# STUDY OF COLD WORKED 304 STEEL FOR SUPERCRITICAL WATER COOLED REACTOR APPLICATIONS

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## 1. Abstract

The design of the Supercritical water cooled reactor requires development and qualification of innovative structural materials. Such materials with high level of advancement are required for the primary components in order to assure safety and service reliability during entire lifetime of the nuclear power plant. Presented research work is focused to the evaluation of modified cold-worked AISI-304 stainless steel. This alloy was cold-worked (20 to 45%) in order to optimise corrosion resistance. The set of samples were analysed by different spectroscopic techniques within the aim to study the microstructural characteristics. In particular, X-ray diffraction and positron annihilation spectroscopy scattering were applied for phase transformation characterization and microstructural behavior. Furthermore, outcomes of corrosion properties of cold-worked AISI-304 stainless steel exposed for 100 and 500 hours in super-critical water reactor conditions (600°C, 25 MPa, controlled $O_2$) are correlated with the obtained results.

## 2. Introduction

The Fukushima Daiichi nuclear power plant accident highlighted the importance of structural integrity of reactor systems. However, newly designed reactors concepts which are being developed in the framework of Generation IV international forum (GIF) offers much better safety characteristics compares to present fleet reactors. The design life-time integrity is critical area for the safety and operational performance point of view and long-term sustainable nuclear energy applications. Considering above-mentioned needs, the Supercritical Water Cooled Reactor (SCWR) design offers excellent characteristics (thermal efficiency up to 45%) with integrated passive safety systems. Besides clear benefits od SCWR concept in terms of important safety enhancements, this design requires extensive development and testing of advanced structural materials which are needed for the primary components. They must withstand operational conditions (mechanical load combined with harsh environment, specifically high radiation level combined with corrosion) as well as designed transient and accident conditions. In principle, there are two key degradation mechanisms which have to be carefully considered in the design of SCWR primary components [1,2]. The presented research work has been carried out in the framework of on-goingEuropean R&D initiatives and it is focused on investigation of candidate materials performance and long-term behaviour in the SCWR environment. Detailed analysis is aimed on microstructural characterisation and study of corrosion dynamics (temperature 600°C and pressure of 25MPa) as well as transient effects. From this point of view, reported research results are important for data validation of tested materials in the framework of SCWR structural materials roadmap.

## 3. Experiments

### *3.1 Materials*

High alloyed steel AISI-304was chosen for investigation and its chemical composition is shown in Table 1.Plasticdeformation due to loading beyond a limiting value, resulting in lattice defects including dislocations, hardening effect has been significantly confirmed for cold-worked AISI-304. This steel has been cold-worked (CW) at different levels of deformations (20, 30, 40 and 45%) in order to increase hardness and yield strength (pre-straining process), corrosion performance and microstructural behaviour. Thereafter, the set of samples were fabricated from each batch of cold-worked AISI-304 by electro-erosion cutting and the surface was polished at level 1 μm. Every sample set was exposed in SCWR environment in order to assess the performance and corrosion phase analysis.

Tab. 1.*The chemical composition of AISI-304 steel.*

| Element | Composition (in mass%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Cr | Ni | Si | Mn | C | Cu | S | P |
| AISI 304 | 19 | 10 | ≤1.0 | ≤2.0 | ≤0.04 | ≤1.0 | ≤0.03 | ≤0.04 |

### *3.2 Methods*

The samples with different level of CW were investigated by analytical methods in order to study microstructural response to plastic deformation. The methods applied for characterisations are described below.X-ray diffraction is method based on analysis of specific diffraction patterns, which constitute evidence for the periodically repeating arrangemen tof atoms in the lattice. The XRD analysis was performed by Phillips instrument (PW3830) with X-ray generator operated at40 kV and 50 mA by using Cu Kα radiation. The Xpert Graphics and identify program was used for analysis of particular phases using JCPDF database. Positron annihilation spectroscopy (PAS) is technique which is very sensitive to open volume defects, especially to vacancies and their clusters. Two different PAS methods were applied in our study, specifically (1) Positron Lifetime Spectroscopy (PALS) and (2) Coincidence Doppler Broadening Spectroscopy (CDBS). For both techniques we used the positron source (1 MBq of $^{22}$Na with kapton encapsulation) in the sandwich geometry (two identical samples were polished at 1 μm level). The PALS spectrometer is based on DRS4 evaluation board (PSI) in combination with BaF2 scintillation detectors coupled with XP2020Q photomultipliers. The evaluation board is controlled by QtPALS software [3]. Time resolution of the PALS setup is around 180 ps (FWHM). The post-processing of lifetime spectra was done by LT10 according to mean life time and two-component analysis. The second PAS techniques was Coincidence Doppler broadening spectroscopy (CDBS) with a digital data read-out system based on PCI 9820 Adlink data acquisition card and signal shaping tasks are performed digitally by QtCDB2 software. Signals from HPGe detectors (two identical Coaxial GC2019 20% rel. efficiency detectors, resolution 1.9keV at 1.33MeV, Peak/Compton 48:1) are sampled at preamplifier outputs and following pulse shaping is done by trapezoidal filter [4].

Corrosion tests have been performed in the SCWR autoclave connected to high- and low-pressure circulation loop. All specimens were loaded into the autoclave and continuously exposed in the conditions of supercritical water environment with the respect of following water chemistry parameters: temperature600°C, pressure 25 MPa, inlet/outlet conductivity 0.1 μS $cm^{-1}$/0.15–1.2 μS cm-1, inlet/outlet dissolved $O_2$<10 ppb/<10 ppb. Parameters, as pH, conductivity and dissolved oxygen were measured continually in low-pressure part of the loop in the outlet from the autoclave. Two different time expositions (100 and500 h) were chosen for experiments. The corrosion layers have been analyzed by the measurement of weight increase, XRD and SEM analysis.

## 4. Results

The microstructural parameters of cold-worked AISI-304 steel were analysed by XRD and PAS measurements. This type of austenitic stainless steel can contain some volume fraction of "strain induced" martensite and this can make the steel partially "ferro-magnetic". The data confirmed that significant phase transformation after CW deformation. The results shown that unstable non-magnetic austenitic phase (γ) was transformed to a magnetic phase martensite (α') after plastic deformation. Furthermore, CW deformation also caused the incubation of a new α'-phase with (bcc) in the structure. The sequence of transformation (γ→ε→α) was only proposed for metastable steels deformed by uniaxial tension and rolling. Presence of martensite in stainless steel increases the work hardening capability and thus reduces the formability of stainless steel. It could also increase the tendency to hydrogen embrittlement and stress corrosion cracking. The analysis of experimental data confirmed the presence of $\varepsilon_{101}$ phase with hexagonal-close-packed (hcp) structure. In addition, the shown the evolution of martensite phase with the level of cold-worked AISI-304 followed by further incubation of $\varepsilon_{100}$ phase to its maximum at level 45% CW. It is expected that such transformations can have direct influence on the corrosion resistance. The qualification and quantification of point defects, their clustering and transformation was specifically investigated by PLAS and CDBS methods. Lifetime spectrum was analyzed by two-component approach. The outcomes of analysis for all samples are summarized in Fig. 1, which shows the lifetime components $\tau_1$ and $\tau_2$, including component's intensities $I_1$and $I_2$. Lifetime parameters reflect change of dislocation density and incubation of vacancy-type defects. The parameter $\tau_1$has significant increase trend-line with higher level of cold-work deformation (142ps / 20% CW, 158 ps/ 45% CW). This change indicates partial modification of bulk features. Most likely, it is due to phase transformation of γ-austenite to ε and α' phases. The parameter $\tau_2$ gives qualitative information regarding point defects and their size. The presence of the tri- and quadri-vacancies($v_3$ and $v_4$)have been confirmed at 20% CW, however this is changing with increase of cold-work level and rather large vacancy clusters have been observed at 45% CW and their size is in the range of $v_{10}$ and $v_{14}$. Another very important observation is decrease of$I_2$parameter which corresponds to vacancy-type defects concentration. The change is about 50% (relative value) for investigated cold-worked deformation range (20 % → 45 % CW).

Further details about electronic structure were extracted from CDBS data.The plot (figure 2) shows the momentum distribution of electron-positron pair with reference defect free system (pure Fe). The S-parameter corresponds to the shell-electrons and it describes the positron annihilation at defects, while W-parameter is sensitive to the chemical surrounding of the annihilation site. The CDBS results also confirmed significant clustering of smaller vacancy-defects which is fully in compliance with PALS data.

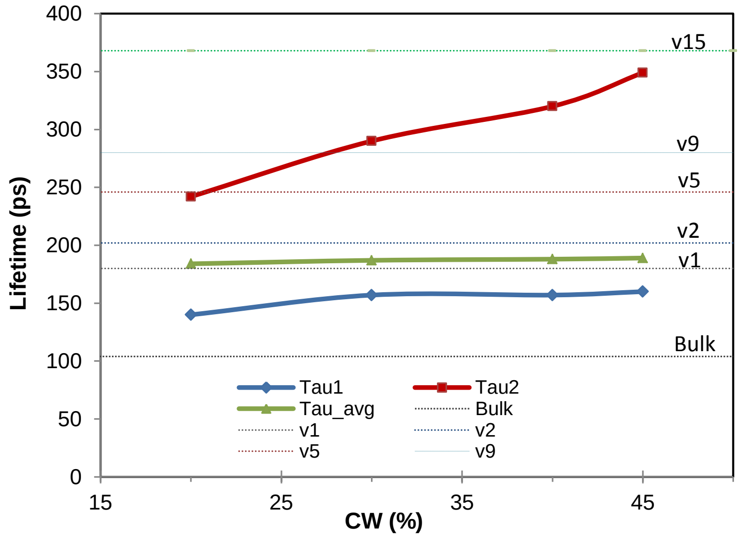


Fig.1: *Two-component positron lifetime analysis of AISI-304 with 20, 30, 40 and 45% cold-worked deformation.*

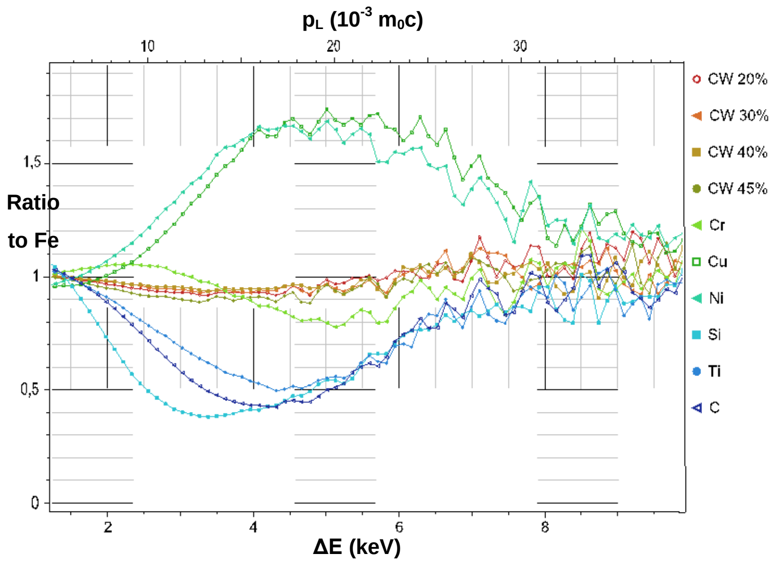


Fig.2: *Doppler broadening spectra for AISI-304 with 20, 30, 40 and 45 % cold-worked and its alloying elements (pure Fe reference, S = ±(0–3.2).$10^{-3}$ $m_0c$, W = ±(9,8-25). $10^{-3}$ $m_0c$).*

The results of experimental tests in the SCWR environment have shown clear impact of CW deformation on AISI-304 corrosion resistance. It is most significant for longer exposure time (500 h) and elevated $O_2$content (200 ppb). The analysis of weight gain parameter ($W_g$) shows that best corrosion resistance is for 45% CW AISI-304 samples, specifically for 500 h of exposure time was difference of $W_g$ parameter for 0 ppb and 200 ppb about 0.87 g/kg in case of 20% CW, while for 45% CW was only 0.38 g/kg. However for highest cold-worked deformation (45% CW), $Cr_2O_3$ has been detected in the corrosion layer, which is caused by higher precipitation kinetics of chromium from near-surface region to the corrosion layer (figure 3).

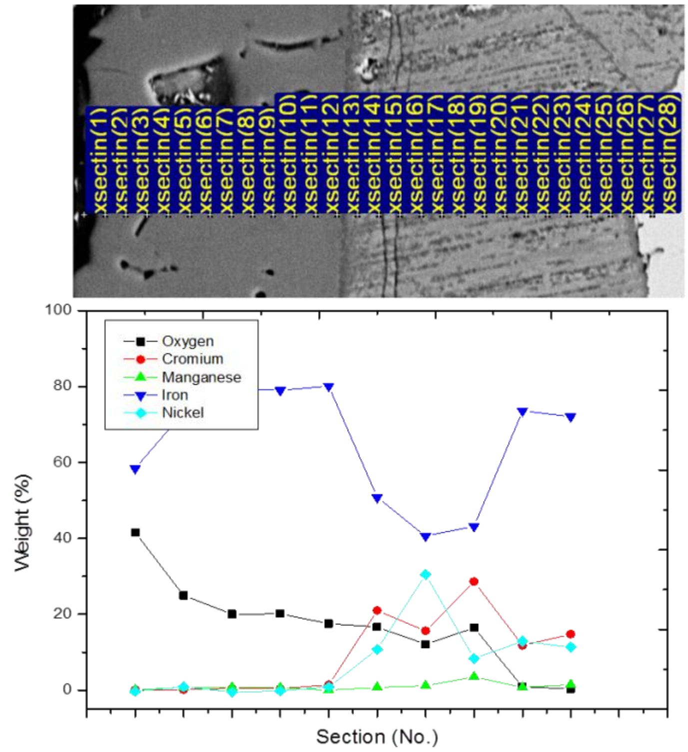


Fig.3:*Corrosion layer profile of AIS-304 40% CW exposed to SCWR environment (500 h).*

## 5. Discussion

In general, structural materials can undergo plastic deformationdue to loading beyond a limiting value, resulting in lattice defects including voids and dislocations. These imperfections can interact with the crystal lattice, producing a higher state of internal stress,also known as residual stress that can induce reduced ductility. The development of internal stresses is often influenced by permanent strain resulting from thermo-mechanical operations associated with plastic deformation. The analysis of PALS and CDBS parameters of the cold-worked iron-based alloys are typically longer than that in the un-worked state. The shorter lifetime is associated with positron trapping at deformation-induced defects such as dislocations, vacancy-impurity complexes, other than the vacancy clusters. It is important to underline that the lifetimes are notably longer for this complex system in comparison with other metals, like Ni and Cu. Moreover, fast deformed (fcc) structures, a phenomenon called stacking fault tetrahedral (SFT) can occur due to nucleation of defect clusters from the migration and coalescence of self-interstitial atoms and vacancies.It is noteworthy that, for the (bcc) iron deformed by using the above three different deformation methods, we observe rather vacancy clusters induced by deformation, while such large vacancy clusters either are completely absent or appear only after some kinds of deformation in the (fcc) metals. The formation of SFT leads to a high density of thermally stable clusters and such clusters prevent the build-up of the vacancy super-saturation state necessary for an efficient nucleation of large vacancy clusters in the (fcc) metals. This is why no large vacancy clusters have been observed in case of investigated AISI-304 cold-worked samples. Reported PAS data gives strong indication that SFTs are created. However direct separation of SFT contribution to the lifetime spectra is rather challenging. As of today, only calculations of positron lifetimes for simple (fcc) metals have been done [5,6], but it is hoped that in near future, simulation of complex systems (alloys) will be carried out in order to support on-going experimental work. In addition there is strong indication that SFTs play important role in the phase-transformation process, since they can act as an incubation sites for ε-phase which was confirmed by XRD measurements. The results of corrosion tests have shown that cold-working deformation has significant effect on long-term behaviour of AISI-304 in the SCWR environment. Better corrosion resistance of AISI-304 with higher cold work deformation level can be assigned to the effect of chromium precipitation from bulk to corrosion layer caused by phase transformation($\gamma \rightarrow \alpha$). This effect is even more significant for high oxygen content (200 ppb). However further study of long-term behaviour will be needed in the future (> 1000 h) in order to assess the chromium precipitation effect.

## 6. Conclusions

The SCWR design is considered as the natural evolution of the water-cooled reactor technology. The qualification of suitable structural materials (e.g. fuel cladding, internals and reactor core components) remains the serious R&D challenge. Currently, the biggest gap remains the behavior of the candidate alloys under irradiation. The effects of the irradiation on material properties will vary significantly across the core. Little work has been done to understand the coupling of the microstructural changes induced by irradiation with thermal aging effects under SCWR conditions. Therefore, screening and testing of candidate materials for primary components have been identified as one of the major hurdles to implementation of this technology. The analysis of experimental results from XRD and PAS testing confirmed the phase transformation of austenite (fcc) to martensite (bcc) due to cold-worked deformation. Furthermore, incubation of ε-phase (hcp) has also been registered at the level of 20% CW. The maximum was detected at 30% CW level. Experimental results bring some insights to microstructural features and possible effects on corrosion resistance of AISI-304. Nucleation of stacking fault and also small fraction of ε-phase with hexagonal-close-packed (hcp) structure has been identified. There is also an indication for the increase of dislocation density and Cr/Cu-precipitation. Taking into account of all complex experimental results, it can be concluded that CW deformation has positive influence to general corrosion and localized corrosion processes resistance. However, further studies focused on SCC phenomenon in SCWR environment are needed to investigate the behavior of AISI-304 for longer exposure time (> 1000h).

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