



Article High-Temperature Oxidation Behaviour of Duplex Fe-Mn-Al-Ni-C Lightweight Steel

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Abstract: Lightweight Fe-Mn-Al-Ni-C steels are an attractive material, due to the combination of low density, high elongation, and yield strength. However, the high Al content is also interesting from the point of view of high-temperature resistance. High-temperature resistance is important for high-temperature applications and oxidation during heat treatment. Oxidation tests at 700, 800 and 900 °C were carried out to investigate the oxidation rates. Oxidation at 700 °C resulted in slight decarburisation, which was reflected in a slight weight loss in the thermogravimetric analysis. In contrast, the weight in the thermogravimetric analysis increased at 800 and 900 °C and the kinetics followed a parabolic law. The higher the temperature, the more weight is gained and the thicker the oxide layer becomes. The oxidation layer at 800 and 900 °C consisted mainly of hematite and magnetite, with minor amounts of wüstite, alumina and hercynite. Preferential oxidation of austenite was also observed, as it has an increased Mn content. In addition, ferrite had an increased content of Al and Ni, which provide additional oxidation resistance.

Keywords: duplex steel; lightweight steel; oxidation; kinetics



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1. Introduction

Lightweight steels have attracted attention mainly because of their low density, as they can achieve up to 20% lower density compared to conventional steels [1–10]. The low density is the result of the high Al content, as each weight percent of Al lowers the density by approximately 1.3% [11,12]. Therefore, these steels typically contain between 5 and 10 wt.% Al, along with Mn contents above 10 wt.%. The unique chemical composition leads not only to low densities, but also to relatively high tensile strengths and elongations. However, there is another interesting aspect of the Fe–Mn–Al alloy system, and that is its oxidation resistance, not only at room temperature, but also at elevated temperatures, so that the steels can also be used at elevated temperatures. Another important aspect is the oxidation that can occur during various heat treatments.

Studies have been carried out on the high-temperature oxidation behaviour of Fe-Mn-Al-C steels. It was found that the addition of Al promotes the formation of an Al₂O₃ layer, which prevents further oxidation and has a high protective effect [13–18]. Furthermore, an increasing C content increases the weight gain per unit area and the thickness of the oxide layer formed, which leads to the deterioration of the high-temperature oxidation resistance [13]. Steels with Mn content lower than 7.5 wt.% formed layers consisting of Al₂O₃ and Fe-like oxides, while the oxide layer was highly enriched in Mn for steels with Mn content greater than 7.5 wt.% [15]. It was also found that the formation of Al₂O₃ and Mn-rich oxides essentially compete with each other [16]. Grain size also plays a role, as grain refinement accelerates phase transformation and promotes the rapid formation of Al₂O₃ layers and slightly improves oxidation resistance [17]. As for the kinetics of high-temperature oxidation, it was found to follow a parabolic law [19]. As for the structure of

the oxide layers formed, the outer layer was mainly composed of Mn_2O_3 and Mn_3O_4 , while the Al_2O_3 was mainly observed in the ferrite layer [20]. Based on previous studies [13,21], internal oxidation is also expected, as it was found that increased C content not only worsens the high-temperature oxidation resistance, but also increases the internal oxidation area and provides more time for decarburisation of the austenite, leading to greater diffusion of Mn to the outside and reaction with O [13]. The preferential oxidation of Mn promotes the phase transformation of austenite to ferrite, which opens pathways for Al diffusion. Therefore, Al_2O_3 is enriched at the boundary of the inner oxidation layer of austenite [13]. The higher the temperature (>850 °C) of oxidation, the more Al_2O_3 -rich oxide layers are formed, providing better oxidation resistance [21].

In this study, we have focused on the high-temperature oxidation of Fe-Mn-Al-Ni-C steel in the temperature range of 700 to 900 °C. In addition to the metallographic analysis of the oxide layers formed at the investigated temperatures, the high-temperature oxidation kinetics were also studied.

2. Materials and Methods

A total of 10 kg of steel was melted in a vacuum induction melting furnace under a 300-mbar Ar protective atmosphere. The pure elements Al, Mn, Ni, and C, as well as mild steel, were used to produce the steel. The steel was cast into a 210 mm long ingot that was 80 mm wide at the bottom and 90 mm wide at the top.

The chemical composition (Table 1) was measured by wet chemical analysis and infrared absorption after combustion with ELTRA CS-800 (ELTRA GmbH, Haan, Germany).

Sample	С	Si	Cu	Ni	Mn	Al	Fe
FeMnAl5.6NiC	0.82	0.20	0.17	5.6	14.8	10.1	balance

Table 1. The chemical composition of the samples is given in percent by weight.

The chemical composition of the samples is given in Table 1.

High-temperature oxidation was studied at 700, 800 and 900 °C in dry air atmosphere for 100 h. For the study of kinetics, oxidation was carried out in a NETZSCH STA Jupiter 449C (NETZSCH-Gerätebau GmbH, Selb, Germany) instrument, in which a TGA (Thermogravimetric Analysis) sample carrier was used to study kinetics. The heating and cooling rate was 10 °C min⁻¹, and air (79 vol.% nitrogen, 21 vol.% oxygen, 0.9 vol.% argon and 0.1 vol.% hydrocarbons and other inert gases) was introduced into the furnace at a flow rate of 30 mL min⁻¹ (during the isothermal section). The samples were on an alumina slip-on plate, and the top of the slip-on plate was covered with a 1 mm thick platinum layer. After the experiment, the obtained TGA data were exported, the weight gain at the specific surface was calculated, and the graph was generated using OriginPro software (OriginLab Corporation, Northampton, MA, USA), version 2016. In addition, before the sample runs, correction runs were performed with an empty Al₂O₃ slip-on plate on which the samples were located during oxidation.

As for the microstructural characterisation of the oxide layers formed, the samples were cooled at a faster rate ($10 \degree C s^{-1}$) than in the kinetics study to preserve the scale structures developed at the elevated temperatures. This is especially true for wüstite, as it can transform back to Fe and Fe₃O₄ [22]. The samples were then prepared for metallographic analysis by grinding and polishing. For electron backscatter diffraction measurements, the polished samples were additionally polished with oxide polishing suspension (OPS) for 5 min. Microstructural characterisation was performed using the scanning electron microscope JEOL JSM 6500-F (Jeol, Tokyo, Japan). Additional microanalysis was performed with energy dispersive spectroscopy (EDS) (Ultim^{®®} Max, Oxford Instruments, Abingdon, UK) and electron backscatter diffraction (EBSD) (HikariSuper EDAX, Mahwah, NJ, USA).

The commercial software Thermo-Calc version 2022a (Thermo-Calc Software AB, Stockholm, Sweden) was used for the CALPHAD calculations [23]. The Thermo-Calc

Software TCFE10 Steels/Fe-alloys database was selected to obtain the thermodynamic data for the calculations. We used the equilibrium calculator and selected the property diagram calculation type, from which we obtained diagrams showing the amount of thermodynamically stable phases in the steel studied.

Density was already determined according to the "principle of Archimedes" [24] and was $6886.54 \text{ kg m}^{-3}$ for the steel studied.

3. Results and Discussion

3.1. CALPHAD Calculations

The CALPHAD calculations (Figure 1) show the amount of thermodynamically stable phases in the steel studied at the oxidation temperatures. At 700 °C, the equilibrium composition of the steel contains the following phases: 46.2 wt.% ferrite (BCC_B2), 44.6 wt.% austenite (FCC_A1) and 9.2 wt.% kappa carbides (KAPPA_E21). At 800 °C, 59.7 wt.% austenite (FCC_A1), 35.5 wt.% ferrite (BCC_B2) and 4.8 wt.% kappa carbides (KAPPA_E21) and at 900 °C, 67.1 wt.% austenite (FCC_A1) and 32.9 wt.% ferrite (BCC_B2) were recorded. Based on the calculated results at 700 and 800 °C, kappa carbides are expected to indirectly influence the high-temperature oxidation behaviour, as the matrix is depleted of alloying elements. At 900 °C, equilibrium calculations show that kappa carbides are no longer present in the matrix, but in practice, i.e., in experiments, this may be different as we are not in equilibrium.



Figure 1. CALPHAD calculations of the equilibrium quantity of phases in the steel studied at oxidation temperatures.

3.2. Thermogravimetric Analysis

The TGA results are shown in Figure 2. At 900 °C, the oxidation proceeds parabolically, the calculated parabolic rate constant k_p is 1.8×10^{-3} mg² cm⁻⁴ s⁻¹, but after 138 min or 2 h and 18 min, the slope of the TGA curve changes and from then on, the parabolic rate constant k_p changes and is 3.3×10^{-4} mg² cm⁻⁴ s⁻¹. At 800 °C, the oxidation proceeds parabolically, the calculated parabolic rate constant k_p is 7.8×10^{-4} mg² cm⁻⁴ s⁻¹, but after 211 min or 3 h and 31 min, the slope of the TGA curve changes and from then on, the parabolic rate constant k_p changes and is 2.3×10^{-4} mg² cm⁻⁴ s⁻¹. At 700 °C, after 13 min of oxidation, there is a decrease in weight and the oxidation is neither parabolic nor cubic, which can also be observed from the change in weight in Table 2. The results were to be expected to a certain extent, i.e., the higher the oxidation temperature, the more weight is gained. This is also confirmed by the calculated rate constants of 3.3×10^{-4} mg² cm⁻⁴ s⁻¹ at 900 °C (after 138 min) and 2.3×10^{-4} mg² cm⁻⁴ s⁻¹ at 800 °C (after 211 min). At 700 °C, the weight starts to decrease (Table 2), which is mainly due to mild decarburisation and partly also to spalling of the oxide layer formed. This means that the steel does not oxidise



as quickly as at 800 and 900 °C and basically only decarburisation takes place, which is confirmed further by the metallographic analyses.

Figure 2. TGA results for all the samples investigated at different oxidation temperatures.

Table 2. Final weight changes in %, mg, and mg cm⁻² (weight change per specific surface area of the samples).

Temperature (°C)	TGA (%)	TGA (mg)	TGA (mg cm ⁻²)
700	-0.030	-0.124	-0.144
800	1.031	4.222	4.935
900	1.310	5.324	6.282

3.3. Scanning Electron Microscopy

The SEM analysis showed that the samples are resistant to oxidation at 700 °C, as there is practically no oxide layer, which is in agreement with the TGA result. There is a slight decarburisation, which can be observed from the weight loss in Figure 2 and Table 2. The absence of an oxide layer can be observed in Figure 3a. Oxidation is more pronounced at 800 and 900 °C, as can be observed in Figure 3b,c. Oxidation of austenite is preferred, as the ferrite contains more Al ~12 wt.% (Figure 4—Spectrum 1, 2 and 5) than austenite ~9 wt.% (Figure 4—Spectrum 3 and 4).

Figures 4 and 5 show the initial microstructure of the Fe-Mn-Al-Ni-C duplex steel containing ferrite and austenite [25], as shown in Figure 4. An EDS analysis of the matrix, i.e., the initial microstructure, was also carried out to show the distribution of elements in ferrite and austenite (Figure 4). As mentioned earlier, ferrite contains more Al ~12 wt.% (Figure 4—Spectrum 1, 2 and 5) than austenite ~9 wt.% (Figure 4—Spectrum 3 and 4). In contrast, ferrite contains more Mn ~15 wt.% (Figure 4—Spectrum 1, 2 and 5) than austenite ~12 wt.% (Figure 4—Spectrum 3 and 4). The Ni content is the same as the Al content, i.e., ferrite contains more Ni ~7 wt.% (Figure 4—Spectrum 1, 2 and 5) than austenite ~4 wt.% (Figure 4—Spectrum 3 and 4). This also explains why the oxidation of austenite is preferred. The C content in the EDS analysis is only informative; the values are only shown to show that more C is present in the austenite.

a) 700 °C



Figure 3. Oxide layers formed after high-temperature oxidation at (a) 700, (b) 800 and (c) 900 °C.

To confirm that ferrite (light areas in Figure 5) contains more Al and Ni than austenite (dark areas in Figure 5), we also performed EDS elemental mapping of Al, Mn, Fe and Ni in the matrix of the steel under study (Figure 5). The results show that the weight percentage of Al and Ni is higher in ferrite and the weight percentage of Mn is higher in austenite.

The EBSD analysis revealed a multiphase oxide layer at 800 and 900 °C. At 800 °C, it consists mainly of hematite and magnetite, with occasional wüstite and alumina at the oxidation front (Figure 6). The enrichment of alumina at the oxidation front is also evident from the EDS elemental mapping in Figure 7. The Al is present in the form of alumina and

FeAl₂O₄ hercynite. The crystal orientations were coloured with the IPF (inverse pole figure) colour coding of orientation maps, using the IPF-Z standard colour triangle. The IPF-Z of the oxide layer shows no preferential growth orientation in the upper oxide layer, while the lower layer shows a preferential orientation and the middle layer cannot be indexed. These layers are only visible by the IPF-Z mapping, while they show no differences in the phase analysis. The EDS mapping also shows that the oxidation-resistant ferrite contains more Ni; therefore, surprisingly, there is no Ni enrichment zone in the steel matrix below the oxidation front, as is the case for tool steels [26].



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-	wt.%						
Spectrum	С	Al	Mn	Fe	Ni	Total	
Spectrum 1	1.2	12.2	11.5	67.9	7.2	100.0	
Spectrum 2	1.1	11.6	11.6	68.9	6.8	100.0	
Spectrum 3	2.2	9.1	15.3	68.9	4.5	100.0	
Spectrum 4	2.3	9.0	14.8	69.6	4.3	100.0	
Spectrum 5	1.1	11.7	12.2	68.8	6.2	100.0	

Figure 4. The areas analysed with EDS are indicated with the corresponding chemical composition in wt.%.



Figure 5. EDS elemental mapping of Al, Mn, Fe and Ni in the matrix of the investigated steel.



Figure 6. EBSD phase analysis of the oxide layer after high-temperature oxidation at 800 °C, phase analysis and the crystal orientations in the oxide layer formed.



Figure 7. EDS analysis of the surface distribution of the elements in the oxide layer formed after high-temperature oxidation at 800 °C.

Oxidation at 900 °C gave similar results (Figure 8), but with more pronounced preferential austenite oxidation. The upper oxide layer was lost during sample preparation, but the lower layer was retained. The wüstite and FeAl₂O₄ hercynite areas are coarser. While hematite and magnetite still make up the bulk, the wüstite is more pronounced and makes up a significant proportion of the oxides. The IPF-Z results correspond to the middle oxide layer formed at 800 °C, as they are difficult to index. The oxidation front is rich in Al and depleted in Ni and Mn (Figure 9), while the oxides are enriched in Mn. Furthermore, areas of Ni enrichment appear in the oxides directly above the Al-enriched areas.



Figure 8. EBSD phase analysis of the oxide layer after high-temperature oxidation at 900 °C, phase analysis and the crystal orientations in the oxide layer formed.



Figure 9. EDS analysis of the surface distribution of the elements in the oxide layer formed after high-temperature oxidation at 900 °C.

4. Conclusions

High-temperature oxidation of lightweight Fe-Mn-Al-Ni-C steel showed that oxidation at 700 °C was relatively slow, with only mild decarburisation. The oxidation layer was too thin for SEM analyses.

However, at 800 and 900 °C, the oxidation rate increased significantly and favoured austenite oxidation. The oxidation at 800 and 900 °C was parabolic. We calculated oxidation rate constants of $2.3 \cdot 10^{-4}$ mg² cm⁻⁴ s⁻¹ at 800 °C (after 211 min) and $3.3 \cdot 10^{-4}$ mg² cm⁻⁴ s⁻¹ at 900 °C (after 138 min).

The oxidation layer at 800 and 900 $^{\circ}$ C consisted mostly of hematite and magnetite, with minor amounts of wüstite, alumina and hercynite. However, the wüstite content increased at 900 $^{\circ}$ C, while alumina and hercynite were only minor trace constituents.

The oxidation front is rich in Al, hence the alumina and hercynite formation, while most of the hematite and magnetite is rich in Mn, mainly due to the preferential oxidation of Mn-rich austenite. As for the matrix, the austenite phase is richer in Mn and C, while the ferrite is richer in Al and Ni, which provide additional oxidation resistance compared to austenite.

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