Thermal Stability of Low-Temperature-Carburized Austenitic Stainless Steel

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Abstract

To study the thermal stability of the “case” (hard layer) that forms on AISI-316L austenitic stainless steel by low-temperature carburization, we exposed carburized specimens to temperatures between 573 K and 648 K (300 and 375 °C) in air for 20.7 Ms (8 months). In spite of a colossal supersaturation with carbon, the austenite does not precipitate carbides. No carbon is lost to the ambient. Carbon diffuses deeper into the alloy, resulting in a flatter carbon-fraction–depth profile. This is realistically simulated assuming temperature- and concentration-dependent carbon diffusion. Exposing to 648 K for 20.7 Ms about doubles the average carbon depth. The near-surface carbon fraction decreases only moderately, particularly as the material appears to assimilate carbon from the ambient. Accordingly, the beneficial effects of low-temperature carburization on mechanical properties and corrosion resistance are retained throughout such long-term heat exposure, implying corresponding service life of low-temperature-carburized parts at temperatures below 650 K.

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1. Introduction

Austenitic stainless steels are highly resistant to corrosion. However, their surface-mechanical properties are less attractive [1]. Therefore, various methods have been employed to surface-harden these alloys [2]. One of the most effective methods is interstitial solid-solution hardening by carbon or nitrogen [2, 3]. The very low equilibrium solubility of carbon and nitrogen and the rapid increase of solubility with increasing temperature seem to suggest that the best strategy for obtaining high concentrations of interstitial solute is solute infusion at high temperature and subsequent quenching. However, such “conventional” carburizing and nitriding inevitably induce precipitation Cr-rich carbides or nitrides, which can have a very negative impact on mechanical properties (stress concentration) and corrosion resistance (“sensitization”). A much more potent approach, which has been developed over the past decades, is infusion of interstitial solute at low temperature. “Low,” in this context, means a temperature at which the metal atoms of the alloy are practically immobile, thus incapable of precipitating with the solute, while the solute, since it resides in interstices between the metal atoms, can still diffuse over technically useful distances within technically feasible processing times. Under such “para-equilibrium” conditions [4], the concentrations of up to 15 at% for carbon and 20 at% for nitrogen can be infused and retained in solid solution. This corresponds to about 10^5 times the equilibrium solubility limit, therefore constituting a “colossal supersaturation.” It is well established that these high concentrations of interstitial solute are highly beneficial for mechanical properties (surface hardness, wear resistance, fatigue resistance) and corrosion resistance. This has found many applications, e.g. in nuclear reactors or chemical plants [5, 6].

Thermodynamically, a colossal supersaturation with interstitial solute leaves the alloy in an unstable (not “metastable”) state, since at supersaturations of order 10^5 , nucleation barriers for precipitation will be small compared to the typical energy $k_B T$ of thermal

fluctuations (k_B : Boltzmann constant, T : absolute temperature). Particularly for applications at elevated temperature, therefore, it is highly important how the case and the related alloy properties respond to heat exposure. For a number of low-temperature-carburized and -nitrided austenitic alloys, tests at elevated temperature have been carried out to determine their stability against carbide- or nitride precipitation [7–11]. The results were organized in the form of TTT (time-temperature-transformation) diagrams [11]. The strong temperature dependence of decomposition kinetics has led to the technically useful (if not physically exact) concept of a “threshold temperature” [7–9, 11–13], below which the case can be assumed to remain free of precipitates for a practically infinite lifetime.

However, even under conditions where precipitation can be neglected, the case may not be stable against redistribution of interstitial solute by diffusion or loss of solute to the ambient. For the example of low-temperature-carburized AISI-316L (austenitic stainless steel), therefore, we investigate the impact of long-term heat exposure on the carbon-AFDP (atom-fraction-depth profile).

2. Experimental Methods and Procedures

Table 1 compiles information on the specimens we studied in this work. “No-C” designates non-carburized, ordinary AISI-316L. “LT-C” designates the specimens in their initial state after LTC (low-temperature carburization), prior to the long-term heat exposure experiments. These specimens were “ferrules” made from AISI-316L and treated by LTC [3]. AISI-316L contains 18.5 at% Cr, 11.6 at% Ni, 2 at% Mo, and balance Fe. LTC had been carried out by a gas-phase (CO , H_2 , N_2) process designed and carried out by the Swagelok Company [3, 14]. The long-term heat exposures were carried out in electric furnaces at 4 different temperatures (Table 1), all for the same time $t = 20.7$ Ms (8 months). To characterize the material before and after temperature exposure, we employed a D8 diffractometer made by Bruker XRD (X-ray diffractometry) in Bragg–Brentano setting and with $\text{Co-K}\alpha$ radiation. For metallographic analysis of the microstructure by LOM (light-optical microscopy), cross-sections of aged specimens were polished, chemically etched using a solution of 25 vol% HNO_3 , 50 vol% HCl , and

25 vol% H₂O. Hardness–depth profiles $h[z]$ were obtained from cross-sectional specimens by NHT (**nano-hardness testing**) using a G 200 nanoindenter, made by Keysight (formerly Agilent). The instrument operated with a load of 1 g. In the non-hardened core of the AISI-316L specimens, this produced indents with a projected area of only $\approx 0.5 \mu\text{m}^2$.

Carbon-AFDPs $X_C[z]$ were obtained by analyzing the cross-sectional specimens with a PHI 680 SAM (**scanning Auger microprobe**), made by Physical Electronics. In order to minimize artifacts introduced by adventitious carbon, we employed an established technique of continuous Ar⁺ sputtering [15, 16]. For precise quantification of the carbon concentration as a function of depth z below the surface, we evaluated the measurements using standard data obtained from specimens with certified carbon concentrations [15, 16]. For concentration–depth profiling determined by SAM, the effect of noise in the contributing Auger-electron energy spectra deserves particular attention. Evaluation of the carbon peak intensity involves differentiation of the spectra and evaluation of the maximum–minimum difference in the region of the differentiated carbon peak. Even in the absence of carbon, spectral noise will produce a non-vanishing derivative and, therefore, an apparent carbon level in regions of vanishing carbon concentration (non-carburized alloy core). To eliminate related artifacts, the experimental data were corrected with a newly developed method for signal-dependent background subtraction [17]. The resulting analytical uncertainty is estimated to be $< 1 \text{ at\%}$ in absolute carbon concentration.

3. Results

The cross-sectional LOM micrograph in Fig 1a shows the microstructure of HT-4. Owing to higher corrosion resistance against metallographic etching, the case (carbon-infused layer) layer appears “featureless.” Carbide precipitates were not discovered in such images. Since the AFDP of carbon is smoothly graded and the resistance against the metallographic etchant requires a minimum carbon fraction (e.g. 5 at%), the apparent case depth ζ_{LOM} i. e. the thickness of the featureless layer, may slightly underestimate the true case depth ζ (e. g. defined as depth where $X_C = 1 \text{ at\%}$). Corresponding LOM

images were obtained from the other specimens listed in Table 1. Figure 1b shows the measured $\zeta_{\text{LOM}}[T]$.

Figure 2 shows X-ray diffractograms acquired in the LT-C (“as carburized”) state and after the long-term heat exposures (Table 1). In the displayed range of the diffraction angle 2θ , the diffractograms exhibit the $\{111\}$ and $\{200\}$ peaks of the austenite. For reference, the figure also shows the corresponding $\{111\}$ and $\{200\}$ peak positions expected for No-C – indicated by vertical dashed lines with corresponding labels. (Their positions follow from the lattice parameter $a_0 = 0.3599$ nm of as-machined, non-carburized AISI-316L ferrules as experimentally determined by XRD and Nelson–Riley correction [18].)

Generally, as interstitially dissolved carbon expands the interatomic distances between the metal atoms, $X_C > 0$ increases the plane spacings of the austenite and shifts the $\{111\}$ and $\{200\}$ peak positions to 2θ values smaller than the corresponding positions of No-C. Thus, the more the peaks of the diffractograms are shifted to lower 2θ compared to the corresponding vertical dashed lines in Fig 2, the higher is the level of interstitially dissolved carbon. (The actual peak position and shape follow from the actual solute distribution $X_C[z]$ and the depth-dependence of the X-ray intensity $I[z]$ in the near-surface zone sampled by the X-rays). Compared to the diffractogram of non-carburized AISI-316L, the peak positions obtained from the as-received low-temperature-carburized are shifted to smaller Bragg angles θ_B , owing to lattice parameter expansion caused by interstitially dissolved carbon [19]. For the heat-treated specimens, the peak shifts are less and anti-correlate with the treatment temperature T . This indicates correspondingly reduced average carbon concentrations in the ≈ 5 μm -thick layer below the specimen surface that is sampled by the X-rays: Upon heat exposure, the near-surface region loses carbon. The higher the heat-treatment temperature T , the more carbon is lost from the sampled zone within the treatment time t . In earlier work, carbide precipitation was apparent from additional peaks in corresponding X-ray diffractograms, particularly in the angular range between the $\{111\}$ and $\{200\}$ austenite peaks. Since such additional peaks are not observed in Fig.2, we conclude that the heat exposures did not cause significant

carbide precipitation. If carbides are present, at all, we estimate their volume fraction below 5 %.

Figure 3 presents the carbon-AFDPs $X_C[z]$ of LT-C and HT-4. They were obtained by quantifying the carbon fraction from Auger-electron energy spectra acquired at every scan point using the procedure described in Section 2. The final profiles are shown as black points. These were obtained from the initial profiles (light grey points) by background subtraction with the method described in Section 2. For LT-C, $X_C[z = 0] = 0.14 \pm 0.01$ – corresponding to $\approx 100,000$ times (!) the equilibrium solubility of carbon room temperature. The profile falls off towards the interior of the specimen and approaches the noise level at an apparent case depth $\zeta_{SAM} \approx 30 \mu\text{m}$. The profile of HT-4 is flatter, but also deeper. It starts at $X_C[z = 0] = 0.11 \pm 0.01$ and exhibits an apparent case depth $\zeta_{SAM} \approx 50 \mu\text{m}$. Figure 3b compares the nanohardness profile $h[z]$ of HT-4 with that of LT-C. Near the surface ($z = 0$), LT-C displays $h = 14 \text{ GPa}$. The hardness prior to LTC can be estimated from the average hardness in the non-carburized alloy core region included in the $h[z]$ graph of the as-carburized ferrules (LT-C). The corresponding level is shown as a horizontal line in Fig 3b, marked with “No-C.”

Consistent with the $X_C[z]$ in Fig 3b, both profiles indicate greatest hardness at the specimen surface ($z = 0$). Similar to the carbon-AFDP, the $h[z]$ of HT-4 is flatter, but also deeper than that of LT-C. In particular, the heat exposure HT-4 has reduced the hardness near the surface from $h = 14 \text{ GPa}$ to $h = 12 \text{ GPa}$, while increasing the apparent case depth from $\zeta_{NHT} \approx 25 \mu\text{m}$ to $\zeta_{NHT} \approx 50 \mu\text{m}$.

4. Discussion

While the three measures of apparent case depth, ζ_{LOM} , ζ_{SAM} , and ζ_{NHT} are physically different, they are reasonably consistent ($\pm 5 \mu\text{m}$) under the conditions considered here. Accordingly, the threshold carbon concentration at which the material becomes etch-resistant is low enough for the case depth ζ_{LOM} apparent from optical micrographs to provide a realistic estimate of the true case depth, which is likely most reliably (though not necessarily most accurately) represented by ζ_{NHT} . ζ_{SAM} , on the other

hand, may be less reliable when the underlying AES (Auger electron spectrometry) data are impacted by spectral noise, which offsets the profiles towards higher carbon levels. Therefore, a reliable method of background subtraction, as applied in this work [17], is important. Figure 3a indicates that in both specimens the maximum carbon fraction occurs at the specimen surface ($z = 0$). This means that no carbon is lost to the exterior – in that case, where carbon diffuses outward (as well as inward), the law of diffusion would cause the regions closer to the surface to lose carbon more rapidly than regions deeper in the alloy, and a maximum of HT-4's $X_C[z]$ would be observed at some finite depth $z > 0$ below the surface. The absence of carbon loss to the ambient is not trivial. For example, low-temperature-carburized IN-718 (Ni-base superalloy), when exposed to higher heat-treatment temperatures, actually exhibits carbon loss to the exterior, which manifests itself as a decrease of $X_C[z]$ near the surface, such that $X_C[0] = 0$ and the maximum of X_C resides at a finite depth of about $5\text{ }\mu\text{m}$ [20].

For the non-carburized core of LT-C, Fig 3b indicates an average hardness of $\approx 5\text{ GPa}$. That this value is higher than typical hardness levels quoted for AISI-316L appears to be a result of the machining by which ferrules are produced. While there is scatter in the hardness data, it appears that the plateau of HT-4 on the right-hand side of Fig 3b is somewhat lower than the plateau of LT-C (5.1 GPa vs 5.3 GPa). Apparently, the long-term heat treatment somewhat softened the non-carburized core of the alloy by recovery.

The shape of both $X_C[z]$ profiles differs significantly from that of a complementary error function as it would be expected from Fick's second law (concentration-independent diffusion coefficient). The reason for the “concave” shape ($z_2 > z_1 \Rightarrow X_C[(1 - \nu)z_1 + \nu z_2] > (1 - \nu)X_C[z_1] + \nu X_C[z_2]$ for $0 \leq \nu \leq 1, \nu \in \mathbb{R}$) observed here in regions $[z_1, z_2]$ of high X_C is the strong increase of the carbon diffusion coefficient with increasing local carbon concentration [21]. While the $h[z]$ of Fig 3b are correlated with the $X_C[z]$, their shapes are different because the local hardness depends on the local carbon fraction in a complicated way, involving solid-solution hardening [22] and work hardening due to plastic deformation induced by relaxation of compressive biaxial stress [4]. While there is much scatter in such hardness data, it appears that the plateau of HT-4 on the

right-hand side of Fig 3b is somewhat lower than the plateau of LT-C. This is expected as heat exposure enables recovery of the non-carburized core region of the alloy.

The evolution of LT-C's AFDP of carbon into that of HT-4 (Fig 3a was modeled using two newly developed C++ programs (extending earlier work) [21, 23, 24] for Boltzman–Matano analysis [21] and numerical modeling of concentration-dependent diffusion. Details are described in the Appendix. Boltzman–Matano analysis of LT-C's $X_C[z]$ suggests that the concentration-dependence of the carbon diffusion coefficient can be realistically modeled in the following form [21]:

$$D[X_C, T] = D_0 \text{Exp} \left[-\frac{Q_0 + \lambda X_C}{k_B T} \right], \quad (1)$$

where D_0 is the “pre-factor” of the diffusion coefficient, Q_0 the activation energy of diffusion, k_B the Boltzmann constant, T the temperature, and λ a factor that characterizes the fraction- (or concentration-) dependence of the diffusion coefficient.

Figure 4a presents a sequence of simulated carbon-AFDPs that were obtained in two steps: (i) Numerically fitting a Bézier curve (“LT-C”) to the experimental data of LT-C in Fig 3a and determining D_0 , Q_0 , and λ in (1) by Boltzman–Matano analysis [21]. The results are indicated in the plot. (ii) Simulating concentration-dependent diffusion (1) with the parameter values determined in the first step. The simulation reproduces the experimentally observed flattening and increased depth of $X_C[z]$. The inset at the top right of Fig 4a shows the MDS (mean of the squared displacement) of the simulated profiles as a function of time t . Accordingly, HT-4 increases the initial MDS of LT-C by a factor of 4. As much as the line connecting the data points is straight (it is not perfectly straight), the usual rule that the MDS is proportional to diffusion time applies to the added depth of carbon in the specimen. The inset also shows the MD (mean displacement – or mean depth) of carbon as a function of time t . Within the simulated time of 20.7 Ms, the MD increases by a factor of 2.

Figure 4b shows a comparison of the experimental data of Fig 3a with the profile fit “LT-C” and the simulated $X_C[z]$ of HT-4 in Fig 4a. The simulation reproduces the experimentally observed flattening of the profile, the reduced carbon fraction at the surface ($z = 0$), and the increased case depth ζ . However, the experimentally observed

carbon fraction at the surface is higher than predicted. In fact, the integrated carbon fraction

$$\int_0^{\infty} X_C[z] dz =: \xi \quad (2)$$

of HT-4 ($2.79 \mu\text{m}$) is 9 % greater than that of LT-C ($2.57 \mu\text{m}$). While this could be an unidentified artifact of SAM, it is also possible that the specimen exposed to LT-4 has in fact assimilated carbon from the ambient. Indeed, the experimental $X_C[z]$ of HT-4 in Fig 4b features a negative slope $dX/dz < 0$ at $z = 0$, indicating ongoing ingress of carbon. The simulated profiles in Fig 4a, in contrast, exhibit vanishing slope $dX/dz = 0$ at $z = 0$, as expected for a surface through which carbon transport does not occur. An obvious source of carbon could be the CO_2 (carbon dioxide) in the air. While CO_2 is a very stable molecule, the thermodynamic data of Table 1 indicate that CO_2 decomposition at 648 K is exothermic if the carbon atom is accepted in an environment energetically comparable to Cr_{23}C_6 and the oxygen atoms are incorporated in an Fe- or Cr oxide. Carburization of austenitic stainless steel by uptake of carbon from ambient CO_2 has been observed earlier for 20/25-Nb alloys, although at higher temperatures (around 900 to 1000 K) [25]. In fact, an equivalent reaction constitutes a major technical challenge for turbines operating with supercritical CO_2 , where it is found that the CO_2 oxidizes and carburizes the turbine blades made from Cr-containing alloys [26]. Similarly, adsorption of CO_2 on the surface of Zircaloy-4 is known to cause dissociation of the CO_2 by formation of surface oxide and carbide carbon [27]. Further, the hypothesis of CO_2 decomposition enabled by metal-oxide formation explains the dark surface scale we observed forming on the HT-4 treated ferrule. The observed 9 % increase in carbon content corresponds to the CO_2 contained in a layer of air with a thickness of 2 m. Considering the likely exchange of air in the ambient within the exposure time of 20.7 Ms, i. e. 8 months, the *availability* of carbon from CO_2 in the ambient air suffices to explain the observed uptake of carbon.

5. Conclusions

Important for the service life of low-temperature-carburized AISI-316L, the results of this work demonstrate that long-term (20 Ms) exposure to temperatures up to 650 K does

not cause significant carbide precipitation and only moderate degradation of properties. The most aggressive heat exposure of this study, 20.7 Ms (8 months) at 648 K (375 °C), increases the mean depth of the carbon atoms present in the “as-carburized” state by a factor of 2 and reduces the carbon fraction at the alloy surface to $\approx \frac{2}{3}$ of the original value. Since no carbon is lost to the ambient (air), the main effect of heat exposure is further inward diffusion of the carbon that low-temperature carburization dissolved in the near-surface layer of the alloy. The resulting evolution of the carbon AFDP (**atom-fraction–depth profile**), including flattening and depth increase, can be realistically simulated assuming concentration-dependent carbon diffusivity, confirming the validity of such calculations for quantitative predictions. In addition to inward diffusion of the carbon dissolved during LTC, the alloy with the strongest heat-exposure in air exhibits additional carbon within a zone adjacent to the surface: The integral of the AFDP of carbon increases by $\approx 10\%$, indicating that heat-exposure in air enables carbon assimilation of from the ambient – apparently from the CO₂ contained in the ambient air. This should actually be beneficial for the alloy properties and mitigate performance degradation by ongoing inward diffusion of carbon. In fact, the loss of surface hardness during the applied heat exposures is not dramatic, indicating a considerable service life of low-temperature-carburized AISI-316L for applications at temperatures below 650 K.

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Appendix

The simulations employed in this work were carried out using two computer programs, BMA and CPE (F Ernst, unpublished). Both programs are coded in C++-11 and were developed under XCode on the Macintosh OS X platform.

BMA performs Boltzmann–Matano analysis on experimentally determined atom-fraction–depth profiles, i. e. the diffusion coefficient as a function of local (carbon or other solute) atom fraction $X[z]$. This requires (i) integration over and (ii) differentiation of the *inverse* $z[X]$ of the experimental atom-fraction–depth profile $X[z]$. This, in turn, $X[z]$ to be a monotonous function, i. e. $z_2 > z_1 \implies X[z_2] < X[z_1]$. To obtain a noise-reduced monotonous representation of the experimentally determined $X[z]$, BMA performs least-square fitting of a monotonous 4-point Bézier curve to the experimental data (8 parameters, 5 of which are independent). Once the parameters of the Bézier curve are determined, BMA performs numerical inversion, differentiation, and integration to determine $D[X]$.

CPE performs numerical simulation of atom-fraction- (concentration-) dependent diffusion, i. e. with a diffusion coefficient $D = D[X]$. Numerical differentiation is carried out by the “finite difference” method [28]. CPE provides great flexibility by allowing for an initial profile $X[z]$ to be provided for computing the further temporal evolution and allowing for *time-dependence* of temperature, surface transparency, and solute activity in the gas phase to be included.

BMA and CPE have been checked for self-consistency: A given diffusion profile $X[z]$ is properly reproduced by running CPE with the concentration dependence $D[X]$ determined by BMA.

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Figure Legends

1. Case depth in low-temperature-carburized AISI-316L as a function of exposure to temperature. (a) Cross-sectional light-optical micrograph, showing the microstructure and apparent case depth of HT-4. (b) Apparent case depth ζ_{LOM} in LT-C (“as-carburized”) condition and after the heat treatments of Table 1.
2. X-ray diffractograms of low-temperature-carburized AISI-316L in the conditions shown in Table 1. The $\{111\}$ and $\{200\}$ peak positions expected for No-C (non-carburized AISI-316L ferrules) are indicated by vertical dashed lines with corresponding markers.
3. Effect of heat treatment on carbon distribution and hardness. (a) Carbon-AFDPs $X_C[z]$ in LT-C (“as-carburized”) condition and after heat treatment HT-4, obtained by SAM. (b) Corresponding hardness–depth profiles $h[z]$, measured by nanoindentation. “No-C” indicates the approximate average hardness of the non-carburized alloy core region of the as-carburized ferrules (LT-C).
4. Temporal evolution of the AFDP of carbon upon heat exposure to $T_4 = 648\text{ K}$. (a) Numerical simulation for time interval $[0, 20.7]\text{ Ms}$. “LT-C” is a Bézier curve *numerically* fitted to the experimentally obtained $X_C[z]$ of LT-C. The other graphs represent the temporal evolution of the profile in equidistant time steps, simulated with the parameters given at the top right. The bold line is $X_C[z]$ of HT-4, after $t = 20.7\text{ Ms}$. The inset at the top right shows the MDS of the simulated profiles. (b) Comparison with the experimental data of Fig 3a.

Figures Enlarged

Figure 1: Case depth in low-temperature-carburized AISI-316L as a function of exposure to temperature. (a) Cross-sectional light-optical micrograph, showing the microstructure and apparent case depth of HT-4. (b) Apparent case depth ζ_{LOM} in LT-C (“as-carburized”) condition and after the heat treatments of Table 1.

Figure 2: X-ray diffractograms of low-temperature-carburized AISI-316L in the conditions shown in Table 1. The {111} and {200} peak positions expected for No-C (non-carburized AISI-316L ferrules) are indicated by vertical dashed lines with corresponding markers.

Figure 3: Effect of heat treatment on carbon distribution and hardness. (a) Carbon-AFDPs $X_C[z]$ in LT-C (“as-carburized”) condition and after heat treatment HT-4, obtained by SAM. (b) Corresponding hardness–depth profiles $h[z]$, measured by nanoindentation. “No-C” indicates the approximate average hardness of the non-carburized alloy core region of the as-carburized ferrules (LT-C).

Figure 4: Temporal evolution of the AFDP of carbon upon heat exposure to $T_4 = 648 \text{K}$. (a) Numerical simulation for time interval $[0, 20.7] \text{Ms}$. "LT-C" is a Bézier curve *numerically* fitted to the experimentally obtained $X_C[z]$ of LT-C. The other graphs represent the temporal evolution of the profile in equidistant time steps, simulated with the parameters given at the top right. The bold line is $X_C[z]$ of HT-4, after $t = 20.7 \text{Ms}$. The inset at the top right shows the MDS of the simulated profiles. (b) Comparison with the experimental data of Fig 3a.

Tables

Table 1: **Specimens**

ID	Temperature T	Time t
No-C	–	–
LT-C	–	–
HT-1	$T_1 = 573\text{ K}$ $300\text{ }^{\circ}\text{C}$	$t_1 = 20.7\text{ Ms}$
HT-2	$T_2 = 598\text{ K}$ $325\text{ }^{\circ}\text{C}$	
HT-3	$T_3 = 623\text{ K}$ $350\text{ }^{\circ}\text{C}$	
HT-4	$T_4 = 648\text{ K}$ $375\text{ }^{\circ}\text{C}$	

Table 2: **Thermodynamic Data**

Reagents	Products	ΔG (MJ/mol)
$23\text{Cr} + 9\text{Fe} + 6\text{CO}_2$	$\text{Cr}_{23}\text{C}_6 + 3\text{Fe}_3\text{O}_4$	−0.67
$23\text{Cr} + 8\text{Fe} + 6\text{CO}_2$	$\text{Cr}_{23}\text{C}_6 + 4\text{Fe}_2\text{O}_3$	−0.58
$23\text{Cr} + 12\text{Fe} + 6\text{CO}_2$	$\text{Cr}_{23}\text{C}_6 + 12\text{FeO}$	−0.69
$23\text{Cr} + 6\text{CO}_2$	$\text{Cr}_{23}\text{C}_6 + 4\text{Cr}_2\text{O}_3$	−1.86
$23\text{Cr} + 6\text{CO}$	$\text{Cr}_{23}\text{C}_6 + 3\text{O}_2$	+0.64
$23\text{Cr} + 6\text{CO} + 6\text{H}_2$	$\text{Cr}_{23}\text{C}_6 + 6\text{H}_2\text{O}$	−1.13
$8\text{Cr} + 6\text{O}_2$	$4\text{Cr}_2\text{O}_3$	−3.88

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Heat Exposure in Air

Carbon Atom-Fraction-Depth Profile