Thermodynamic Prediction and Experimental Verification of Multiphase Composition of Scale Formed on Reheated Alloy Steels

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The structure, phase, and composition of scale formed on a continuously cast steel slab during reheating depend on intrinsic factors (steel chemistry, microstructure, and as-cast surface condition) and extrinsic parameters (temperature, time, composition, and velocity of combustion gas atmosphere). The scale that forms on a slab normally has several layers with differing compositions and phases and knowledge of this scale structure is important in subsequent descaling and hot rolling processing steps. Formation of multiphase scale structures on steel during high temperature oxidation in reheat furnace proceeds according to a local thermodynamic equilibrium, while thickness of layers depends on kinetic conditions (mostly by diffusion). In this study, the local thermodynamic equilibrium conditions through the scale layer were simulated using different oxygen/steel ratios, which mimicked the conditions for scale formation at the external, internal, and sublayer oxide region at metal/scale boundary. Experiments were performed in a simulated combustion atmosphere using typical industrial reheat time/temperature conditions. The phases that developed in layered scale structure were documented using SEM/EDX and Raman spectroscopy. The predicted scale compositions and phases were in good agreement with the experimental results for studies with Mn and Si-alloyed carbon steel, Cr-alloyed ferritic, and Cr, Ni-alloyed austenitic steels.

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I. INTRODUCTION

SCALE formation in a typical steel processing plant begins during the continuous casting of a slab and continues through slab reheating and hot rolling of the steel. Scale formation during reheating is a complex phenomenon which has been described in numerous studies conducted over the past several decades.^[1–6] The formation of oxide scale on steel at various processing stages is affected by a combination of intrinsic factors (steel grade, microstructure, segregation, grain boundary, surface roughness) and extrinsic factors (gas atmosphere, gas flow, furnace pressure, temperature, exposure time, furnace throughput, and mechanical and thermal stresses).^[4–9] With a combination of these factors, the formed oxide scale might be easily removed by water jet descaling or it may be sticky and hard to remove from the steel surface, leaving a residual scale after descaling that interferes with subsequent processes

such as hot rolling.^[10,11] To promote surface cleanliness of the steel, water jet descaling^[12,13] is most commonly conducted in multiple stages to improve the efficiency of scale removal using both primary and secondary descaling steps. This descaling normally occurs after slab reheating and prior to the final hot rolling pass. In some cases, depending on the severity of the scale formed on the as-cast slab, descaling is carried out at the exit of the caster to remove scale and mold flux residues or the slab is scarfed or surface ground in cases of extreme scale formation. This slab surface conditioning is sometimes performed to minimize the development of complex scale structures at scale/metal boundary during slab reheating in a combustion gas atmosphere.

Due to the demand for steels with improved properties for various applications in the automotive, manufacturing, construction, and other industry sectors, steel producers have adjusted steel chemistry with increasing levels of alloying elements (Si, Mn, Ti, Cr) and have increasing restricted impurity levels (Cu, S, P) to meet modern demands for improved steel properties. Reheating of such steels in furnaces with combustion atmospheres (CO₂, O₂, H₂O, N₂) promotes the formation of multilayered scale structures with strong adhesion to steel surface, particularly in the case of high Si and Al steels,^[14] which interferes with water jet descaling and leads to inefficient scale removal. The complexity of such

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scale structures has been reported for different steel compositions, such as low to medium carbon steels,^[4,6,15–18] ferritic stainless steels,^[19–21] and austenitic stainless steels.^[7,22–25] These high temperature oxidation studies were performed to document the scale growth kinetics and the mechanisms of scale formation. Characterization of the scale was performed using scanning electron microscopy coupled with energy-dispersive X-ray (SEM/EDX), Raman spectroscopy, transmission electron microscopy (TEM), and X-ray diffraction to document microstructure, chemistry, and oxide phases present in the scale layers for the different steels.

The rate of scale formation for the different steel grades during oxidation is controlled by kinetics,^[26,27] while phases that form are defined by the local thermodynamic conditions. The transport mechanisms responsible for oxidation rate are often driven by solid state or gas pore diffusion; however, the total mass transfer can also be limited by a chemical reaction step or convective mass transport and/or starvation of oxygen in the gas atmosphere near the slab surface. These mechanisms depend on oxidation time and temperature, atmosphere composition, gas flow rates, as well as steel chemistry which promotes the formation of complex structures. Unlike kinetics, thermodynamic approach to study oxidation utilizes the initial and final macroscopic states assuming global or local equilibrium conditions^[28] without considering mass transfer. Irrespective the kinetics, thermodynamics is a powerful tool that can be used to predict the feasibility of an oxidation reaction and to qualitatively identify the possible oxide phases that can form during oxidation.^[28]

Thermodynamic software utilizing the fundamental principle of Gibbs free energy minimization has been used for analyzing various steelmaking processes and experimental reports support its reliability.^[29–36] Common areas in steelmaking that have employed thermodynamic studies include refining and non-metallic inclusion formation in the melt, as well as precipitate formation in the solid. The feasibility of thermodynamic studies for a large volume of processed liquid steel relates to (i) intensive mixing during sufficient time and (ii) high melting temperature, both factors that allow the chemical reactions to proceed close to equilibrium. In

contrast, precipitate formation in the solid state typically occurs without mixing and at lower temperatures. However, microscale distances also allow the use of thermodynamic tools to predict equilibrium precipitate formation when assuming fast diffusion.

Considering the case of steel oxidation during reheating, gas/solid oxidation reactions occur at high temperatures over a time frame of several hours, but the substantial thickness of the oxide that forms provides sufficient kinetic resistance which prevents the achievement of a global thermodynamic equilibrium, preventing access of oxidant to the whole metal volume. However, the actual process of multiphase scale formation occurs according to a local thermodynamic equilibrium at each reaction boundary. Therefore, thermodynamic methods can be employed to predict the phases that form at different distances from external metal/gas boundary without reference to the actual thickness of the formed layers. This approach has been used in several studies of alloy oxidation and has been found to be useful to predict the sequence of phases that form in scale during steel reheating.^[37]

In this study, FACTSAGE thermodynamic software^[38] was used to simulate the local equilibrium conditions for scale formation for different steel grades to predict multiphase composition and these results were compared to experimentally observed scale structures.

II. PROCEDURES

A. Steels and Oxidation

A variety of industrially produced steels were used in this study (Table I). The steels studied included carbon steels (Class 1) with varying alloying elements (Si, Mn, Cr, and Ni), advanced high strength steels (Class 2) with high alloying elements (Si and Mn), ferritic stainless steels (Class 3) with varying Cr, Al and Ti contents, and high Ni and Cr austenitic stainless steel (Class 4). These cast steels were supplied by industrial sponsors. Samples used for the oxidation test were machined to 50×20×3.5 mm and finished using wet machine grinding with 60 grit silicon carbide, the surface quality of the

Table I. Composition of Studied Steels

Steel Class	Code	Composition (Wt Pct)							
		C	Mn	Si	Cr	Cu	Ni	Ti	Al
Carbon	1a	0.17	0.84	0.06	0.14	0.26	0.13	—	0.03
	1b	0.06	1.30	0.33	0.07	0.34	0.10	—	0.04
Advanced High Strength	2a	0.19	2.51	0.99	0.04	0.02	0.02	—	0.04
	2b	0.19	2.97	2.52	0.04	0.02	0.02	—	0.04
Ferritic	3a	0.04	0.43	0.39	16.19	0.25	0.19	—	0.01
	3b	0.04	0.41	0.53	16.02	0.25	0.18	—	0.20
	3c	0.01	0.30	0.32	11.03	0.18	0.13	0.19	0.02
Austenitic	4	0.02	7.10	0.56	15.94	0.80	4.57	—	—

ground sample was measured to have Ra of $0.271\ \mu\text{m}$ using 3D optical profiler (Nanovea, Model PS50 Micro Photonic Inc.)

Oxidation testing was carried out using a laboratory thermo-gravimetric setup in a vertical MoSi₂ resistance-heating tube furnace (Model D900438 ATS Inc.). The oxidation tests were conducted in a combustion gas atmosphere by mixing gases in proportions that reproduced the reacted natural gas + air combustion atmosphere used in an industrial furnace (Table II). Thermal conditions (temperature and time) and combustion atmosphere were designed to mimic a typical industrial reheating used these grades before hot rolling.

Samples after oxidation were mounted in epoxy to protect scale layer, carefully cross-sectioned using wet cutting, and mechanically polished using diamond paste. The morphology, thickness, microstructure, and chemistry of the oxide layers were analyzed using a scanning electron microscopy (SEM) with an ASPEX-PIXA 1020 system equipped energy-dispersive spectroscopy (EDS). EDS analysis was performed using several points in each scale layer. HORIBA Jobin-Yvon Raman spectroscopy (LabRam ARAMIS) was also used to identify the oxide phases that were present and compared to reported phases in RRUFF database.^[39]

B. Thermodynamic Simulation

FactSage 7.2 thermodynamic software^[38] was used to simulate steel oxidation under the local equilibrium conditions. The databases used included FSsteel, FToxid, and FasctPS. The local equilibrium condition was examined by making stepwise oxygen additions into

the simulated streams from previous step assuming irreversible reactions. The predicted stable oxide phases were identified at each calculation step. This method allows one to predict different phases that form at low (inner layer) and high (outer layer) added oxygen levels. The thermodynamic simulations were performed assuming that the local equilibrium conditions were reached between gas component, the formed oxide phases, and the steel. Preliminary simulations showed that for the studied thermodynamic conditions, oxygen was the predominant oxidant in the combustion gas. Using different oxygen/steel mass ratio, different oxide phases which form under the local equilibrium condition during oxidation were traced from low to high added oxygen levels and compared to the oxide phases reported from the experiments. The equilibrium oxygen partial pressure after formation of the various oxides phases was also reported for each oxygen/steel ratio. The temperatures used in the thermodynamic simulations were similar to those used in laboratory experimental oxidation.

III. EXPERIMENTAL RESULTS AND THERMODYNAMIC PREDICTIONS

A. Carbon Steel

Figure 1 shows the cross-section microstructure of the scale that formed after 60 minutes at 1230 °C in a laboratory-simulated combustion gas atmosphere (Table II) for two carbon steels having different alloying elements (Table I). Average scale thickness on these

Table II. Industrial Reheating Conditions Simulated in Laboratory Oxidation

Steel Code	Combustion Gas (Vol Pct)	Temperature (°C)	Time (Minutes)
1, 2	8 CO ₂ , 17 H ₂ O, 2 O ₂ , N ₂ bal.	1230	60
3a, b	8 CO ₂ , 17 H ₂ O, 3 O ₂ , N ₂ bal.	1150	120
3c	8 CO ₂ , 17 H ₂ O, 1 O ₂ , N ₂ bal.	1205	60
4	8 CO ₂ , 17 H ₂ O, 2 O ₂ , N ₂ bal.	1260	60

Fig. 1—Low (left) and high (right) magnifications BSE image of cross-sectional scale structure in carbon steels: 1a (a) and 1b (b). Number indicated formed layers: 1—outer, 2—intermediate, 3—inner, and 4—sublayer joined with metal matrix.

Table III. Characterization of Scale Chemistry and Oxide Phases: Carbon Steel

Steel	Layer	Scale Chemistry (Wt Pct)							Oxide Phases
		Fe	O	Si	Mn	Cr	Ni	Al	
1a	Outer (1)	49	50	—	1	—	—	—	Fe ₂ O ₃ , Fe ₃ O ₄
	Intermediate (2)	54	45	—	1	—	—	—	Fe ₂ O ₃ , Fe ₃ O ₄
	Inner (3)	55	44	—	1	—	—	—	Mn ₂ SiO ₄ , Fe ₃ O ₄
	Subsurface (4)	43	51	4	2	—	—	—	Mn ₂ SiO ₄
		38	54	5	2	—	—	—	
		53	46	—	1	—	—	—	
		82	10	—	7	1	—	—	
1b	Outer (1)	45	52	—	3	—	—	—	Fe ₂ O ₃ , Fe ₃ O ₄ ,
		41	57	—	2	—	—	—	
	Intermediate (2)	46	51	—	2	—	—	—	Fe ₃ O ₄ , Mn ₂ SiO ₄
		59	38	—	3	—	—	—	
	Inner (3)	31	60	6	3	—	—	—	Fe ₃ O ₄ , MnO, Mn ₂ SiO ₄
		96	—	—	2	—	2	—	
	Subsurface (4)	45	53	—	2	—	—	—	Fe ₂ SiO ₄ , MnO, Mn ₂ SiO ₄
		52	38	7	3	—	—	—	
		46	36	4	13	—	—	1	
		46	41	1	11	1	—	—	
		69	20	1	9	1	—	—	
		55	44	—	1	—	—	—	

steels was between 500 μm and 700 μm for steel 1a and 1b, respectively. The scale structure was stratified into 4 different layers (1—outer, 2—intermediate, 3—inner, and 4—subsurface). Each layer was completely (Figure 1(a)) or partially (Figure 1(b)) separated from the other. Both the outer and intermediate layers had dense structures with mainly iron oxide as the predominant oxide phase. The inner scale layer had voids and porosity and also included entrapped droplets of unoxidized metal. This layer was formed next to scale/metal boundary and had isolated islands composed of different oxides of Mn and Si (Table III). In steel 1b, which had higher Si and Mn when compared to low alloyed steel 1a, Si and Mn oxide, droplets of entrapped metal (Fe-Ni-Mn) and porosity in the scale structure increased toward the subsurface layer which had an uneven boundary at the scale/metal interface. A randomly scattered dotted oxide structure was formed in subsurface area below scale/metal interface in the steel 1b. In this case, the subsurface oxidized layer in the metal substrate had a depth ranging between 15 and 50 μm .

Table III reports the composition of the oxide scale layers formed in the two studied carbon steels. In both steels, precipitates of alloying element oxides were observed to be more frequent in the inner layer and subsurface layer compared to the outer and intermediate layers. The compositions of the oxides were obtained using EDX point analysis to report chemistry differences in the various scale layers, and the oxide phases were identified by Raman spectroscopy analysis. Fayalite (Fe₂SiO₄) and tephroite (Mn₂SiO₄) were the predominant phases in the inner and subsurface scale layers. The alloying elements in the steels affected the oxide phases

formed in subsurface layers, with the higher alloy steel (1b) exhibiting an increased presence of Si-containing fayalite and Mn and Si-containing tephroite phases.

Thermodynamic simulations of the local equilibrium at different positions through the multiphase oxide layers were performed by varying the amount of oxygen available to react using different oxygen/steel mass ratios, as shown in (Figure 2). Approximately, four different phases were predicted at low oxygen/steel ratios that mimicked the local equilibrium conditions for oxide phase formation in the subsurface and inner scale layer. The oxide phases predicted at this low ratio showed strong presence of oxides of alloying elements (Mn and Si) as well as impurities (Al). Complexity of the oxide phases decreased toward the external (intermediate and outer) scale layers having higher oxygen/steel ratio with the predicted oxide phase being predominantly hematite (Fe₂O₃) with some traces of tephroite (Mn₂SiO₄). Thermodynamics predicted the formation of different oxides in the inner scale layers (subsurface and inner) but similar oxides in the external layers (intermediate and outer) for the two alloy steels. In the steel 1b with an elevated concentration of alloying elements, simulations predicted formation of complex Mn and Si oxides in the form of MnSiO₃ and Mn₃Al₂Si₃O₁₂ in the inner scale layer, while mono-oxides MnO and Cr₂O₃ and also spinel-MnAl₂O₄ were predicted in the lower alloy steel 1a.

B. Advanced High Strength Steel (AHSS)

In the case of AHSS, the cross-section of the scale layer in Figure 3 revealed a dense continuous scale structure with partial detachment of outer and intermediate layers from inner and sublayer in steel 2a and

Fig. 2—Thermodynamic prediction of oxide phases formed during reheating carbon steel at different oxygen/steel mass ratio: (a) carbon steel 1a with low Mn and Si and elevated Cr and (b) carbon steel 1b with elevated Si and Mn and low Cr.

Fig. 3—Low (left) and high (right) magnifications BSE image of cross-sectional scale structure in advanced high strength steels: 2a (a) and 2b (b). Number indicated formed layers: 1—outer, 2—intermediate, 3—inner, and 4—sublayer joined with metal matrix.

Table IV. Characterization of Scale Chemistry and Oxide Phases AHSS

Steel	Layer	Scale Chemistry (Wt Pct)						Oxide Phases
		Fe	O	Si	Mn	Ni	Cr	
2a	Outer (1)	42	55	—	3	—	—	Fe ₂ O ₃ , Fe ₃ O ₄
	Intermediate (2)	39	53	5	3	—	—	Fe ₂ O ₃ , Fe ₃ O ₄ , Fe ₂ SiO ₄
	Inner (3)	96	—	—	3	1	—	MnO, Fe ₂ O ₃
	Subsurface (4)	27	62	7	4	—	—	MnO, SiO ₂ , Fe ₂ SiO ₄
		33	59	5	3	—	—	
2b	Outer (1)	45	52	—	2	—	—	Fe ₂ O ₃ , Fe ₃ O ₄
		32	45	5	17	—	1	
	Intermediate (2)	45	52	5	3	—	—	Fe ₂ O ₃ , Fe ₃ O ₄
	Inner (3)	40	52	5	3	—	—	Fe ₂ O ₃ , Fe ₃ O ₄ , Fe ₂ SiO ₄
	Subsurface (4)	32	59	6	3	—	—	SiO ₂ , MnO
		45	52	—	3	—	—	Fe ₂ O ₃ , SiO ₂ , Fe ₂ SiO ₄ , MnO
		31	59	6	4	—	—	
		37	48	5	10	—	—

Fig. 4—Thermodynamic prediction of oxide phases present during reheating AHSS at different oxygen/steel mass ratio: (a) steel 2a with medium Mn and Si, and (b) steel 2b with high Mn and Si.

Fig. 5—Low (left) and high (right) magnifications BSE image of cross-sectional scale structure in ferritic steels 3a (a), 3b (b), and 3c (c). Number indicated formed layers: 1—outer, 2—intermediate, 3—inner, and 4—sublayer joined with metal matrix.

Table V. Characterization of Scale Chemistry and Oxide Phases in Ferritic Stainless Steels

Steel	Layer	Scale Chemistry (Wt Pct)									Oxide Phases
		Fe	O	Si	Mn	Cr	Ni	Al	Ti	Cu	
3a	Outer (1)	43	57	—	—	—	—	—	—	—	Fe ₂ O ₃
	Intermediate (2)	53	44	—	1	2	—	—	—	—	Fe ₂ O ₃ , Cr ₂ O ₃
		33	53	—	—	14	—	—	—	—	
	Inner (3)	46	49	—	1	4	—	—	—	—	Cr ₂ O ₃ ,
		32	57	4	—	7	—	—	—	—	
	Subsurface (4)	16	60	—	—	24	—	—	—	—	Cr ₂ O ₃ , SiO ₂ , FeCr ₂ O ₄
3b	Outer (1)	43	57	—	—	—	—	—	—	—	Fe ₂ O ₃
		54	43	—	1	2	—	—	—	—	Fe ₂ O ₃ , Cr ₂ O ₃
	Intermediate (2)	31	54	—	—	15	—	—	—	—	
		45	50	—	1	4	—	—	—	—	Fe ₂ O ₃ , Cr ₂ O ₃
	Inner (3)	46	49	—	—	5	—	—	—	—	
		29	57	5	—	9	—	—	—	—	FeCr ₂ O ₄ , Cr ₂ O ₃ , Fe ₂ SiO ₄
	Subsurface (4)	28	43	—	1	21	—	7	—	—	
		17	58	1	—	24	—	—	—	—	
3c	Outer (1), Intermediate (2)	53	46	—	1	—	—	—	—	—	Fe ₂ O ₃
		26	52	—	—	22	—	—	—	—	Fe ₂ O ₃ , Fe ₂ SiO ₄
	Inner (3)										FeCr ₂ O ₄
		50	45	—	1	4	—	—	—	—	
	Subsurface (4)	36	51	5	1	8	—	—	—	—	
		81	1	—	1	5	10	—	—	2	
		48	44	—	1	7	—	—	—	—	Fe ₂ SiO ₄
											FeCr ₂ O ₄
		25	54	—	—	23	—	—	—	—	
		32	56	4	—	8	—	—	—	—	
		50	46	—	1	3	—	—	—	—	

complete detachment in higher alloyed by Si and Mn steel 2b. The average scale thickness on the AHSS after 60 minutes at 1230 °C in the combustion atmosphere noted in Table II was between 870 and 950 μm with a thicker scale layer observed on high alloy steel 2b. The internal porosity observed in the scale layers formed on the carbon steels was not observed in the scale structure formed in AHSS and penetrating “root-like” dark oxide phases originating from the intermediate and outer layers into the inner and subsurface layers of the sample were observed. The round shape of subsurface oxides indicated possible liquefaction. The results from composition analysis and Raman spectroscopy on the various phases in scale layers are reported in Table II. The dark continuous oxide phases present in the inner and subsurface layers were identified as fayalite (Fe₂SiO₄) and silica (SiO₂). The inner and subsurface layers contained thick continuous dark Fe-Si oxide phases of about 100 μm with embedded metal (Fe-Ni-Mn) entrapment and scattered precipitated gray Fe-Mn oxide phases were observed by adjusting contrast in SEM/BSE analysis. The subsurface structure contained a superimposed oxide scale in the metal substrate with strong adhesion to inner layer and minimal porosity, cracks, and voids. The oxide phases identified by Raman spectroscopy were similar in the two steels (2a and 2b) with the major difference being the presence of SiO₂ oxide in the inner layer of the high Si and Mn steel 2b, which was not observed in the medium Si and Mn steel 2a (Table IV). Both steels contained phases of MnO and Fe₂SiO₄.

Figure 4 reports the thermodynamically predicted solid oxides and liquid oxide solutions (slags) at varying oxygen/steel mass ratio for the AHSS samples under the local equilibrium conditions at reheating temperature. The outer oxide phase in both AHSS grades was predicted to be pure iron oxide (about 95 pct) with traces of solid Mn-Si oxide-based phases. The phases predicted in the subsurface and the inner layer contained a mixture of solid oxides of alloying elements (Si and Mn) and liquid oxide phases. A greater amount of silicon-based solid oxide phases and liquid oxide solutions in the subsurface through to the intermediate layer were predicted in steel 2b which had higher Si and Mn concentrations in the steel. These liquid solutions had average compositions: Slag 1 (51 wt pct SiO₂, 34 wt pct MnO, 15 wt pct Al₂O₃), Slag 2 (69 wt pct FeO, 15 wt pct SiO₂, 11 wt pct MnO, 5 wt pct Fe₂O₃), and Slag 3 (33 wt pct Fe₂O₃, 32 wt pct SiO₂, 18 wt pct MnO, 13 wt pct Mn₂O₃, 4 wt pct FeO).

C. Ferritic Stainless Steel

Three stainless steels with low Al (steel 3a), high Al (steel 3b), and Ti-bearing (steel 3b) were studied. All these steels were highly alloyed with Cr in addition to Mn. Cross-section analysis of the oxidized steels revealed a complex scale structure that could best be classified into four layers: 1—outer, 2—intermediate, 3—inner, and 4—subsurface (Figure 5). The average total scale thickness for these 3 stainless steels oxidized under the conditions noted in Table II was measured to

Fig. 6—Thermodynamic prediction of oxide phases present during reheating *studied* ferritic steels at different oxygen/steel mass ratio: (a) steel 3a with low Al, (b) steel 3b with high Al, and (c) steel 3c with Ti.

be 1000, 900, and 600 μm for the steels 3a, 3b, and 3c, respectively. The wide variation in scale thickness was due to the different steel chemistry and the different applied industrial oxidation conditions (Tables I and II). In all cases, the outer, intermediate, and inner layers represented nearly 95 to 96 pct of the total scale thickness and the subsurface layer made up of the remaining 4 to 5 pct. The typical structure of the outer scale layer on the ferritic stainless steels consisted of dense continuous layers containing iron oxide without any traces of alloying elements. However, the intermediate layer structure had porosity and voids coupled

with microscopic and macroscopic transverse and lateral cracks. The chemistry and oxide phases in the intermediate layer were predominantly hematite (Fe_2O_3) and chromia (Cr_2O_3), while the inner layer contained a mixture of chromite (FeCr_2O_4), hematite (Fe_2O_3), chromia (Cr_2O_3), and fayalite (Fe_2SiO_4) phases with impurities of Ni and Cu (Table V). The subsurface scale layer was strongly attached to the metal substrate with heavily superimposed oxides in the metal matrix. In general, two Cr-based phases were observed in the subsurface region, high Cr with traces of Si, and low Cr with high Si content (Table V). The stainless steel with Al (steel 3b) developed

Fig. 7—Low (left) and high (right) magnifications BSE image of cross-sectional scale structure in austenitic steel (4). Number indicated formed layers: 1—outer, 2—intermediate, 3—inner, and 4—sublayer joined with metal matrix.

Table VI. Characterization of Scale Chemistry and Oxide Phases in Austenitic Stainless Steel (4)

Steel	Layer	Scale Chemistry (Wt Pct)						Oxide Phases
		Fe	O	Si	Mn	Cr	Ni	
4	Outer	45	49	—	4	2	—	MnO, Fe ₂ O ₃ , Fe ₃ O ₄
	Intermediate	28	52	—	3	15	2	MnO, Fe ₂ O ₃ , Fe ₃ O ₄
	Inner	52	42	—	2	4	—	MnO, Mn ₂ SiO ₄ , Fe ₂ O ₃ , Cr ₂ O ₃ ,
		16	57	—	2	25	—	
		8	57	—	5	30	—	
		28	47	4	7	14	—	
	Sub	29	53	5	6	7	—	SiO ₂ , FeCr ₂ O ₄ , Cr ₂ O ₃ , MnSiO ₃
		14	52	—	8	26	—	
		44	47	—	4	5	—	
		37	51	—	2	10	—	
		32	54	5	6	3	—	

a subsurface scale layer with a significant presence of Al oxides. Titanium oxide was not detected in analysis of the scale chemistry in the Ti-bearing steel 3c.

Thermodynamic simulations (Figure 6) of the oxidation sequence in these steels predicted the formation of specific oxides at the scale/metal boundary at low oxygen/metal ratios. In the case of the low Al steel 3a,

Fig. 8—Thermodynamic prediction of oxide phases present during reheating austenitic steel 4 with high Ni and Cr at different oxygen/steel mass ratio.

the predicted subsurface oxides phases where predominantly Cr and Si-based oxides with trace of Al-Mn-Si oxide phase. Aluminum oxide (Al_2O_3) and other Al-based complex Al-Mn-Si oxide were formed in the subsurface layer of the high Al steel 3b. In the case of steel grade 3c having traces of Ti, thermodynamics predicted a complex multicomponent subsurface scale formation, having evidence of Ti-based oxides mixed with Al and Si-based oxide phases which extended to the inner scale layer. A mixture of Cr- and Fe-based oxide phases identified in the experimental investigation was predicted by thermodynamic for these steels in the intermediate to outer scale layer with traces of a Si-based phase mixture as described in Table V.

D. Austenitic Steel

Scale structures formed on the studied austenitic stainless steel that was highly alloyed with Cr, Ni, and Mn are shown in Figure 7. This scale at the outer and intermediate layers was completely separated from the inner and subsurface layers and high levels of porosity were observed in the intermediate scale layer. The inner-subsurface layer had a thickness of about $270\ \mu\text{m}$ with a dense oxide structure superimposed in the metal matrix. The total scale thickness in this steel averaged about $900\ \mu\text{m}$. The composition and phases measured in these two layers consisted mainly of Fe- and Mn-based oxides (Table VI). The inner and subsurface layers where fused together and strongly attached to the base metal substrate, having a complex oxide chemistry comprising of different ratios of Fe, Mn, Si, and Cr (Table VI).

Thermodynamic simulation of the oxidation of this stainless steel predicted the formation of several layers with different oxide phases (Figure 8). A monoxide phase (Mn_2SiO_4) was predicted in the subsurface and through to the inner oxide layer. Multiphases having Cr, Mn, Fe, and Ni-based oxides were predicted in the intermediate and outer scale layer.

Table VII. Experimental vs Thermodynamic Prediction of Oxide Phases in Studied Steel Grades

Steel	Phases Present in Various Oxide Scale Layers			
	Outer	Intermediate	Inner	Subsurface
1b	Experimental Fe ₂ O ₃ , Fe ₃ O ₄ , Simulated Fe ₂ O ₃ , Mn ₂ SiO ₄	Fe ₃ O ₄ , Mn ₂ SiO ₄	MnO, Mn ₂ SiO ₄ , Fe ₃ O ₄ , MnO, Fe ₂ O ₃ , MnAl ₂ O ₄ , Cr ₂ O ₃ , Fe ₂ SiO ₄	Fe ₂ SiO ₄ , MnO, Mn ₂ SiO ₄ Mn ₂ SiO ₄ , MnO, MnAl ₂ O ₄ , Cr ₂ O ₃ , Al ₂ O ₃
2b	Experimental Fe ₂ O ₃ , Fe ₃ O ₄ Simulated Fe ₂ O ₃ , Slag 3 (Fe ₂ O ₃ , SiO ₂ , MnO, Mn ₂ O ₃ , FeO ₂)	Fe ₂ O ₃ , Fe ₃ O ₄ , Fe ₂ SiO ₄ , Slag 2 (FeO, SiO ₂ , MnO, Fe ₂ O ₃)	SiO ₂ , MnO SiO ₂ , Mn ₂ SiO ₄ , Mn ₃ Al ₂ Si ₃ O ₁₂	MnO, Fe ₂ O ₃ , SiO ₂ , Fe ₂ SiO ₄ Al ₂ O ₃ , SiO ₂ , Slag 1 (SiO ₂ , MnO, Al ₂ O ₃)
3b	Experimental Fe ₂ O ₃ Simulated Cr ₂ O ₃ , Fe ₂ O ₃	Fe ₂ O ₃ , Cr ₂ O ₃ Cr ₂ O ₃ , Fe ₂ O ₃ , Fe ₂ SiO ₄ , MnAl ₂ O ₄	Fe ₂ O ₃ , Cr ₂ O ₃ Cr ₂ O ₃ , SiO ₂ , Mn ₂ Al ₄ Si ₅ O ₁₈	Fe ₂ SiO ₄ , FeCr ₂ O ₄ , Cr ₂ O ₃ Al ₂ O ₃ , SiO ₂ , Mn ₂ Al ₄ Si ₅ O ₁₈
4	Experimental Fe ₂ O ₃ , Fe ₃ O ₄ , MnO Simulated Cr ₂ O ₃ , Fe ₂ O ₃ , Mn ₂ SiO ₄ , NiO, Mn ₂ O ₃	MnO, Fe ₂ O ₃ , Fe ₃ O ₄ Cr ₂ O ₃ , Fe ₂ SiO ₄ , Fe ₃ O ₄ , MnO	Mn ₂ SiO ₄ , Cr ₂ O ₃ , MnSiO ₃ , Fe ₃ O ₄ Mn ₂ SiO ₄	SiO ₂ , FeCr ₂ O ₄ , Cr ₂ O ₃ , MnSiO ₃ Mn ₂ SiO ₄

IV. DISCUSSION

The scale formed in the different steels had a multilayered structure and complex phase compositions, as well as defects such as cracks, pores, and delamination from the metal matrix. Formation of the different scale layers is governed by mixed thermodynamic and kinetic oxidation mechanisms. However, considering reheating process time and high temperature, local thermodynamic equilibrium can be used to predict multilayered scale structure and characterize phase composition in the external, internal, and subsurface layers. The experimental work characterized the type of scale formed in different steel grades and identified structure, phases, and compositions of the different oxide layers formed in scale during reheating in a combustion furnace atmosphere. Thermodynamic simulations of the local equilibrium at different oxygen/steel ratios were used to predict the phases that formed at different distances from the sample surface. These simulations showed strong similarities with experimentally observed phases in scale. However, there were also some differences between the actual scale structure and the theoretical thermodynamic predictions. These differences may be due to assumptions used in the simulation of the local equilibrium as well as limitations of the analytical method used in this study for the oxide phase identification. Additional methods such as electron diffraction and high-resolution TEM might be needed to explain these differences. Table VII presents the details of these findings. One steel from each studied steel type was selected for this comparison. Steels 1b and 2b were selected for carbon steels and AHSS due to the presence of Si and Mn alloying element in these steels. For stainless steel, chemistry 3b was selected due to the high Al content in this steel.

In carbon steel 1b with elevated Mn and Si, thermodynamics predicted Fe_2O_3 , Mn_2SiO_4 , MnO, and Fe_2SiO_4 oxide phases in the different scale layers. This layered structure was also observed in the experimental scale and supported by EDX chemistry analysis and Raman spectroscopy phase identification. Thermodynamics predicted the formation of small amounts of phases such as Cr_2O_3 , Al_2O_3 , and MnAl_2O_4 at low oxygen/steel mass ratio. However, these phases were not detected in experimental scale using the Raman spectroscopy analysis. In contrast, trace levels of these elements were detected using EDX chemistry analysis of inner and subsurface of the oxide scale (Table III).

For AHSS, thermodynamics predicted the formation of Fe_2O_3 , SiO_2 , and MnO solid oxide phases in the scale layers which were also identified in the experimental scale structure. Differences observed between thermodynamics predictions and experimental investigations where the predicted formation of predominant Mn_2O_3 and FeO in the external scale layers and $\text{Mn}_2\text{Al}_4\text{Si}_5\text{O}_{18}$, and mono Al_2O_3 in the internal layers. These phases were not identified in experimental Raman spectra, whereas EDX chemistry analysis of the external (outer and intermediate) scale layers did detect the presence Mn and Si (Table IV). Also, it was difficult to identify the complex phases which were present as complex liquid solutions.

Thermodynamics predicted the formation of Cr_2O_3 , Fe_2O_3 , Fe_2SiO_4 , Al_2O_3 , SiO_2 , MnAl_2O_4 , $\text{Mn}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ in the ferritic stainless. Similar oxides of (Cr_2O_3 , Fe_2O_3 , and Fe_2SiO_4) phases were observed in experimental scale phase identification. At the same time, experimental investigations observed the presence of iron chromite FeCr_2O_4 occurring in the subsurface region. Thermodynamics predicted phases of SiO_2 , Al_2O_3 , $\text{Mn}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ in the internal (subsurface and inner) scale layers at low oxygen/steel mass ratio. The space resolution (10x) of the Raman spectroscopy method did not allow identification these phases, while elements forming these phase (Mn, Si, Al) were reported in the EDX scale chemistry analysis (Table V). These results support the possibility of forming thermodynamic predicted oxide phases in the subsurface structure.

In austenitic stainless steels with high Mn, Cr, and Ni, thermodynamics predicted the formation of (Fe_2O_3 , MnO, Cr_2O_3 , Mn_2SiO_4) phases in the scale layers were also identified in experimental investigations. Thermodynamics predicted the formation of a mono-oxide phase in the inner and subsurface layers (Mn_2SiO_4), while experimental scale phase identification reported the formation of a multiphase composition (Mn_2SiO_4 , Cr_2O_3 , MnSiO_3 , Fe_3O_4 , FeCr_2O_4) with elements making up these phases, in good agreement with EDX chemistry analysis of this scale layers (Table VI). The external (outer and intermediate) scale layers predicted by thermodynamics indicated the formation of NiO and Cr_2O_3 . These oxides were not identified in the experimental scale by Raman spectroscopy, possibly due to the small amounts present. However, EDX analysis did show evidence of Ni, Cr, and O in the collected spectra. (Table VI).

The experimental and simulation results presented in this article are limited to oxidation during reheating of a clean milled surface. However, our research has shown that mold flux residues and the roughness of the as-cast surface can have a significant impact on scale formation and scale morphology. The effects of slab surface quality on oxidation will be presented in a future publication.

V. CONCLUSION

Oxide scale structures, phases, and compositions that formed during the reheating of four classes of low alloyed carbon, AHSS, ferritic stainless, and austenitic stainless steels were investigated experimentally and using thermodynamic simulations applying the local equilibrium approach by varying oxygen/steel ratio. The experimentally observed scale structures were documented and the oxide phases formed in the various steels during oxidation were in good agreement with thermodynamic predictions. At the same time, experimental results showed that the formation of multilayered scale structures on the different steel grades is associated with unique structural characteristics such as crack, void, porosity, and detachment, which cannot be revealed by thermodynamics because mostly depend on the physical properties of formed oxides and reaction kinetics. The current study demonstrates the potential of using a

thermodynamic simulation methodology to predict multiphase oxide scale composition in alloys steels to provide reasonable guidance for subsequent technological processes such as descaling and hot rolling.

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