_{AC} coefficients for nitrided and non-nitrided substrates

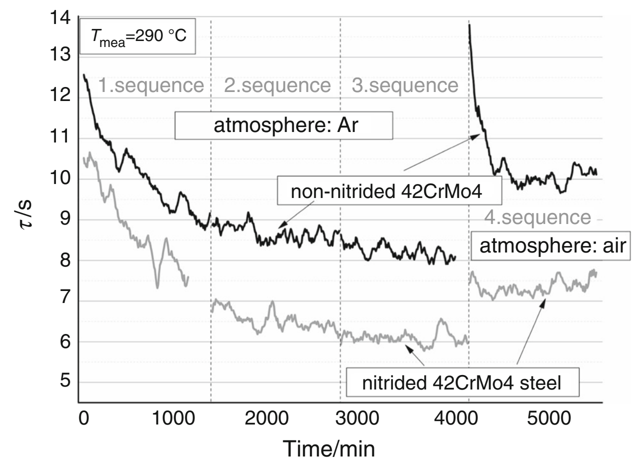

Fig. 5 Dependence of the value of time delay τ as a function of annealing time for the nitrided and non-nitrided substrate

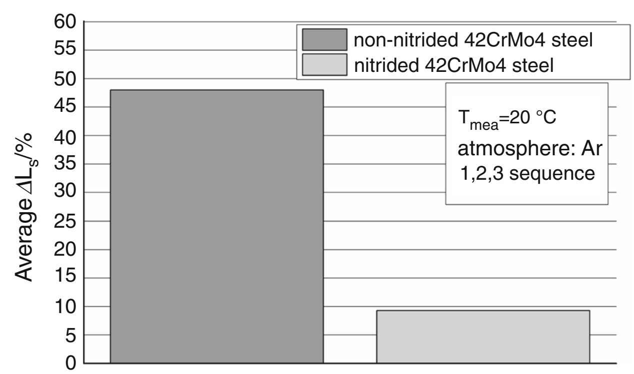

Fig. 6 Summary of average changes of linear expansion ΔL_s of nitrided and non-nitrided samples after annealing processes according to the curve in Fig. 1

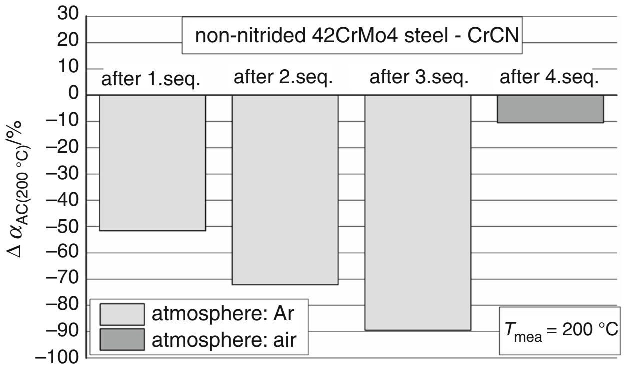

Fig. 7 Summary of results of changes of $\Delta\alpha_{AC}$ after subsequent sequences of annealings, for non-nitrided substrate–CrCN coating system

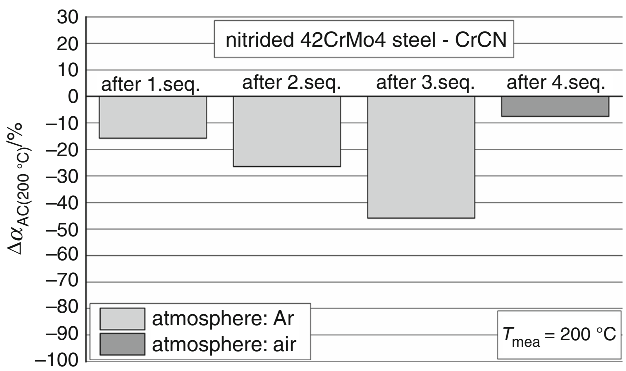

Fig. 8 Summary of results of changes of $\Delta\alpha_{AC}$ after subsequent sequences of annealings, for nitrided substrate–CrCN coating system

Conclusions

Objects of study were samples of 42CrMo4 steel, nitrided and non-nitrided. It was shown that the nitriding of steel substrates significantly enhances their thermal stability as compared to non-nitrided substrates. It was further found that the nitrided substrate is characterized by smaller changes in the ΔL_S indicator—correlated with changes in stiffness and internal stress, relative to the non-nitrided substrate. This means that the nitrided substrates are less susceptible to heat-induced deformations. In addition, results obtained using presented method (MT TMA) enabled the identification of the influence of gas atmosphere in which annealing sequences were carried out, on rheological properties of substrates. In particular, there was a discontinuity of changes in the α_{AC} and τ parameters as a function of annealing time at the moment of change the gas atmosphere from argon to air. Values of step change of these parameters for the nitrided sample were significantly lower compared to the non-nitrided sample (Figs. 4 and 5). This reflects directly in increment of service life of nitrided tools and machine parts. Nitrided substrates also provide improvement of thermal stability of substrate–CrCN coating systems, because changes of $\Delta\alpha_{AC}$ after subsequent sequences of annealings (Figs. 7 and 8) were lower compared to systems with non-nitrided substrates.

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