

# Internal Chromizing – The Benefits

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## Abstract

The layer of oxide that forms on the internal surface of alloy steel pressure parts (e.g., tubing, headers, steamline piping) as an inevitable part of their operation at elevated temperatures constitutes an insidious form of degradation that can severely limit the serviceability of costly tubing and piping materials and can cause damage to critical boiler and turbine components. For pressure part materials operating in heat transfer service the presence of the internal oxide results in a gradual increase in metal temperature that should be – but often is not - factored into design in order to insure acceptable component life, resulting in a limitation on service that can force designers into selecting more highly alloyed – and, in some cases, less suitable – materials for given applications. In addition, particles of the internal oxide inevitably exfoliate from the surface of the pressure part, which can result either in blockage of steam flow through tubing if the exfoliated scale accumulates at bends, welds or changes in internal diameter, or can cause solid-particle erosion damage due to the abrasive effect of the impact of the hard particles on the unprotected surface of critical valve and turbine components. A technical solution to this problem has existed for many years – i.e., the diffusion-controlled enrichment in chromium of the internal surface of the pressure part to a level where the rate of oxidation at elevated temperatures is reduced to negligible amounts. In the past this “chromizing” solution has been prohibitively expensive to carry out on pressure part components, but recent advances in diffusion coatings technology have made it possible to chromize the internal surfaces of pressure parts at costs that are only incrementally higher than the base material. In this paper the problems caused by the internal oxidation of ferritic and austenitic pressure parts at elevated temperatures will be reviewed and the benefits of internal chromizing as an effective means of controlling that internal oxidation will be discussed in detail.

## Introduction

The various problems that electric power producers have encountered as a result of the formation of oxide

on the internal surface of pressure parts operating at elevated temperatures have been known for more than 25 years.<sup>1,2</sup> Whether it is mechanical damage to valve internals or turbine blades caused by the impact of exfoliated scale particles (i.e., Solid Particle Erosion) or the short-term overheating failures caused by accumulations of exfoliated scale in the bottom of superheater tube assemblies, there is a general understanding that the internal oxidation of pressure part surfaces is detrimental for operators of steam-generating equipment.

In fact, the problem is more significant than generally is understood, because in addition to the adverse effects of internal oxidation that are immediately apparent to operators in the form of malfunctioning valves, eroded components and ruptured pressure parts, there is the more insidious long-term effect of the oxidation that manifests itself in the form of substantially reduced pressure part life.

In the discussion that follows, the various aspects of the internal oxidation of pressure parts will be reviewed as they bear on equipment reliability. The discussion will cover the basics of oxide formation and growth, the exfoliation of the oxides, differences in oxide behavior based on material type, and the types of damage directly attributed to exfoliated oxide. The benefits of internal chromizing then will be discussed, with a brief review of the history of chromizing and an explanation of why chromizing is so effective in dealing with the more punitive effects of internal oxidation.

## Oxide Structures and Exfoliation

When the internal surface of a steel pressure part is exposed to steam at elevated temperatures the surface will oxidize at a rate that is a function of the temperature of the surface, the partial pressure of oxygen in the steam, and the alloy content of the pressure part. The fundamental reactions by which this oxidation occurs have been well understood for many years.<sup>3,4</sup> However, it has only been in recent years that the characteristics of the oxide that forms on the surface have been more fully considered, and particularly those properties of the oxide that influence

the manner in which the oxide adheres, or fails to adhere, to the internal surface of the pressure part.

It now is generally understood that the oxide layers that form on pressure parts will vary in structure and, therefore, in mechanical behavior depending on the alloy. Wright and Dooley, et.al.,<sup>5,6,7</sup> have provided excellent descriptions of how the oxide layers on different alloy groups form and how the structure of the oxides influences the manner in which exfoliation occurs. For example, the oxide that forms on the internal surface of low alloy steel tubing, such as T22

(2-1/4Cr-1Mo) develops initially as a two-layered structure - an inner spinel layer of oxidized base metal that is enriched in the major alloying elements, particularly chromium, and an outer layer of iron oxide, predominantly magnetite although some hematite may be present (see left photo, Figure 1). Subsequent growth of the scale often results in transformation of this bi-layered structure into a multi-layered structure consisting of alternating layers of the spinel and the iron oxide, as shown in the right photo in Figure 1.

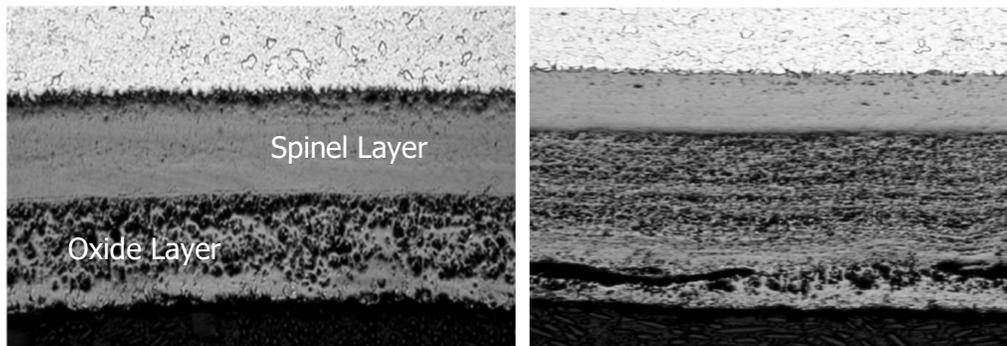


Figure 1. (left) A bi-layered oxide that has formed on T22 tubing following > 50K hours of service at elevated temperatures; (right) a multi-layered oxide that has formed on T22 tubing after a similar period of service.

When exfoliation occurs in these scales, the separation is likely to occur at the alloy/oxide interface and the particles released tend to be relative small.

In contrast to the scale that forms on 2-1/4Cr-1Mo material, the scale that forms on the austenitic stainless grades is different in certain important respects. The structure of the scale on the austenitic steels again is bi-layered, with an inner spinel layer and an outer layer of iron oxide, but with the austenitics the spinel layer develops in a “saw-tooth” type profile, due primarily to differences in the rate of oxidation of material immediately adjoining grain boundaries and material away from the boundaries. Voids form at the interface between the inner spinel layer and the outer oxide layer gradually increasing in density with time until there is a full separation between the layers, as shown in Figure 2. When exfoliation occurs in austenitic tubing the separation typically occurs through the voids at the interface and the particles released tend to be relatively large.

The structure of the oxide that forms on the modified 9Cr ferritic steels, such as Grade 91, varies in important ways from the oxide that forms on other steels, whether it be the low alloys, such as Grade 22, or the austenitic grades. The Grade 91 scale generally is bi-layered, with an inner layer of spinel and an outer layer of oxide, but the spinel frequently consists of sub-layers of varying chromium content, as indicated in the left photo in Figure 3. In addition, between the layer of spinel and oxide concentrations of voids can develop, similar to those that form in the austenitic materials. When exfoliation occurs, the separation typically occurs at the interface between the inner and outer layers and the particles of oxide released are relatively large; alternatively, the two layers may separate while the outer layer remains intact (see Figure 4), which promotes local overheating due to the complete disruption of heat transfer.

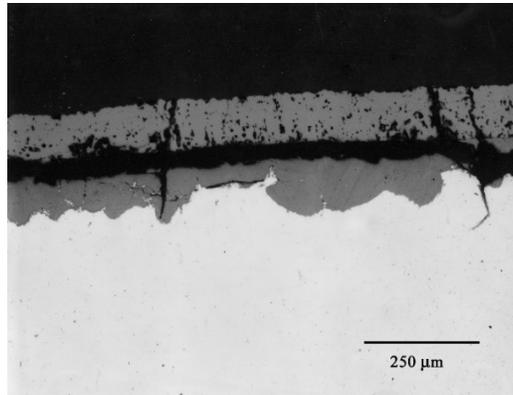


Figure 2. Oxide that has formed on TP304H tubing following extended elevated temperature service; note the irregular profile of the spinel layer in contact with the base metal and the complete separation at this location of the outer magnetite layer from the spinel layer.

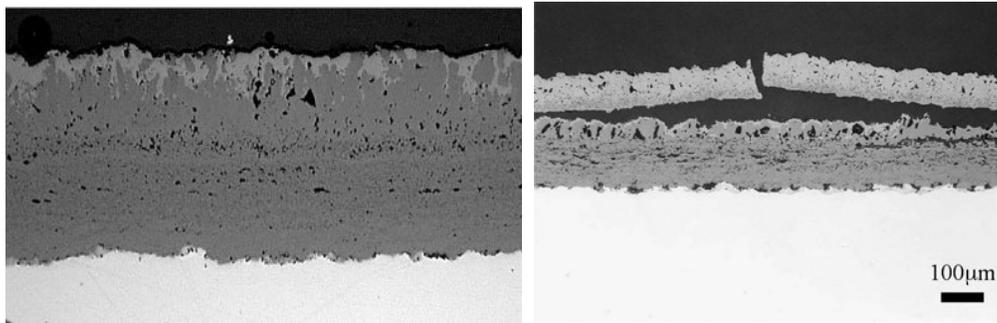


Figure 3. (left) Oxide formed on T91 tubing following extended service at elevated temperatures; (right) delamination of internal oxide on T91 tubing at the interface between oxide layers.<sup>7</sup>

Research into scale behavior has shown that as the thickness of the scale layers increases, internal stresses develop in the layers due to the increase in volume that occurs with formation of the oxide as well as due to differences in the thermo-physical properties of the scale and the base metal, particularly the coefficient of thermal expansion (CTE). The formation of hematite at the outer surface of the magnetite can influence the tendency to exfoliate, since the hematite has a lower CTE than does the magnetite. As the various stresses acting on the scale layer increase, the likelihood of portions of the scale separating from the surface of the pressure part increases also. When the internal stresses in the oxide approach a critical level, any external influence, such as a rapid change in temperature of the pressure part, can trigger a massive release of the scale.

Another aspect of the properties of the internal oxides that adversely affects the pressure part is the insulating

character of the scale. The oxides that form have poor thermal conductivity relative to the metal substrate so that the “cooling” effect of the steam gradually diminishes as the thickness of the oxide layers increases. As a result, for tubing operating within the heat transfer area of the furnace as the scale increases in thickness the tubing metal temperature also increases. It is estimated that for every 25 $\mu$ m of scale that forms on the ID surface of a tube in the heat transfer area, the metal temperature increases by 2-2.5 $^{\circ}$ C (3-4 $^{\circ}$ F). Considering the general observation that the creep life of a component decreases by a factor of roughly 2X for every increase in metal temperature of 15 $^{\circ}$ C, then it could be expected that the life of a tube with an internal oxide thickness of 500 $\mu$ m (+50 $^{\circ}$ C) would be reduced by a factor of more than 6X. For tubing with below average as-installed creep strength, this could mean failure by long-term overheating in less than 10 years, assuming no other damage mechanisms (e.g., external corrosion) are active.

The increase in metal temperature that occurs with the growth of the oxide layer has one further potential disadvantage in oil and coal-fired units: because the susceptibility to certain types of fuel-related external corrosion, such as coal-ash attack, is a function of metal temperature, it can be the case that a boiler that during the early years of operation suffers no

significant external wastage, because metal temperatures were below the range of susceptibility, suddenly experiences aggressive corrosion and rapid wall loss because the metal temperature has increased to the point that the tubing is within the range of susceptibility.

## Chromium and High Temperature Oxidation

Both the rate and manner of growth of oxide layers on the surface of pressure parts is influenced by the alloy content of the pressure part material. In terms of the inhibition of the growth of the oxide layers, the three common alloying elements that potentially have the greatest inhibiting effect are chromium, aluminum and silicon. There is an abundance of data in the technical literature that describes the beneficial effect of chromium on high temperature corrosion and

oxidation; see for example Figure 4. The inhibiting effect of chromium is achieved through a modification of the structure of the oxide, so that the oxide produced becomes more effective in reducing interaction between the metal substrate and the environment. At a chromium content of 25% or greater, a continuous layer of chromia ( $\text{Cr}_2\text{O}_3$ ) forms on the surface of the part, and this chromia layer is stable to temperatures in excess of 680°C.

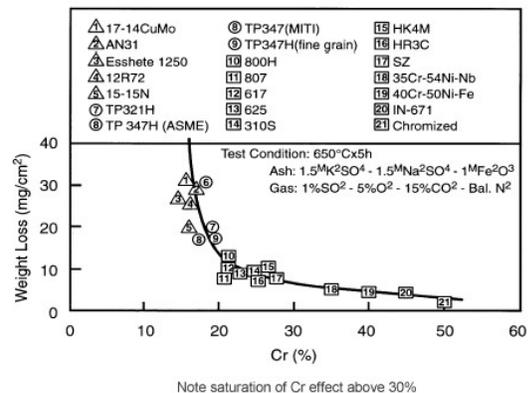
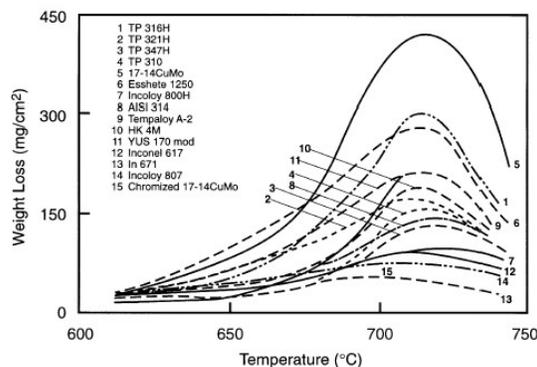


Figure 4. Data from two different studies indicating the beneficial effects of chromizing (Cr content > 30%) on resistance to aggressive conditions of corrosion.

The amount of chromium that can be added as an alloying element to non-austenitic pressure part materials is limited by the potentially adverse impact on the mechanical behavior of the material, particularly ductility and toughness. However, this limitation can be overcome if the alloying is restricted to a relatively thin layer of material at the surface of the component; in such cases relatively large amounts of the element can be added without compromising the safe and reliable operation of the component. In addition, the thermo-physical properties of the base metal are retained when a steel part is chromized, so that there is no increased vulnerability to thermal-fatigue damage or to stress-corrosion cracking.

## Chromizing: The History and Nature of the Protection

The term “chromizing” covers any process in which chromium is diffused into the surface of a component in sufficient amounts to substantially alter the corrosion and/or erosion resistance of that component (see Figure 5).

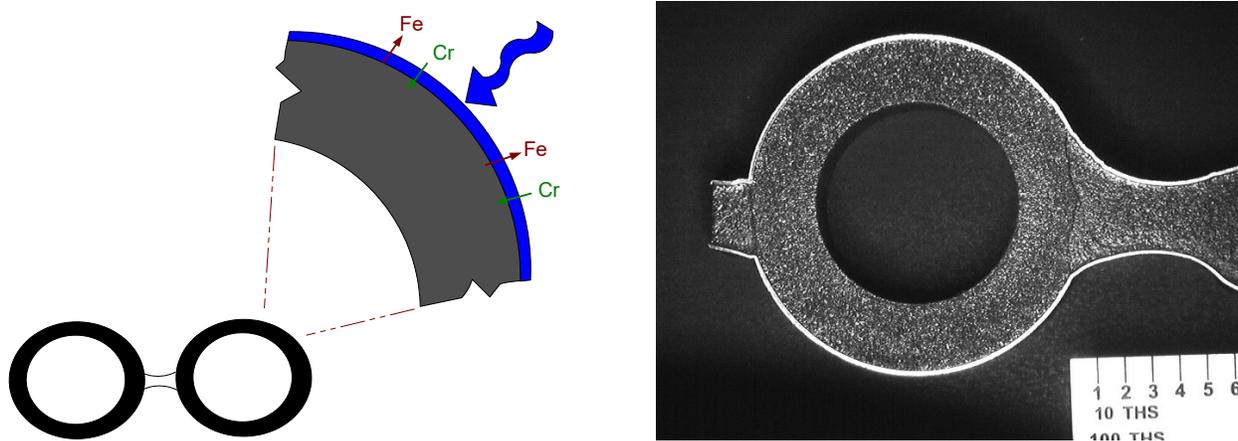


Figure 5. (left) a schematic illustration of what happens during the chromizing process: chromium ions diffuse into the surface of the part, substituting for iron ions, which diffuse outward; (right) an externally chromized waterwall tube from a membrane-welded panel.

As a commercially viable method of surface treatment, chromizing has been available for more than 70 years, with some of the earliest applications involving the chromizing of steam turbine components.<sup>8,9,10,11,12,13</sup> In the past, both gaseous and pack processes have been used to chromize parts, and by the far the greatest amount of chromizing has been carried out by the pack process in which the component to be treated is embedded in a chromium-rich powder mixed with an activator and a parting agent in a sealed retort. In the traditional pack process, the powder serves two obvious functions: first, it is the source of the chromium diffused into the component surface and, second, it supports the components throughout the high temperature processing, which minimizes deformation. The retort containing the powder and the parts is heated to a specified temperature, in the course of which the activator reacted with the constituents of the powder to produce a halide gas that serves as the mechanism of transport of the chromium to the surface of the component. Contact between the surface of the part and the powder was not required for the surface enrichment to occur provided there was a sufficient amount of the chromium-rich gas present to fully develop an optimum protective structure. However, because components of the powder are refractory in nature, processing times for large components tend to be quite long and the process of loading and unloading the powder is labor intensive, which substantially increases the cost of the process.

Recently a slurry-based method for chromizing has been developed that both eliminates a substantial portion of the labor associated with the powder handling and facilitates the use of more economical methods of heating, thereby significantly reducing the cost of the internal chromizing of pressure parts. In

addition, through careful control of the slurry composition, the amount of chromium added to the surface can be tailored to meet the requirements of specific applications, such as the ID surface of pressure parts.

Depending on the carbon content of the base material and the temperature of diffusion, the chromium that is diffused into the surface of the component may combine with carbon in the base metal to form a thin but hard and wear-resistant layer of chromium carbide, or it may “dissolve” into the base metal structure to form a surface layer of single-phase high-chromium material. Since the chromized layer is an integral part of the base metal structure, the chromized layer cannot spall off, as occurs with other coatings that are not metallurgically bonded. In addition, for the ferritic-based steels, the thermo-physical properties of the chromized layer are fully compatible with those of the base metal, so that there is no increase in susceptibility to thermal-fatigue damage, nor is the chromized layer susceptible to stress-corrosion cracking, as is the case with many of the austenitic overlay materials.

For common pressure part alloys, including low carbon steels, low alloy steels (e.g., Grade 22), modified 9-12%Cr steels (e.g., Grade 91), and austenitic stainless steels (e.g., TP304H) the objective typically is to produce a surface layer of material that is enriched with a sufficient amount of chromium that the corrosion or oxidation resistance is fundamentally changed. To achieve this the temperature/time combinations are carefully selected, first, to insure that the minimum chromium content at the surface of the component is in the range of 30-35% (by weight) and, second, that the desired thickness of the layer is achieved. For the more severe applications involving

protection from external corrosion of pressure parts the thickness of the chromized layer typically is a minimum of 0.010” (0.25mm), while for less aggressive environments, involving protection from

high temperature oxidation at the internal surface of boiler tubing, much thinner chromized layers provide the required degree of protection (see Figure 6).



Figure 6. Showing the surface-enriched chromizing layer produced for two different applications: on the left the application was designed to combat aggressive external corrosion in carbon steel tubing in a chemical recovery boiler; on the right the application was designed to minimize internal oxidation in a Grade 91 superheater tube in a utility boiler.

With proper control during processing, the through-thickness chromium “profile” established during the process is independent of the chromized layer thickness, with the chromium content at the surface of

the part exceeding 30% and gradually decreasing to the etching boundary, at which point the chromium content is approximately 13% (see Figure 7).

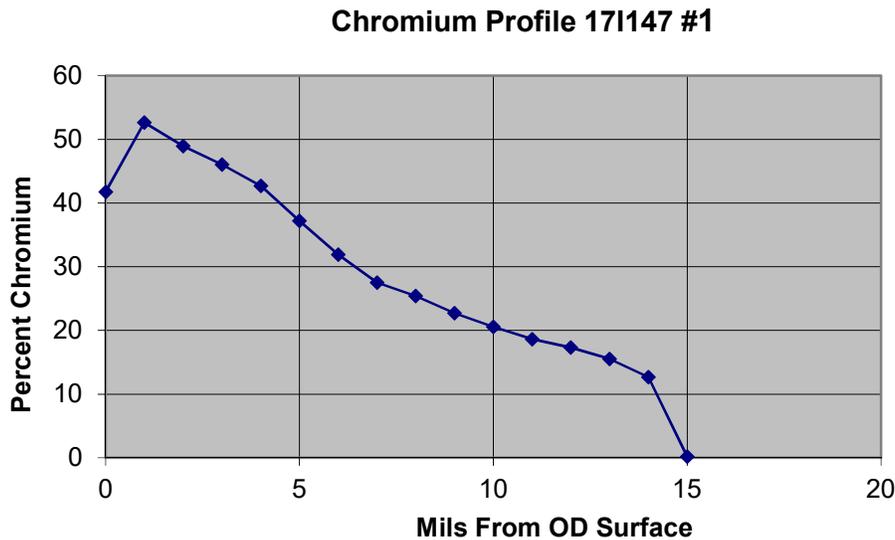


Figure 7. A typical chromium profile for a 0.014” (0.36mm) thick chromized layer.

## Summary

The oxide that forms on the internal surface of pressure parts that operate at elevated temperatures adversely affects the operation of steam generating equipment in a number of ways. First, for pressure parts operating in a heat transfer area (e.g., a superheater) the oxide acts as a thermal barrier disrupting the cooling effects of steam, so that over time as the thickness of the oxide layer increases the metal temperature of the pressure part also increases. This results in a significant reduction in total component life regardless of fuel type and, for coal-fired and oil-fired boilers, can lead to enhanced susceptibility to external corrosion. Second, the oxide eventually will exfoliate, which can result in erosion damage to valves and turbine components and can cause short-term overheating failures if the exfoliated

scale accumulates at pinch points in the circuit and blocks steam flow.

Chromizing is a very effective way of eliminating the problems associated with the growth of internal oxide, since the chromium content at the surface of a chromized part is sufficiently high to greatly reduce the rate of oxide growth. Processing restrictions that in the past had substantially increased the costs of chromizing the internal surface of pressure parts have been overcome in part through the development of a slurry technology that substantially reduces handling and in part through a modified heating procedure that permits accelerated processing of individual tubes.

## References:

- Grobner, P.J., Clark, C.C., Andreae, P.V. and Sylvester, W.R., "Steamside Oxidation and Exfoliation of Cr-Mo Superheater and Reheater Steels," Corrosion/80, Paper No. 172, 1980.
- Fry, A., Osgerby, S., and Wright, M., "Oxidation of Alloys in Steam Environments – A Review," NPL Report MATC (A) 90, NPL Materials Centre, 2002.
- Viswanathan, R., Sarver, J., and Tanzosh, J.M., "Boiler materials for ultra-supercritical coal power plants—steamside oxidation," Journal of Materials Engineering and Performance, 2006, Springer
- Ennis, P.J. and Quadackers, W.J., "Mechanisms of Steam Oxidation in High Strength Martensitic Steels," International Journal of Pressure Vessels and Piping, 2007 – Elsevier
- I. G. Wright, A.S. Subau, and R.B. Dooley, "Development of Strain in Oxides Grown in Steam Tubes", Materials Science Forum, Vols. 595-598, pp. 387-395, 2008
- Wright, I.G. and Dooley, R.B., "A Review of the Oxidation Behavior of Structural Alloys in Steam," International Materials Reviews, 2010, Taylor & Francis
- Wright, I.G. and Dooley, R.B., "Morphologies of Oxide Growth and Exfoliation in Superheater and Reheater Tubing of Steam Boilers," Materials at High Temperatures, 28(1), 45-62 (2011)
- Plumley, A.L., Henry, J.F., and Cullen, T.M., "Long Term Performance of Chromizing for Corrosion Protection of Utility Boilers," presented at the Power-Gen Americas Conference in Orlando, FLA, 1994.
- Henry, J.F., and Daoust, N., "Chromizing: An Alternative Solution for Recovery Furnace Protection," presented at the 1994 TAPPI Engineering Conference in San Francisco, CA.
- Nakahama, S., Saitoh, K., Kawasaki, M., Yakuwa, H., and Miyasaka, M., "Chromized Coating for Preventing High-Temperature Sulfidation Corrosion of FCC Power Recovery Turbine," NACE International, 2000.
- Palka, K., & Weronki, A., "Some Properties of Chromized Stainless Steels, Inzynieria Materialowa, 25(3), 5-6, aendix, 2004.
- Behrani, V.R. and Singh, P.M., "Corrosion Behavior of Aluminized and Chromized Carbon Steel in Fluctuating Oxidizing-Sulfidizing Environments," NACE, 07209, 2007 CP.
- Alia, F.F., Kurniawon, T., Asmara, Y.P., Ari, M.H.B., and Nandiyanto, "High Temperature Oxidation in Boiler Environment of Chromized Steel," IOP Conference Series, Materials Science and Engineering, Volume 257, Conference 1, 2017.