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**In-depth oxide scale growth analysis of B and Ti microalloyed AISI 304 in
oxygen-containing furnace atmospheres and CH₄ burn-simulating
furnace atmospheres**

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Abstract

The effects of boron and titanium microalloying on scale-layer formation and structure on AISI 304 austenitic stainless steel are studied. The research is focused on a steel slab's oxide scale formation in a reheat furnace prior to hot rolling. The studied boron microalloying amounts are 7, 35 and 55 ppm and the studied titanium microalloying amounts are <100 and 400 ppm. In-depth temperature and atmosphere tests span from 1100 °C to 1300 °C for an O₂-containing atmosphere and 1100 °C to 1250 °C in an H₂O-containing atmosphere, both using 25 °C increments. Research shows that microalloying 55 ppm B reduces scale growth at above 1175 °C in an H₂O atmosphere, all microalloying elements show significant scale growth reduction at 1175 °C in an O₂ atmosphere, microalloying 35 and 55 ppm B increases scale growth amounts at above 1225 °C in an O₂ atmosphere, while microalloying 400 ppm Ti reduced it. The inhibiting effect on scale growth that results from boron microalloying is tied to silicon oxide infiltration of the steel substrate.

1. Introduction

In stainless steels, the usual approach in microalloying elements' use is to control precipitate formation (e.g. nitrides) and austenite grain properties. Boron's and titanium's usage through alloying or coating have long been studied for both steel and stainless steel; titanium's microalloying amount affects railroad steel segregation^[1], and boron's alloying affects the self-hardenability on steel^[2], both date to 1924. Older research on boron, focusing on the 1 to 5 wt-% alloying effects of boron, uncovered boron's effects: the deposition of thin boron films improved dry sliding wear and the acid-caused corrosion of mild steel^[3], and increased austenitic stainless steel wear resistance due to boron ion implantation-induced martensite formation^[4]. More recent general research on boron's alloying effects, putting prominence on its microalloying amounts, has shown very good results in increasing the hardness (and thus the wear resistance) of welding-deposited Fe-Cr-Ti-C^[5] and Fe-Cr-Si-C^[6] hardfacing alloys. On the effects and phenomena concerning iron and steel, research has been made on boron content in the diffusion mechanism of Fe-B-based alloys (containing silica and manganese) in 1073 K for a duration of 100 hours and has shown the formation of a B₂O₃-SiO₂ scale that has increasing cyclic oxidation resistance with increasing boron alloying amounts^[7], while research on low-carbon steel microalloyed with boron (29–105 ppm B) shows a decrease in critical stress and strain resulting from increasing the boron microalloying amounts^[8].

Focusing on stainless steels' namesake, corrosion resistance, recent developments regarding boron alloying's effects have shown that boron alloying decreases pitting potential and increases the probability of the stable pitting of AISI 304H^[9]; microalloying boron between 29 and 105 ppm shows the increased hot ductility of conventional steel with increasing boron

content^[10]; an addition of 0.6 wt-% of boron to 316L stainless steel reduces oxide layer porosity and improves cyclic oxidation resistance at 900 °C^[11]. Additionally, nuclear- and maritime-focused research has shown that alloying 60 ppm B to Fe-15CR-30Ni-1.2Mo-2Ti-0.26Al-0.2Si-0.02C austenitic stainless steel alloy reduces its hydrogen embrittlement sensitivity^[12] through boron carbides and/or borides precipitating the grain boundaries; boron segregation with carbide and/or boride precipitation is a reoccurring phenomenon in many studies^[13,14,11,9,6,7].

The purpose of this research is twofold. Firstly, it is focused on the temperature-wise high-resolution observation of scale formation on a timespan usual for an industrial reheat furnace operating cycle for one slab in both an oxygen-containing atmosphere and an H₂O-containing atmosphere. Secondly, it is focused on the unstudied effect of multiple microalloying amounts of boron and titanium on the scale formation of commonly used AISI 304 austenitic stainless steel. As was established earlier in this chapter, boron and titanium alloying and microalloying have multiple effects on the properties of steels. As such, this research also contributes to the wider knowledge we have on the end-product properties and options available in steel production phases. This is invaluable information in producing precision-engineered steels in the future. The earlier research on this subject^[15] was made at three different temperatures and in one atmosphere containing 5 % oxygen. It was shown that boron and titanium alloying had effects on the end scale-formation amounts, as well as on the scale-formation rates within the three-hour experiment's time. The present research focuses on the temperature range of 1100 to 1300 °C in an O₂-containing atmosphere and the range of 1100 to 1250 °C in an H₂O-containing atmosphere in order to gain further insight into the effects of boron and titanium microalloying on the scale growth properties of AISI 304 stainless steel.

2. Materials and methods

The effects of water vapour and free oxygen in the atmosphere on the scaling of boron and titanium microalloyed AISI 304 stainless steel in the simulated atmosphere of a walking beam slab reheating furnace were studied. The studied boron microalloying amounts were 7, 35 and 55 ppm and the studied titanium microalloying amounts were <100 and 400 ppm. The O₂-containing atmosphere was selected to have 5 % free oxygen in order to simulate the oxygen content in an industrial walking beam furnace. The H₂O-containing atmosphere in this work is based on the atmosphere produced by burning CH₄ according to reaction in equation (1) in 20 % excess air, assuming the complete combustion of CH₄ and where the air flow is 21 % O₂ and 79 % N₂. The assumption of 20 % excess air, based on the operation of an industrial-size walking beam furnace assuming having no CO form inside the furnace, having no latent CH₄ inside the furnace and not losing heating power to excess air. The atmosphere for the results referred to as having been done in an O₂ containing atmosphere was 76.19 % CO₂, 18.81 % N₂ and 5 % O₂ vol.-% using the ideal gas assumption. Additionally, the atmosphere for the results referred to have been done in an H₂O containing atmosphere in this work was 8.0 % CO₂, 72.6 % N₂, 16.1 % H₂O and 3.2 % O₂ in vol.-% using the ideal gas assumption. Isothermal temperatures for the O₂ atmosphere experiments were set to range from 1100 °C to 1300 °C in 25 °C increments. The isothermal temperatures for the H₂O atmosphere were set to range from 1100 °C to 1250 °C, also in 25 °C increments.

The detailed microalloying process, sample preparation method and sample chemical composition analysis can be found in our earlier paper^[15] and an overview of the

microalloying method and experimental setup is shown in **Figure 1**. The thermogravimetric (TG) practice is also the same. The difference in this paper is the addition of H_2O (g) to the TG chamber for the H_2O atmosphere tests. This was done with a calibrated precision peristaltic pump feeding a deionized water flow of 0.259 ml/min through a preheater to the oven chamber. Sample preparation was the same as it was before^[15]. Oxide detachment or spallation was not observed during the test as it would have been seen as sharp momentary decreases in weight gain on the TG-graphs. Additionally, no flaked oxide was found in bottom of the oven. Chromium volatilization is acknowledged in the used temperature regions, but assumed as a minor component to the weight gain (loss) behaviour in the time window in the time window used in this research: Cr evaporation through pure Cr_2O_3 would, at highest place the amount at 0.04 kg/m^2 at $1300 \text{ }^\circ\text{C}$ in vacuum ^[16] and at 0.003 kg/m^2 at $1300 \text{ }^\circ\text{C}$ in 20 % O_2 atmosphere^[17] for the three-hour period.

Figure 1. Slab cut-off evolution: a) scrap from AISI 304 slabs, b) melting of the scrap and addition of boron and/or titanium, c) cast laboratory-scale slab, d) cut from a scrap cross-section (dark), e) cut of the sample bulk piece (grey) and f) cut of the final samples (light grey). The thermogravimetric (TG) oven setup is shown in g); the arrow points to the sample in the oven, black boxes are mass flow controllers, Gas lines and H_2O line from pump are connected to a preheater. Schematic illustration, modified from source^[15].

Due to the high amount of TG graphs involved in this research, the scaling amounts and the differences between the boron and titanium microalloying amounts, as well as the differences between different atmospheres, were presented as colour map images. The area-normalised scaling amounts are presented in absolute numbers, and comparative figures are presented as percentage differences between normalised scaling amounts.

The sample surface areas (SSAs) calculated from samples' side measurements are presented in **Table 1** (with O₂ in the atmosphere) and **Table 2** (with H₂O in the atmosphere). Each sample's side thicknesses were measured with an electronic digital calliper from three points (end, middle, end) and the averaged value for each side was used in the area calculation (the indicated values are in mm²). The sample areas noted here are from tests used in further area-normalised scale growth figures. To ascertain of proper sample preparation and experiment setup, double tests were performed in some of the O₂ and H₂O atmospheres. Table 1 and Table 2 show an asterisk (*) next to the test temperatures where double tests were performed.

3. Results

Based on the TG tests, the normalised scale-growth curves were classified to one of the four generic shapes presented in **Figure 2**. Shape I represents for a linear, or near linear, curve shape. Shape II denotes a sigmoidal shape with two linear stages separated by another linear stage that has a higher slope value. Shape III is also a sigmoidal curve, but unlike shape II, the last stage is almost horizontal due to a very low slope value, and the sigmoidal behaviour happens sooner. Shape IV is also sigmoidal, but with the final stage being parabolic instead of

linear. Should the scale-growth curve have had two sigmoidal stages, this is denoted with the suffix '2', (e.g. 'IV-2'). For each of the curve shapes, the final stage of oxidation was determined to have started after the ratio between the experimental delta m value and the fitted regression delta m differed by 20 percent or more. Filtering out the sigmoidal behaviour in the beginning, the final stage regression was calculated from 7800 seconds onward, and the equation was set to be linear ($y = k_l x$) for curve shapes I, II and III. For curve shape IV, the regression equation was parabolic ($y = c + k_p x^2$), where k_l is the slope, k_p is the parabolic constant and c is the experimental constant.

Figure 2. General oxidation curve shapes: approximately linear (I), sigmoidal (II), sigmoidal with a plateau (III) and sigmoidal with a parabolic final stage (IV).

3.1. 1100—1300 °C tests in an O₂-containing atmosphere

The TG results for the different samples in the 5 % O₂ atmosphere are presented in **Figure 3**, showing the area-normalised weight gain (in kg/m²). In the figure, there are two colour areas, from 0 to 0.3 kg/m² and from 0.3 to 1.5 kg/m²; the colours for the amounts of the former area are presented on the right-hand side, and the colours for the latter amounts are presented above the images. The ranges of each colour subset are the same in the image in order to better compare the results between microalloying amounts.

Figure 3. Area-normalised weight gain (in kg/m²) for tests between 1100 and 1300 °C in the 5 % O₂-containing atmosphere for AISI 304 stainless steel microalloyed with (a) 7 ppm B and <100 ppm Ti, (b) 7 ppm B and 400 ppm Ti, (c) 35 ppm B and 100 ppm Ti and (d) 55 ppm B and 100 ppm Ti.

The TG test parameter table for the O₂-containing atmosphere tests is presented in **Table 1**. Shown in the table are the sample ID, the test temperature (in °C), the microalloying amount of B and Ti (in ppm), the curve shape (as described earlier and as shown in Figure 2), the direction of the area-normalised end-scaling amount (ESA; with a plus sign for more, a minus sign for less) compared to the previous temperature of the same sample, the final oxidation stage start time (in seconds after the experiment's start), the measured SSA and the area-normalised ESA (in kg/m²).

Table 1. The O₂-containing atmosphere's test result table, showing the sample ID, temperature (T, in °C), the microalloying chemical (in ppm), curve shape (I to IV), the area-normalised end-scaling amount (ESA; in kg/m²), measured sample surface area (SSA; in mm²), the relative direction of the test temperature's ESA in regard to the ESA of the previous temperature and the time when the final stage of oxidation began.

Sample	T (°C)	B (ppm)	Ti (ppm)	Curve shape	ESA vs. previous T	Final stage start (s)	SSA (mm ²)	ESA (kg/m ²)
1510L	1100*	7	<100	I			1216	0.084
	1125	7	<100	II	+	3050	1168	0.181
	1150	7	<100	II	+	2790	1367	0.197
	1175*	7	<100	II	+	2210	1361	0.215
	1200	7	<100	III	-	1280	1334	0.141
	1225	7	<100	III	-	770	1368	0.118
	1250*	7	<100	IV	+	4770	1362	0.38
	1275	7	<100	II	+	4280	1252	1.057
	1300	7	<100	II	+	3190	1256	1.432
1511L	1100	7	400	II		3610	1283	0.143
	1125	7	400	II	+	3500	1370	0.174
	1150	7	400	II	+	2800	1395	0.187
	1175	7	400	III	-	2210	1418	0.162
	1200	7	400	III	-	1020	1330	0.126
	1225*	7	400	III	-	1040	1398	0.105
	1250*	7	400	IV	+	4940	1361	0.313
	1275	7	400	IV	+	4450	1396	0.779
	1300	35	100	II	+	3030	1300	1.421
1512L	1100	35	100	I		5050	1221	0.132
	1125	35	100	II	+	3490	1351	0.17
	1150	35	100	II-2	-	3080	1398	0.108
	1175	35	100	II-2	-	2120	1321	0.09
	1200*	35	100	IV-2	+	1840	1416	0.119
	1225*	35	100	IV-2	+	3920	1308	0.207
	1250	35	100	IV-2	+	3250	1317	0.474
	1275	35	100	II-2	+	2590	1343	1.162
	1300	35	100	II-2	+	2740	1247	1.46
1513L	1100	55	100	II		4960	1351	0.135
	1125	55	100	II-2	+	5300	1391	0.18
	1150*	55	100	III-2	-	4730	1386	0.155
	1175	55	100	III-2	-	2280	1362	0.089
	1200	55	100	IV-2	+	1550	1398	0.108
	1225	55	100	IV-2	+	4110	1393	0.186
	1250*	55	100	IV-2	+	5680	1382	0.591
	1275	55	100	I	+	3610	1372	1.057
	1300	55	100	I	+	2970	1244	1.409

3.2. 1100–1250 °C tests with water vapour in the atmosphere

The H₂O atmosphere TG tests' results are presented in **Figure 4**. For added clarity, because the overall scaling is significantly higher and because the H₂O tests were done in up to 1250 °C (vs. 1300 °C for the O₂ tests), this figure has different colours than the figure for the oxygen atmosphere results. As with the oxygen atmosphere shown in Figure 3, (a) is the non-alloyed baseline 1510L with 7 ppm B and <100 ppm Ti, (b) is the 400 ppm Ti alloyed sample with 7 ppm B, (c) is the mid-boron alloyed 1511L with 35 ppm B and (d) is the high-boron microalloyed 1512L with 55 ppm B. ESAs for the H₂O atmosphere tests can be found in **Table 2**.

Figure 4. Area-normalised weight gain (in kg/m²) for tests between 1100 and 1250 °C in the 16.1 % H₂O-containing atmosphere for AISI 304 stainless steel microalloyed with (a) 7 ppm B and <100 ppm Ti, (b) 7 ppm B and 400 ppm Ti, (c) 35 ppm B and 100 ppm Ti, and (d) 55 ppm B and 100 ppm Ti.

Table 2. The H₂O-containing atmosphere's test result table, showing the sample ID, temperature (in °C), the microalloying chemical (in ppm), the curve shape (I to IV), the area-normalised end-scaling amount

(ESA, in kg/m²), the measured sample surface area (SSA, in mm²), the relative direction of the test temperatures' ESA in regard to the ESA at the previous temperature and the time when the final stage of oxidation began.

Sample	T (°C)	B (ppm)	Ti (ppm)	Curve shape	ESA vs. previous T	Final stage start (s)	SSA (mm ²)	ESA (kg/m ²)
1510L	1100	7	<100	II		2540	1392	0.147
	1125	7	<100	II	+	2220	1380	0.198
	1150	7	<100	II	+	2430	1391	0.207
	1175*	7	<100	II	+	1330	1358	0.223
	1200	7	<100	II	+	1220	1361	0.252
	1225*	7	<100	II	+	440	1353	0.28
	1250	7	<100	II	+	1000	1363	0.34
1511L	1100	7	400	I		3400	1327	0.127
	1125*	7	400	I	+	2680	1333	0.155
	1150	7	400	II	+	3530	1353	0.198
	1175	7	400	II	-	2130	1334	0.187
	1200	7	400	II	+	1050	1351	0.217
	1225	7	400	II	+	430	1315	0.235
	1250*	7	400	II	+	640	1329	0.286
1512L	1100	35	100	II		1240	1379	0.171
	1125	35	100	II	+	1240	1398	0.213
	1150	35	100	II	+	490	1389	0.222
	1175	35	100	III	-	290	1400	0.167
	1200	35	100	III-2	+	190	1361	0.217
	1225*	35	100	IV	+	4710	1368	0.326
	1250*	35	100	II	+	330	1306	0.665
1513L	1100	55	100	II		1620	1337	0.152
	1125	55	100	II	+	1480	1345	0.178
	1150	55	100	II	+	970	1394	0.192
	1175*	55	100	III	-	550	1348	0.14
	1200	55	100	III	+	230	1375	0.146
	1225*	55	100	IV	+	5490	1352	0.212
	1250*	55	100	IV	+	3390	1377	0.315

3.3. Microscopy and EDS analysis

Microscopy analysis was decided to be done on the basis of TG data. For the O₂ atmosphere, temperatures of interest were 1175 °C and 1250 °C, because of their very interesting behaviour with boron alloying, and also 1225 °C, in order to see the contrast between O₂ and H₂O atmospheres. For the H₂O atmosphere, temperatures of interest were 1225 °C, for contrast with the O₂ atmosphere, and 1250 °C, for the reduction in the scaling amount with

the microalloying amounts of 55 ppm B and 400 ppm Ti. As with the previous research, the terminology used in the description of the sub-zones in the oxide layer remains the same. Starting from the metal substrate and going towards the outer surface of the sample, there are four distinct oxidation sub-zones: the inner oxidation zone, intermediate oxidation zone, differentiating oxidation zone and outer oxidation zone.

The most peculiar temperature is 1175 °C. As with the other lower temperatures, at this temperature the oxide layer is non-continuous and as such exhibits pockets of oxides. **Figure 5** shows FESEM imagery of the sample 1510L (7 ppm B, <100 ppm Ti) with two distinct oxide pocket types that are found; (a) oxides of Fe and Cr ($\text{Fe}_x\text{Cr}_{2-x}\text{O}_3$ or $\text{Fe}_x\text{Cr}_{3-x}\text{O}_4$)^[18–20], and Fe and Si oxide area. Within the oxide pocket type in Figure 5 (a), a metal phase is also found that includes iron, chromium and nickel and has no oxygen. The metal phase's composition is of iron, around 3 wt-% Cr and the rest is nickel (with the nickel's wt-% being strongly dependent on the depth of any one metal particle relative to the original surface of the sample). The closer a metal particle is to the original surface, the higher the nickel wt-% is, ranging up to 90 wt-%. The other pocket type Figure 5 (b) has no metal particles embedded and, surprisingly, includes a nickel oxide phase, along with a Fe and Cr oxide area ($\text{Fe}_x\text{Cr}_{2-x}\text{O}_3$ or $\text{Fe}_x\text{Cr}_{3-x}\text{O}_4$)^[18–20]. This nickel oxide phase was not previously found and is not found at higher temperatures where the inner oxide layer is continuous. For example, at 1225 °C the only nickel found in any oxide phase is in the phase that also contains Si, and in that, the nickel content is around 1–2 wt-%. As can be seen from **Table 3**, the nickel oxide phase EDS analysis shows a relatively large weight percentage ranging from 9.27 wt.-% (Spectrum 5) to 13.53 wt.-% (Spectrum 8).

Figure 5. FESEM images of 1510L (7 ppm B, <100 ppm Ti) from a 1175 °C sample in the O₂ atmosphere: (a) shows the oxide pocket with metal particles embedded and (b) shows the oxide pocket without metal particles and with a nickel oxide phase. Also shown is the general look of the mounting epoxy, oxide, metal inclusions and substrate steel.

Figure 6 shows the samples 1510L (a) and 1513L (b) at 1250 °C in the H₂O atmosphere. At the 1510L steel–oxide interface (a) is a small band of oxide-containing Si. The same oxide is seen in the sample 1513L (b), but in larger quantities and having a different oxide morphology on the upper side of the scale–oxide–epoxy axis. The Fe,Cr oxide area has a nearly identical composition in both samples (e.g. spectra 16 for 1510L and 21 for 1513L in Table 4). The metal inclusions can be seen to follow the approximation of having a higher nickel wt.-% amount (e.g. spectra 23) the closer the inclusion is to the original sample surface (seen at the edge of the oxide, next to the black epoxy in Figure 6b).

Figure 6. FESEM BSE images of the samples (a) 1510L and (b) 1513L, both at 1250 °C in the H₂O atmosphere.

Table 3. EDS analysis spectrums as non-normalized weight percent (wt.-%) for Figure 4 and Figure 5.

Spectrum	O	Si	P	Cr	Mn	Fe	Ni	Total
1		0.28		16.46	1.82	69.62	8.59	96.77
2	27.98	12.02	0.97	4.15	1.96	45.54	1.24	93.86
3				3.1		14.86	77.67	95.64
4	27.58			32.58	0.68	34.05	3.61	98.5
5	28.33			24.56		36.37	9.27	98.53
6		0.32		15.75	0.62	75.01	8.43	100.12
7	30.46			65.63		2.92		99.01
8	26.3			30.14	0.92	26.91	13.53	97.79
9	30.09			46.54		22.65	0.8	100.07
10	31.35			53.54		15.77	0.87	101.53
11	27.15			28.96		29.77	13.31	99.19
12	27.81			24.63	0.9	33.08	12.82	99.25
13	28.51	1.33		43.5	4.14	19.99		97.46
14	27.63	0.34		51.58	3.89	16.12		99.55
15	27.96	2.31		43.72	2.35	22.22	0.51	99.07
16	26.45	1.2		40.22		28.53		96.4
17	39.16	26.51		18.78		11.5	0.56	96.51
18	38.73	23.84		19.87		13.14	0.69	96.27
19	31.69	0.85		62.54		4.03	1.2	100.3
20				4.14		12.48	76.47	93.09
21	27.11	0.22		39.37	0.91	27.36	2.92	97.89
22				3.32		12.45	78.5	94.27
23		0.48		3.33		12.2	78.19	94.19

4. Discussion

Figure 7 shows the percentage differences to scaling when changing the boron microalloying from 7 to 35 ppm and from 7 to 55 ppm in O_2 and H_2O atmospheres. It can be seen that the effect of microalloying boron ranging from 7 ppm to either 35 or 55 ppm in an O_2 atmosphere leads to a similar change. The increases in scaling amounts from the microalloying amounts of 7 to 35 ppm B (Figure 7a) and 55 ppm B (Figure 7b) are most pronounced between the 1225 °C and 1275 °C temperature regions in the O_2 atmosphere, especially from 75 minutes (4500 seconds) onward. Interestingly, between 1150 and 1200 °C, the scaling amounts for 35 ppm B and 55 ppm B microalloying are considerably less than the amounts for 7 ppm B microalloying. The largest difference is seen at 1175 °C, with the scaling amount being around 60 percent less for both the microalloying amounts of 35 ppm and 55 ppm B

Figure 7. The effects on the AISI 304 scaling amount due to boron microalloying differences when changing the alloying amount from (a) 7 ppm B to 35 ppm B in the 5 % O_2 atmosphere, (b) 7 ppm B to 55 ppm B in the 5 % O_2 atmosphere, (c) 7 ppm B to 35 ppm B in the 16.1 % H_2O atmosphere and (d) 7 ppm to 55 ppm B in the 16.1 % H_2O atmosphere. The colour map indicates the change in percentage when compared to the 7 ppm B-alloyed AISI 304.

The effect of titanium microalloying on the scaling amount when changing from <100 ppm to 400 ppm Ti can be seen in **Figure 8** with the oxygen effect showing in (a) and the H₂O effect in (b). For the quantitative scaling of AISI 304 in the 5 % O₂ atmosphere, the overall effect for microalloying titanium from <100 ppm to 400 ppm is a lower ESA and rates in all other temperatures except 1100 °C. The most obvious decreases in scaling amounts are seen at 1275 °C and 1175 °C. As seen in Figure 8b, the overall effect of titanium microalloying in the H₂O atmosphere is a reduced scaling amount at almost all temperatures for the whole duration of the tests. Considering ESAs, the highest reducing effect is seen at 1100, 1125, 1175 and 1250 °C.

Figure 8. The effects on the AISI 304 scaling amount due to titanium microalloying differences when changing the alloying amount of Ti from <100 ppm to 400 ppm in a) the 5 % O₂ atmosphere and b) the 16.1 % H₂O atmosphere. Difference in percentage when comparing the 400 ppm Ti scaling amounts to <100 ppm Ti scaling amounts.

Considering the curve shapes in both O₂-containing and H₂O-containing atmospheres, in consecutive temperatures the transition from curve type II to type III leads to a lower ESA, even though the temperature is increased. Also, in both atmospheres the transition from curve type III to type IV leads to a higher scaling amount than the previous temperature. Only the

boron microalloyed samples 1512L and 1513L showed the double sigmoidal behaviour in either of the atmospheres. Based on these observations, boron seems to momentarily cause oxidation inhibition characteristics at high temperatures, although less so in the H₂O-containing atmosphere.

Figure 9. The effects on the amount of AISI 304 scaling when changing the atmosphere from 5 % O₂ to 16.1 % H₂O for a) 7 ppm B-alloyed AISI 304, b) 35 ppm B-alloyed AISI 304 c) 55 ppm B-alloyed AISI 304 and d) 400 ppm Ti-alloyed AISI 304.

Error! Reference source not found. shows the difference in scaling amounts (in %) when changing the atmosphere from O₂ to H₂O. For the microalloying amount of 7 ppm B (a), the ESA is increased by 30 to 60 percent at 1100 and 1125 °C. For the temperatures 1150 and 1175 °C, the ESAs are unchanged. Increases in the ESA are observed in temperatures of 1200, 1225 and 1250 °C, with the most prominent increase (of more than 150 percent) occurring at 1225 °C. The differences in the amount of scaling during the three-hour period show clear

differences during the start of the tests, with the H₂O atmosphere having a very high scaling rate at the beginning of the test at all temperatures except 1175 °C.

For the 35 ppm B microalloying in **Error! Reference source not found.** (b), when going from O₂ atmosphere to H₂O, the ESAs are mostly worse with end scaling amounts being least affected at temperatures of 1100, 1125 and 1250 °C. The beginning of the tests show much higher scaling rate in the H₂O atmosphere.

For the microalloying amount 55 ppm B (c), the ESA is increased by 60 percent at 1175 °C and by 30 percent at 1150 and 1200 °C. The ESA remains the same at 1100 and 1125 °C. The most interesting phenomenon happens at 1250 °C, where changing the atmosphere from O₂ to H₂O leads to a 30 percent decrease in ESA at 1250 °C. During the three-hour period, the scaling rate difference between the O₂ and H₂O atmospheres shows the same, but more pronounced, behaviour as with 7 ppm B in Figure 9 (a). The scaling rate during the first hour of the test for the temperatures 1100, 1125 and 1150 °C in the H₂O atmosphere is very high when compared to the O₂ atmosphere. For temperatures between 1175 and 1250 °C, the high scaling rate differences of the atmospheres is only observed during the first seven minutes.

For the titanium microalloying amount of 400 ppm in Figure 9 (d), going from O₂ to H₂O atmosphere, the ESAs are nominally worse in the H₂O atmosphere. The only decrease is observed in the middle of the test at 1125 °C.

As was seen in the FESEM imagery and EDS analysis of Figure 6, the metal-inner oxide layer interface of the sample 1513L in H₂O containing atmosphere at 1250 °C had substantially different morphology, wherein there was a highly Si-rich oxide phase directly in contact with the substrate metal. At 1250 °C in the H₂O containing atmosphere, 400 ppm Ti microalloying

seems to have an even greater diminishing effect on scale growth than 55 ppm B microalloying by providing a slightly different oxide structure for the initial Ni-based oxide phase. Based on EDS analysis, the Ti content rises up to 1.11 wt-% in the Ni oxide phase.

The differences between 7 ppm B 1510L and 55 ppm B 1513L samples' morphology in a similar oxide pocket are shown in **Figure 10**. As can be seen in Figure 10 (a) and (b), the sample 1510L has a plethora of small pockets of Si-enriched oxide crept in to the substrate metal at the metal—oxide interface. As opposed to the 55 ppm B sample 1513L, the substrate metal at the interface is free of these Si-enriched oxide pockets and the Si is concentrated as larger areas in contact with the inner oxide layer. SiO₂ phase has been shown to stay at the base of Cr₂O₃ scale and be formed through the oxidation of Fe₂SiO₄ to SiO₂ in H₂O atmosphere and low H₂ contents at high temperatures^[21]. The infiltration of SiO₂ into the steel substrate occurs through the steel grain boundaries^[22,21], and Fe₂SiO₄ adheres to the steel surface strongly^[23]. The temperature of 1175 °C coincides with the melting point of Fe₂SiO₄ at 1177 °C^[24], and Si-rich oxide areas was found in the inner oxidation layer of the scale layer. When alloyed, boron segregates to grain boundaries^[13,14] as discontinuous boron carbides^[12,13], as M₃B₂ borides^[12] or as boron atoms^[12]. As such, it seems plausible that the boron carbides, borides and/or atoms inhibit the Si oxide infiltration (as SiO₂), although the exact boron compound is hard to detect at these alloying quantities. The oxidation inhibiting effect could particularly be seen at 1175 °C with both boron microalloying amounts, as well as with the titanium microalloying, in the oxygen atmosphere and, to some extent, in the H₂O atmosphere.

Figure 10. Backscattered detector FESEM images and Si wt.-% EDS map images of 1250 °C H₂O atmosphere sample 1510L (a) BSE image and (b) EDS Si map, and 1513L (c) BSE image and (d) Si map.

At high temperatures (1250 °C in O₂ and up), the oxide scale growing on the alloy is shown to have an even structure with distinct layers, and in two of these layers there are metal inclusions throughout the parallel of the metal-oxide interface. At lower temperatures, the occurrence of two pocket types in the inner oxide layer (an only-oxide structure and an oxide with metal inclusions structure) leaves no debate about there being oxidation; there also has to be reduction during the test period. One such mechanism for reduction could be the starvation of readily available oxidation agent O⁻ anion; the outgrowing Fe₂O₃ outer oxidation layer inhibits the oxygen diffusion rate and the Ni oxide phase in the inner oxidation layer is reduced by Fe⁺ cation movement towards the outer oxidation layer. This is further illustrated in **Figure 11**, where a FESEM image, taken with a backscattered electron (BSE) detector, is shown of sample 1510L in a 1225 °C O₂ atmosphere. This temperature, atmosphere and sample showed a very linear and not very steep TG curve, indicating that after the initially

1 fast, diffusion-controlled oxidation, it was later limited by chemical reactions. In the image is
2 what could presumably be called *the annihilation of the oxide pocket with no metal inclusions*.
3 In Figure 11, it can also be clearly seen that porosity is mostly occurring in the oxide layer (or
4 pocket) with metal inclusions. Further, it is most likely the Kirkendall porosity^[25] occurs
5 around the metal inclusion areas, and this is caused by diffusion speed mismatches between
6 different metal anion or cation movements. For example, the diffusion speeds of Cr^{3+} , Fe^{2+}
7 and O_2^- vary in the (Fe,Cr) spinel^[26–28], and the general diffusion speed of the same ions
8 through magnetite is faster than through hematite^[26,29,30].

10
11 **Figure 11. An FESEM BSE image from sample 1510L at 1225 °C in an O₂ atmosphere.**

12
13 In addition to natural gas (96 % CH₄ in dry natural gas^[31]), propane is also widely used in slab
14 reheat furnace operation. The usage of propane as a burning agent versus using methane as
15 the burning agent in a slab reheat furnace produces an atmosphere of varying H₂O content.
16 Using the calculation method described for the tests in this paper, fully burning methane with
17 20 % excess air produces an atmosphere with 16.1 % H₂O. Using the same 20 % excess air
18 for a full propane burn produces an atmosphere with 13.1 % H₂O. Preliminary research^[32] on

the subject shows that at 1260 °C, the difference between these two atmospheres mostly affects the inner oxide layers' thickness and has no effect on the outer oxide layer's thickness. Additionally, the inner oxide layer's morphology is most affected by a substantial increase in porosity when transitioning from there being 13.1 % H₂O in the atmosphere to there being 16.1 % H₂O. Research done by others in the field has shown that, in addition to the scale layers' chemical composition, increased porosity promotes scale removal^[33]. Taking this in account, and the large difference in the amount of methane needed versus the amount of propane needed to produce the same amount of heat, there is a good opportunity to be had in finding the subtle differences in oxide scale growth in different atmospheres. Boron microalloying was already seen to reduce Si-based oxide penetration in the steel-oxide interface. Adding the scale removal benefit of having less Si-oxide penetration and increased porosity will lead to a decrease in slab scale originated defects in the end product.

5. Conclusions

AISI 304 austenitic stainless steel boron and titanium microalloying's effects on scaling properties were studied in this research. Base AISI 304 had 7 ppm B and <100 ppm Ti alloyed with it. Comparative boron microalloying amounts were 35 ppm B and 55 ppm B, and the comparative titanium microalloying amount was 400 ppm. Temperature regions were between 1100 °C and 1300 °C in the O₂-containing atmosphere (76.19 CO₂, 18.81 % N₂ and 5 % O₂) and between 1100 °C and 1250 °C in the H₂O atmosphere (8.0 % CO₂, 72.6 % N₂, 16.1 % H₂O and 3.2 % O₂). In both atmospheres, temperature intervals were 25 °C. The holding time was 180 minutes, and temperatures were isothermal. The following conclusions can be observed based on this research and when compared to base AISI 304 with 7 ppm B and <100 ppm Ti:

In the O₂ containing atmosphere:

- Microalloying with 35 ppm B incites lower scale-formation amounts at 1150 and 1200 °C and substantially lower formation at 1175 °C. Additionally, it causes scale formation amounts to increase at 1250 and 1275 °C, having a high difference in the peak scale-formation amount (100 % more) at 1250 °C, at the 90-minute mark, but with the difference levelling off towards the end of the test.
- Microalloying with 55 ppm B incites lower scale-formation amounts at 1150 and 1200 °C and substantially lower formation at 1175 °C. An even more vigorous scale-formation peak than for 35 ppm B microalloying is observed at 1250 °C, 90 minutes into the test (150 % higher), with the difference levelling off towards the end of the test, but to a lesser extent than the microalloying amount of 35 ppm B. Additionally, there is negligible change in scale-formation amounts from 90 minutes onwards at 1275 °C.
- Microalloying with 400 ppm Ti only causes an increase in scale formation at 1100 °C. At temperatures of 1175 and 1275 °C, there is a decrease in scale formation for the whole duration of the test and for the last third of the test at 1250 °C. Overall, 30 % less scale formation is observed at 1175 °C and 60 % less scale formation is observed between 30 and 135 minutes into the test at 1275 °C, with 30 % less scale formation otherwise.

In the H₂O containing atmosphere:

- Microalloying with 35 ppm B decreases ESAs at 1175 °C and 1200 °C, and increases ESAs at 1100 and 1250 °C, while having a negligible effect on the ESA at other tested temperatures.
- Microalloying with 55 ppm B decreases ESAs between 1175 °C and 1250 °C. At 1225 °C and around 90 minutes into the test, the scaling amount is considerably

1 less than with 7 ppm B. Between 1100 and 1150 °C, the end-scaling difference is
2 negligible. At 1250 °C, a Si-oxide area that is directly in contact with the steel
3 substrate is observed in the 55 ppm B sample.

- 4 - Overall, microalloying with 400 ppm Ti has a decreasing effect on the amount of
5 scale formation throughout the tests, with decreases to ESAs at 1125 °C, 1175 °C,
6 1225 °C and 1250 °C.

7
8 Additionally, a nickel oxide phase is found, predominantly in the boron and titanium
9 microalloyed samples in the O₂ atmosphere at 1175 °C. This nickel oxide phase is not found
10 at higher temperatures and indicates a transition oxide area that is annihilated during the
11 three-hour test at other temperatures.

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