



Effect of Short-Term Overheating on the Isothermal Oxidation Behavior of P91 Steel

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Abstract

P91 ferritic-martensitic steel is widely used in fossil-fired power plants because of its high creep strength and oxidation resistance at elevated temperatures. However, transient overheating above the design temperature can accelerate oxidation, damage the protective oxide scale, and adversely affect component reliability. In this study, the isothermal oxidation of P91 steel under short-term overheating was investigated in dry air at 600°C and 800°C for up to 350 h using weight gain measurements, SEM, cross-sectional analysis, and EDS. The results showed that oxidation increased with both exposure time and temperature, with temperature having a stronger effect. At 600°C, P91 steel formed a thin, compact, and adherent oxide scale with low weight gain. In contrast, at 800°C, the weight gain increased markedly and a much thicker oxide scale developed, accompanied by localized cracking and partial delamination. Cross-sectional SEM confirmed more rapid oxide growth at the higher temperature, while EDS mapping revealed a duplex oxide structure consisting of an Fe-rich outer layer and a Cr-rich inner layer. The chromium-rich inner layer provided better protection at 600°C, however, its effectiveness decreased at 800°C due to rapid oxide growth and enhanced diffusion of oxygen and iron ions. Overall, short-term overheating significantly accelerates the oxidation of P91 steel by promoting oxide growth and weakening the protective chromium-rich oxide layer. These findings help explain the oxidation behavior of P91 steel during transient overheating in power plant service.

Keywords: High temperature oxidation, Isothermal oxidation, Short-term overheating, Oxidation kinetics, Oxide spallation, Ferritic-martensitic steel.

1. Introduction

During the last fifty years, steam pressure and temperature in fossil-fired power plants have been continuously increased to improve thermal efficiency [1]. The thermal efficiency of steam power plants can be significantly improved by increasing the temperature and pressure of the steam entering the turbine inlet from 580 to 620°C, resulting in an increase in thermal efficiency from 38% to 42% [2]. These efficiency gains reduce fuel consumption as well as CO₂ emissions [2,3]. At such high temperature, conventional low-alloy steels and 12% Cr steels can no longer be used as construction materials for live steam piping systems because of the lack of creep resistance of these materials at service temperatures [4]. Consequently, numerous studies on heat resistant steels have been actively conducted since the early 1970s, leading to significant progress of both 9-12% Cr steels and austenitic steels [1]. Among these, ferritic-martensitic (F-M) steels are preferred over austenitic stainless steels because of their higher thermal conductivity, lower thermal expansion coefficient, reduced neutron irradiation-induced swelling, and lower cost [5]. Several modified 9% Cr steels, such as 9Cr-1MoVNb steels (P91/T91), have been developed for high-temperature applications. The high temperature strength is enhanced through the addition of strong carbide and carbonitride forming elements such as vanadium (V), niobium (Nb) and titanium (Ti) leading to the precipitation of various particles, including M₂₃C₆ and MX-type precipitates [1, 6]. In particular, modified 9Cr-1Mo (also denoted as Grade 91) steel is a promising candidate material

for high-temperature power plant applications. P91 steel is widely used in steam and gas turbine systems and boiler components operating at elevated temperatures in fossil-fired thermal and nuclear power plants [6, 7]. For P91 steel, oxidation protection is mainly achieved through the formation of a protective chromia scale on the alloy surface during high-temperature exposure [8]. The approximately 9 wt.% Cr in P91 promotes formation of dense Cr-rich oxides that slow long-term oxidation [5]. Mathiazhagan and Khanna reported that P91 follows parabolic oxidation kinetics in the 600-800°C temperature range, with comparatively lower weight gain and better scale adherence than P92 and E911, consistent with diffusion-controlled oxide growth [9]. Schütze et al. [10] observed stable oxidation of P91 at 650°C in dry synthetic air for exposures up to 10,000 hours without breakaway oxidation. This stability was attributed to the formation of a thin, protective chromium oxide layer and the presence of Mn-rich outer oxides, while Si formed only discrete silica islands at the metal-oxide interface. However, long-term service examinations, have revealed more complex oxide-scale structures [10]. Zhong et al. [11] found a two-layer oxide scale on the inner walls of P91 superheaters, consisting of an outer Fe_2O_3 rich layer with no detectable Cr and an inner $(\text{Fe, Cr})_3\text{O}_4$ layer with a Cr-enriched transition zone. Continuous Cr_2O_3 coverage was incomplete, thereby enabling trans granular oxidation. Yonghao et al., [12] compared oxidation behavior in dry-air and steam environments and reported that T91 exhibited lower mass gain in dry air, remaining relatively stable up to 600°C and reaching approximately $\sim 0.6 \text{ mg/cm}^2$ at 700°C. However, rough, uneven oxide morphologies were observed, along differences in oxidation resistance between steam and dry-air conditions. Short-term oxidation studies at the design temperature of 650°C are limited. Swaminathan et al. [6] reported rapid, non-parabolic oxidation during the first 100 hour, while Schütze et al. [10] observed the early formation of a protective chromium-rich scale that may crack after a few hundred hours. These findings indicate that the short-term oxidation kinetics and scale stability at the design temperature still require further investigation. However, relatively few studies have addressed the short-term overheating behavior of P91 at temperatures above the design value, despite the fact that transient exposure can subject boiler components to much more severe conditions than those normal service [13,14]. In the present study, the isothermal oxidation behavior of P91 steel under short-duration overheating conditions is systematically investigated. The work focuses on understanding the influence of elevated temperature exposure on oxide scale formation, growth kinetics, and spallation behavior. Isothermal oxidation tests conducted at 800°C for different exposure durations to evaluate the oxidation behavior under normal service and overheating conditions. Special emphasis is placed on evaluating the stability and protectiveness of the Cr_2O_3 rich oxide layer under elevated temperature exposure. The findings provide deeper insight into the degradation mechanisms of P91 steel and contribute to a better understanding of its oxidation behavior during transient overheating, which may support the safe design and operation of high-temperature steam power plant components.

2. Experimental procedure

Sample specimens were cut from P91 steel. The chemical composition of the steel is presented in Table-1.

Table 1: Compositional specification for modified 9Cr-1Mo steel [14].

Element wt. %	
C	0.08-0.12
Mn	0.30-0.60
P	<0.020
S	<0.010
Si	0.20-0.50
Cr	8.00-9.50
Mo	0.85-1.05
Nb	0.06-0.10
V	0.18-0.25
N	0.03-0.070
Ni	<0.40
Al	<0.04
Fe	Balance

For the oxidation studies, the specimens were mechanically polished using SiC papers up to 1200 grit to obtain a smooth and uniform surface finish. The polished specimens were ultrasonically cleaned in acetone to remove surface contaminants and then air dried prior to oxidation exposure. The microstructure of the modified 9Cr-1Mo steel was revealed by immersion etching in Vilella's reagent,

consisting of 1 g picric acid, 5 ml HCl and 90 ml ethanol). Each specimen was weighed before oxidation using a digital analytical balance with an accuracy of ± 0.0001 g. High temperature oxidation tests were performed in an electrically heated muffle furnace under an open-air atmosphere. The furnace was capable of operating at temperatures up to 1200°C and was equipped with a PID temperature controller to maintain the temperature accuracy of $\pm 2^{\circ}\text{C}$. The prepared specimens were placed in alumina crucibles and positioned in the uniform temperature zone of the furnace. The oxidation experiments were carried out at fixed temperatures of 600°C and 800°C for exposure duration of 50 h, 100 h, and 350 h to investigate the oxidation behavior. After completion of the exposure, the furnace was allowed to cool naturally to room temperature. The oxidized specimens were then carefully removed and reweighed to determine the weight gain due to oxidation. The measured weight gain was used to evaluate the oxidation behavior of P91 steel. Hardness tests were conducted on the oxidized specimens. The oxidized surfaces and cross sections were examined using an optical microscope and a Scanning Electron Microscope equipped with Energy Dispersive X-ray Spectroscopy (SEM/EDS) to characterize the oxide morphology and elemental composition.

3. Result and Discussion

The isothermal oxidation behavior of P91 ferritic-martensitic steel was investigated in dry air at 600°C and 800°C for exposure durations of 50 h, 100 h, 350 h. The oxidation behavior was evaluated through weight gain measurements, surface and cross-sectional Scanning Electron Microscope (SEM), oxide-scale thickness, and Energy-Dispersive X-ray spectroscopy (EDS). The results demonstrate a pronounced effect of temperature on the oxidation behavior of P91 steel, particularly under the short-term overheating condition of 800°C .

3.1 Oxidation Behavior

Table 2: weight gain and percentage weight gain of P91 steel after isothermal oxidation at 600°C and 800°C .

Temperature ($^{\circ}\text{C}$)	Exposure Time (h)	Weight Gain (g)	Weight Gain (%)
600	50	0.0100	0.02
600	100	0.0148	0.04
600	350	0.0477	0.11
800	50	0.3436	1.09
800	100	0.7705	2.60
800	350	1.4208	4.35

Table 2 summarizes the weight gain and percentage weight gain of P91 steel after oxidation at 600°C and 800°C . A continuous increase in weight gain with exposure time was observed at both temperatures, confirming progressive oxide formation during isothermal exposure. However, the extent of oxidation was strongly dependent on temperature. At 600°C , the weight gain remained relatively low throughout the exposure period. The weight gain increased from 0.0100 g after 50 h to 0.0477 g after 350 h, while the corresponding percentage weight gain increased from 0.02% to only 0.11%. This relatively small increase in mass indicates comparatively slow oxide growth and suggests that the oxide scale formed at 600°C provided an effective barrier against further oxidation.

A substantially different behavior was observed at 800°C . The weight gain increased from 0.3436 g after 50 h to 0.7705 g after 100 h and reached 1.4208 g after 350 h. The corresponding percentage weight gain increased from 1.09% after 50 h to 4.35% after 350 h. Thus, increasing the temperature from 600°C and 800°C resulted in a pronounced increase in oxidation. At 350 h, the percentage weight gain at 800°C was approximately higher than that at 600°C (4.35% compared with 0.11%). The strong temperature dependence can be attributed to the increased rates of ionic and oxygen transport through the developing oxide scale at elevated temperatures. The higher temperature promotes oxide nucleation and growth and facilitates the transport of iron and oxygen ions through the oxide scale. Under these conditions, the formation and growth of Fe-rich oxides become increasingly significant, while maintaining a continuous and Protective Cr-rich barrier becomes more difficult. The present weight gain data clearly demonstrates the detrimental effect of overheating at 800°C on the oxidation resistance of P91 steel. Although the increase in weight gain with exposure time suggests progressive oxide growth, the available exposure interval data do not provide sufficient evidence to assign a specific kinetic law. Therefore, no definite conclusion regarding parabolic, linear oxidation kinetics is drawn in the present study.

3.2 Surface Morphology of Oxidized Samples

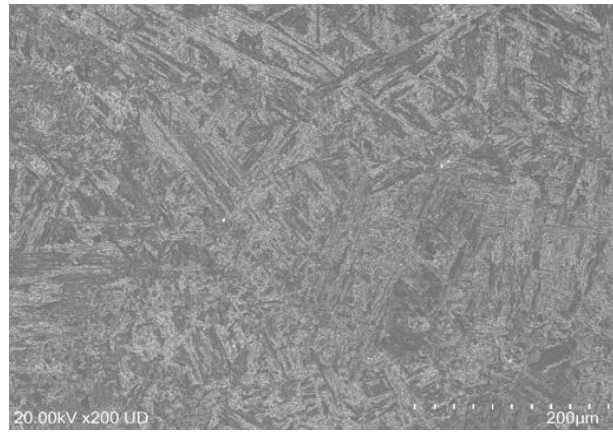


Figure 3.1 Shows the SEM micrograph of the unoxidized P91 sample.

The SEM image shows that the unoxidized P91 steel had a smooth, polished surface, characteristic of its tempered martensitic microstructure. The oxidation temperature strongly influenced the morphology and development of the oxide scale.

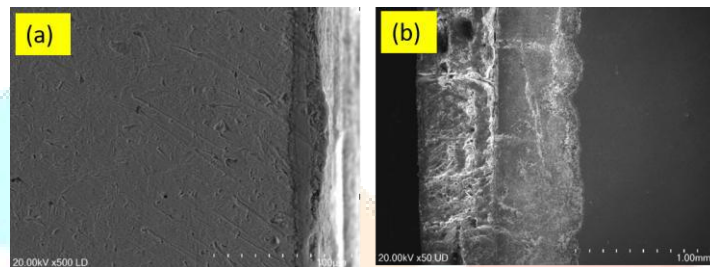


Figure 3.2 SEM Cross-Sectional micrographs of P91 steel after isothermal oxidation, showing oxide scale development: (a) 600°C-350 h, (b) 800°C-350 h.

SEM image of the oxidized P91 samples showed that the oxide-scale morphology varied significantly with temperature. After oxidation at 600°C for 350 h, the oxide scale was relatively thin, compact, and continuous, with very few cracks or signs of peeling. This observation is consistent with the low weight gain measured at 600°C and indicates that the oxide layer provided effective protection against further oxidation. In contrast, the sample exposed at 800°C for 350 h developed a much thicker and more uneven oxide layer with several cracks and partially detached regions. These defects may have resulted from the rapid growth of the oxide scale and the stresses generated during oxidation. The presence of cracks and detached regions likely reduced the protective nature of the oxide layer, facilitating further oxidation of the underlying steel. The difference in the oxide morphology between 600°C and 800°C is consistent with weight change measurements. The compact and continuous scale observed at 600°C corresponds to the relatively low weight gain, whereas the thicker and locally damaged scale at 800°C corresponds to the substantially higher weight gain. These observations indicate that the protective effectiveness of the oxide scale deteriorated under the overheating condition at 800°C, resulting in enhanced oxidation of the P91 steel.

3.3 Oxide Scale Composition and Elemental Distribution

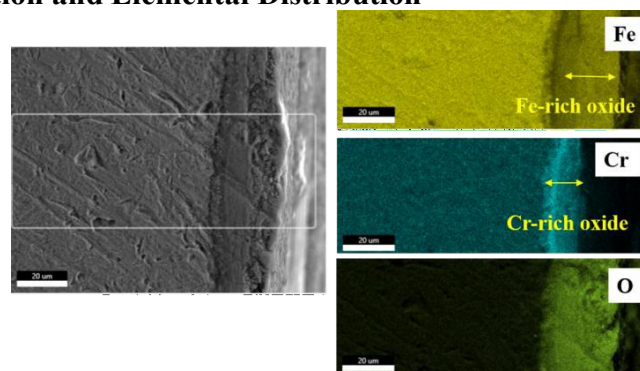


Figure 3.3 Cross-Sectional SEM micrograph and corresponding EDS elemental maps of Fe, Cr and O for P91 steel oxidized at 600°C for 350 h.

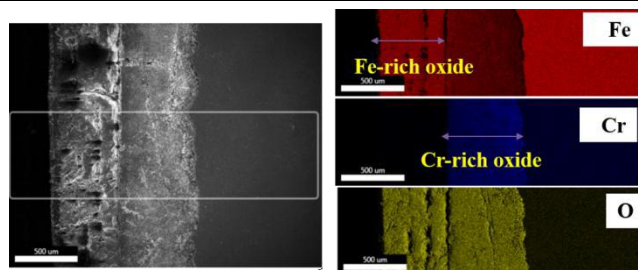


Figure 3.4 Cross-Sectional SEM micrograph and corresponding EDS elemental maps of Fe, Cr and O for P91 steel oxidized at 800°C for 350 h.

The EDS elemental distribution revealed the development of a chemically differentiated oxide scale. An Fe-rich outer region and a Cr-enriched inner region adjacent to the steel substrate were observed at both temperatures. The presence of these regions indicates that selective oxidation and redistribution of alloying elements occurred during the oxidation process.

Table 3: Thickness of the outer Fe-rich oxide layer and inner Cr-rich layer formed on P91 steel after 350 h of isothermal oxidation.

Temperature	Outer layer	Thickness (μm)	Inner layer	Thickness (μm)
P91-600°C-350 h	Fe-rich oxide	50	Cr-rich layer	44
P91-800°C-350 h	Fe-rich oxide	90	Cr-rich layer	103

The thickness of the Fe-rich outer layer increased from approximately 50 μm at 600°C to 90 μm at 800°C. Similarly, the thickness of the Cr-rich inner layer increased from approximately 44 μm to 103 μm. The increase in oxide thickness with temperature is consistent with the corresponding increase in weight gain. The formation of a thicker oxide scale at 800°C indicates enhanced oxidation and increased transport of ions through the growing oxide scale. The substantial growth of the Fe-rich outer region is particularly important because Fe-rich oxides generally provide less effective protection than a continuous and stable Cr-rich barrier. The Cr-enriched inner layer contributes to the oxidation resistance of P91 steel. At 600°C, this layer remained relatively compact and, together with the thin Fe-rich outer layer, provided effective protection against further oxidation. At 800°C, although the Cr-enriched layer became thicker, the Fe-rich outer oxide also grew significantly and exhibited cracks and delamination. Therefore, the protective effect of chromium depends not only on the thickness and stable of the Cr-rich barrier.

3.4 Oxide Growth Mechanism

The combined weight gain measurements, SEM observations, Cross-Sectional analysis, and EDS result provide insight into the oxide growth mechanism of P91 steel. The results are consistent with a diffusion-assisted oxidation process in which oxygen and metal ions are transported through the developing oxide scale. The EDS maps indicate the formation of an Fe-rich outer region and a Cr-enriched inner region, suggesting that different ionic species participate in oxide growth at different locations within the scale. At 600°C, oxidation proceeds relatively slowly, as indicated by the small mass increase and limited oxide scale thickness. The Cr-enriched inner region remains comparatively compact and, together with the outer oxide layer, provides a relatively effective barrier to further ionic transport. Consequently, the oxide scale remains largely continuous and adherent and, and the overall oxidation rate remains low. At 800°C, the substantially higher temperature accelerates the processes responsible for oxide formation and growth. The resulting scale contains a significantly thicker Fe-rich outer layer region and Cr-enriched inner regions. The rapid growth of the oxide scale can generate stresses within the scale, which may contribute to localized cracking and partial delamination. Once these defects develop, the protective effectiveness of the scale is reduced, facilitating continued oxidation and contributing to the substantially higher weight gain observed at 800°C. The proposed oxide-growth sequence is therefore characterized by the development of a Cr-enriched region near the metal/oxide interface followed by substantial growth of Fe-rich oxide toward the outer surface. At the normal service related-temperature investigated here, 600°C, the resulting oxide scale remains comparatively thin and compact. Under the short-term overheating condition 800°C, accelerated oxide growth and scale damage become more pronounced, resulting in reduced oxidation resistance. Overall, the results demonstrate that the oxidation resistance of P91 steel is strongly associated with the integrity of the Cr-enriched inner region and the ability of the oxide scale to remain continuous and adherent. The degradation of this protective configuration at 800°C explain the substantially greater weight gain and oxide scale development observed under the overheating condition.

3.4 Conclusion

1. Oxidation increased with both exposure time and temperature.
2. P91 exhibited comparatively good oxidation resistance at 600°C.
3. Short term overheating at 800°C substantially accelerated the oxidation of P91 steel.
4. The oxide scale exhibited a chemically differentiated structure consisting of an Fe-rich outer region and a Cr-enriched inner region.

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