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**Forschungszentrum Karlsruhe**  
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**Wissenschaftliche Berichte**  
FZKA 6973

**Available Metallurgical  
and Process Parameters/  
Treatments for Reduction  
of General Corrosion/  
Stress Corrosion Cracking for  
In- and Ex-vessel Application**

**J. Konys, S. Leistikow, K. Ehrlich**  
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## Zusammenfassung

### **Metallkundliche und prozessspezifische Maßnahmen bzw. Vorbehandlungen zur Reduzierung der allgemeinen sowie der Spannungsrisskorrosion von in-vessel und ex-vessel Anwendungen**

Maßnahmen, die der Verminderung der Korrosion unter HPLWR-spezifischen Bedingungen dienen sollen, müssen dabei das gesamte Kühlsystem des Reaktors berücksichtigen. Das bedeutet für die eingesetzten Werkstoffe, dass am Beispiel von Hüllrohren vor allem der Zustand ihrer Oberflächen, die im Kontakt z. B. mit dem wässrigen Kühlmedium auf der Außenseite bzw. mit dem Brennstoff und den Spaltprodukten auf der Innenseite stehen, eine besondere Beachtung erfahren müssen.

Beispiele für mögliche präventive Methoden zur Korrosionsverminderung werden vorgestellt. Dabei wird besonderer Wert auf Maßnahmen wie z. B. die Kaltumformung von Oberflächen gelegt, da hiermit der natürliche Oxidationsschutz von Stählen durch dünne Chromoxid-schichten wesentlich verbessert werden kann.

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## Abstract

Measures to avoid corrosion under HPLWR service conditions have to take into account the whole cooling system. In principal, it consists of the material and its surfaces exposed to the aqueous medium, especially of the fuel cladding material, internally in contact with fuel and its fission products, externally exposed to the water as heat transfer medium.

Examples of preventive corrosion protection methods are listed. Preference of applications is given to methods, creating metal surface grain refinement, which increases the number of surface piercing grain boundaries. They act as free diffusion paths for protective  $\text{Cr}_2\text{O}_3$  thin layer formation.

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**TABLE OF CONTENTS:**

Page

Abbreviations

Zusammenfassung

Abstract

1.	Introduction	1
2.	Principles	1
3.	Mechanical surface treatment to minimize corrosion	3
4.	Surface modification using the Pulsed Electron Beam Facility (GESA)	5
5.	Conclusions	5
6.	References	6

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## **Abbreviations**

CVD	Chemical Vapor Deposition
GESA	Gepulste Elektronenstrahlanlage (Pulsed Electron Beam Facility)
HAZ	Heat Affected Zone
HT	High Temperature
HCF	High Cycle Fatigue
HPLWR	High Performance Light Water Reactor
LCF	Low Cycle Fatigue
PVD	Physical Vapor Deposition



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## 1. Introduction

It is the intention to show that metallurgy, production, and construction of in- and ex-vessel parts and components and their service as fuel element cladding, supporting in-reactor structure, pressure vessel, heat exchange components and piping have to be optimized under supercritical water corrosion conditions. These aspects are only partially known as pointed out in HPLWR-D8 [1]. The principal requirements are therefore reviewed in the following report. Some new aspects of metal surface cleaning and deformation to promote super-protective layers growth are reported. Claim is not laid to substantial completeness and an unapproved application of the proposed methods.

## 2. Principles

Measures to avoid corrosion can be taken within the whole system, consisting of material, interface, medium and service conditions - as items of heat generating and transporting systems and according to their service in the large engineering scale. There is a need to analyze each system component behavior separately.

- a) Material choice is strongly influenced by corrosion considerations, like resistance against general corrosion and local corrosion. The first type of corrosion can be described by various laws of uniform surface metal loss, transformed to oxide, which can be totally adherent or partially lost to the system. The second type is of electrochemical character and has the formation of anodic sites (for dissolution) and cathodic sites (for reduction) in a medium of adequate conductivity as driving mechanism to local corrosion. Appropriate corrosion resistivity results from
- alloy composition and homogeneity
  - matrix structure
  - component construction and production
  - welding
  - heat treatment

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- b) Inter-(Sur-)faces are improved to guarantee a passive surface character by cleaning, removal of roughness, and preformed layers. Protective layers can be deposited by means of physical and chemical methods.
- c) Medium considerations have to include the given physical properties of the coolant. Frequently chemical conditioning concerning suitable chemical properties is needed, i.e.
- filtering from corrosion products, cleaning by ion-exchange, degasification, oxygen removal by hydrazine addition, etc.
  - pH-adjustment by additives for neutralization, alkalization
  - boron-addition for shim control and/or hydrogen addition for suppression of water radiolysis
- d) Service conditions have strong influence on material corrosion in an aqueous system
- coolant temperature and pressure
  - flow velocity
  - phase transformation (liquid/steam, sub- to supercritical)
  - transport phenomena
- In case of materials, especially those under heat transfer,
- surface temperature and temperature distribution
  - temperature gradients within the components and coolant thermal load leading to stress/creep deformation, especially under transient or cycling conditions
- In case of materials application in nuclear technology, additionally the influence of neutron and fission product irradiation on fuel elements, construction materials, pressure vessel, heat exchangers, piping, and the coolant itself has to be considered.

General recommendations to avoid water/steam corrosion must be defined specifically for the materials under consideration according to their composition related corrosion resistance and passivity in a low aggressive medium which proved to be harmless. Mainly protecting oxide layers are produced on the Cr-alloyed steels, austenitic steels and nickel base alloys, designed for application in superheated steam. Preferably adherent oxide layers are formed

this way which avoid spalling and mass transport to lower system temperature/pressure regions, narrow coolant channels or into valves, where they could cause plugging by deposition or limitation of heat flow. If radioactive corrosion products are transported from the core into the system they act as sources of irradiation and thus cause non-accessibility of components for repair work. Further measures to limit or even prevent corrosion are listed in Table 1.

**Table 1: Measures to minimize corrosion**

<b>Actions</b>	<b>Measures</b>
Alloying	Increase of Cr, Mo and Ni content, stabilizing with Ti, Ta, Nb, reducing of C, S, P, minor additions of Ce, Y
Melting	Homogeneity → electroslag remelting process
Heat treatment	Tempering, solution annealing, normalization, quenching, anneal for recovery, recrystallization, residual stress relief, HT grain size refining treatment
Surface treatment	Etching, pickling, passivation, preoxidation, protective layer deposition (galvanic, CVD, PVD), plating, GESA
Construction	No crevices, smooth surface, welding followed by solution annealing to avoid sensitized heat affected zone (HAZ)
Operation conditions	No stagnant or very fast coolant flow, no concentration gradients in the medium, no cycling of T, p (LCF, HCF), no deposits under which uncontrolled chemistry can develop
Coolant purity	No aggressive components and salts, low O <sub>2</sub> , high pH, additives, few corrosion products

As mentioned above measures as alloying, remelting heat treatments, protective layer deposition, coolant purification and corrosion minimizing operation conditions are recommended.

By superficial cold deformation [2-4], a highly defective metal surface structure is being created so that in case of dry HT-oxidation along innumerable "easy diffusion paths" chromium diffusion and protective, Cr-rich oxide layer formation takes place at the interface to the oxidizing medium and acts this way for 24,000 h [5]. By dissolution or evaporization (oxide loss-to-the-system), because of chemical reaction in oxygen containing water/steam, as well as in wet air, the soluble ionic product CrO<sub>4</sub><sup>2-</sup> or the volatile CrO<sub>3</sub>-aq. are formed [6]. The same mechanism is effective when by application of a high temperature treatment, prior to the

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normal cold work and solution treatment , a fine grained steel is produced and oxidized in steam [4, 7].

### **3. Mechanical surface treatment to minimize corrosion**

#### Benefits for ferritic/martensitic and austenitic steels

- High number of grain boundaries in near-surface layer (3-10  $\mu\text{m}$ ) leads to an increase of selective Cr outside diffusion  $\Rightarrow$  preferential formation of thin  $\text{Cr}_2\text{O}_3$  or  $\text{MnCr}_2\text{O}_4$  surface layers, instead of  $\text{Fe}_3\text{O}_4$  scales
- Hence, protection against further oxidation is strongly improved

#### Risks of mechanical treatment for both kinds of steels

- $\text{Cr}_2\text{O}_3$ -loss due to volatile  $\text{CrO}_3$  formation in oxygen containing steam  $\Rightarrow$  distinct surface degradation  
At higher temperatures, recovery, recrystallization and grain growth due to fine grain structure transformation, can take place
- Alkaline additives can attack  $\text{Cr}_2\text{O}_3$  layers and destroy protectiveness.

The mentioned Cr(VI)-oxides and  $\text{Fe}_2\text{O}_3$  (hematite) turned out to be the thermodynamically stable oxide phases in the transition region from sub- to supercritical conditions of temperature and pressure in an aqueous environment [8]. Under hydrogen addition a lower oxidation potential would favor  $\text{Cr}_2\text{O}_3$  stability.

By chromium oxide loss-to-the-system (surface chromium depletion), surface depassivation takes place in a supercritical water system so that the electrochemically measured current densities of pure iron and CrNi stainless steel becomes of comparable extent [9].

So the authors claim to have proven that at critical temperatures and pressures thermodynamic considerations on water system and corrosion product stability on unalloyed and Cr-alloyed steels are in agreement with kinetic results, measured by electrochemistry (exchange and corrosion current density).

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However, it must be mentioned that approximations on long-term have to take into account that in principle high temperature corrosion in steam leads to an overgrowth of chromium-rich inner oxide phases by iron-rich outer oxides. Corrosion resistivity is assured by Fe/Ni-Cr-spinel inner scale formation. That explains why under critical and supercritical conditions on long-term very similar corrosion results are observed, which depend clearly on alloy composition and degree of cold work as well.

All these methods have been tested successfully at laboratory scale for the group of austenitic stainless steels and have partially been applied on an engineering level, too. For instance, a routine procedure exists for reducing tensile stresses in needle-shaped steam generator tubing made of Incoloy 800.

#### **4. Surface modification using the Pulsed Electron Beam Facility (GESA)**

A surface modification of steels to increase their corrosion resistance against strong oxidation (in water or other oxidizing media) can be carried with the so-called GESA facility (gepulste Elektronenstrahlanlage) at FZK. A detailed description of this process is given in [10]. GESA is a pulsed electron beam facility that consists of a high voltage generator with a pulse duration control unit, a multipoint explosive emission cathode, a controlling grid and an anode, which form a triode system. The electron kinetic energy can be varied in the range of 50 to 150 keV with an energy density up to 50 J/cm<sup>2</sup> at the target. This is sufficient to melt metallic materials adiabatically up to a depth of 10 to 50 μm. The beam diameter is 6 to 10 cm and this is the area of surface melting by applying one single pulse. Due to the high cooling rate on the order of 10<sup>7</sup> K/s, very fine grained or even amorphous structures develop during solidification of the molten surface layer.

Another possibility to modify the materials surface in order to increase the corrosion resistance is the alloying of Al into a surface layer of about 15 μm thick. For this purpose, a thin Al-foil is placed on a steel surface. It melts and mixes with the molten material surface layer (typically steels). A great part of the Al evaporates during this process, but the remainder, about 25 atom %, is alloyed into the surface. Therefore, in strongly oxidizing media, the formation of Al<sub>2</sub>O<sub>3</sub> as an outer oxide layer will be promoted.

Surface modification using the GESA facility is a very promising technique to treat small but thermally highly loaded surfaces like heat exchanger tubes or claddings.

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Due to this surface treatment, either restructuring or Al-alloying, the oxide layer formation on steels is enhanced and therefore, the corrosion resistance can be increased significantly.

## 5. Conclusions

It can be stated that for austenitic stainless steels proposed as reference material for cladding and in-core structures the described mechanical surface treatments can be applied to minimize general and localized corrosion. This treatment allow to establish systems of residual compressive stresses in a superficial layer of metallic parts or components. It reduces by "surface hardening" the tensile load by superposition, even under alternating stress conditions. By surface treatment a fine grain structure can be generated, the corrosion reaction activated. Refining the grain size is another metallurgical treatment to get the same effect.

For 12 % Cr-containing ferritic-martensitic steels, which are presently used in conventional power plants and for austenitic CrNi stainless steels  $\geq 16$  % Cr content, cold work is very successful in promoting the formation of a stable chromium, manganese, and silicon rich protective oxide layer upon subsequent exposure to steam. During further oxidation these layers can develop into spinels of various compositions. Chromium and manganese depletion profiles equally exist beneath the oxide layers. Nickel-chromium alloys do not respond reproducibly in the same way when oxidized after cold deformation.

All other statements on material corrosion and potential anti-measures are principal in nature and must be tested further on under the special aspects of supercritical coolant conditions and nuclear systems service.

In respect to a possible increase of stress corrosion sensivity by superficial tensile stress creating mechanical pretreatments, only compressive stress generating methods, like ball peening etc., should be applied. The superposition of residual compressive stress systems with a tensile load can reduce the maximum effective tensile stress component.

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