Pitting corrosion behavior of a laser hardened, high-alloyed steel

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Abstract. Laser hardening provides significant advantages in processing time, and energy consumption compared to conventional hardening processes, especially for small batches. In addition, the functional characteristics can be adjusted locally for different applications. However, the differences of the microstructural states in the laser-treated areas and the surrounding untreated base material may result in corrosion issues. In this paper, the corrosion behavior of the high-alloyed, laser-treated steel X153CrMoV12 (1.2379) used in the meat-processing industry is investigated in Hanks’ balanced salt solution, a simulated body fluid, globally by immersion tests and locally by microelectrochemical investigations, depending on the measured temperature in the laser spot. Differences of the susceptibility to pitting, as well as correlation to thermodynamic calculations were found. Thus, the application-related corrosion behavior can be estimated numerically.

1. Introduction
Cutting tools in the meat-processing industry are often produced from high-alloyed steels. These materials provide several advantages, such as good food compatibility, non-toxicity, and hardenability. High hardness of knives is expected to be one of the most important properties and is usually correlated with long service life. However, during service, the knives are exposed to meat and the related corrosive media (e.g., blood), which can cause corrosion issues. Especially, pitting corrosion will occur in these media because the passive layer receives mechanical damage during cutting and is chemically attacked by Cl⁻ ions.

For conventionally produced knives, annealed high-alloyed steel with low hardness is machined in order to obtain the basic shape of the knife with low tool wear. This is followed by hardening in a furnace with subsequent quenching and tempering. A high hardness of the cutting edge while maintaining good ductility of the knife’s body can be achieved by local hardening with a laser. Especially for small batches, the laser hardening provides low machining time in combination with easy adaption to different shapes of the knives. Thus, a time- and energy-efficient machining is possible. However, chromium carbides are present (especially in the non-hardened base material) and the local chromium content is not sufficiently high for the formation of a stable passive layer. As a result, in the body and the transition zone to the laser-hardened areas, the knife is expected to be susceptible to corrosion. As laser hardening is a non-equilibrium process, the laser track’s pitting resistance depends on the temperature in the laser spot (“laser temperature”) in combination with the laser feed. In addition, the volume of the surrounding material impacts the heating and cooling rates, leading to a complex lateral and in-depth temperature distribution. This is of major importance as the
thermodynamic behavior of some high-alloyed steels show specific characteristics that do not occur for low-alloyed materials. As an example, the solubilities of C, Mo, and Cr in the austenite during the austenitization of the material X153CrMoV12 (1.2379) are very sensitive to the temperature (see Figure 1 in section 3). Thus, when laser treated, it is expected that laser temperature and laser feed rate (laser travel speed) during the laser-hardening process will greatly impact the local chemical composition of the austenitic solid solution. In consequence, local differences of the corrosion resistance of the laser-treated areas are expected.

According to furnace hardening processes, the hardening temperature of X153CrMoV12 is set to 1050 °C. However, when applying laser hardening, the above-mentioned temperature distribution within the work piece results in hardness gradients and very low hardening depths when using a laser temperature of 1050 °C. In order to achieve sufficient hardness levels and hardening depths, it is usually recommend using a laser temperature that is 150 K above furnace hardening temperatures, i.e., 1200 °C for the selected base material [1]. However, this value as well as the heating and cooling rates strongly depend on the laser feed rate. Thus, even higher laser spot core temperatures might be necessary. The required adaptions of the laser-hardening process are barely investigated. Especially for high-alloyed steels, only insufficient data for laser hardening are available.

Besides hardness and hardening depth, further properties of X153CrMoV12 are scarcely considered in the literature [2]. Thus, in the present study, the corrosion behavior of this material is analyzed. By means of local current-density–polarization measurements with a microcapillary tube, the pitting potential is investigated for different laser temperatures and feed rates in order to determine the influence of the laser-hardening process on the pitting resistance. The experiments are supported by thermodynamic calculations.

2. Experimental and materials
The chemical composition of the material used for the production of the specimens is summarized in Table 1. Sheets with the size of 280 mm × 30 mm and a thickness of 8.5 mm were laser-hardened centered on the surface of the sheet along the long axis with a 3 kW diode laser. The laser hardening was performed with laser temperatures of 1050 °C, 1200 °C, 1280 °C, and 1350 °C each with a laser feed rate of 1 mm/s or 6 mm/s. Subsequently, the sheets were cut into specimens with the size of ≈10 mm × 30 mm × 8.5 mm and were grinded and polished according to standard procedures.

Table 1. Chemical composition of the used material X153CrMoV12 (main elements).

| Element | C  | Cr  | Mo  | V  | Mn  | S   | P   | Fe  | Other |
|---------|----|-----|-----|----|-----|-----|-----|-----|-------|
| Mass fraction (%) | 1.59 | 11.62 | 0.84 | 0.55 | 0.39 | 0.014 | 0.012 | 84.1 | 0.88  |

Two corrosion-testing methods were applied at room temperature utilizing the electrolyte Hanks’ balanced salt solution (HBSS) [3], a simulated body fluid that can be used for emulating the corrosive media present during the cutting of meat. As first testing method, immersion tests were carried out for six days in 100 ml of the solution. The solution was replaced after 48 h and 96 h. Only the top surface was exposed to the HBSS. The bottom and the four sides were covert by lacquer. Three different samples were tested for each laser temperature. From this, the samples’ general susceptibility to pitting was analyzed by optical microscopy with regards to the different areas: laser-hardened material (center line of the laser track), base material, and transition region. Potentiodynamic polarization tests were performed as the second testing method with the microcapillary technique using a capillary tube with a diameter of 800 µm, a potentiostat IMP83 PCT-BC (Jaissle Elektronik GmbH), and a potential scan rate of 1 mV/s. The stabilization of the open-circuit potential (OCP) took about 5–6 min before each measurement. At least three measurements were performed in the center of the laser track. Before the measurements were performed, the surfaces were metallographically prepared according to standard procedures and polished using an OP-S suspension (active oxide polishing suspension, Struers) directly prior to the measurements.
Thermodynamic calculations were done using the software JMatPro V7.0 (Sente Software Ltd.). Within this software, the CALPHAD method [4, 5] was used. Hereby, using a thermodynamic database, the phase equilibria are calculated for given chemical compositions and temperatures. As a result, the phase fractions and their individual chemical equilibrium compositions are determined. For the calculations in the present investigation, the chemical composition shown in Table 1 was used in the stainless steel mode. It is important to note that a thermodynamic equilibrium state is assumed in the CALPHAD method.

The pitting-resistance equivalent numbers (PRENs) were calculated based on the results of the thermodynamic calculations. For alloys without tungsten, DIN EN ISO 15156-3:2015 defines the PREN by

\[
\text{PREN} = 1 \cdot w_{\text{Cr}} + 3.3 \cdot w_{\text{Mo}} + 16 \cdot w_{\text{N}}
\]  

with the mass fractions \(w\) of Cr, Mo, and N, respectively. The nitrogen content of the alloy is not considered within the present investigation.

3. Results and discussion

Figure 1 shows the results of the thermodynamic calculations. In X153CrMoV12, austenite occurs in the temperature range of 793–1394 °C (Figure 1, left). Due to the ferrite-to-austenite phase transformation, there is a steep increase of the austenite mass fraction to about 82 % between 793 °C and 813 °C. Type M7C3 and M23C6 carbides constitute the remaining 18 %. These carbides decompose with increasing temperature and are fully dissolved above 1251 °C. At 1236 °C, the maximum of the austenite mass fraction (94 %) is reached. While the carbides are dissolved, the released C, Cr, and Mo atoms diffuse into the austenitic solid solution (Figure 1, right). The maximum equilibrium solubilities for these elements occur at 1233 °C (Mo), 1237 °C (C), and 1252 °C (Cr), respectively.

![Equilibrium phase composition and mass fractions](image)

**Figure 1.** Equilibrium phase composition (left) and equilibrium mass fractions of Cr, Mo, and C that can be dissolved in the austenite (right) for the material X153CrMoV12 depending on the temperature (calculated using JMatPro).

Optical-microscopic images for laser-treated samples after immersion tests are shown in Figure 2. The zones with constant laser temperature are marked by red dashed lines. The width of transition zones and the remaining base material are marked in blue, and green, respectively. The laser track width is larger than the region with constant laser temperature due to quick self-quenching in the outward rim of the laser track. The transition region is characterized by a strong temperature gradient. The base material is not affected by the laser induced heat.
Figure 2. Optical-microscopic images of corroded samples (immersion tests in HBSS, laser feed 6 mm/s) after 6 d.

Within the laser track, corrosion pits are small, which indicates that pitting and repassivation occurs simultaneously within these areas. In contrast, in the transition zone, a large number of wide pits can be observed. Compared to that, the number of pits in the base-material region is lower, but pits are more developed than within the laser track. Within the temperature range that occurs in the transition zone, the precipitation of carbides or their incomplete dissolution (see Figure 1) is expected. Thus around the carbides, the mass fraction of Cr solved within the matrix is considerably below 12 %. As a result, the passive layer exhibits imperfections that promote the formation of large pits, while repassivation cannot occur. In the transition zone, this susceptibility to pitting is observed for all laser temperatures. However, it is shifted toward the laser track rim by about 1 mm for a laser temperature of 1350 °C. Similar results could be observed for the laser feed rate of 1 mm/s. As a result of the higher duration time of the material in the laser spot, visible oxidation products occurred in the center (2–3 mm) of the laser track for 1280 °C and 1350 °C.

To determine the optimum of the laser temperature with regards to pitting resistance, the pitting potential was determined in the center of the laser track by electrochemical measurements. Typical current-density–potential curves of the samples treated with different laser temperatures and feeds are shown in Figure 3.
Figure 3. Current-density–potential curves of samples with different temperatures of the laser and laser feed rates of 1 mm/s (left) or 6 mm/s (right).

Due to the different solubility behavior of the alloying elements, the corrosion potential varies slightly for different laser temperatures. The pitting potential is clearly visible by the remarkably sharp increase of the current density. This is caused by the small area underneath the microcapillary tube (about 0.5 mm²) that increases the method’s sensitivity for the occurrence of pitting. The averaged pitting potentials are shown in Figure 4 along with the calculated PREN (from Equation (1) and Figure 1). As the PREN significantly changes in the temperature range of 1000–1400 °C, the pitting resistance is also strongly affected by the heat treatment temperature. The reason for this PREN change is the strong change of both the Cr and Mo solubilities in the austenitic matrix of the X153CrMoV12 material with increasing temperature.

Figure 4. Pitting potentials for different laser temperatures and feed rates in comparison to the calculated PREN for equilibrium conditions. The black and red lines are shown to guide the eye and have no physical meaning. The error bars represent standard deviations.

For both laser feed rates, the temperature 1050 °C hardly affects the pitting potential, which is equal within the laser track and the base material. Only above about 1100 °C, the pitting potential exceeds the value of the base material. Using the laser feed rate of 1 mm/s, there is a maximum of the pitting potential (i.e., the most pitting-resistant state) at around 1280 °C. It slowly decreases towards lower temperatures.
temperatures and strongly towards higher temperatures. The pitting potential and the PREN exhibit similar curve shapes and their maxima occur at similar temperatures (around 1280 °C and 1240 °C, respectively). The minor difference of about 40 K is caused by the non-equilibrium conditions during the laser treatment. In the literature, shifts of Ac3 of up to 150 K compared to equilibrium conditions were reported [1, 6–8]. The resulting value depends on the heating rate and the time of the heat exposure. Due to the non-equilibrium conditions, the applied temperature has to be larger for the fast, local heat treatment by laser compared to a bulk heat treatment. This is related to the necessary diffusion of C, Cr, and Mo: The short-time heating process only allows for a short-time diffusion. However, when increasing the temperature, the diffusibility of the atoms increases [1]. As a result, the higher temperature compensates the shorter diffusion time and the resulting material state is similar to an equilibrium condition, but it occurs at a higher laser temperature. The steep decrease of the pitting potential for temperatures above 1280 °C is caused by the above-mentioned oxide formation on the surface in the center of the laser track. These oxidized areas are more susceptible to pitting due to related imperfections of the passive layer as well as differences of the electrochemical potential between small oxidic regions (hematite, magnetite) and the surrounding austenitic phases. For the low laser feed rate, the best pitting resistance of the laser track can be achieved in the temperature range of 1250–1300 °C. However, the oxidation in the center of the laser track limits the applicable laser temperature to about 1200 °C.

For a laser feed rate of 6 mm/s, the pitting potential steadily increases with increasing laser temperature within the considered temperature range. Due to the high feed rate, the treated samples do not reach the maximum pitting potential which leads to a steadily increased curve progression with increasing laser temperature. A shift of Ac3 as observed for a laser feed rate of 1 mm/s can be estimated to be at least 100 K. Hence using 6 mm/s, the heating and cooling rates apparently are in the same order of magnitude (> 1000 K/s) as described by Kostov [1]. The results prove that a high laser feed rate and a high laser temperature are advantageous for achieving good pitting resistance in the laser track for the material X153CrMoV12.

4. Conclusions

Pitting corrosion of the material X153CrMoV12 was studied in HBSS after laser hardening. The conventional hardening of this high-alloyed steel is usually conducted at 1050 °C. The thermodynamic calculations using the PREN indicate that the pitting resistance can be improved by increasing the hardening temperature to about 1250 °C. This is a consequence of significant changes of the behavior of the alloying elements regarding their solubility in the austenitic matrix in the temperature range of 800–1400 °C, which is much less pronounced in many other materials. Thus, the properties of X153CrMoV12 are very sensitive to the selected hardening temperature. Utilizing laser hardening with the related lateral and in-depth temperature gradients, the laser temperature for reaching the best pitting resistance strongly depends on the laser feed rate. A high feed rate results in large heating rates (non-equilibrium conditions) and to a shift of Ac3 of more than 100 K compared to conventional hardening. As a consequence, the usually assumed 150 K temperature increase required in laser-hardening processes does not result in the optimal pitting resistance, when using a high laser feed rate.

For a low laser feed rate of 1 mm/s, the pitting resistance in the center of the laser track is highest in the temperature range of 1250–1300 °C, but due to visible oxidized areas, a laser temperature of about 1200 °C should not be exceeded.

The most pitting-susceptible area is located in the transition region next to the laser track as the temperature is not sufficiently high for dissolving the initially present carbides. The related imperfections of the passive layer and differences in the electrochemical potential cause the observed strong pitting. As the temperature gradient is characteristic for the laser treatment, an appropriate heat treatment (dissolution of carbides) of the base material before laser hardening would result in an increase of the pitting resistance alongside the laser track.

Under consideration of the observed shift of about 40–70 K, the PREN can be used for predicting the laser temperature in order to gain good pitting resistance within the laser track when using a low
laser feed rate. Thus, for minimized pitting, the determination of the PREN based on thermodynamic calculation is suitable for estimating required temperatures during laser treatments.

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References
[1] Kostov V 2014 Untersuchungen zur zeitaufgelösten Spannungsentwicklung und Eigenspannungsentstehung beim Laserstrahlstandhärten am Beispiel des Stahls 42CrMo4 PhD thesis Karlsruher Institut für Technologie (in German)
[2] Oppenkowski A 2011 Cryobehandlung von Werkzeugstahl PhD thesis Ruhr-Universität Bochum (in German)
[3] Hanks J H and Wallace R E 1949 Relation of oxygen and temperature in the preservation of tissues by refrigeration Proc. Soc. Exp. Biol. Med. 71 196–200
[4] Kaufmann L and Bernstein H 1970 Computer Calculation of Phase Diagrams with Special Reference to Refractory Metals vol 1 (New York: Academic Press)
[5] Bleck W and Moeller E 2018 Handbuch Stahl: Auswahl, Verarbeitung, Anwendung vol 1 (München, Carl Hanser Verlag) (in German)
[6] Schlicht H 1974 Beitrag zur Theorie des schnellen Erwärmen und schnellen Abkühlens von Stahl Härterei-Techn. Mitt. 29 184–192 (in German)
[7] Miokovic T, Schulze V, Löhe and Vöhringer O 2003 Experimentelle Analyse und Modellierung des Kurzzeitumwandlungsverhaltens von Stählen am Beispiel von 42CrMo4 Härterei-Techn. Mitt. 58 304–313 (in German)
[8] Pyzalla A, Bohne C Heiterkemper M and Fischer A 2001 Influence of laser rapid heat treatment on the corrosion resistance of the high nitrogen steel X30CrMoN15 1 + 0,3%N Materials and Corrosion 52 99–105