Original Article

Effect of high-temperature degradation on microstructure evolution and mechanical properties of austenitic heat-resistant steel

Jaegu Choi¹, Chang-Sung Seok¹,*, Soo Park¹, Gayeon Kim⁶

¹ Graduate School of Mechanical Engineering, Sungkyunkwan University, 2066, Seobu-ro, Jangan-gu, Suwon 16419, South Korea
⁶ Iron & Steel Development Team, Hyundai-Kia Motors Company, 150, Hyundaiyeonguso-ro, Namyang-eup, Hwaseong 18280, South Korea

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ABSTRACT

21-4N austenitic heat-resistant steel is widely used as the material for automobile engine valves because of its high strength, excellent creep resistance, oxidation resistance and corrosion resistance under high-temperature circumstances. Engine valves, which are exposed to high temperatures for long periods, undergo material degradation in which the initial microstructure of the material is changed, resulting in deterioration of mechanical properties. This degradation can cause valve failure. Therefore, the microstructure and mechanical characteristics of degraded valves are important issues in designing the hot-section engine components. In this study, the changes in the microstructure evolution and mechanical properties of 21-4N austenitic steel were investigated after exposure at high temperature (1123 K) for 10–200 h, using accelerated degradation testing. To evaluate the degradation characteristics of 21-4N austenitic heat-resistant steel, we analyzed the microstructure evolution (e.g., grains, surface oxides, carbides, and phase) and the change in mechanical properties (e.g., tensile strength and hardness) for virgin and degraded specimens. Finally, analyses and tests results demonstrate the correlation between microstructure evolution and changes in mechanical properties.

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1. Introduction

Austenitic heat-resistant steel has been widely used as a structural material in elevated-temperature applications such as for boilers, nuclear reactors, super-heater tubes in ultra-supercritical power plants, and automobile engines because of its excellent high-temperature properties (e.g., high strength, creep resistance, oxidation resistance and corrosion resistance) [1-6]. Iron is the main component of austenitic steel; nickel must be added to enhance the stability of austenite and chromium is added to protect the material from oxidation and corrosion in service circumstances. When substantial amounts of nickel and chromium are added austenitic heat-resistant steel is produced [7]. Nickel has been the most
important alloying element in the production of austenitic heat-resistant steels. However, because the price of nickel is high, steel makers have developed alternative austenitic stainless steels containing little or no nickel. In this respect, nitrogen-containing austenite heat-resistant steel with little or no nickel is expected to be more widely used in the future [8].

5Cr21Mn9N4N (21-4N) nitrogen-containing austenitic heat-resistant steel has a face centered cubic (FCC) crystal structure containing elements such as Ni, Si, Cr, Mo, N, and Mn. The FCC structure of 21-4N is maintained by the Ni, Mn and N alloying additions, all of which are austenizing elements. 21-4N is usually used as the material for valves and turbocharger rotors in automobile engines. This material offers an excellent balance of characteristics including high strength, high resistance against creep and fatigue, and oxidation resistance at room temperature and elevated temperature (up to 1150 K) [9–11].

With the adoption of the Paris Convention in December 2015, regulations on greenhouse gas emissions have become an important environmental issue globally. The increase in operating combustion gas pressure and temperature of automobile engines will result in increasing the efficiency of automobiles. The increase in efficiency leads to less fuel consumption and thereby reduces carbon dioxide emission [12–14]. Therefore, ensuring the durability of engine valves at elevated temperatures, under high stress, and in corrosive circumstances is indispensable. The intake and exhaust valves exposed to high-temperature conditions for a long period undergo material degradation in which the initial microstructure of the material is changed by damage from high-temperature oxidation, thermo-mechanical fatigue, and creep, resulting in deterioration of mechanical properties. As the degradation progresses, the valves become highly damaged, which can cause failure of the engine. Therefore, it is very important to evaluate the effects of microstructural changes such as changes in crystal grain size, internal defect generation, and growth, phase changes, and precipitates on the deterioration of mechanical properties. In the case of heat-resistant steel, several researchers have conducted individual studies on changes in the microstructure and mechanical properties of materials from high-temperature degradation [15–19].

In this study, the microstructure and mechanical properties of 21-4N austenitic heat-resistant steel were studied after exposure at high temperature (1123 K) for 10–200 h, using accelerated degradation testing. To evaluate the degradation characteristics of 21-4N austenitic heat-resistant steel, we analyzed the microstructure evolution (e.g., grain boundary, surface oxides, precipitates, and phase) and the change in mechanical properties (e.g. tensile strength and hardness) for virgin and degraded specimens. Finally, analyses and test results demonstrate the correlation between microstructure evolution and changes in mechanical properties.

### 2. Experimental procedure

The 21-4N steel, used in this study, is treated by aging after solution annealing at 1433 K to strengthen the matrix by a solution-precipitation strengthening mechanism. As a result, 21-4N steel has austenitic grains and some dispersed carbides at the grain boundary [20]. The nominal composition of 21-4N austenitic steel is listed in Table 1.

Specimens for the hardness measurement and microstructure analysis were machined in the form of Ø7 × 13 mm round bars. Specimens for the tensile test were machined in accordance with the specimen specifications given in ASTM E 8/E 8M [21]. Fig. 1 shows the shape and dimensions of the tensile test specimen.

To reduce experimental costs and make efficient use of time, an accelerated degradation test of the virgin specimen was performed in harsh conditions instead of a long-term test. The accelerated degradation test was conducted on the machined specimens for 10–200 h, using an electric muffle furnace. By artificially accelerating degradation at a higher temperature (1123 K) than the actual operating temperature (1023 K) of the material, the specimen can be made to have the same microstructure as the material used for a long time at actual operating temperature. To set the amount of self-diffusion of iron at the accelerated degradation temperature be the same as that at the actual operating temperature, the accelerated degradation time was calculated using the following equation [22,23]:

\[
t_2 = t_1 \exp \left[ \frac{Q}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right]
\]

where \(T_1\) is the actual operating temperature (1023 K), \(T_2\) is the accelerated degradation temperature (1123 K), \(t_1\) is the actual operating time (in hours) at \(T_1\), \(t_2\) is the accelerated degradation time (in hours) at \(T_2\), \(Q\) is the activation energy of iron (272 kJ/mol), and \(R\) is the universal gas constant (8.3143 J/mol/K). Table 2 gives the accelerated degradation time.

### Table 1 - Nominal composition of 21-4N austenitic steel (wt.%).

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>S</th>
<th>Mn</th>
<th>N</th>
<th>P</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>0.6</td>
<td>0.3</td>
<td>9.9</td>
<td>0.4</td>
<td>0.04</td>
<td>4.3</td>
<td>23.4</td>
<td>0.5</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

### Table 2 - Degradation time at 1123 K for equivalent microstructures serviced at 1023 K.

<table>
<thead>
<tr>
<th>Degradation time (h) at 1123 K</th>
<th>0</th>
<th>10</th>
<th>25</th>
<th>50</th>
<th>100</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Actual operating time (h) at 1023 K</td>
<td>0</td>
<td>172</td>
<td>431</td>
<td>862</td>
<td>1723</td>
<td>3447</td>
</tr>
</tbody>
</table>
at 1123 K needed to obtain the same microstructure as that for a long time at actual operating temperature (1023 K).

The virgin and degraded specimens were prepared by cold mounting, grinding, and polishing for microstructure analysis. Microstructure analysis was performed on the grains, surface oxides, and precipitates of both virgin and degraded specimens using optical microscopy (OM) and scanning electron microscopy (SEM). The possibility of a phase change in 21-4N steel during isothermal degradation was examined by powder X-ray diffractometry (XRD) using Cu-Kα radiation at a glancing angle of 0.01°. For microstructure observation, chemical etching was performed in a solution of CH₃OH (90 mL) + CuSO₄ (1.5 g) + HCl (3 mL) for 3 s.

Vickers hardness of each specimen was measured using an MVK-H2 hardness tester (Akashi Corporation) after microstructure analyses. The test load was set at 5 N and the center of the specimen, which had no influence on the surface oxide layer, was measured 25 times and then the measurements were averaged.

Tensile tests were performed at 1023 K for the virgin and degraded specimens. The test equipment was an electric-motor-type testing machine (Simadzu Corporation model AG-250 kN X Plus) and an electric furnace with the allowable temperature of 1673 K. The load and displacement were measured using a ceramic-type extensometer and measurements were saved using a data acquisition system in real time. The temperature of the specimen was maintained by feedback control using a K-type thermocouple. The specimen was maintained at 1023 K for 1 h to prevent formation of a temperature gradient. The tensile tests were performed by setting the cross-head speed at 0.4 mm/min to satisfy the strain-rate condition of ASTM E21 [24].

3. Results

3.1. Observation of carbides

To predict dissolution and precipitation behavior of various precipitation phases, the mole fraction of all phases according to temperature was calculated using Thermo-Calc software and the TCFE database. Simulation results for 21-4N austenitic steel are shown in Fig. 2. Cr-rich M₂₃C₆ carbides are predicted to be present at a fraction of 10% at 1123 K, the accelerated degradation temperature.

Fig. 3 shows X-ray diffraction pattern of the virgin and degraded specimens as a function of degradation time. It can be seen from Fig. 3 that the all specimens are mainly composed of an austenite (γ) phase and granular carbides (Cr₂₃C₆) and partially composed of a sigma (σ) phase. In addition, according to the peak intensities, it can be seen from Fig. 3a–f that the content of Cr₂₃C₆ carbides increased with increasing degradation time. This indicated that the amount of Cr₂₃C₆ carbides increased with increasing degradation time.

Analyses of the SEM images were performed on the virgin and degraded specimens to analyze the morphology of Cr₂₃C₆ carbides. A representative SEM image of a specimen degraded for 50 h is shown in Fig. 4. Various shapes and sizes of Cr₂₃C₆ carbides in the grain boundaries can be observed and

![Fig. 2 - Calculated phase fraction diagram as a function of temperature.](image1)

![Fig. 3 - XRD patterns after exposure for (a) 0 h, (b) 10 h, (c) 25 h, (d) 50 h, (e) 100 h, and (f) 200 h at 1123 K.](image2)

![Fig. 4 - SEM images of the morphology of intragranular carbides.](image3)
the result of elements analysis using SEM energy-dispersive spectroscopy (EDS) is listed in Table 3. In addition, a few plate-like Cr$_2$C$_6$ carbides within the grains can be observed. These carbides were maintained independently at the beginning of degradation. As the degradation progressed, the carbides that were present within the grains gradually disappeared, and the carbides at the grain boundaries became coarse. As a result, it was confirmed that the continuous carbides at the grain boundaries were gradually dispersed. The absence of carbides distributed dispersively at the grain boundaries and within the grain would lower the strength at high temperatures [25]. Because the precipitates were separated from each other, these changes are related to losses in tensile strength.

3.2. Measurement of the grain size

The grains of virgin and degraded specimens were observed using an optical microscope at a magnification of 1000×. OM images of the grains and grain boundaries at different degradation times are shown in Fig. 5. As shown in Fig. 5a, 21-4N steel in its virgin state exhibits a fine grain size and grains are homogeneously distributed. Micrographs for the degraded specimen are shown in Figs. 5b–f as a function of degradation time, where it is observed that the grains coarsen gradually compared to the virgin state with increasing degradation time.

The average grain diameter was calculated using the intercept method according to ASTM E112 [26]. The average grain diameter of the virgin specimens was determined to be 5.7 μm. Fig. 6 shows the changes in the average grain diameter as a function of degradation time. With increasing degradation time, the average grain diameter increased and the frequency of coarsened grains increased. For the specimen degraded for 200 h, its average grain diameter was 7.6 μm. However, the growth rate of grains continuously decreased. This is judged to be the effect of the Cr$_2$C$_6$ carbides present at the grain boundaries [27].

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Mn</th>
<th>O</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt.%</td>
<td>4.2</td>
<td>6.0</td>
<td>4.9</td>
<td>0.7</td>
<td>66.9</td>
<td>17.3</td>
</tr>
</tbody>
</table>

Table 3 – Composition analysis results for the intragranular carbides in the grain boundaries.
3.3. Observation of surface oxides

Fig. 7 shows the X-ray element distribution mapping images of the surface oxides of the degraded specimen. The results of elements analysis near the surface of the specimens using SEM-EDS are shown in Fig. 8 and are listed in Table 4. It was confirmed that Mn oxide was the most principal oxides among the surface oxides but a small amount of Cr oxides was also found. This indicates that the base metal is mainly protected by Mn oxide. The Mn oxide is a chemical compound with the formula Mn₃O₄ and is thermodynamically in its most stable phase between 773 and 1173 K [28]. Additionally, high-temperature degradation makes solid-solution-strengthening elements such as Mn and Cr diffuse to the surface of the layer from under the oxidation layer, producing a depletion zone. The thickness of the surface oxide layer increases with increasing degradation time. However, it is difficult to quantify the increase in layer thickness because the layer was peeled off by the stress resulting from the difference between thermal expansion coefficients in the microstructure of the specimen during cooling [29].

Therefore, the surface oxide layer thickness was indirectly measured by measuring the thickness of the zone where the content of the solid-solution-strengthening element was depleted. To measure the thickness of the depletion layer under the surface oxide layer, the Mn composition was analyzed using SEM-EDS and each element near the specimen surface was investigated by a line scan. Fig. 9 shows the line scan results for the Mn composition of the specimens degraded for 50 h. Section 1 indicates the Mn oxides formed on the specimen surface. Section 2 indicates the Mn-depleted zone formed by diffusion of Mn to the surface. Section 3 indicates the matrix.

The changes in thickness of the Mn-depleted zone with increasing degradation time are plotted in Fig. 10. The thickness of the Mn-depleted zone was ~15.5 μm for the specimens.
degraded for 10 h and the thickness of the Mn-depleted zone was ~28.5 μm for the specimens degraded for 200 h. It was confirmed that the depletion of Mn in the matrix progressed continuously by the growth of surface oxide layer with increasing degradation time. The growth of the surface Mn oxides layer resulting from high-temperature degradation depletes the solid-solution-strengthening elements in the matrix. As a result, the stacking fault energy increases and cross-slip easily occurs, which affects the mechanical properties of the material [30]. It is assumed that the hardness and tensile strength decrease when the surface oxides layer grows.

3.4. Tensile tests and hardness measurement

The changes in the uniaxial tensile properties and hardness with increasing degradation times are plotted in Figs. 11 and 12, respectively. The changes in ultimate stress, yield stress and hardness with increasing degradation times all exhibited a similar tendency. With increase degradation time, the ultimate stress, yield stress and hardness decreased, but very little change was observed after 100 h of degradation. However, the elongation tends to increase continuously with increasing degradation time. For the specimen degraded for 200 h, its ultimate stress, yield stress and hardness decreased by 15%, 23% and 9%, respectively, compared to the virgin specimen but elongation increased by 23%. This means that the material has softened as the degradation progresses. Such reductions normally amount to an erosion of the design safety factor in terms of tensile properties, but can also be reflected in terms of reduced fatigue strength, because fatigue strength is related to both tensile strength and ductility [27].

Fig. 9 – Line scan results for surface Mn oxides after exposure for 50 h at 1123 K.

Fig. 10 – Changes in Mn-depleted zone thickness as a function of degradation time.

Fig. 11 – Changes in tensile properties as a function.

Fig. 12 – Changes in hardness as a function of degradation time degradation time.
4. Discussion

4.1. Plastic flow behavior

Tensile flow and work-hardening behavior attract significant scientific and technological interest with a view to optimizing appropriate conditions for material processing and ensuring safe performance during service [31]. Plastic flow behavior of metals and alloys is commonly analyzed with the aid of the empirical mathematical equations, e.g., the Hollomon equation [32], which is given by

\[ \sigma = K_0 \varepsilon^n \]

where \( \sigma \) is the true stress, \( \varepsilon \) is the true plastic strain, \( K_0 \) is the strength coefficient and \( n \) is the strain-hardening exponent. It has been suggested that the plastic flow behavior of austenitic stainless steels and many other FCC metals and alloys with low stacking fault energy (SFE) frequently cannot be adequately analyzed by the Hollomon equation owing to the existence of a positive stress deviation in the low-strain region [33]. To give appropriate consideration for this stress deviation, a modified equation, i.e., the Ludwigsen equation, was proposed by Ludwigsen; it can be expressed as [34]

\[ \sigma = K_1 \varepsilon^{n_1} + \exp(K_2 + n_2 \varepsilon) \]

where \( K_1 \) and \( n_1 \) have the same meanings as \( K \) and \( n \) in the Hollomon equation, \( \exp(K_2 + n_2 \varepsilon) \) is an additional term that accounts for the contribution of the stress deviation, \( K_2 \) is the initial yield stress at \( \varepsilon = 0 \) or at the onset of plastic flow and \( n_2 \) is the strain-hardening exponent in the low-strain region. Besides \( K_1, n_1, K_2 \) and \( n_2 \), the transition strain \( \varepsilon_C \) is also important [33]. Soussan et al. [35] defined a transition strain \( \varepsilon_C \) where the deviation parameter in the Ludwigsen equation \( \exp(K_2 + n_2 \varepsilon) \) becomes very small in comparison with the Hollomon equation. \( \varepsilon_C \) was calculated using the following equation:

\[ r = \frac{\exp(K_2 + n_2 \varepsilon)}{K_1 \varepsilon^{n_1}} \]

The parameters involved in the Ludwigsen equation have been used to investigate the underlying mechanisms and the changes in microstructure that occur during deformation. The physical interpretation of each parameter is as follows: \( K_1 \) expresses the ability of strengthening by deformation, \( n_1 \) indicates the intensity of the work-hardening phenomena. Similarly while \( K_2 \) signifies the short-range stress inducing the movement of the first mobile dislocation, \( n_2 \) expresses the rate at which the ratio between the short-range and long-range stress decreases. The critical strain \( \varepsilon_C \) corresponds to the strain below which planar slip is prevalent and above which multiple slip becomes dominant [36]. In this study, \( \varepsilon_C \) was determined at \( r = 0.05 \). The various flow curve parameters of the Ludwigsen equation \( K_1, n_1, K_2, n_2, \) and \( \varepsilon_C \), are summarized in Table 5.

The decrease in the value of \( K_1 \) with degradation time may be related to the combined resistance to dislocation motions from the dislocation structure that results from the interaction of dislocations. Because the parameter \( K_2 \) does not present a clear trend, it is not obviously influenced by degradation. However, there is an obvious influence of degradation on the parameters \( n_1, n_2, \) and \( \varepsilon_C \). The increase in the value of \( n_1 \) means that the strain hardening is active and the decrease in the value of \( |n_2| \) means an increase of plastic strain. The increase in the value of \( \varepsilon_C \) means the short-range stresses act up to high strain with increasing degradation time. The dependence of \( \varepsilon_C \) on grain size can be rationalized in terms of Ludwigsen’s suggestion that \( \varepsilon_C \) represents the strain at which transient (planar-glide) behavior decays and steady-state (cellformation) behavior becomes predominant [37]. An important consequence of this behavior is that, while strain compatibility induces the operation of many slip systems, this causes the rate of strain hardening to increase. The softening is probably caused by the grain coarsening with increasing degradation time and results in a decreased tensile strength and increased ductility.

### Table 5 – Summary of flow curve parameters of the Ludwigsen relation.

| Degradation time (h) | \( K_1 \) (MPa) | \( n_1 \) | \( K_2 \) | \( |n_2| \) | \( \varepsilon_C \) |
|----------------------|----------------|----------|----------|----------|----------------|
| Virgin               | 573            | 0.153    | 1.98     | 7.46     | 0.206          |
| 10                   | 552            | 0.188    | 1.95     | 7.31     | 0.225          |
| 25                   | 537            | 0.196    | 2.01     | 7.27     | 0.318          |
| 50                   | 518            | 0.229    | 2.11     | 4.98     | 0.331          |
| 100                  | 498            | 0.251    | 2.12     | 4.59     | 0.338          |
| 200                  | 503            | 0.287    | 2.22     | 3.78     | 0.360          |

4.2. Hall–Petch relation

To evaluate the effect of grain coarsening, yield stress and hardness were measured to represent the strength of 21-4N steel as a function of grain size. Generally, in a polycrystalline material, the grain boundary itself does not have inherent strength, and strengthening by grain boundaries occurs by interfering with the slip in the grain. Therefore, as the grain size decreases, the strength of the material increases. The relation between tensile yield stress and grain size is described mathematically by the Hall–Petch equation, which can be expressed as

\[ \sigma_y = \sigma_0 + \frac{k_y}{\sqrt{d}} \]

\[ H = \sigma_0 + \frac{k_y}{\sqrt{d}} \]

where \( \sigma_y \) is the yield limit (usually equivalent to Vickers hardness), \( \sigma_0 \) is the lattice friction stress of mobile dislocation, \( H \) is the Vickers hardness, \( \sigma_0 \) is the intrinsic hardness, \( k_y \) defines the characteristic constant that depends on the content of impurities and alloying elements and \( d \) is the average grain size [38,39]. Fig. 13 shows the relationships between yield stress and grain size and Fig. 14 shows the relationship between hardness and grain size. The Hall–Petch coefficient \( (k_y) \) and the lattice friction stress \( (\sigma_0) \) derived from the relationship between yield stress and grain size are 761 MPa \( \mu \mathrm{m}^{-1/2} \) and \(-54.6\) MPa, respectively. The Hall–Petch coefficient \( (k_y) \) and the intrinsic hardness \( (\sigma_0) \) derived from the relationship between hardness and grain size are 745 MPa \( \mu \mathrm{m}^{-1/2} \) and Hv 48.3, respectively. The Hall–Petch coefficient \( (k_y) \) derived from yield stress and hardness exhibited almost the same value within 2.0% error. Therefore, it is valid to regard the yield stress as an evidence...
and hardness as equivalent parameter in the Hall–Petch relation. The equations of the Hall–Petch relation were derived through a linear regression analysis and can be expressed as

\[ \sigma_y = -54.6 + \frac{761}{\sqrt{d}} \]

\[ H = 483 + \frac{745}{\sqrt{\Delta}} \]

As the degradation time increased, continuously the grain coarsens and the grain boundaries decrease. The yield stress and hardness as a function of grain size fit the Hall–Petch relation very well. This means that the change of yield stress and hardness with degradation time can be predicted by the grain size. As shown in Fig. 15, the yield stress calculated by using the Hall–Petch relation were compared with the values measured according to the degradation time. Comparing the results, one can see that the yield stress calculated by the Hall–Petch relation fit well with actual measured values within 4.0% error. However, after 100 h of degradation, the error exhibited a tendency to increase gradually. These results are judged to be insufficient to reduce the strength associated with grains growth resulting from the effects of strengthening the grain boundaries by the solid solution strengthening and precipitation of carbides at grain boundaries. Nevertheless, both the tensile yield stress and the hardness during degradation are consistent with the Hall–Petch relationship. Therefore, it is possible to predict the change of the yield stress and hardness through the change of the grain size, as grains are coarsened during degradation, and, at the same time, the degradation time can be predicted.

5. Conclusion

In this study, the effects of high-temperature degradation on the microstructure evolution and changes in mechanical properties of 21-4N austenitic heat-resistant steel were investigated. The conclusions were as follows.

1. The Cr23C6 carbides were observed in various sizes and shapes at the grain boundaries and in the grain at the beginning of degradation. With increasing degradation time, the content of Cr23C6 carbides increased and the size of Cr23C6 carbides located at grain boundaries became coarse.

2. With increasing degradation time, the average grain diameter increased and the frequency of coarsened grains increased. However, the growth rate of grains gradually decreased. This is judged to be the effect of carbides present at the grain boundaries.

3. Composition analysis of the surface oxides for the degraded specimens revealed that most were Mn oxides (MnO2); some Cr oxides were also observed. A Mn-depleted zone was observed under the Mn oxide layer. As the degradation time increased, the thickness of the Mn-depleted zone increased with the growth of the surface oxide layer, thereby continuously depleting the matrix of Mn content.

4. With increasing degradation time, the ultimate stress, yield stress and hardness decreased, but very little change was observed after 100 h of degradation. However, the elongation tends to increase continuously with increasing degradation time. This means that the material softened as the degradation progressed.

5. Plastic flow behavior using the Ludwigson equation revealed that the decrease in the value of K1, and |n2| with
increasing degradation time, but the increase in the value of \( n_1 \) and \( \epsilon_c \) with increasing degradation time. However, the parameter \( K_2 \) does not present a clear trend, it is not obviously influenced by the degradation. The softening is probably caused by the grain coarsening with increasing degradation time and results in a decreased tensile strength and increased ductility.

6. Tensile yield stress and hardness during degradation are consistent with the Hall–Petch relationship. Therefore, it is possible to predict the change of the yield stress and hardness through the change of the grain size, as grains coarsen during the degradation, and at the same time, the degradation time can be predicted.

Conflicts of interest

The authors declare no conflicts of interest.

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