

## **CORROSION BEHAVIOR OF STEELS WITH REDUCED EFFECTIVE CHROMIUM CONTENT**

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### **Abstract**

The paper deals with the corrosion behavior of steels with reduced effective chromium content in the matrix, with the intent to estimate their long-term behavior in low aggressive environments, typical for the secondary and primary circuits of nuclear power plants. Materials for this research were steels with varying characteristics of influence of effective chromium content precipitation of chromium carbides or spinodal breakdown of chromium / martensitic steels, creating other types of chromium-rich phases, e.g. borides in austenitic steels. In addition, materials used as additional welding material or high alloy steel bolts were used. In these mentioned materials is chromium released by various mechanisms and the content of effective chromium in the solid solution is reduced (up to several units of wt. %), which may cause the overall passivity of the steel, to sensitivity to intergranular corrosion.

Based on the basic techniques of material identification, the causes of different behavior of both types of steels after sensitization or tempering were estimated. They are described as being risky in terms of heterogeneity in the chromium content, which manifest themselves as active ways of corrosion.

**Keywords:** Corrosion behavior, steels with reduced chromium content, low aggressiveness environment, reduced corrosion resistance, intergranular corrosion, heterogeneity of chromium content

### **1. INTRODUCTION**

Damage of metallic construction materials during their application is a consequence of the complex influence of operating conditions, so-called stress / stressors acting on metallic material [1-6]. Depending on the extent of the effects of the stressors (on the whole or on the surface of the metal), various manifestations of their effect can be observed [7-12]. From the degradation of the material properties to the more or less intense material loss, are observed; the ultimate consequence of load effects on structural materials can be to damage the integrity of the material and failure of a component. That has often a localized character [13-18].

The general cause of localized damage is the existence or formation of heterogeneities in the system material-environment, as well on the material side as on the environment side. In the power plants, are created specific conditions for the application and co-operation of both types of heterogeneity in the occurrence and development of damage.

### **2. DESCRIPTION OF CORROSION SYSTEM**

During the exposure of all types of that steels in the energetics industry, changes in the material properties may occur. The causes of changes in properties can be divided into two groups according to application temperature. Steels exposed in temperature range  $t < 300 - 350$  °C are subject to damage with a significant environmental impact, typical of nuclear plant facilities or part of the pressure circuit of conventional power plant. Steels exposed at temperature  $t > 350$  °C often fail due to degradation of material properties with minimal environmental effects, as is the case in particular blocks power classical and supercritical.

On the environmental side, heterogeneity is generated during all operating modes, most notably when changing the physicochemical conditions of the work environment. These are the volumes of transient condensation, with the formation of the first condensate, by erosion - corrosion, the cavitation effect of condensing vapor, the evaporation of the working medium, the formation of a thickened environment,

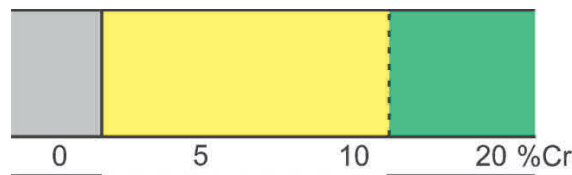
The influence of heterogeneity on the environment side on heterogeneous joint of materials may be different, with the greatest risk of intensification of the corrosion process being assumed for carbon steel with low chromium regions, especially in the temperature range  $t < 130-160$  °C.

Generation of material heterogeneities during operation are often manifested by a change in the uniform distribution of the elements in the steel, the surface layer of the steel, or by the increase in the transport of one of the elements, by creating specific fast transport paths in the steel.

The most pronounced are those in highly alloyed steels where the uneven distribution of Chromium in steel dominates the steel behavior. The following text will focus on high alloyed steels at application temperatures  $t < 30$  °C (conditions typical of nuclear power plants), where the low temperature of material heterogeneity is difficult to produce, hence heterogeneity in the distribution of chromium in steel to the system introduced, e.g., besides events leading to redistribution of chromium occur in opposite transporting atoms and segregation activities P, S and others:

- using martensitic quenched steel in varying degrees of tempering (bonding of chromium to different types of carbides),
- using high boron steel (bonding of chromium to borides and, to a lesser extent, carbid-borides),
- using ChN35VDVT / Cr15Ni34Ti1W3 (chromium bonding to carbides, formation of Ni-Al-Ti intermetallic reinforcement),
- using Ch16N25AM6 / Cr16Ni25Mo6 steel (chromium bonding to carbides, segregation processes on contact of ferrite-austenite structural blocks),
- in heterogeneous weld joints, carbon steel - corrosion resistant (formation of the transition zone at the fusion boundary).

For these steels or joints, the change in the uniform distribution of Cr is so significant that the tests used to verify metallurgical quality (resistance to intergranular corrosion) can exclude most of the material variants from use. In the event of failure of these steels, very often with in intergranular form, a low resistance to intergranular corrosion is indicated as the cause of the failure. In order to assess the "hazard" of chromium-modified regions with respect to the nominal in the matrix, it is possible to use a Fe-Cr material spectrum with a  $w(\text{Cr}) \approx$  content of 0 % by weight up to  $w(\text{Cr}) \approx 30$  % w / w. This spectrum includes both the component of heterogeneous weld joints (carbon steel), their transit region and areas with reduced chromium content around chromium-rich particles (precipitates, eutectic components), **Figure 1**.



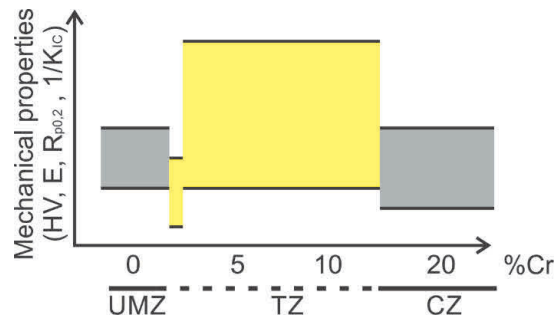
**Figure 1** Model spectrum of Fe - Cr materials; areas of non-affected metals are indicated with a solid line (carbon - gray / stainless steel - green area); areas with reduced chromium content are marked with a dashed line

### 3. PROPERTIES OF MATERIAL SPECTRUM Fe - Cr (Ni)

The Fe - Cr material spectrum is a localized region introduced or formed in a material with different chromium content from the matrix. This can vary from 0 % to 30 % by weight. Cr, which is accompanied by a variable

and structurally, dependent carbon content and typical impurities, P, S and the like. The contradictory transport of chromium and carbon can lead to the formation of areas with altered mechanical and corrosion properties, **Figure 2**, decarburization, occlusion areas, carbide zones etc.

The content of chromium in steel is dominated mainly by the properties of corrosion; with chromium content in steel  $w(\text{Cr}) > 10 - 12 \text{ wt. } \%$  the properties of the steel are changing, it becomes easier to pass through, and this effect is also reflected at the limit of high temperature oxidation (it moves to higher temperatures).



**Figure 2** Qualitative estimation of mechanical properties of individual Fe - Cr spectrum bands

#### 4. CORROSION RESISTANCE OF MATERIAL VARIATIONS IN THE ENVIRONMENT OF NUCLEAR POWER PLANTS

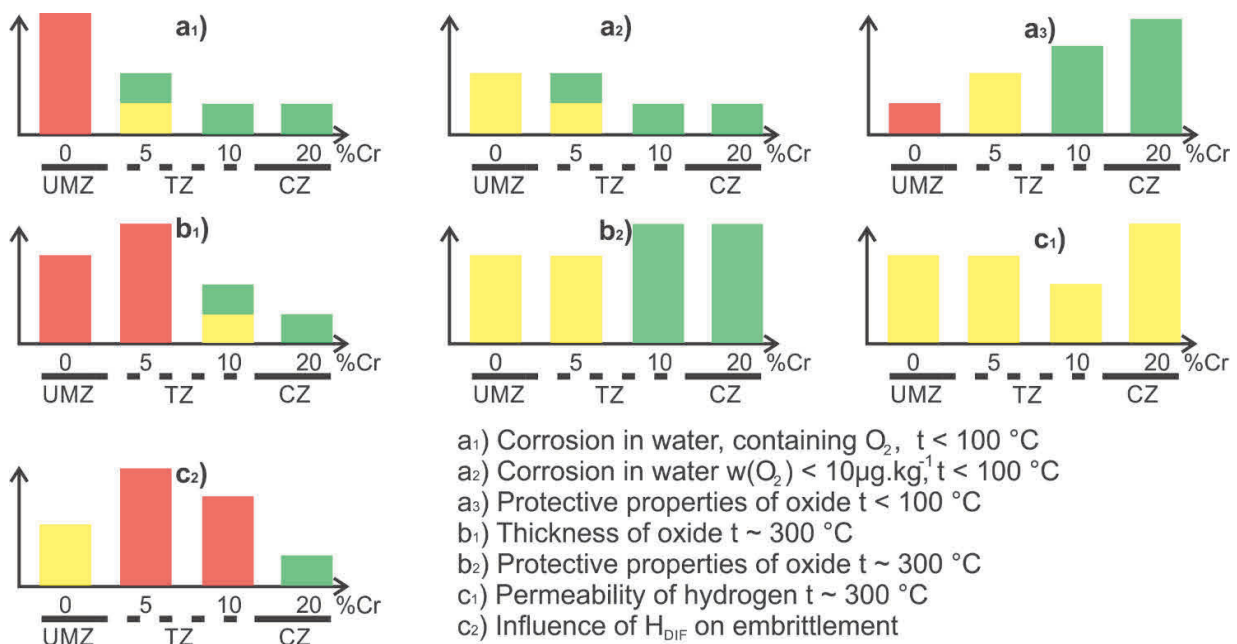
For corrosion behavior of Fe-Cr steels in aqueous environments, the amount of alloying elements available in steel is critical; especially chromium. Variable Ni content slightly reflects the behavioral change in corrosion of steel in the active state and in high temperature oxidation. From the point of view of the influence of the environment on two corrosively different materials of the model spectrum Fe - Cr their behavior should be determined by the different corrosion resistance of the partial components (Fe - CrNiMo), ie. the lifetime of the material (steel, Chromium Depletion Area, etc.) with a lower corrosion resistance should be decided. All possible material spectrum, with generally different chemical activity (resistance), however, exhibits acceptable and usable durability up to maximum operating temperatures in correct typical nuclear power plants environments (secondary and primary circuit). The origin of the resistance of both extreme material variants (Fe - CrNiMo) is either:

- in passivity ( $t < 160 - 200 \text{ }^\circ\text{C}$ ), the metal is covered with an oxide layer, the thickness does not change over time,
- in "high temperature passivity", the protection of the steel surface by high temperature oxidation ( $t > 200 \text{ }^\circ\text{C}$ ), which especially increases on carbon steel at temperatures up to  $350 \text{ }^\circ\text{C}$  measurably increases with temperature and time.

The resulting protective layers, oxides, act as a barrier to direct contact of the metal surface with the environment. When the integrity of the protective layer is impaired, it is possible to detect metal this process is called activation, followed by a different episode of more intense corrosion-oxidation. Uninterrupted sealing of the damaged site will result in a decrease in pumping intensity, metal loss and passivity, or low rate of high temperature oxidation. The protective layer may be interrupted repeatedly, in a mechanical way (deformation of the metal - protective layer, shock effect of the flowing working medium, etc.) or chemical (occlusion solution, oxygen cells, evaporation medium, etc.). Frequency of disturbance under given conditions determines the rate of stable propagation of subcritical defect. On high-alloy steels (containing chromium, this effect is applied at  $w(\text{Cr}) > 5 - 8 \text{ wt. } \%$ ), both states (the resulting layers) are much more resistant to local or total chemical or mechanical disturbances compared to carbon steel. On high-alloyed material, in most typical environments for nuclear power plants, the breakthrough of the protective layer is impossible by chemical action, or after mechanical damage, the defect is so quickly encapsulated, passivating that no significant metal loss occurs.

Depending on the content of alloying elements, especially Cr, the corrosion resistance of individual material variants can be characterized by:

- different corrosion behavior (different value of spontaneous corrosion potential,  $E_{KOR}$ ), possibility of creating galvanic cell: active - active, active - passive,
- variable spontaneous passivating ability ( $v_{KOR\_PAS} \approx f(1/Cr)$ ,  $w_{LIM} > 10$  to 12 wt.%) in aqueous medium at a temperature  $t < 100$  °C (regardless on the oxygen content in the aqueous environment), **Figure 3a**,
- carbon steel stability is determined by the concentration of oxygen in water, **Figure 3a**; in environments with a very low concentration of oxygen in water,  $t < 100$  °C ( $k < 0.1$  mS / m), corrodes with very low corrosion rates in activity and passivity, higher chromium steel is passive,
- in the aqueous phase,  $t < 100$  °C, ( $k < 0.1$  mS / m),  $w(O_2) > 400$   $\mu\text{g}\cdot\text{kg}^{-1}$ , are higher chromium steels in passivity, carbon steel can pass from the passive state and succumb to local activation, the higher conductivity of the environment accelerates the activation of carbon steel,
- different rates of high temperature oxidation at temperatures  $t > 250$  °C,  $v_{HT\_OX} = f(1/Cr)$ , characterized by parabolic constant,  $k_P$ , **Figure 3b**,
- different resistance to localized corrosion ( $\approx f(Cr, Mo, Ti / Nb: C)$ ),
- different permeation behaviors and level of embrittlement by diffusible hydrogen, **Figure 3c**.



**Figure 3** Semi-quantitative evaluation of the actions that can be applied in stable defect spreading in areas with reduced chromium content (situation around zone of fusion in heterogeneous weld. UMZ - unmixed metal zone. TZ - transition zone, CZ - composite, negative expression with possible maximum loss of steel (red), neutral or negligent negative expression with slight loss of steel (Yellow). Positive expression with minimal steel loss (Green) (the height of the column is proportional to the degree of positive or negative effect)

## 5. DISCUSSION

On propagation of defects may also be involved phenomena conditional deformability of steel, forming a transition region, e.g. in influencing the steel atomic hydrogen or the high temperature oxidation, disruption of the protective layer. When deformation occurs in the area of maximum deformation of the steel with high ductility (area decarburized etc.), and high-temperature cracking of the cured regions or vice versa may occur

first crack in this field (with minimal compliance) oxide, and then damage on its surface. Repeating this process is the cause of the so-called high temperature oxidation and the intensive loss of metal, locally subcritical stable spread of the defect.

In another way, the different mechanical properties of the steel (e.g. in the weld transition area) can be manifested when the steel is affected by atomic hydrogen. In parts of the transition region where is the structure ferritic-pearlitic, quenched structure and their decay products can occur, these areas can be locally fragmented by atomic hydrogen. Small amounts of hydrogen can enter into the material through reductive water decomposition (relatively low intensity) and high temperature oxidation. The embrittlement intensity is proportional to the hardness / hardness of the quenched area and the HV limit is HV 350 where the areas are cracked with hydrogen in a neutral water environment (10 -100 x higher salinity than boiler water) or already in a humid atmosphere (RH > 80 %) in the case of extremely hardened areas - HV 500. Quenched areas are cracked at a lower hydrogen concentration, compared to areas with lower hardness. The influence of hydrogen may also be reflected in interaction with specific segregates, most significantly segregated with sulfur, even in the highly alloyed zone of the weld metal.

The galvanic effect in the joint resulting from the different corrosion resistance of the welded steels is only applicable to carbon steel activation, its more intense corrosion, near the fusion boundary, or the initiation of a defect of atypical effect due to segregation in weld metal. However, the presence of an oxidizing agent (typically O<sub>2</sub> at temperatures up to 130 °C) or multiple cycles of so-called high temperature oxidation (at temperatures above 160 °C - but without the influence of galvanic contact) is necessary for the subcritical propagation of a stable carbon steel defect.

## 6. CONCLUSION

In nuclear power plants constructions (especially in the secondary circuit environment) may cause problems steels with Chromium reduced area, often resulting in reduced resistance to intergranular corrosion. However, chromium reducing is not a direct cause of a failure (under standard operating conditions) of a stable growth of subcritical defect, and other possible material or environmental heterogeneity needs to be responsible for this responsibility.

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