# Substrates and temperatures in relation to coatings

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## Introduction

Heat resistant coatings are used for many applications covering multiple industries and segments. These coatings face various operational conditions and are applied on different substrates. The purpose of heat resistant coatings depends on the application, but some main categories are atmospheric corrosion protection and protection against corrosion under insulation (CUI). Further, when used for stainless steel, heat resistant coatings reduce the chances for chloride stress corrosion cracking (CSCC) and oxidation.

The performance of a heat resistant coating highly depends on the duration of exposure to heat and corrosive environments, and the substrate’s thermal expansion and oxidation process. Various substrates respond differently when exposed to heat. Differences in thermal expansion of the substrate and the coating may cause the coating to crack and/or delaminate from the substrate. Different metal substrates can also form a significant oxide layer on the surface between the coating and the steel that may lead to delamination. This calls for tailormade coating solutions that can not only withstand elevated temperatures and highly corrosive conditions, but also the thermally induced stresses caused by differences in thermal expansion. To cope with the oxidation process, Jotun states “where substrates allow” limiting the continuous operational temperatures for the heat resistant coatings to the substrates’ nature given limitations.

## 2. Corrosive conditions

Heat resistant coatings for atmospheric corrosion protection of carbon steel, alloyed steel and stainless steel are important to protect against corrosion. This can be during the manufacturing phase until commissioning of e.g. a hydrocarbon processing industry plant, during production shutdowns and cyclic conditions during the operational phase. For such applications it is crucial that heat resistant coatings provide corrosion protection at ambient temperatures both before and after being exposed to high operating temperatures.

Heat resistant coatings are also frequently used as one of the few effective measures against CUI. CUI is known to be a high risk for all processing plants operating at elevated temperatures with insulated piping or processing equipment. For such applications, the heat resistant coatings must withstand elevated temperatures while also being exposed to highly corrosive environments. These environments are formed in the presence of moisture from water leaking through the insulation jacket/casing or condensation, combined with impurities and salts from the surrounding atmosphere and the insulation material. Above the boiling point of water, the surface of the piping will dry out, however, the insulation material surrounding the pipe may still hold moisture. Since many operations in process plants are cyclic, CUI challenges can often be encountered although the operating temperatures are above 100°C. NACE SP0198 defines the CUI range from –4 to 175°C.[1]

Stainless steel is used for piping in process plants when operating conditions requires. This can either be because the operating temperature is above the temperature where the structural integrity and strength of carbon steel is reduced.[2] Stainless steel might also be preferred because the liquid or gas inside the piping is highly corrosive. Stainless steel is inherently well protected against general corrosion; however, other forms of corrosion may occur under certain circumstances such as chloride stress corrosion cracking (CSCC). Heat resistant coatings are often used as a measure to protect stainless steel against different forms of intergranular corrosion by reducing the concentration of detrimental ions and molecules at the surface of the stainless steel substrate (e.g. chloride ions and oxygen, respectively).

## 3. Thermal expansion

In addition to the various corrosive environments heat resistant coatings must withstand and protect the substrate against, these materials also must perform under mechanical loads such as stresses induced by the difference in thermal expansion between the coating and the steel substrate. The thermal expansion of a heat resistant coating can be many times larger than the thermal expansion of the metallic substrate. This difference in thermal expansion will induce mechanical stresses predominantly at the steel-coating interface and will increase as a function of temperature. The coating can only cope with these stresses by having sufficient internal strength and adhesion to the substrate to withstand the built-up stress. However, if the dimensional difference exceeds the coating material's internal strength and/or the coating material's ability to adhere to the substrate, the thermal expansion may cause the coating to crack and/or delaminate from the substrate. This calls for tailormade coating solutions that can not only withstand elevated temperatures and highly corrosive conditions, but also the thermally induced stresses caused by differences in thermal expansion.

## 4. High temperature oxidation

Metals oxidize. The reaction between metals and oxygen is one of the simplest chemical reactions[3,4]. The oxidation reaction is initiated by adsorption of oxygen on the metallic surface, followed by an initial transient stage where components in an alloy will oxidize. During the initial nucleation and growth, a thin oxide layer forms and covers the entire metal surface. Surface defects and impurities in the metal and/or the gas will influence the adsorption of oxygen, nucleation, and formation of the oxide.

The stability of an oxide, and thereby whether it will form or not, can be determined by considering the Gibbs free energy of the system[5]. A useful presentation of standard free energies for the formation of selected oxides is an Ellingham-Richardson diagram as shown in Figure 1. The most stabile oxides in such a diagram will be characterized by the most negative ΔG values. This information can be used to identify which element of an alloy that will form the most stable oxide and is thereby likely to act as a protective corrosion resistant oxide layer on the base alloy.

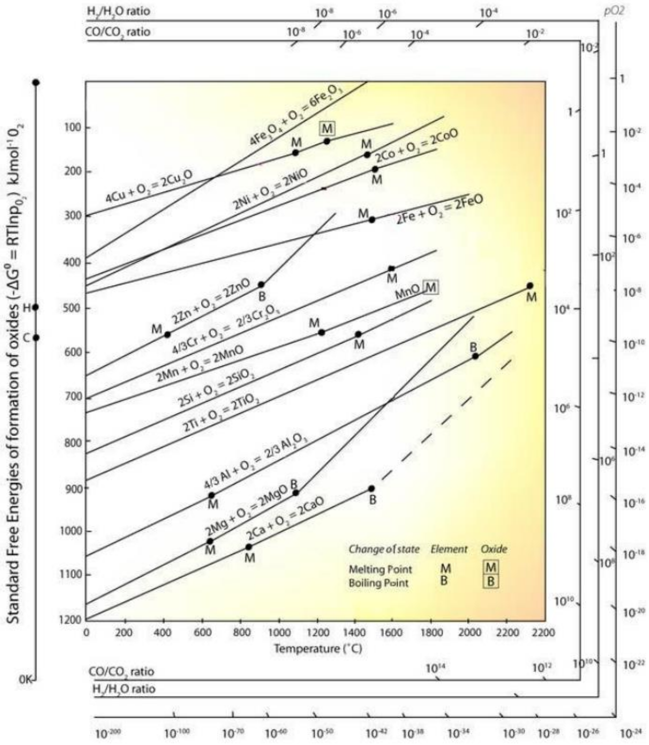

*Figure 1. Ellingham-Richardson diagram showing free energies for formation of selected oxides*

Although the thermodynamic stability of an oxide dictates whether it will form or not, the rate of oxidation and scale growth is given by the kinetics of the oxidation process. The kinetics of oxidation is highly temperature dependent, and the increase in oxidation rate as a function of temperature is often logarithmic. Isothermal high temperature oxidation is often following a parabolic rate law as most high temperature oxidation is limited by either cation or oxygen diffusion through the forming oxide scale[6]. So, the higher amount of a component that will easily form a stable oxide, e.g. chromium, the higher oxidation rate.

At the steel-coating interface there will initially be enough oxygen to the onset and progress of oxide scale formation. However, depending on the oxygen permeability of the coating and the composition of the steel alloy, the oxide scale growth can be reduced as time increases or continue following a parabolic growth rate. For temperatures of 200°C and lower the oxidation at the steel-coating interface will be insignificant as coatings used in that temperature usually holds good barrier properties as well as the temperature not being high enough to sustain substantial oxide growth even for highly alloyed materials. However, at higher temperatures above 450 °C the oxide scale growth on highly alloyed stainless steels, meaning alloys with more than 17 wt. % of chromium, can continue as the coatings used for such conditions will have a higher permeability of oxygen due to the more porous structure the coating material due to lack of organic components.

Thorough testing and verification of Jotun’s findings with third party test institutes concludes that when stainless steel alloys containing enough chromium are exposed for an extensive duration to temperatures exceeding 450°C and there is sufficient access to oxygen at the coating-steel interface, a continuous growth of oxide scale will form a significant oxide layer between the coating and the steel causing delamination regardless of the coating type or technology [7].

*Figure 2. Cross cut test and pull off test of heat resistant coating on carbon steel (S355)*

Most organic binder polymeric material compounds will start to be thermally degraded at temperatures above 230°C, and at temperatures above 400°C organic polymers will be decomposed[8]. Consequently, the remaining coating material after such decomposition of the organic polymeric binder structure will have an increased porosity. Increased coating porosity will increase the oxidation rate of the substrate.

A coating can perform for some time even if the surface of the steel has started to oxidize, however continued heat exposure will eventually result in delamination. Figure 2 shows cross cut and pull-off tests of a heat resistant coating on carbon steel (S355) after continuous exposure to 650°C. The cross cut test result seems acceptable, however a pull off test reveals lack of adhesion between the oxidized carbon steel substrate and the coating. High temperature exposure over time will therefore likely result in complete delamination from a substrate with significant oxide scale formation, regardless of the coating type or technology.

Consequently, Jotun sets the continuous operational temperature limits based on the substrate's natural heat resistant properties and state "where substrates allow" limiting the continuous operational temperatures to the substrates' nature given limitations. For shorter time periods a heat resistant coating may tolerate higher temperatures than the given continuous operational temperature limit.

Jotun are also extending the test time for heat exposure to 1 000 hours to better represent in-field exposure. The performance of Jotun's heat resistant coatings is verified by third party test institutes documenting 1 000 hours dry heat exposure and various tests for anti-corrosive properties on carbon steel, alloyed steel- and various stainless steel-substrates.

## 4. Conclusion

The performance of a heat resistant coating highly depends on the duration of exposure to heat, corrosive environments, thermal induced stresses, and the substrate's natural oxidation process. Jotun acknowledge that substrates respond differently to high temperature exposure and have therefore developed tailor made solutions to optimize performance on various substrates and temperatures, and to meet customers' needs in the best way possible.

# References

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