Recent progress in advanced plasma-assisted thermochemical treatments of steels

S. M. Jafarpour A. Dalke, H. Biermann

In plasma-assisted thermochemical treatments of steels, reliable and precise control of the generated treatment-relevant gas species and consequently the resulting material response, requires decoupling of the components heating from the species generation. This paper features recent developments in modified reactor configurations for both hot and cold wall technologies as well as in the real-time monitoring of discharge compositions using a compact laser-based absorption sensor during plasma nitrocarburizing. A combination of a plasma-activated carbon electrode inside a hot wall reactor with a compact LAS sensor for in-line evaluation of discharge composition, allows achieving a full control of the species generation and the resulting material response.

KEYWORDS: THERMOCHEMICAL SURFACE TREATMENT, PLASMA NITROCARBURIZING, EXPANDED AUSTENITE

INTRODUCTION

As a representative of stainless steel, AISI 316L is widely used in chemical facilities, food industries, medical equipment, stents, etc. Such diverse applications are attributed mainly to the outstanding corrosion resistance resulting from the passive film formed on the steel surface [1,2]. However, modification of the surface properties of AISI 316L is required to improve the surface hardness, tribological properties, fatigue resistance, and resistance to the localized corrosion in specific environments. These properties can be significantly improved by thermochemical surface treatment, in which nitrogen (N) and/or carbon (C) diffuse into the austenitic crystal lattice at elevated temperatures [3]. Thus, improved surface properties can be achieved by enriching the near-surface region by interstitial N and/or C atoms to develop an apparently homogeneous solid solution in the austenite crystal lattice, the so-called expanded austenite or S-phase [4–6]. As a result of expanded austenite formation, the surface hardness, mechanical properties as well as wear resistance of AISI 316L significantly increase without compromising its high general corrosion resistance [5,7,8]. It is worth to mention that in order to perform an effective thermochemical diffusion treatment of AISI 316L, an activation of the surface is required to remove

S. M. Jafarpour,
A. Dalke,
H. Biermann
Institute of Materials Engineering,
Technische Universität Bergakademie Freiberg,
Germany - Center for Efficient High Temperature
Processes and Materials Conversion (ZeHS),
Technische Universität Bergakademie Freiberg, Germany

saeed.jafarpour@iwt.tu-freiberg.de

the passive oxide film prior and/or during the treatment [9,10]. In addition, during thermochemical diffusion treatment of AISI 316L at relatively high temperature and/or long duration, the kinetics of chromium nitrides and/or carbides precipitations are accelerated and consequently, chromium nitride and/or carbide may precipitate [11,12]. As long as the precipitation of chromium nitrides and/or carbides is a diffusion-controlled process, it can be suppressed by a sufficiently low temperature and/or short duration, according to the temperature-time (T-t) threshold curve of the treated steel, thus, the good corrosion resistance is maintained [13,14].

Different plasma-assisted thermochemical treatments such as plasma nitriding (PN) [15], plasma carburizing (PC) [14], and plasma nitrocarburizing (PNC) [16] were realized by introducing feed gas compositions of H_2:N_2, H_2:CH_4 or H_2:N_2:CH_4, into the plasma-enhanced treatment atmosphere, respectively. In addition, depending on the way of the reactor heating, treatments can be performed either in a cold wall reactor or in a hot wall reactor [17]. Generally, plasma-assisted treatment in a conventional cold-wall reactor unavoidably causes issues such as overheating in components with different area/volume ratio, arcing, edge effect, hollow cathode effect and high energy consumption due to the high plasma power required to heat the components to the desired treatment temperature [18]. In addition, only a minor fraction of the applied plasma power (about 10-20%) is required to activate the chemical reactions and generate reactive gas species, while most of the plasma energy (about 80-90%) is dissipated in the form of heat to increase the temperature and adjust the required treatment temperature [17,19]. Therefore, during plasma-assisted treatments in conventional cold-wall reactors, the electrical plasma parameters for heating and for generating reactive gas species are directly coupled and cannot be controlled separately resulting in a weak control of the generated treatment-relevant species and consequently a limited response of the treated material. This issue is less significant for treatments in a conventional hot-wall reactor where the heating of the components to the target temperature is performed mainly by the heating elements at the wall. However, even in this case, it is still not possible to fully decouple the heating and species generation in order to get a precise control of the material response [17]. Besides, in both reactor types, during plasma-assisted thermochemical diffusion treatments, in particular PNC, different treatment-relevant reactive species such as HCN, NH_3, CH_4 can be produced where the HCN is considered as a most crucial product due to its dual application [20]. On the one hand, HCN can de-passivate the AISI 316L surface by gas-surface reactions, and on the other hand, it can act as a source for providing diffusible N and C atoms [21,22]. Thus, it is crucial important to have knowledge about the resulting discharge composition inside the treatment zone with respect to the generated reactive species during each type of treatment (PN, PC and PNC) as well as their corresponding concentrations. This can be done by utilizing plasma diagnostic techniques, in which laser-based absorption spectroscopy (LAS) shows great potentials for in-situ monitoring of the resulting discharge compositions and evaluation of absolute concentrations of generated species with high spectral resolution [23].

In order to overcome the aforementioned issue occurring during plasma-assisted treatment in a conventional cold wall, i.e. heating and species generation are coupled together, modification with respect to the reactor configuration is required. Georges patented the use of an active screen (AS) technology for plasma nitriding (ASPN) in 1999 [24,25]. He showed that by utilizing a plasma-activated metal mesh screen, i.e. active screen (AS) initially made of steel (steel-AS), in a conventional cold wall reactor, the high plasma power is relocated from the workload table to the steel-AS which can significantly reduce the negative issues in connection with the high plasma power at the treated samples [25]. Several years later in 2017, further modification in reactor configuration was made in the authors' laboratory by utilizing an AS made of carbon fiber-reinforced carbon (CFC) instead of a steel-AS for PNC inside an industrial-scale conventional cold wall reactor (Fig. 1a) [26]. PNC treatment utilizing an AS made of CFC (CFC-AS) in a cold wall reactor eliminates the issues of high plasma power at the treated steels similar to the treatment with steel-AS, but also additionally produces the required carbon-containing species, i.e. HCN, by the chemical sputtering of CFC-AS with N_2-H_2

plasma [27,28]. However, during treatment with CFC-AS, a weak plasma power can be applied at the samples, i.e. P_{Bias}, which enables surface cleaning and activation as well as acting as a new treatment parameter to control and adjust the resulting material response [29].

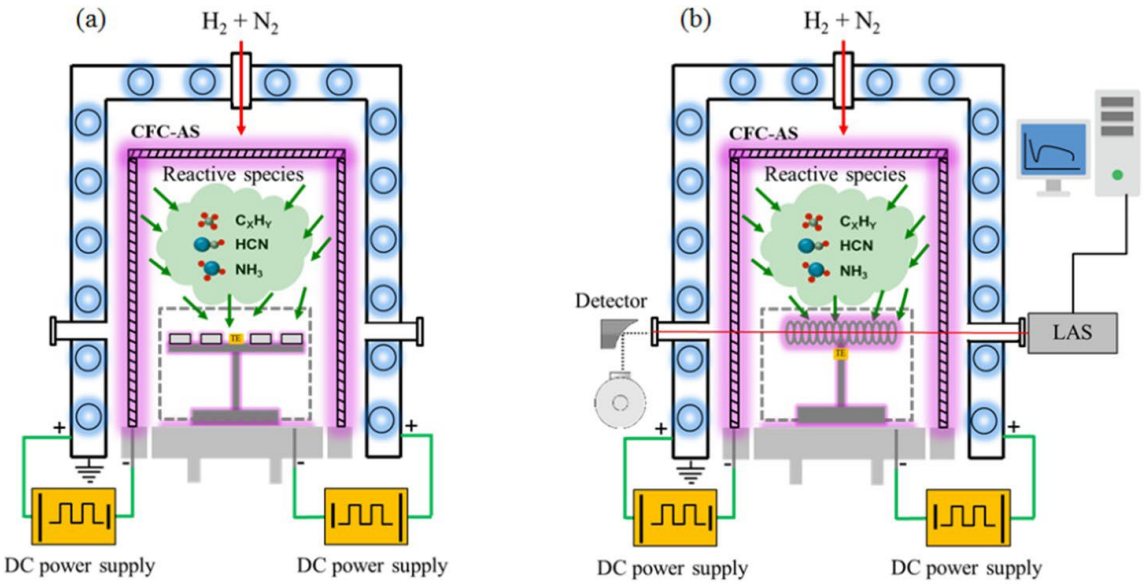

Fig.1 - Schematic drawings of (a) the material treatment setup in a cold wall reactor using a CFC-AS and the workload table, and (b) laboratory scale LAS setup in a cold wall reactor consisting of laser sources (LAS), detector, monitoring panel and model probe. The grey dashes indicate the active treatment zone which (a) surrounds the treated steels and (b) surrounds the model probe.

Reliable and precise control of the generated treatment-relevant species and consequently the resulting material response requires (i) modified reactor configuration aiming to decouple the crucial treatment parameters, and (ii) monitoring discharge compositions to get real-time information regarding the type and the concentration of generated treatment-relevant species. Therefore, this study addresses the recent developments and progress in plasma-assisted treatments with respect to the aforementioned aspects in both hot wall and cold wall reactors aiming reliable control of the generated species and the resulting material response under industrial conditions.

EXPERIMENTAL DETAILS

Commercial steel grade of AISI 316L (chemical composition in wt.%: C0.03, Cr16.9, Ni10.3, Mo2.19, Mn1.72, Si0.28 and Fe balance) was used in this work. Disc-shaped samples of 20 mm diameter and 5 mm thickness were machined from a cylindrical bar. All samples were mechanically ground with SiC paper down to 800 grade, cleaned with ethanol in an ultrasonic bath and dried in hot air prior to the treatments. A first set of PNC treatments was carried out in an industrial-scale cold wall reactor with a CFC-AS (effective surface area of 4.5 m^2) similar to the reactor configuration which was used in our previous publications [30]. The effect of different plasma powers applied at the treated samples, i.e. bias plasma power; P_{Bias}, of 0, 0.6 and 1.25 kW corresponding to the AS plasma power; P_{AS}, of 6.6, 5.4 and 4.6 kW, respectively, were investigated during PNC of AISI 316L samples treated with the treatment parameters of N_2:H_2= 1:1, p= 3 mbar, Φ= 80 slh, T= 460 °C and t= 5 h (Fig. 1a). In addition, laboratory scale LAS was applied in separate experiments but under comparable conditions to the material treatments. Here, the major part of the LAS diagnostic path was aligned through the active treatment zone inside the reactor during ASPNC (Fig. 1b). Spectroscopic lines of HCN

and NH3 were recorded and their concentrations were evaluated [23,31]. A second set of PNC treatments were carried out using an industrial scale hot wall reactor with a plasma-activated carbon electrode inside the reactor. First, the effect of different voltages applied at the carbon electrode; $U_{Carbon\ electrode}$, (effective surface area of 0.3 m^2) ranging from 410 V to 480 V on the concentration of HCN produced was investigated using the treatment parameters N_2:H_2= 1:1, p= 2.5 mbar, Φ= 100 slh, P_{Bias}= 1.5 kW and T= 440 °C. At the same time, a compact LAS sensor was integrated at the reactor (Fig. 3) in such a way that the measured transmission spectra can be evaluated during the treatment by comparing data with the HITRAN database allowing quick and precise measurements of the discharge composition (Fig. 4a) [32]. Finally, an exemplary results of a PNC treatment of AISI 316L was conducted using a selected voltage of 420 V at the carbon electrode for the duration of 2 hours under the described treatment conditions. The author's aim is to highlight the potential advantages of each modified reactor configuration for hot and cold wall technologies. Exemplary results are shown for each of these technology variants using plasma nitrocarburized AISI 316L. For metallographic analysis, cross-sections were mechanically polished and chemically etched (Beraha II etchant) to light optically assess the thickness of the expanded austenite layers. Concentration-depth profiles of N and C were measured by glow discharge optical emission spectroscopy (GDOES). Surface hardness measurement was performed by Vickers hardness indentation applying a load of 0.4903 N ($HV_{0.05}$), cf. Fig. 2 and 4.

RESULTS

Cold wall reactor with an active screen made of solid carbon

Fig. 2a-f shows the results of the ASPNC AISI 316L samples treated under three different settings for the P_{Bias} of 0, 0.6 and 1.25 kW while the result of LAS measurements is presented in Fig. 2g. The LAS results reveal that with increasing P_{Bias}, there was a slight increase in NH3 concentration and a slight decrease in HCN concentration. In case of HCN, its variation can be explained due to the lower plasma power at the CFC-AS (P_{AS}= 4.6 kW) in case of treatment with P_{Bias}= 1.25 kW and consequently lower HCN production as compared to the treatment with P_{Bias}= 0 kW (P_{AS}= 6.6 kW). However, the overall molecular concentration of HCN was high enough, around 1.9 x 10^{15} cm^{-3}, for all three bias conditions investigated to effectively activate the surface of AISI 316L and provide the surface with sufficient diffusible N and C atoms. Thus, roughly similar values for the total thicknesses of the generated expanded austenite layers of around 17 µm were achieved for the three investigated cases (Fig. 2a-c and e). In addition, by utilizing different settings of P_{Bias}, it is possible to adjust the thicknesses of N- and C-expanded austenite (γ_N and γ_C) layers (Fig. 2a-c and e) as well as the content of dissolved N and C atoms in the austenite crystal lattice (Fig. 2d). As a result, different values for the surface hardness of the PNC AISI 316L were achieved depending on the applied bias conditions (Fig. 2f). It is worth to mention here that although PNC treatment with CFC-AS in a cold wall reactor enables tuning the material response by bias plasma power management as it was shown here, there is still a lack of reliable control of the concentration of the generated treatment-relevant species. In fact, during ASPNC treatments with CFC-AS, species concentrations, in particular HCN, is a function of the AS plasma power which is regulated according to the desired treatment temperature. Due to this dependency, the concentrations of the species cannot be independently controlled, leading to high species concentrations and consequently to oversaturation of the treatment environment.

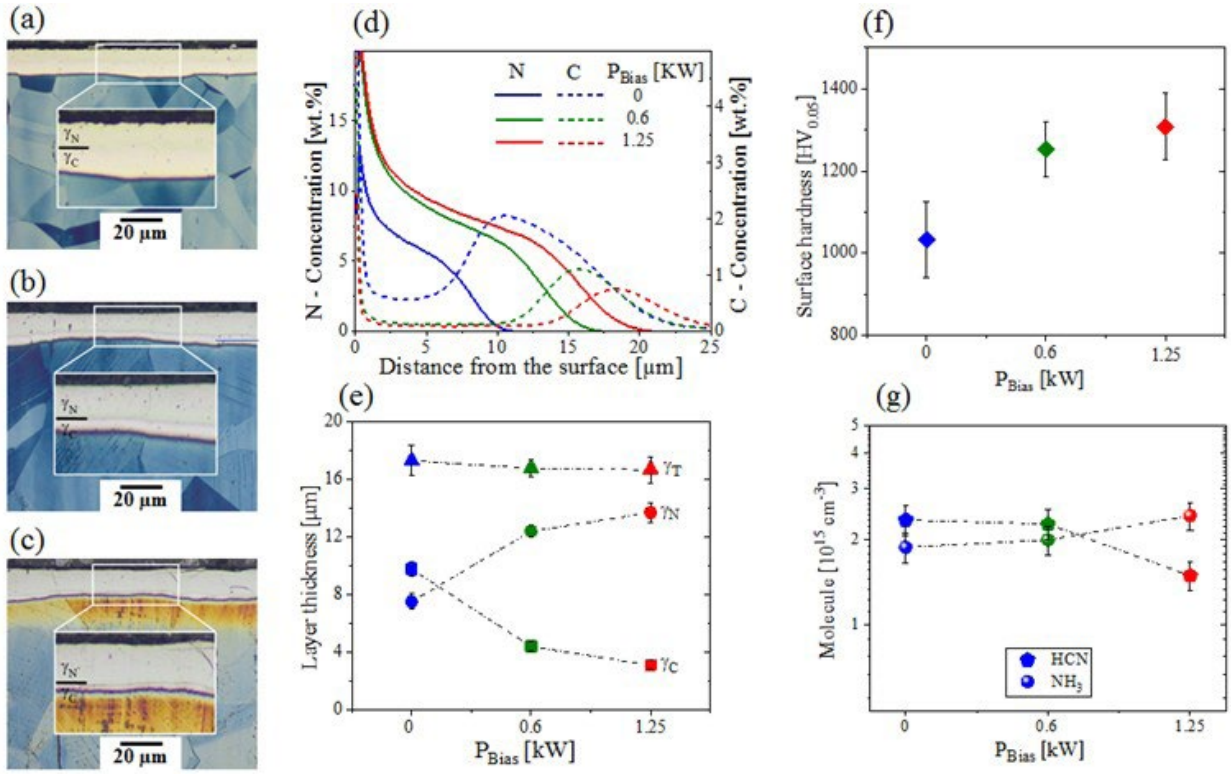

Fig.2 - Cross-sectional light optical microscopy images (a-c), the resulting concentration-depth profiles (in wt.%) of N and C (d), the expanded austenite layers thicknesses, i.e. γ_N, γ_C and γ_T (e) and the resulting surface hardness measured by $HV_{0.05}$ at the surfaces (f) of PNC AISI 316L samples treated with CFC-AS using three different bias plasma powers of 0 kW (a), 0.6 kW (b) and 1.25 kW (c) applied at the treated samples as well as the resulting concentration of treatment-relevant species measured by laboratory scale LAS (g) under the treatment conditions of T= 460 °C, p= 3 mbar and t= 5 hours using CFC-AS (some of the images are adopted/replotted from Ref. [29]).

Hot wall reactor with a plasma-activated carbon electrode

Recent technological developments in plasma-assisted treatment in a hot wall reactor enable unique possibilities of reliable adjustment in the concentration of the treatment-relevant species inside the active treatment zone, and consequently tuning the properties of the treated steels. Here, by introducing a plasma-activated carbon electrode made of graphite, as a solid carbon precursor, inside a conventional hot wall reactor, a modification in configuration of hot wall reactor was done where the carbon electrode can be independently activated by a DC power supply (Fig. 3e). As a result, during PNC treatment in such a reactor configuration, the generation of carbon-containing reactive gas species, in particular HCN, can be adjusted and optimized independently, based on the design and the surface area of the graphite electrode as well as the applied voltage. At the same time, a recently developed compact LAS sensor can be coupled to the reactor for real-time monitoring of the discharge compositions and in-line evaluation of the generated species concentration (Fig. 3b-d). Combining this reactor configuration with a compact LAS sensor (Fig. 3a) enables a full control of the concentration of the generated species as well as the resulting material response.

Fig. 4a shows the variation of the HCN concentration, measured by the compact LAS sensor, as a function of the applied voltage at the carbon electrode during PNC treatments while the other treatment paraments kept constant. Fig. 4a reveals that by performing PNC treatment in a hot wall reactor using a plasma-activated carbon electrode, a reliable adjustment/control of the HCN concentration is enabled upon the variation of the voltage applied at the carbon electrode. In addition, it was revealed that the concentration of the generated HCN in this case, i.e. PNC treatment with plasma-activated graphite electrodes in a hot wall reactor, was one order of magnitude lower (Fig.

4a), compared to the HCN concentration achieved during PNC treatments with CFC-AS in the cold wall reactor (Fig. 2g). Although the treatment conditions T and t were slightly different during PNC using the modified reactor configurations of cold and hot wall technologies in this work, a major reason for the significantly reduced HCN concentration in case of treatment in the modified hot wall reactor can be correlated to the smaller surface area of the applied solid carbon source and the resulting lower plasma power (about an order of magnitude) as compared to the one in the modified cold wall reactor. In addition, even by PNC treatment at such a moderate concentration of HCN, it was shown that the generated expanded austenite layer achieved a total thickness of around 8 µm (440 °C, 2 h) reflecting a relatively high growth kinetics (Fig. 4b and c).

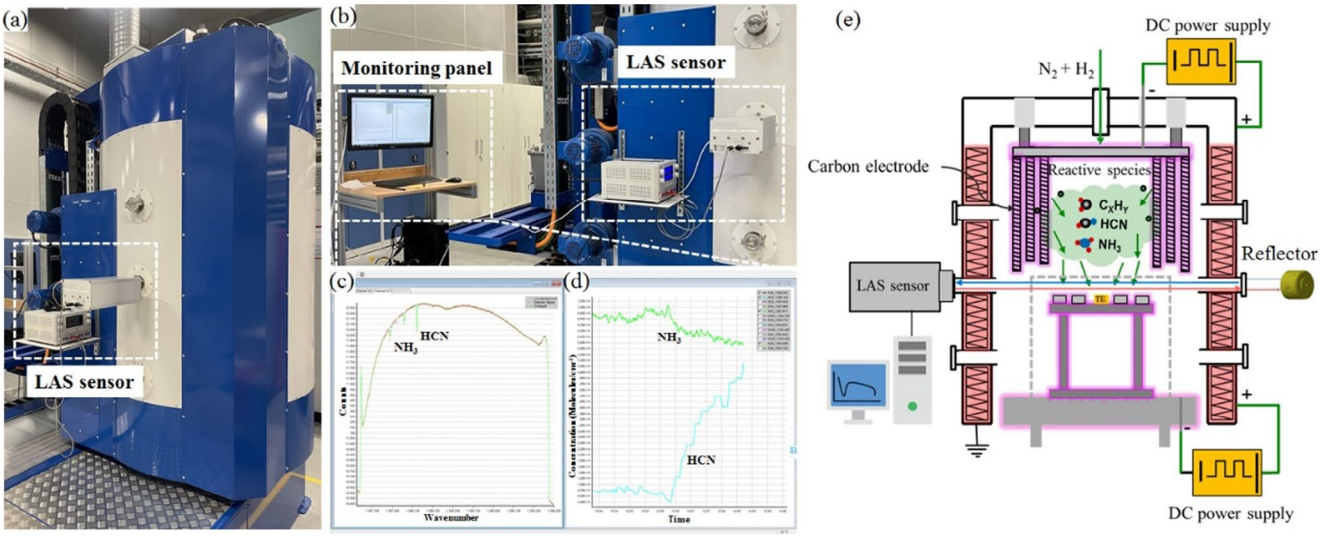

Fig.3 - Photographs and schematic of an industrial-scale hot wall reactor coupled with a compact LAS sensor (a, b and e), where the in-situ generated species during treatment can be monitored and identified (c) while the corresponding absolute concentrations can be evaluated in-line (d).

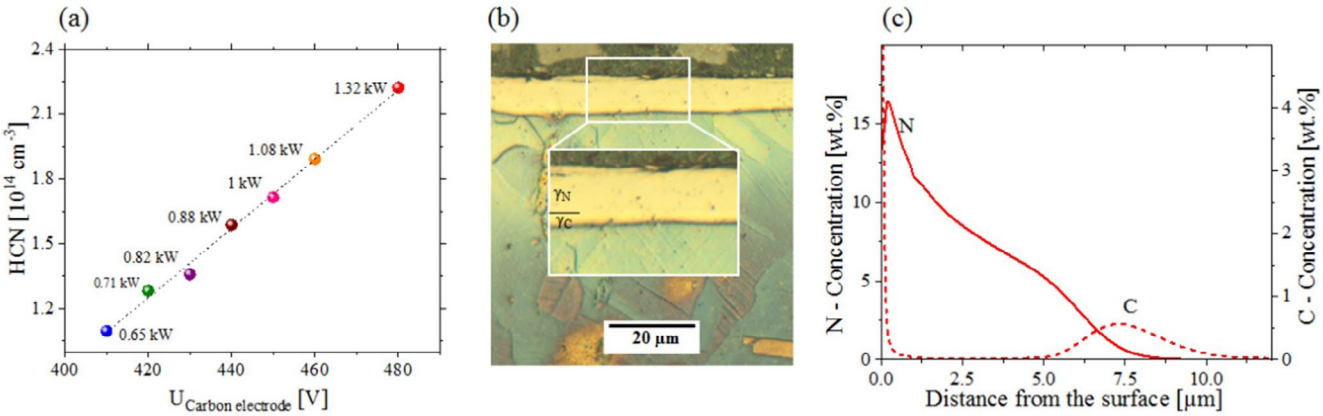

Fig.4 - Variation of HCN concentration measured by compact LAS sensor as a function of applied voltage $U_{Carbon\ electrode}$ at the carbon electrode during PNC treatments in a hot wall reactor (a). Cross-sectional light optical microscopy images (b) as well as the resulting concentration-depth profiles (in wt.%) of N and C (c) of PNC AISI 316L sample treated under the treatment conditions of T= 440 °C, p= 2.5 mbar, t= 2 hours, and $U_{Carbon\ electrode}$= 420 V. In subfigure (a), the values inside the graph represent the resulting plasma power of the carbon electrode.

CONCLUSIONS

The combined use of a plasma-activated carbon electrode in a hot wall reactor with a compact LAS sensor allows a control of the species generation. This also enables the control of material properties, which will be investigated in more detail in future studies. The decoupling of the component heating from the species generation in a hot wall reactor is promising for achieving more reliable treatment control and process optimization. In addition, it enables better understanding of the basic principles of plasma-assisted thermochemical treatments of different steels.

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