Thermal decomposition of austenite in medium manganese high carbon steels

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Abstract: Medium manganese steels can become soft and formable by making them fully austenitic. This can be done by increasing their carbon concentration to more than approximately 1 mass-% followed by quenching from a high austenitization temperature. In this condition, they can be cold-forged to manufacture balls for bearing applications. For the final application, however, the hardness must be raised by an appropriate thermal treatment to decompose austenite into harder product phases. The present contribution discusses changes in the microstructure and hardness of aluminum- and silicon-added medium manganese high carbon steels due to isothermal treatment at 650 °C. Due to the formation of fine pearlite, the hardness exhibited a maximum for holding times between 1 h and 5 h, depending on the Al and Si contents. Prolonged isothermal treatment resulted in the coarsening and partial spheroidization of pearlite, thereby a reduction in hardness. After isothermal treatment for 48 h, carbides were enriched with Mn and Si and depleted of Al.

Introduction
Due to their superior strength and ductility combination, steels containing raised Mn contents receive an ever-increasing attention among the scientific community and steelmakers. Such steels are of particular interest to the automotive industry, where enhanced passenger safety and reduced weight without substantial increase in manufacturing and materials costs drives the industry [1]. The presence of high Mn concentrations in TWIP steels impairs their weldability and galvanizability, increases production costs and decrease their productivity, which are responsible for their limited industrialization [2,3]. Therefore, many researchers have attempted to decrease the Mn concentration of TWIP steels without significant sacrifice of the mechanical properties [2,4,5]. If the reduction in Mn content is not compensated for by the addition of other alloying elements, the microstructure will additionally contain some ferrite or martensite. For example, medium Mn steels containing low C concentrations commonly exhibit austenitic-ferritic microstructures [6]. As long as the carbide formation is suppressed, the formation of ferrite/martensite in medium Mn steels can be inhibited by an increase in the C concentration [7]. In such cases, a soft and formable austenitic microstructure can be achieved by quenching from high austenitization temperatures to retain austenite with an appropriate mechanical stability[8].

In the manufacturing process balls for ball bearings, feedstock in the form of wire is rolled into a machine that cuts off a short piece and then smashes both ends towards the middle. This process is called cold heading and requires raw steel with a low hardness and good formability. These criteria can be met by using medium Mn high C steels with fully austenitic microstructures. For the final application, the hardness of the bearing steel (AISI 52100) can be raised to 58–62 HRC by induction hardening [9]. Based on a prior study using Fe–1.4C–8Mn–(2,3)Al steels (concentrations in mass-%), medium Mn steels can become fully austenitic at RT by raising the C content, which in turn reduces the $M_s$ temperature. The addition of Al decelerates the kinetics of cementite formation in medium Mn steels and facilitates obtaining a fully austenitic microstructure at lower cooling rates compared to the ternary Fe–Mn–C steels. Meanwhile, Al-added medium Mn high C steels exhibit a high resistance against the
formation of martensite by thermal and mechanical treatments, which is necessary for the ready cold 
heading of wires into balls. For the final bearing application, however, the hardness must be raised by 
an appropriate thermal treatment to decompose austenite into harder product phases. Alloying with Al 
can enhance the driving force for the transformation of austenite to pearlite and result in the formation 
of fine pearlite [8]. This is a possible mechanism to make the cold-headed balls hard enough for the final 
application as bearing. The present contribution reviews changes in the microstructure and hardness 
caused by the isothermal treatment at 650 °C of medium Mn high C steels containing Al and Al + Si. 
The results enable to evaluate the suitability of isothermal treatment at 650 °C to attain the hardness 
levels required for bearing applications.

Experimental procedure
Chemical compositions of the medium Mn high C steels studied in the present work are given in table 1. 
The ingots were produced using a vacuum induction melting and casting facility. The cast ingots were 
homogenized at 1250 °C for 2 h under vacuum. To dissolve the carbides possibly formed during N2 gas 
cooling to RT, small specimens taken from homogenized ingots were austenitized at 1150 °C for 30 min 
and then quenched in brine. Specimens in this condition were isothermally treated at 650 °C for times 
up to 48 h. Ferromagnetic phase fractions after different isothermal treatments were quantified by 
magnetic measurements in a magnetic field of nearly 3.5 kOe. These measurements were done using a 
Metis MSAT device equipped with a Lakeshore 480 fluxmeter. Hardness of specimens was measured 
using a 430 SVD Vickers hardness tester with a pyramid-shaped diamond indenter. The applied 
load and the indentation time were 10 kgf and 10 s, respectively. XRD was used to identify 
crystalline phases and determine lattice parameters. Measurements were done in a Seifert-FPM-6 
diffactometer using Co-Kα radiation. The scanning range (2θ) and step size (Δ2θ) were 20-150 ° 
and 0.01 °, respectively. Microstructural examination were done using a LEO 430 type scanning 
electron microscope (SEM) and a Zeiss Neophot 30 light optical microscope.

Table 1. Chemical composition of steels used in the present study (mass-%).

<table>
<thead>
<tr>
<th>Steel ID</th>
<th>C</th>
<th>Mn</th>
<th>Al</th>
<th>Si</th>
<th>Fe + impurities</th>
</tr>
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<tbody>
<tr>
<td>2Al</td>
<td>1.44</td>
<td>8.0</td>
<td>1.9</td>
<td>0.005</td>
<td>Balance</td>
</tr>
<tr>
<td>3Al</td>
<td>1.47</td>
<td>7.8</td>
<td>3.3</td>
<td>0.005</td>
<td>Balance</td>
</tr>
<tr>
<td>2Al2Si</td>
<td>1.43</td>
<td>7.7</td>
<td>2.00</td>
<td>1.98</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Results and Discussion
Figure 1 shows the microstructure of the steels in the as-quenched condition. All steels develop an 
austenitic microstructure with no obvious carbide formation. Nevertheless, the presence of thin films of 
cementite at grain boundaries cannot be excluded [9]. The particles with an approximate diameter of 2- 
3 μm dispersed in the matrix of all alloys were found by energy-dispersive X-ray spectroscopy (EDS) 
in SEM to be sulfides rich in Mn and Se. By examining the microstructure in the polished condition, the 
presence of a small fraction of graphite in the microstructure of the 2Al2Si steel was confirmed. This is 
consistent with the reported effect of Si on the stabilization of graphite in both cast irons and high C 
steels [10,11]. Quantitative image analysis yielded average grain sizes of 1.13 mm, 1.92 mm, and 0.6 
mm for the 2Al, 3Al, and 2Si2Al steels, respectively. The hardnesses in the as-quenched condition are 
marked on the micrographs. Hardness values below approximately 230 HV are required for the ready 
cold forging of rods into balls for bearing applications [12]. The present steels in the as-quenched 
condition are soft enough to qualify for such cold forging operations.
Figure 1. Light optical micrographs and hardness values after water quenching from 1150 °C. Nital was used as etchant.

Figure 2a shows the hardness evolution during isothermal heat treatment at 650 °C. Heat treatment time varied between 15 min and 48 h. The hardness evolution was similar for all steels; it initially increased to a peak value followed by a decrease at longer annealing times. For the 2Si2Al steel, the hardness increase was already noticeable after the shortest holding time of 15 min and the maximum hardness of 526 HV was reached after a relatively short holding time of 1 h. For the 2Al and 3Al steels, the initial hardness increase was moderate and the respective peak hardnesses were reached after a prolonged holding time of 5 h. In figure 2a, the peak hardness values are highlighted by solid symbols. The accelerated decomposition of pearlite in the 2Si2Al steel compared to the 2Al and 3Al steels can be related to multiple factors including the smaller grain size of the 2Si2Al steel, the presence of pre-existing graphite, and the higher thermodynamic driving force for the pearlite formation (high undercooling for pearlite formation due to the high ferrite potential of the alloy).

Figure 2. Evolution of (a) hardness and (b) ferromagnetic phase content during isothermal treatment of steels at 650 °C.

In order to study the microstructural changes responsible for the hardness increase, specimens heat treated to peak hardness—as marked by solid symbols—were studied by light optical microscopy. As shown in figure 3, the microstructure is almost fully pearlitic for the 2Si2Al and 3Al steels. The bright spots marked θ in the microstructure of the 2Si2Al steel are presumably cementite, which replaces the graphite particles in the as-quenched condition. For the specimen of the 2Al steel treated to peak hardness (5 h), large regions with a bright contrast resembling austenite were also found in the microstructure. The presence of austenite is compatible with the magnetic measurement results in figure 2a, where the ferromagnetic phase fraction for the 2Al steel treated to peak hardness remains lower than those for the 2Si2Al and 3Al steels. Even for the 2Si2Al and 3Al steels, the maximum ferromagnetic phase fraction does not exceed 80 vol.%. This can be justified by the presence of high fractions of paramagnetic or weakly-ferromagnetic cementite [13] in the microstructure of all steels, either as isolated particles or as a constituent of pearlite. Accordingly, XRD peaks fairly matching the...
Theoretical positions of Fe₃C peaks were identified in the diffraction patterns (figure 4). The XRD results do not exclude the possibility of the presence of carbides other than cementite.

Figure 3. Light optical micrographs in the peak-hardened condition. Nital was used as etchant.

40 50 60 70 80
Intensity, a.u.

\[
\begin{align*}
2\text{Al}, 48\text{ h}, \alpha &= 2.877 \pm 0.0001\text{ nm} \\
2\text{Al}, 1\text{ h}, \alpha &= 2.873 \pm 0.0001\text{ nm} \\
3\text{Al}, 48\text{ h}, \alpha &= 2.884 \pm 0.0001\text{ nm} \\
3\text{Al}, 1\text{ h}, \alpha &= 2.885 \pm 0.0002\text{ nm} \\
2\text{Si}_2\text{Al}, 48\text{ h}, \alpha &= 2.873 \pm 0.0001\text{ nm} \\
2\text{Si}_2\text{Al}, 1\text{ h}, \alpha &= 2.873 \pm 0.0002\text{ nm} \\
\end{align*}
\]

Theoretical Fe₃C (\(a=0.45235\text{ nm}, \ b=0.50890\text{ nm}, \ c=0.67433\text{ nm}\))

The observed hardness increase of specimens at relatively short isothermal treatment times is attributed to the austenite decomposition to pearlite. Apart from possible differences in the interlamellar spacing of pearlite, the higher peak hardness for the 2Si2Al steel compared to the 3Al steel might be due to the solid solution strengthening effect of Si[14]. The ferrite lattice parameters marked in figure 4 indicate lattice expansion and contraction of ferrite upon alloying with Al and Si, respectively.

The hardness of all steels decreased upon extended exposure to 650 °C. This softening was not associated with any noticeable change in the ferromagnetic phase fraction for 3Al and 2Si2Al steels. This suggests that the observed hardness decrease is due to microstructural changes which leave the phase balance uninfluenced. Figure 5 shows the microstructures after isothermal treatment for 48 h. Comparison of the microstructures with those in the peak-hardened condition indicate the coarser size of pearlite after treatment for 48 h, leading to a more ready resolution of pearlitic lamellae. The SEM micrographs in figure 5 also suggest the breakdown and partial spheroidization of carbides.

Figure 4. XRD patterns and ferrite lattice constants in the peak-hardened condition and after isothermal treatment for 48 h. Symbols indicate the theoretical peak positions for Fe₃C, \(\alpha\), and \(\gamma\), calculated using the marked lattice constants.
For the 2Al steel, the ferromagnetic phase fraction increased from 52 vol.% to 61 vol.% as the holding time increased from 5 h to 10 h. In spite of the increase in the pearlite fraction, the hardness decreased slightly. Therefore, the softening due to the coarsening and spheroidization of pearlite has more than offset the hardening due to the increase in its fraction. At longer holding times, the ferromagnetic phase fraction remains almost constant but changes in the size and morphology of pearlite lead to a constant softening. The coexistence of austenite and pearlite after isothermal treatment for 48 h indicate that austenite has been a stable phase at 650 °C. The higher ferrite potential for the 3Al and 2Si2Al steels, on the other hand, leads to austenite-free microstructures after prolonged heat treatment at 650 °C.

The partitioning of alloying elements between microstructural constituents in the steels treated at 650 °C for 48 h was studied by EDS analysis in SEM (figure 6). The elemental concentrations were quantified by excluding C and impurity elements. In other words, the sum of Fe, Mn, Al, and Si concentrations added up to 100%. The concentrations of the main alloying elements varied significantly in different regions of the microstructure, even in the same phase distributed in different regions. Nevertheless, the concentration of Mn in carbides was invariably higher than the average Mn concentration. Especially in the case of the 2Si2Al steel whose microstructure contained coarse carbide particles suitable for EDS analysis, the Mn concentration of carbides was significantly higher than the average Mn concentration. The Mn enrichment of cementite is a well-documented phenomenon [15,16]. There was a large scatter in the quantified Al concentrations of carbides. Nevertheless, except for a few spots such as the one marked EDS 3 in the 3Al steel, majority of the carbide particles analyzed—including the large ones in the 2Si2Al steel—contained relatively low Al concentrations. This is in agreement with the reported partitioning behavior of Al between ferrite/martensite and cementite [17]. EDS analysis of the 2Si2Al steel further revealed the Si enrichment of carbides. This partitioning behavior is in clear contrast to the reported literature results for cementite [17,18]. If the large carbides are cementite, the coexistence of Si and Al might be responsible for the anomalous partitioning of Si. The inability of ferrite to accommodate both Al and Si can be a possible explanation for the Si enrichment of cementite. Finally, EDS analysis of austenite in the 2Al steel indicated that its chemical composition was similar to the average chemical composition.
Conclusions
Thermal decomposition of austenite in medium Mn high C steels alloyed with Al (2Al and 3Al) and Si + Al (2Si2Al) was studied by hardness and magnetic measurements, microstructural examinations, and XRD of specimens isothermally treated at 650 °C. The following conclusions were drawn:

1. Peak hardness was reached subsequent to austenite decomposition to pearlite. The decomposition of austenite was quickest in the 2Si2Al steel. Prolonged treatment of all steels led to softening caused by the coarsening and spheroidization of pearlite.
2. Some austenite was retained in the microstructure of the 2Al steel treated for 48 h, indicating its stability at 650 °C.
3. XRD results indicated a decrease in the lattice parameter of ferrite upon an increase in the Al concentration. In contrast, Si decreased the ferrite lattice parameter.
4. Partitioning of alloying elements was confirmed by SEM-EDS analyses of specimens treated for 48 h. Mn was invariably enriched in carbides. Carbides were almost always depleted of Al and enriched with Si.

Acknowledgements
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<table>
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<th>Mn (mass-%)</th>
<th>Al (mass-%)</th>
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<tr>
<td>EDS 1</td>
<td>11.37 ± 1.24</td>
<td>1.13 ± 0.29</td>
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<tr>
<td>EDS 2</td>
<td>8.75 ± 0.99</td>
<td>1.48 ± 0.28</td>
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<tr>
<td>EDS 3</td>
<td>12.53 ± 1.40</td>
<td>1.10 ± 0.25</td>
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<tr>
<td>EDS 4</td>
<td>6.99 ± 0.89</td>
<td>1.71 ± 0.29</td>
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<tr>
<th>Spot</th>
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<th>Si (mass-%)</th>
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<tr>
<td>EDS 1</td>
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<td>2.59 ± 0.39</td>
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<tr>
<td>EDS 2</td>
<td>9.43 ± 1.08</td>
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<tr>
<td>EDS 3</td>
<td>13.11 ± 3.62</td>
<td>4.46 ± 1.31</td>
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<tr>
<td>EDS 4</td>
<td>9.21 ± 1.02</td>
<td>3.38 ± 0.41</td>
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<table>
<thead>
<tr>
<th>Spot</th>
<th>Mn (mass-%)</th>
<th>Al (mass-%)</th>
<th>Si (mass-%)</th>
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<tbody>
<tr>
<td>EDS 1</td>
<td>17.89 ± 1.97</td>
<td>0.92 ± 0.32</td>
<td>3.22 ± 0.38</td>
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<tr>
<td>EDS 2</td>
<td>6.95 ± 0.99</td>
<td>1.66 ± 0.36</td>
<td>1.64 ± 0.29</td>
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<tr>
<td>EDS 3</td>
<td>14.16 ± 1.65</td>
<td>0.52 ± 0.27</td>
<td>2.30 ± 0.37</td>
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<tr>
<td>EDS 4</td>
<td>18.45 ± 1.96</td>
<td>0.69 ± 0.33</td>
<td>3.20 ± 0.41</td>
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Figure 6. Quantitative SEM-EDS analyses of steels after isothermal treatment for 48 h.
References


