

HOT CORROSION STUDY OF STAINLESS STEELS FOR NUCLEAR REACTORS

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1. Introduction

Research and development of advanced nuclear reactors in Generation IV (GEN IV) are limited by the selection of proper construction materials. Suitable candidate materials are still under extensive investigation as their properties must be excellent to achieve a high level of reactor system safety. New austenitic steels and oxide dispersion strengthened (ODS) steels are appropriate materials for construction of pipelines, heat exchangers or reactor internal parts in GEN IV. These alloys have improved properties in compare to recently used AISI steels, but they have not yet been tested in real thermal and radiation conditions. Therefore, this study is focused on the investigation of their stability at high temperatures with emphasis on microstructural analyses, especially presence of vacancy defects.

2. Experiment

In this paper, four different steels are investigated: austenitic steel NF 709 manufactured by NIPPON Steel in Japan [1], austenitic oxide dispersion strengthened steel ODS 316 formed at University Beijing (China) by strengthening of AISI 316 [2] and two ferritic ODS steels as commercial products of USA company INCO (MA 957 and tempered MA 956) [3]. The chemical composition of the studied steels is listed in Tab. 1. These kinds of materials demonstrate better mechanical, corrosion and thermal properties than AISI steels (reference materials) recently used in nuclear power plants [1-4]. The measured samples were prepared by common procedure used for positron annihilation spectroscopy [5].

Tab. 1. *Chemical composition of austenitic steels (in % wt.).*

Steels	C	Mn	Ni	Mo	Cr	Ti	Si	Nb	N	Al	Y2O3
NF 709	0.03	0.92	25.34	1.40	22.22	0.05	0.38	0.24	0.17		
ODS 316	0.08	2.00	10.00	2.00	16.00	0.50	0.75		0.10		0.35
MA 957	0.03	0.09	0.13	0.03	13.70	1.00	0.04			0.03	0.30
MA 956	0.07	0.12	0.07	0.10	19.97	0.30	0.04	0.01	0.04	1.30	0.50
AISI 316	-	ref.	0.08	2.00	10.00		2.00	16.00		0.75	0.10
AISI 316L	-	ref.	0.03	2.00	10.00		2.00	16.00		0.75	0.10

The investigated steels were loaded by a thermal treatment typical for the primary circuit of gas cooled GEN IV reactors, which was simulated in autoclave at 1000°C in inert argon atmosphere (99.996 %) for 24 hours. The thermal experiment was performed in autoclave owned by Slovak Academy of Science. The pressure during the annealing was 8 MPa, which should have simulated the pressure in nuclear reactor of GEN IV.

The samples were investigated by positron annihilation lifetime spectroscopy (PALS) sensitive to small vacancy defects and to their changes in size or concentration due to thermal strain. The PALS measurements were done in a fast-fast mode [6] with the FWHM parameter close to 190 ps. The variance of fit (reduced chi-square) achieved value in range of <1; 1.2>. The PALS can determine defect size and defect concentration in the investigated samples up to a depth of 120 µm.

The annealed samples changed the colour of surface from glossy metallic into black/grey mat, which indicated a growth of a new layer. A scanning electron microscope JEOL JSM 7600F with an energy wave dispersive spectrometer (EDX) was used for observation of this layer in a cross-section view. For this purpose, the cross-section samples were prepared by polishing with Ar ions using the cross-section polisher device (JEOL SM-9010).

3. Results and Discussion

The high temperature annealing of samples took a long time (24 hours), therefore we assumed that the structure can transform or thermal vacancies can appear during the treatment. Although the annealing was performed in very pure argon gas with negligible concentration of impurities, an influence of environment was observed. This was demonstrated by the growth of new surface layers tested later by SEM.

The investigated steels were firstly observed by positrons in as-received state (after the process of production) and then after the annealing for the simulation of the thermal strain. The PALS spectra were evaluated by software LifeTime9 (LT9), where the positron data were decomposed into 2 components - lifetimes (LT) and their intensities (I). The shortest lifetime (LT_1) represents positrons annihilated mostly in the defect-free bulk (theoretical value in iron 110 ps) or positrons affected by small defects. The second positron lifetime (LT_2) characterizes the vacancy type defects and is dependent on the size of three dimensional vacancy clusters V_n consisting of n vacancies. Intensities (I_1, I_2) belonging to the individual lifetimes characterize percentage of positrons annihilated with that lifetime.

In Fig. 1, LT_1 of reference AISI samples goes around the value of pure iron. Austenitic steel NF 709 and tempered ODS steel MA 956 have reduced LT_1 below bulk value. The ODS 316 and MA 957 demonstrated an existence of dislocations and mono-vacancies [7], which have probably been annealed out in MA 956 during the process of tempering. LT_1 stayed mostly constant for steels after the annealing; only AISI 316L and NF 709 showed its small increase. The growth of LT_1 for AISI 316L was into the area for bulk and dislocations, which indicated also accumulation of small defects due to the thermal strain.

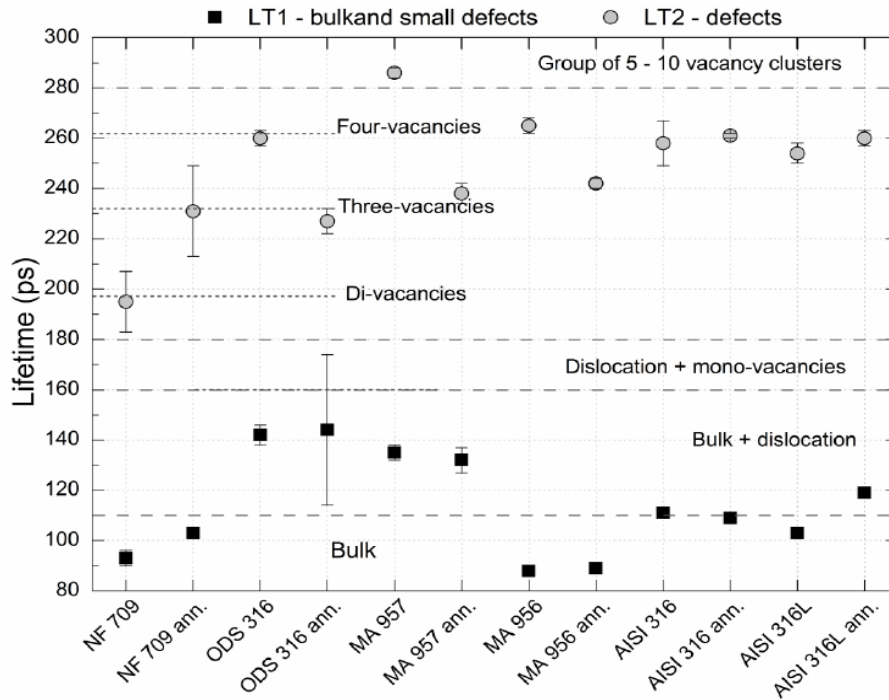


Fig. 1: Positron lifetimes: LT1 for defect-free bulk and small defects, LT2 for bigger vacancy defects.

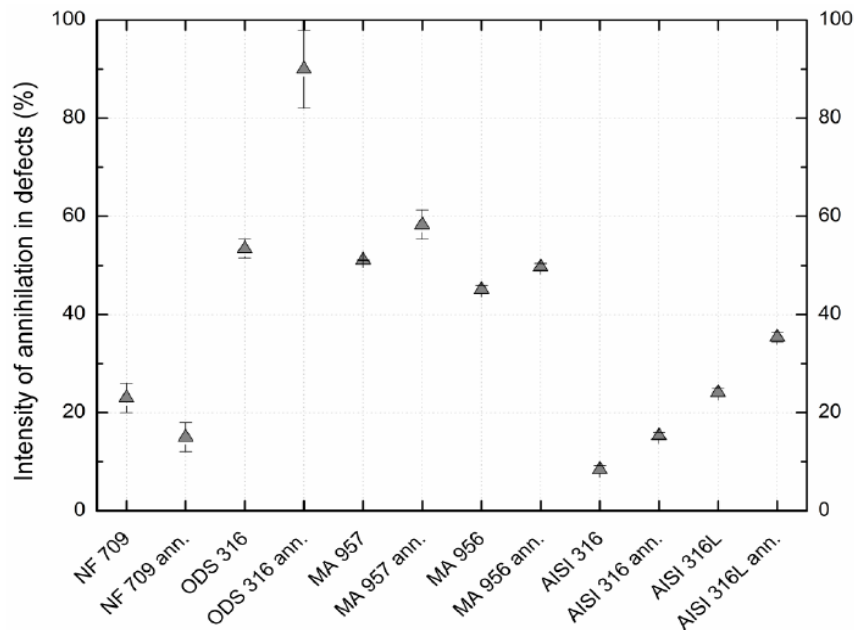


Fig. 2: Intensity of positrons annihilated in defects proportional to defect concentration.

LT₂ of all investigated samples is proportional to defect size. As is visible from Fig. 1, the size of defects is mostly between three and four vacancies. Only NF 709 in as-received state contains di-vacancies and MA 957 five vacancy clusters. After the annealing, the defect size of reference samples stayed constant, four-vacancies in predominance, although their concentration significantly increased (See Fig. 2). The defects of NF 709 grew probably from di-vacancies to three-vacancies, but their concentration slightly decreased in consideration of I₂ error bars. This could indicate that smaller defects were merged into bigger ones during the

annealing or new defects could have been joined to the existed ones. The defect size for all ODS steels – ODS 316, MA 956 and MA 957 even decreased from four-vacancies to three vacancies; resp. from five-vacancies to four-vacancies for MA 957. However, the concentration of these defects increased which indicates formation of new small defects or slight decomposition of bigger defects into smaller ones.

From the results, we can see an existence of different types of behaviour, which can be typical for the individual group of steels – the ODS steels and classic austenitic AISI steels. Only the steel NF 709 differs, although it is austenitic steel. Its different behaviour is probably due to much higher content of chromium and mostly nickel can slightly shift it into nickel chromium-iron alloys. The process of quenching could affect the thermal response of this steel, too.

SEM results (shown in Fig. 3) detected oxide layers on the surface of the annealed samples, although minimal oxygen content ($< 4 \times 10^{-3} \%$) was present in the autoclave during the experiment. This implies that a process of hot oxidation happened during the thermal treatment. The EDX chemical analyses proved a presence of chromium oxide layer with different thickness for all individual steels. In some samples (ODS 316 and both AISI steels), an additional layer of iron oxide was created on the chromium oxide surface. The MA 956 sample was covered with homogeneous layer of aluminium oxide, on which very thin layer of chromium oxide was detected. It was caused probably by higher content of Al as well as it could be previously existed as passive layer there.

The most rapid degradation of surface was found for the steel ODS 316. In case of this sample, the created iron oxide layer started to come off from the rest of the sample; therefore we can note that the manufacturing of this ODS steel was probably not optimal. By the comparison of the ferritic ODS steels, MA 957 has better disposition to growth the oxidation layer than MA 956 due to smaller content of chromium. MA 956 and NF 709 have the highest chromium content, therefore they resist to oxidation better than other studied materials.

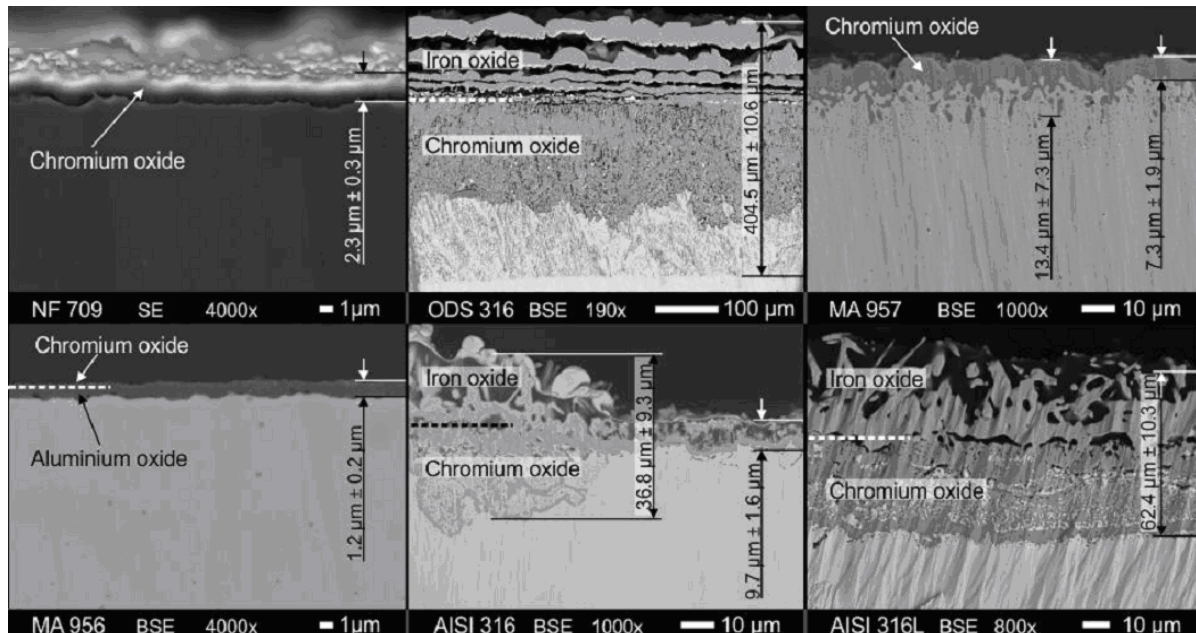


Fig. 3: SEM images of investigated steels after annealing at 1000°C during 24 h in Ar atmosphere (cross-section view).

4. Conclusion

In this paper, thermal stability at high temperatures for four Gen IV materials were studied and compared to classic AISI steels in term of vacancy defects. Although it was assumed that all these advanced steels should have had better thermal properties, ODS 316 strengthened by yttria/ titanium particles demonstrated worse thermal resistance than its non-ODS version - AISI 316. Also oxide layer and post thermal brittleness of ODS 316 were the most significant from all investigated steels (reference steels included). On the contrary, ferritic ODS steels indicated very good thermal stability; even they demonstrated annealing out of some vacancy defects due to the thermal strain. Therefore, their structure was probably additionally regenerated after the process of manufacture, which was mostly seen for MA 957 without the previous tempering. The oxide layer was also sufficiently small and it is probably dependent on chromium content for these ferritic ODS steels. The chromium content also plays important role in the new austenitic steel NF 709 (together with high nickel content), which assigns very good oxidation and thermal resistance at temperature of 1000 °C, too.

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