



Compatibility of steel No. 1.4970 with liquid sodium at high temperatures

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Abstract

The sodium corrosion and the influence of liquid sodium at 873 and 973 K on the creep strength of cladding tubes of steel No. 1.4970 was studied in a sodium loop. The corrosion and creep tests with cladding tube specimens were extended up to 10 000 h. The mass losses showed an effect of the oxygen content in the sodium loop which was controlled by means of a cold trap. The exposure to sodium caused chemical changes as losses of chromium, nickel and manganese and the carbon concentrations were increased in the outer zones of the material. The boron content of the steel was significantly reduced. Despite the changes of the chemical composition of the material, the time to the creep deformation of 1% at 973 K was not influenced by the sodium corrosion. This might be due to the carburization of the steel. All corrosion effects were only marginal at 873 K.

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1. Introduction

The Ti stabilized stainless steel X10NiCrMoTiB1515 with the German number 1.4970 was proposed as material for cladding of fuel elements of a sodium-cooled fast reactor by Böhm and Heß [1]. Their recommendation was based on the superior creep resistance at high temperatures; the titanium content caused a reduced sensitivity to intercrystalline fracture and parallel to this behavior also a lower radiation induced high-temperature embrittlement had to be expected. The further development showed that the steel needed an optimization by means of a thermo-mechanical treatment in order to increase the creep strength in the temperature range 673–1073 K [2]. The excellent creep-rupture behavior of the steel No. 1.4970 up to 973 K and a time of about 42 000 h was reported by Schirra and Ritter [3].

An effect of liquid sodium which was recently again recommended as a coolant of reactors operated with fast neutrons [4] on the allowable stress limits of austenitic stainless steels has been considered as a possible corro-

sion effect of liquid sodium at high temperatures. A reduction of the high-temperature strength of steels may be due to the carbon transfer by sodium which tends to decarburization of steels at high temperatures [5]. This tendency is minimized in the case of stabilized austenitic steels. However, changes in interstitial element concentration in such steels may cause effects on their creep rupture behavior. The study of these possible sodium effects was performed by tests in a sodium loop in which sodium could be circulated at high flow velocities and high temperatures under well defined chemical conditions. The aim of the tests was the generation of corrosion and creep data of the steel No. 1.4970 under conditions close to those in the reactor core.

2. Experiments

The sodium loop which was designed for this type of corrosion and creep-rupture tests in Forschungszentrum Karlsruhe was described in [6]. The specimens of steel No. 1.4970 were placed in three parallel high-temperature tubes of this loop which could be operated at different temperatures. The tube-shaped specimens were

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mounted to stacks of five specimens. These stacks were fixed in the central position of the tubes of 10 mm inner diameter in the test sections. The specimens were cladding tubes of 50 mm length in original dimensions with 6.0 mm outer diameter and 0.38 mm wall thickness. They were closed with welded end plugs, and one of them was connected to a capillary, which was finally closed by welding near the plug. This capillary served to pressurize the specimens with helium gas before testing. The pressure was calculated to produce a certain tangential stress at the temperature of the exposure to sodium. The maximal tangential stresses generated in this way were 220 MPa at 873 K and of 120 MPa at 973 K.

The sodium loop was equipped with a cold trap to keep the concentration of impurities low. Oxygen was continuously measured by means of solid electrolyte electrochemical cells. A sampling device allowed to take samples for the determination of other impurities of the sodium, mainly of carbon. Since the carbon concentrations were very low, the equilibration of 18–8 CrNi steel foils with sodium at 973 K was additionally used to estimate the chemical activity of carbon in the sodium during these corrosion tests [7]. The foils of that steel were exposed to sodium at 973 K for at minimum 48 h, that the carbon activities in the solid and the liquid metal came into equilibrium. The analytical determination of carbon in the foils allowed the calculation of the chemical activity of carbon in the steel at the temperature of equilibration. This carbon activity is equal to that in the liquid sodium at the same temperature.

The parameters of these tests in the high-temperature sodium loop are presented in Table 1. The composition

Table 1
Parameters of the sodium corrosion tests with specimens of steel 1.4970

Parameter	High-temperature loop
Max. temperature/K	873/973 ^a
Temperature gradient/K	280/380
Flow velocity/m s ⁻¹	5
Reynolds number	9 × 10 ⁴
Cold trap temperature/K	423
Exposure time/h	1250, 2500, 5000, 7500, 10000
Oxygen/10 ⁻⁴ mass%	6.3 ± 3.5
Carbon/10 ⁻⁴ mass%	0.1–0.2
Stress at 973 K/MPa	70–118

^a Two test sections were operated at 973 K, the third one at 873 K.

Table 2
Composition of the steel No. 1.4970 exposed to sodium/mass%

C	Si	Mn	P	S	Cr	Ni	Fe	Mo	Ti	B
0.11	0.3	1.40	0.005	0.01	15.13	14.97	Bal.	1.14	0.48	2.9 × 10 ⁻³

of the stainless steel No. 1.4970 with boron content is listed in Table 2. The cladding tubes were solution treated at 1323 K and then 10–15% cold worked; finally they were tempered 2 h at 1073 K. The grain size after this typical thermal treatment to reach optimal strength was ASTM 8–9 (10–20 μm).

Mass losses due to sodium corrosion as well as the creep deformation of the tubes were discontinuously measured during interruptions of the tests. The specimens were cleaned in methanol and ultra pure water after the exposure in the sodium loop. The weight of the specimens before and after test was determined. The deformation of the tubes was determined over the whole length using inductive probes which were moved helically along their lengths. At the end of the test periods, corrosion and creep effects were studied by means of analytical and metallographical methods. Changes of the chemical composition of the steel were determined using the glow discharge spectroscopy and the Auger electron spectroscopy. Scanning electron microscopy with energy dispersive X-ray analysis was also applied to evaluate particular effects [8].

3. Results of tests

3.1. Mass losses

The specimens were weighed before immersion into sodium and at interruptions of tests after complete removal of traces of sodium with a sensitivity of 10⁻⁴ g. Weight changes were divided by the surface areas of the specimens in order to gain weight changes in g cm⁻². The results of weight measurements are shown in Fig. 1 as a function of exposure time. The functions do not show linearity due to the fact that the oxygen concentrations were slightly different in the different partial runs of the whole test.

The mean values of the linear mass loss rates can be expressed by the equations valid for the two test temperatures and the oxygen concentration of (6.3 ± 3.5) 10⁻⁴ mass%.

$$\Delta W(\text{mg cm}^{-2}) = 1.65 - 6.073 \times 10^{-4} \cdot t(\text{h})$$

at $T = 873 \text{ K}$ (1)

$$\Delta W(\text{mg cm}^{-2}) = 2.967 - 1.716 \times 10^{-3} \cdot t(\text{h})$$

at $T = 973 \text{ K}$ (2)

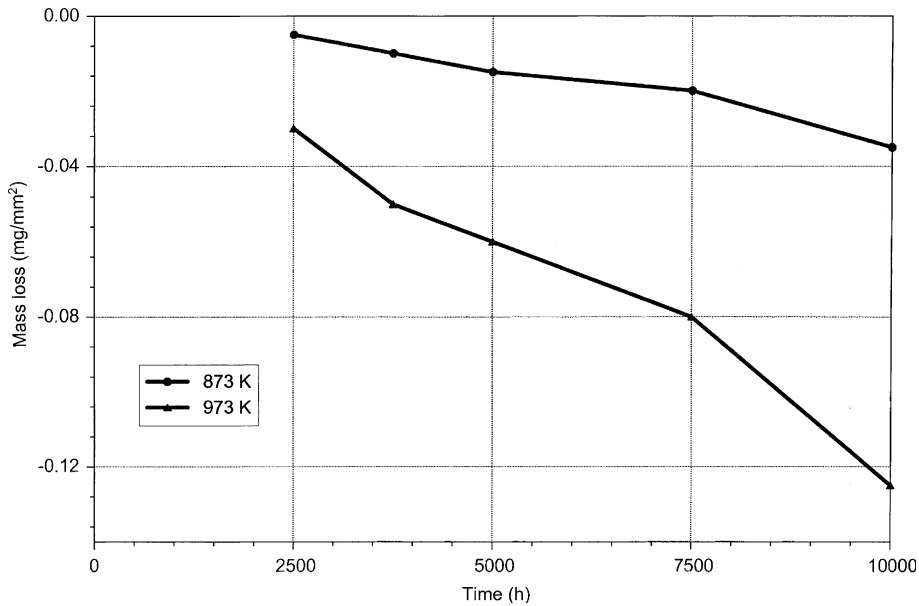


Fig. 1. Mass losses of the specimens of steel No. 1.4970 at 873 and 973 K in the first position of the test sections.

Within the narrow band of oxygen concentrations in sodium ($3.5\text{--}9.0 \cdot 10^{-4}$ mass%) the corrosion rate constants could be related to these oxygen concentrations

$$\log k \text{ (kgm}^{-2}\text{h}^{-1}\text{)} = -2.066 + 0.931 \log c_{\text{O}} \text{ (}10^{-4}\text{mass}\% \text{)} \\ \text{at } T = 873 \text{ K} \quad (3)$$

$$\log k \text{ (kgm}^{-2}\text{h}^{-1}\text{)} = -1.6615 + 0.922 \log c_{\text{O}} \text{ (}10^{-4}\text{mass}\% \text{)} \\ \text{at } T = 973 \text{ K} \quad (4)$$

The Eqs. (3) and (4) indicate that the dependence of the mass losses on the oxygen concentration was nearly linear within the range of values which were found during the tests. The activation energy of the material dissolution based on the two test temperatures is in the order of 65 kJ mol^{-1} . Fig. 1 shows the mass losses during the five periods of testing at 873 and 973 K.

3.2. Changes of the chemical composition

Surface near layers of the corroded specimens were examined by means of glow discharge emission spectrography, energy dispersive X-ray diffraction analysis and Auger electron spectroscopy. These analyses showed for specimens exposed up to 10000 h in sodium selective losses of alloying elements. The metal losses, the thicknesses of the corroded layers and the changes in chemical composition were only small at 873 K. The surface concentrations of chromium were reduced to 12%, those of nickel to 13.5%, and the contents of titanium and manganese were also decreased in the surface

regions. Molybdenum and iron were somewhat enriched in surface layers. The regions of changed composition were only 0.02 mm thick. The selective leaching of chromium, nickel, manganese and titanium reached a depth of 0.015–0.020 mm at 973 K. Molybdenum was not leached at this temperature; thus the element was enriched as well as iron at the surface. The thickness of the depleted layers did not further grow after 2500 h of sodium exposure at this temperature. The glow discharge emission spectrography revealed also information on the behavior of non-metallic elements as carbon and boron in steel No. 1.4970 exposed to sodium at 873 and 973 K [9].

Losses of boron were detected over large areas of the cross sections of the tubes even at lower temperature. The surface concentration decreased to nearly zero, and the matrix concentrations were also somewhat reduced. The leaching effects were more significant at 973 K, at which temperature the mean values of the boron concentration were found to be around 1.0×10^{-3} mass%.

Changes of the carbon concentration were determined over large ranges of the cross sections of the corroded tubes. Only very low carbon contents were found in the ferritic surface zones of specimens exposed at 973 K; after about 0.015 mm in depth, a steep positive gradient occurred, which reached a maximum carbon concentration with a level about three times higher than the initial content. A flat negative concentration gradient was measured from that maximum to the centres of the tube walls. The austenitic tube material was carburized during 10000 h of reaction with sodium at 973 K up to the center of the cross-section (see Fig. 2). The

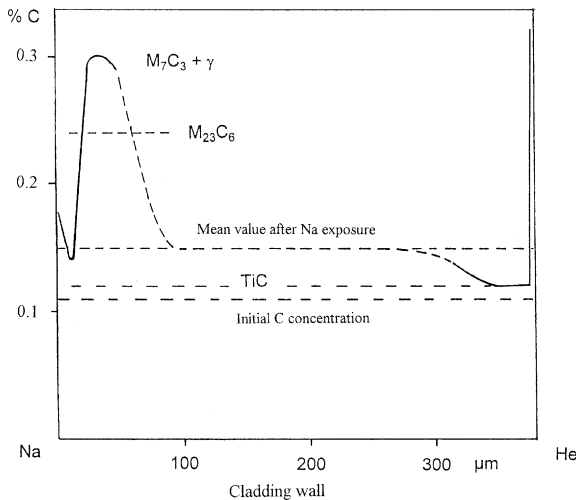


Fig. 2. Concentration profile of carbon in steel No. 1.4970 after exposure to sodium for 5000 h at 973 K.

carbides TiC and M_7C_3 may be present in the region of the maximum concentration of 0.3 mass% carbon, while M_{23}C_6 should be stable in the region below 0.25 mass% carbon. Exposure at 873 K caused an increase of the carbon concentration from the surface to the maximum, the gradient to the center of the tubes was steeper, and the carburized region was smaller at the lower temperature. The carbide M_7C_3 may be expected in the region of highest carbon concentrations, while M_{23}C_6 may be dominant in the region of mean values of the carbon contents. TiC should be completely precipitated even at small amounts of carburization.

The surface areas suffered also structural changes as was shown by metallographic examinations of cross-sections of the tubes. Very thin layers and grain boundaries in the outer layer of grains were changed to ferritic structure due to the leaching of those elements by sodium at 973 K which stabilize the austenitic structure. Some surface grains were completely changed to ferritic structure within this layer of up to 0.025 mm thickness. The ferritic surfaces appeared, however, smooth and uncorroded. The carbon contents in these ferritic layers were much lower than in the uncorroded austenitic material. The low carbon contents in the ferritic layers are due to the higher chemical activity of carbon in this region compared to that in the austenitic steel. This fact causes a higher mobility of carbon in the ferritic layer. Carbon is gettered by the following austenitic zones.

High amounts of carbide precipitates were observed in the region of grain boundary ferrite on slip planes of grains. A high density of carbide precipitates was also found at the border of the austenitic structure at which the maximum of carbon content and hardness was measured. The density of precipitates decreased with increasing depth. σ -phases which occurred in similar

steels due to long exposure to sodium were not precipitated in steel No. 1.4970 [6].

3.3. Changes of the surface structure

Scanning electron microscopic studies reveal that the ferritic surfaces became smooth due to the sodium corrosion. The grain boundaries were visible in this structure, and some small crystals with high molybdenum contents appeared on the grain surfaces. Cavities were found at triple grain boundaries. Fig. 3 shows the surface of such a specimen which was exposed 5000 h at 973 K. The bright areas are rich in molybdenum and iron, and some holes were formed in the surface layers. Metallographic flat angle cross sections were prepared by means of mounting the specimens in an angle of 6° to the plane of grinding in order to enlarge the corrosion layers. Examinations of such cross sections by means of scanning electron microscopy showed that the cavities extended over the whole ferritic corrosion zone.

3.4. Changes of the tube diameters

The growth of the tube diameters of the pressurized specimens of steel No. 1.4970 which were tested in sodium and in vacuum was identical at the test temperature of 873 K. The tests at 973 K showed nearly the same situation, when the high stress applied caused a relatively short time to reach a strain of 1%, while the specimens exposed in sodium were somewhat stronger in

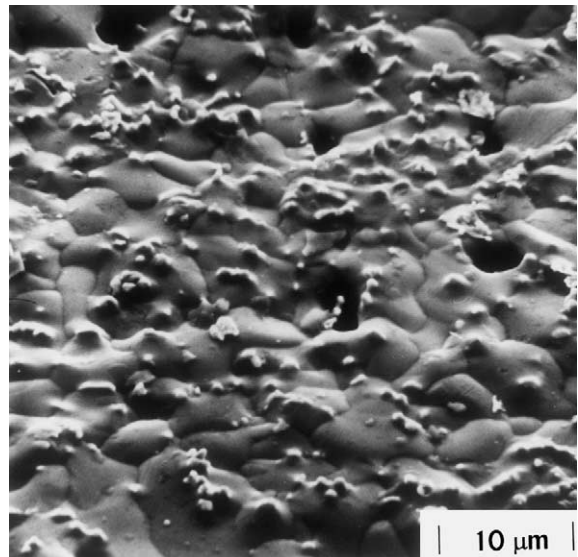


Fig. 3. Surface of a specimen of steel No. 1.4970 exposed 5000 h at 973 K to the sodium in the test section of the high-temperature loop (1100:1).

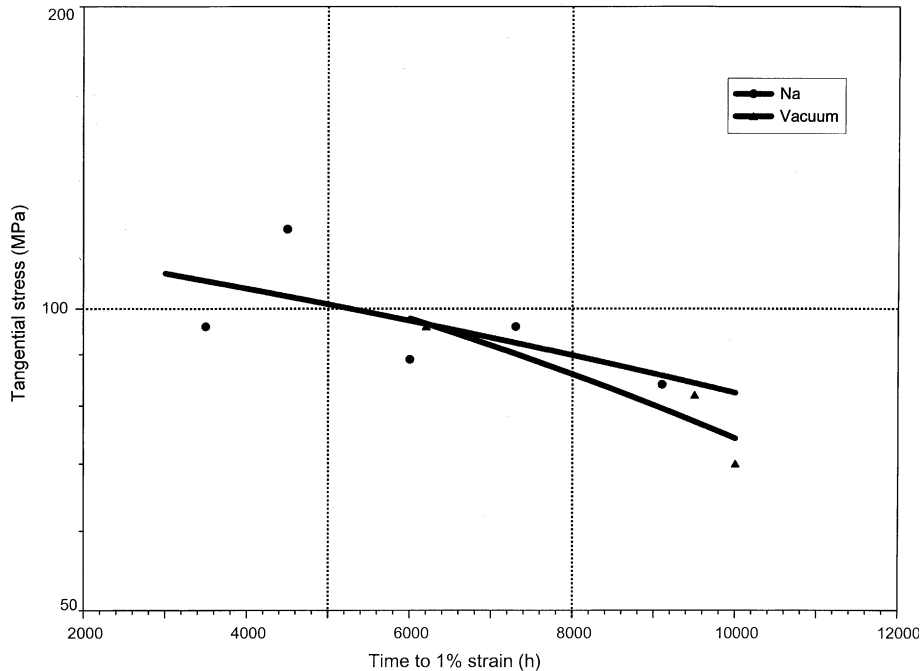


Fig. 4. One percent tangential strain limit of cladding tubes of steel No. 1.4970 tested at 973 K in sodium and in vacuum.

tests of longer duration. This is shown in Fig. 4, in which the time to 1% strain was related to the applied stress. The creep to 1% strain was chosen as parameter, since rupture did not occur with specimens of this steel during the test period. This was due to the fact that the applied tangential stresses were in the order of only 20–30 % of the short-time 0.2 % strain limit of the material at 973 K.

4. Discussion

The mass loss data gained in these tests with a mean oxygen content of (6.3 ± 3.5) ppm were at the lower border of the scatter band of values which are reported for 10 ppm oxygen in the literature [10]. The sodium corrosion of steel No. 1.4970 at 873 and 973 K and 5 m/s flow velocity is not higher than that of other austenitic steels, but significantly lower than that of steel No. 1.4301 (AISI 304) [10].

Losses of thickness of ≤ 5 μm per year at 873 K do not influence the life time of fuel elements. Even at higher oxygen contents of 10×10^{-4} mass% corrosion rates were found within the scatter band of data [10]. The corrosion effects on a cladding tube of steel No. 1.4970 up to the life time of two years are schematically shown in Fig. 5. With respect to the mass losses due to sodium corrosion, steel No. 1.4970 is a good choice.

Even the significant losses of boron did not cause any influence on the creep strength of the cladding tubes of

steel 1.4970. The carburization of the outer parts of the tubes may have compensated the losses of boron with respect to the strength of the material. Though large parts of the cross sections of the tubes were changed in their chemical composition, there was no negative influence of sodium corrosion on the creep behavior.

The parameters of testing in the high-temperature sodium loop were comparable with parameters of the reactor core with the exception of the higher test temperature 973 K. This parameter can only be considered as the hot-spot temperature at the boundary of fuel element clads with the coolant.

The relation of boundary areas steel–sodium to the volume of the liquid metal is significantly larger in the cooling channels of the reactor core than in the loop. This fact would reduce the capacity of the coolant to dissolve components of the solid metals. A downstream effect which occurs in narrow channels due to saturation of the liquid with corrosion products decreases the corrosion at the highest temperature level in the reactor core. Thus, the test results can be considered to be conservative.

An effect of the neutron irradiation in the reactor core could not be studied. However, the scarce data published on the irradiation influence on sodium corrosion [11] are not indicating a strong effect of the irradiation. The irradiation results in the transformation of some of the alloying elements, as it is shown in the following relations [12]:

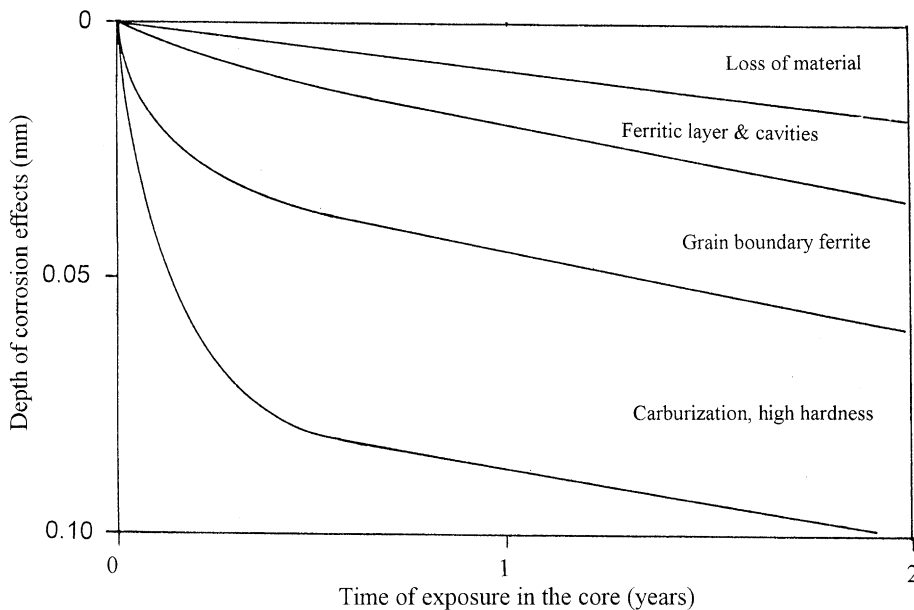
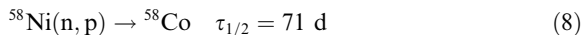
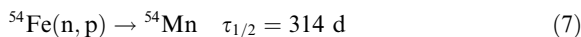
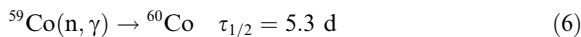
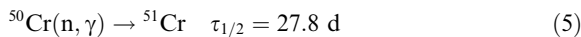


Fig. 5. Schematic graph of effects on the cladding tubes due to sodium corrosion at 973 K.



These activated isotopes are characterized by relative long half-life times and intensive radiation. Together with the initial alloying elements the activated products are dissolved by sodium within the limit of the corrosion rate. They are transferred into cooler regions of the cooling circuit where they can be precipitated. The build-up of activated inner surfaces at the heat exchanger between the primary and secondary systems makes the maintenance more difficult. This is mainly due to the transfer of manganese, which is more soluble in sodium than the other alloying elements. The deposition of manganese on surfaces of tubes of the experimental circuit was shown after its dismantling [13]. Cobalt is retained in the cladding steel due to its low solubility in sodium, while chromium is oxidized, forming sodium chromite NaCrO_2 or chromium oxide Cr_2O_3 ; these non-metallic substances are dissolved or suspended in sodium and transported into the purification systems. The activation and transfer of activated corrosion products of steel No. 1.4970 is, however, comparable to those of AISI 316. One may expect comparably low problems with steel No. 1.4970 due to the relative low corrosion rates.

Thus, the design of the cladding tubes does not need any corrections with respect to the corrosion rates or influences on the creep behavior of steel 1.4970 in sodium up to temperatures in the range 873–973 K.

Acknowledgements

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