

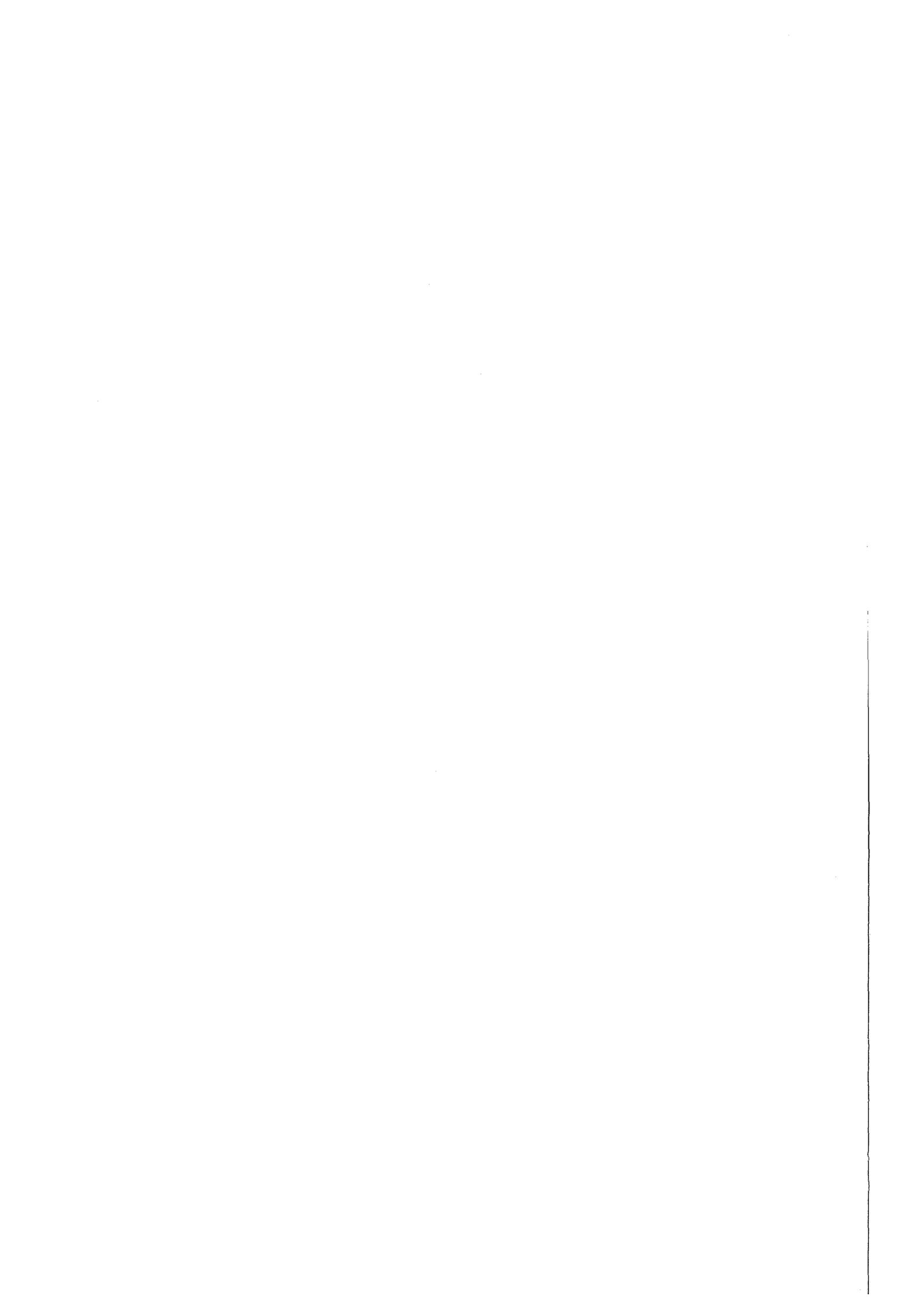
KfK 4595
Juli 1989

Standard and Applied Material Testing Methods of Austenitic CrNi Stainless Steels in Different Nitric Acid Media

Procedures and Results

S. Leistikow, R. Kraft, G. Schanz
Institut für Material- und Festkörperforschung
Projekt Wiederaufarbeitung und Abfallbehandlung

Kernforschungszentrum Karlsruhe



KERNFORSCHUNGSZENTRUM KARLSRUHE

Institut für Material- und Festkörperforschung
Projekt Wiederaufarbeitung und Abfallbehandlung

KfK 4595
PWA 41/89

**Standard and Applied Material Testing Methods of Austenitic
CrNi Stainless Steels in Different Nitric Acid Media -
Procedures and Results**

S. Leistikow, R. Kraft, G. Schanz

Kernforschungszentrum Karlsruhe GmbH, Karlsruhe

Als Manuskript vervielfältigt
Für diesen Bericht behalten wir uns alle Rechte vor

Kernforschungszentrum Karlsruhe GmbH
Postfach 3640, 7500 Karlsruhe 1

ISSN 0303-4003

Abstract

Extended ASTM Standard Huey Testing has been performed in at 120°C boiling 14.4 molar (65%) nitric acid during 15 periods (15 x 48 = 720 h duration) for quality control of numerous commercial nitric acid resistant austenitic CrNi steels. It was shown how sensitively the chosen testing conditions could differentiate between CrNi steels of the same nominal composition as specified for DIN W.Nr. 1.4306 (AISI Type 304 L), but with varying residual element contents. Within an attempt to differentiate within this group of steels by application of electrochemical methods, potentiostatic tests at 1250 mV in nitric acid of equal concentration and temperature were able to detect remarkable differences in corrosion behavior already after one hour.

Another approach, more typical for the electrochemical potentials during materials application in reprocessing plants of nuclear fuel, gave preference to long-term immersion tests, which were performed in nitric acid of lower concentration and temperature. Reference tests in pure 7 molar, 90°C nitric acid could only reveal by surface attack small differences in steel quality by exposures of 720 h duration. To shorten the test time by an increase of the redox potential chromium (VI) ions were added to the nitric acid. In a solution of 0,5 g Cr(VI)/l at 90°C remarkable differences in corrosion behavior of the steels - similar to the Huey Test results - became measurable by means of gravimetry and metallography already during a short-term exposure of 24-72 h. The recommendations to perform as standard method short-term testing in nitric acid solutions of oxidizing ions at those or even higher redox potentials are discussed in the light of these results.

Notice:

Paper presented to the International Symposium on "Corrosion Resistant Alloys", organized by the Faculty of Foundry Engineering, Academy of Mining and Metallurgy and the Association of Foundry Engineers, Kraków, Poland, November 24-26, 1988

Standard und angewandte Material-Prüfmethoden von austenitischen, rostfreien CrNi-Stählen in verschiedenen salpetersauren Medien - Verfahren und Ergebnisse

Kurzfassung

Umfassende ASTM Standardprüfung nach Huey wurde zur Qualitätskontrolle von zahlreichen salpetersäurebeständigen austenitischen CrNi-Stählen in bei 120°C siedender 14,4 molarer (65%) Salpetersäure über 15 Perioden (15 × 48 h = 720 h) durchgeführt. Es wurde gezeigt, wie empfindlich die angewandten Prüfbedingungen in der Lage sind, zwischen CrNi-Stählen derselben nominellen Zusammensetzung DIN W.Nr. 1.4306 (AISI Type 304 L), aber unterschiedlichem Gehalt minorer Elemente zu unterscheiden. Bei einem Versuch, innerhalb dieser Stahlgruppe durch Anwendung elektrochemischer Methoden zu differenzieren, waren potentiostatische Tests bei 1250 mV in Salpetersäure gleicher Konzentration und Temperatur erfolgreich, bemerkenswerte Unterschiede im Korrosionsverhalten bereits nach einer Prüfzeit von 1 h aufzuzeigen.

In einem anderen Anlauf, der typischer ist für die Lage der elektrochemischen Potentiale beim Materialeinsatz in Wiederaufarbeitungsanlagen für Kernbrennstoff, wurde der Vorzug Langzeit-Eintauchversuchen gegeben, die in Salpetersäure bei mittlerer Konzentration und Temperatur durchgeführt wurden. Referenz-Versuche in reiner 7 molarer Salpetersäure bei 90°C konnten zwar durch Oberflächenangriff kleine Unterschiede in der Stahlqualität über Expositionszeiten von 720 h Dauer erkennbar machen. Um jedoch durch Redoxpotential-Erhöhung die Testzeit zu verkürzen, wurden der Salpetersäure Cr(VI)-Ionen zugesetzt. In einer Lösung von 0,5 g Cr(VI)/ℓ, 90°C konnten bereits nach 24-72 h - in tendenzieller Übereinstimmung mit den Ergebnissen des Huey-Tests - bemerkenswerte Unterschiede des Korrosionsverhaltens der Stähle durch Gravimetrie und Metallographie meßbar gemacht werden. Die Empfehlungen, Kurzzeitversuche in salpetersauren Lösungen oxidierender Ionen bei diesen oder sogar höheren Redoxpotentialen als Standardmethode auszuführen, werden im Lichte dieser Ergebnisse diskutiert.

Hinweis:

Bei dem vorliegenden Bericht handelt es sich um einen Vortrag, der auf dem Internationalen Symposium "Korrosionsbeständige Legierungen" gehalten wurde, das vom 24.-26. November 1988 von der Fakultät für Gießereiwesen, Akademie für Bergbau und Metallurgie und der Vereinigung der Gießereingenieure in Kraków, Polen veranstaltet wurde.

Disposition

1.	Introduction	1
2.	Experimental	2
2.1	Material Composition, Specimen Shape and Pretreatment	2
2.2	Chemical Testing	2
2.3	Supporting Actions	3
2.3.1	Analytical Chemistry	3
2.3.2	Electrochemical Testing	3
2.3.3	Metallography	4
3.	Experimental Results	4
3.1	Pure 7 molar HNO ₃ at 90°C	4
3.2	7 molar HNO ₃ containing Chromium (VI)-Ions	5
4.	Discussion	6
5.	Conclusions	8
6.	Acknowledgements	9
7.	References	9
	Tables	11
	Figures	16

1. INTRODUCTION

Since long time the unstabilized austenitic CrNi Steel DIN W. Nr. 1.4306 = AISI Type 304 L is generally applied as vessel, container and tubing material in the chemical industry and reprocessing plants of nuclear fuel. However, corrosion problems have been reported of those parts of the reprocessing plants (dissolver, evaporator etc.) which are exposed to an environment consisting of nitric acid or nitric acid solutions containing fuel and fission products at higher temperatures. The insufficient corrosion resistance could be explained as caused by the alloy composition, especially in respect to the content and the inhomogeneous distribution of minor elements as consequence of steel production and processing.

The German chemical industry has initiated the development of improved versions of the above mentioned steel by optimizing the chemical composition, full use of secondary metallurgy, and improved heat treatment within the production process. The result of a successful development was a fully austenitic and homogeneous product, rich in Cr and Ni, and very poor in minor elements as C, P, S, Si, Mo. It is appropriate for service in nitric acid of concentrations up to the azeotropic composition and the corresponding boiling points. This CrNi steel is commercially available under the designation DIN W.Nr. 1.4306 in different versions: in the normal quality (n) and the special nitric acid grade (s). The abbreviation ESU is added to the s in case that an electroslag remelting process was applied for quality improvement of the steel in respect to purity and especially homogeneity.

Within a first effort (Table 1) to differentiate between the above mentioned grades by an appropriate test method the ASTM Standard Huey Testing (1) was successfully applied during an extended duration of 15 periods (Fig. 1), which is equal to $15 \times 48 = 720$ h (2). A much faster result in respect to the ranking order of nitric acid corrosion resistance of these grades (Fig. 2) was achieved by one hour electrochemical polarization tests (3).

This paper deals with the response of these different versions to another group of chemical tests in which oxidizing metal ions are added to nitric acid of medium concentration and temperature as corroding medium. Thus, the chosen conditions of testing are more typical for the chemical

"load" put on materials which are applied for reprocessing purposes of nuclear fuel.

2. EXPERIMENTAL

2.1 Material Composition, Specimen Shape and Pretreatment

Three different austenitic CrNi steels within the specification of AISI Type 304 L (DIN W.Nr. 1.4306) of normal (n), special (s), and electroslag remelted (s(ESU) quality were delivered in the solution annealed condition as plates of 2-5 mm thickness. Their chemical composition is given in Tab. 2. Rectangular specimens (30 x 30 mm) and disc specimens (20 \varnothing x 5 mm) were cut of these plates and tested in the mill solution-annealed (as-received), laboratory solution (re-) annealed (3 min, 1050°C) and sensitized (30 min, 700°C) condition. Instead of surface grinding or pickling as pretreatment, the specimens were electropolished in a mixture of sulfuric and phosphoric acid. In that way the surfaces became smooth and shiny. Etching did not take place under the chosen conditions.

2.2 Chemical Testing

In principle, the so-called chemical corrosion testing was performed similarly to the ASTM Standard Huey Test, however in pure and 0,5 g Cr(VI)/l containing nitric acid ($c(\text{HNO}_3) = 7 \text{ mol/l}$). It lasted 15 periods each, being equal to $15 \times 48 = 720 \text{ h}$, as longest time of testing and was performed in a thermostatically controlled bath, interrupted periodically for weight measurements and the renewal of the acid or acidic solution. During the exposure to the media the specimens were suspended on glass hooks. The surface/volume ratio was 1 cm² metal surface area/20 ml liquid. The extent of metal dissolution was measured by weighing, then calculated in terms of rate of metal loss of specimen weight or thickness. The sequence of testing was: initial weight measurement, exposure, final weighing, data transfer directly from the balance to the computer, program controlled data processing. Further details are given in (4).

The calculated corrosion rate (as given in tables and figures) is an averaged and extrapolated value of surface metal loss in thickness, which seems to originate from the uniform surface corrosion. In reality, numerous compositional and microstructural phenomena contribute to the appearance of local non-uniform metal dissolution in surface and matrix: at grain and twin boundaries, precipitates and inclusions, segregations and other micro- and macro-heterogeneities. In principle CrNi steels of lower minor element content - at least in the solution annealed condition of heat treatment - are corroding more uniform and often slower.

2.3 Supporting Actions

2.3.1 Analytical Chemistry

After preparation of a concentrated master solution by dissolution of CrO_3 in nitric acid, the exact quantity for a solution of 0,5 g Cr(VI)/l in nitric acid ($c(\text{HNO}_3) = 7 \text{ mol/l}$) was calculated and the acid test solution made by dosage for direct use. Concerning the quantitative analysis of the Cr(VI)-content before and after the corrosion reaction an appropriate procedure based on back-titration was elaborated. Under reduced acid concentration the Cr(VI)-content to be analyzed was reduced by the addition of surplus 0,1 molar Fe(II)-solution. Afterwards the surplus Fe(II)-quantity (not reacted) was potentiometrically measured by oxidation with a 0,1 molar Ce(IV)-sulfate solution. For that purpose the Titroprocessor 682 of the METROHM Company with automatic end point finding and calculation of the results was applied.

2.3.2 Electrochemical Testing

To perform electrochemical corrosion tests in nitric acid a special electrochemical cell was built up and used, which consisted of the following items:

- a thermostat for heating of the acid containing flask or directly by an electric heater,
- the reference electrode and the conductive connection to the Luggin capillary,

- a nitric acid resistant specimen holder.

Under certain conditions however, the specimens were directly connected by spot welding to a CrNi steel wire, holding it into position and avoiding crevice corrosion between the metal surface and the sealing of the specimen holder. Otherwise the usually applied electrochemical periphery (as potentiostat etc.) was used. Further details are given in (3).

The free corrosion potential of the CrNi steels in both nitric acid solutions and the corresponding redox potential of the media were measured as function of time and temperature.

2.3.3 Metallography

Metallography of the corroded specimens was performed after cut and polish of the cross-section. Surface microscopy was performed by means of light and scanning electron microscopy (SEM). Especially under the aspect of short-term testing the very first traces of attack became important features to be evaluated by metal surface microscopy.

3. EXPERIMENTAL RESULTS

3.1 Pure 7 molar HNO₃ at 90°C

Before chromium (VI)-ion containing solutions were used as corroding media a basic study of CrNi steel corrosion in 7 molar nitric acid was performed during 15 periods equal to $15 \times 48 = 720$ h. Like in Huey testing the specimens were taken off the acid after each test period of 48 h duration, weighed and then brought back into fresh acid to continue the exposure.

Fig. 3 shows the measured rate of weight loss as function of time of the three different steel qualities. Very small weight changes, hardly measurable after each period, sum up to a total metal loss of W.Nr. 1.4306 n of only about $0,82 \mu\text{m}$ after 720 h. The curves show considerable scattering which was due rather to experimental limitations than to weight changes because of loss of whole grains from the corroding surfaces. Comparing the material quality, it is clearly shown only that the

normal (n)-quality is corroding about twice as fast as the two other ones do ($n = 0.009$, $s = 0.005$, $s(\text{ESU}) = 0.004$ mm/a). Fig. 4 shows three pictures of the SEM evaluation of the metal surfaces after the total exposure of 720 h. They show etched steel surfaces, but only in case of the normal quality the grain structure is fully developed and clearly visible, much weaker is the etching of the special steel surface and hardly visible is the response of the special remelted one.

Thus it was found that there is a definite chance to differ these steel qualities only by a long-term exposure to 7 molar HNO_3 at 90°C , combined with a of periodic-gravimetric and a post-test metallographic evaluation. But since the effects of weight change and surface attack are weak and the testing time as long as for Huey testing there is no significant advantage to report.

3.2 7 molar HNO_3 Containing Chromium (VI)-Ions

0,5 g Cr(VI)/l are added to 7 molar HNO_3 to increase the redox potential of the corroding medium from 1320 mV to 1425 mV (Table 3), as measured at 90°C . In this way the free corrosion potentials of the steels became increased from about 1015 mV to 1225 mV. Both potentials are a bit higher than the initial ones of Huey testing at 120°C ($\sim 1100/1380$ mV). Like in nitric acid the test duration lasted 15 periods = 720 h, interrupted by weight measurements of the specimens and their re-exposure to fresh acidic solution.

The results achieved (Fig. 5) showed that all steels corroded at a much higher rate than in pure 7 molar HNO_3 . The corrosion rate of the special quality came close to the normal one and the remelted special quality again was much better ($n = 4.13$, $s = 3.77$, $s(\text{ESU}) = 0.92$ mm/a). Especially for the normal and special quality it takes quite a long time (4 periods) until some kind of equilibrium surface morphology has developed which is corroding at a constant rate. The better the material the longer it lasts until this process has completed.

After each test period the chemical analysis of the test solution in respect to the remaining, non-reduced Cr(VI) content - performed as function of time and steel quality - revealed very interesting findings: For all three

steels the percentage of Cr(VI) being reduced to Cr(III) within one period increases from the first to the third period ($n = 46 \rightarrow 88$, $s = 39 \rightarrow 88$, $s(\text{ESU}) = 17 \rightarrow 34\%$). During the following periods (4.-15.) and due to the development of an equilibrium surface structure constant values of Cr (VI) reduction were measured for each quality ($n = 93$, $s = 92$, $s(\text{ESU}) = 50\%$), showing nearly total (n , s) and half Cr(VI) reduction (Table 3) of the initial Cr(VI) addition. An empirical function (Table 4) based on experiments during which the redox potentials of six different Cr(VI)-ions containing 7 molar nitric acid solutions were measured in the temperature range of 30 to 90°C (Fig. 6), allows to calculate the related drop of redox potential ($n = 33$, $s = 31$, $s(\text{ESU}) = 9 \text{ mV}$), which in fact creates at least in case of $n + s$ quality steels between the 4. and the 15. test period periodically transient potential conditions going down to the Huey test level.

That was the reason why a closer look was taken to a shorter duration of exposure, e.g. 24, 48 and 70 h. Already 24 h-corrosion tests (Fig. 7) showed very different results of metal loss and Cr(VI)-reduction (Table 5) which gave strong indication that a real chance exists that short-term tests at nearly constant corrosion potential conditions are able to differentiate materials of same nominal composition but - due to small differences in minor elements - different corrosion behavior /5/.

After a 70 h-exposure pictures (Fig. 8) were taken from the corroded steel surfaces showing in case of the normal quality steel a deeply etched structure and a lot of grains which are dissolved and/or fallen out of the metal surface. In case of the special quality steel a deeply etched surface grain structure showed numerous sites where whole grains were missing, while the remelted special quality showed only an etched surface grain structure without loss of grains. Thus it was proven that after gravimetry and analytical chemistry also surface microscopy is able to select very similarly composed materials according to the phenomenology of nitric acid surface attack.

4. DISCUSSION

Starting from the corrosion results gained in 7 molar HNO_3 it can be recognized that the ranking order of steel of quality n , s , $s(\text{ESU})$ is equal to

that of the Huey testing. The special quality (s) behaves similarly to s(ESU), despite of all scatters. The reaction is very slow and grain boundary corrosion specific. Surface micrographs taken after 15 periods show a distinct difference between the three versions: a stepwise decrease of grain boundary dissolution (etching) from n to s(ESU), on which only general uniform dissolution and no localized could be recognized.

For Huey testing in 14,4 molar HNO_3 it is normally agreed that a test duration of 5 periods is not long enough to judge of quality. About 15 (or even more) periods are needed. After an initial period the attack has established some kind of equilibrium surface morphology and proceeds at a constant rate. Mainly grain boundary, but also some dissolution within grains is being recognized by microscopy. Nitric acid attack creates a surface structure which on the premises of composition and heat treatment is occasionally able to accelerate on long-term the corrosion rate by grain boundary dissolution and enrichment of corrosion products within it.

The attack by chromium containing 7 molar HNO_3 is faster than the Huey test and very similar to the potentiostatic test at 1250 mV. Less than twenty-four hours are sufficient to develop a typical picture of the initial surface corrosion attack. The fact that later on the attack on version s is much faster than in all other tests at lower redox potentials (Fig. 5) seems to go along with a long-term tendency to unspecific general surface dissolution. That is also typical for the attack of the high potential nitric acid Ce(IV)-ion containing solution which does not more allow to differentiate the different steel versions after a certain test duration.

In so far we can make the following statements:

- 1.) In nitric acid of medium concentration and at medium, nearly boiling temperature the attack of the steels is slow, but is measured on long-term to be grain boundary-active and specific towards the minor element content.
- 2.) In boiling azeotropic concentrated nitric acid the attack on steels is faster, however sufficiently moderate so that mainly grain boundary attack as an indicator of steel quality and state of heat treatment can be measured after about 5-15 periods = 240-720 h.

- 3.) In chromium (VI) ions containing 7 molar nitric acid of medium temperature the specific kind of grain boundary attack takes place within 0,5-1,5 periods = 24-72 h. Surplus time of testing can annul the effect of quality-related differences in the grain boundary specific initial dissolution.
- 4.) Less specific dissolution is the tendency of attack by nitric acid solutions at even higher redox potentials. Its appearance is controlled mainly by the number of grain/twin boundaries within the metal surface, but also by all other surface and matrix heterogeneities.

In spite of the fact that this minor element specific corrosion behavior of our steels has a strong reverse proportional time/redox potential relationship, it was tried, based on long-term results to show trends by plotting in a half-logarithmic scale the corrosion rate/corrosion potential curve (Fig. 9). The diagram underlines the practical advantages of testing close to the Huey Standard Test conditions. At lower potentials the dissolution is too slow to be measurable in a reasonable time span, at higher values too fast to be specific in respect to the minor element content and state of sensitization.

Similar results have been shown by M. Okubo et al. (6) for the SUS 310 Nb (25Cr20Ni) steel in boiling 3 molar HNO₃ containing various oxidizing ions.

5. CONCLUSIONS

Standard Huey Testing of CrNi steels has been performed successfully to detect effects of minor element content, impurities or inhomogeneity on nitric acid corrosion. Three versions of the austenitic CrNi stainless steel of the same nominal composition as specified for W.Nr. 1.4306 = AISI Type 304 L could be differentiated by nitric acid corrosion tests (65% HNO₃, 120°C, 720 h). The method seems to be easy, but is complicated to be performed reproducibly and is manpower (time) consuming.

It was decided to look after less demanding methods. The one hour electrochemical potentiostatic test at 1250 mV in nitric acid (65% HNO₃,

120°C) proved to be (at least for preselection purposes) an appropriate method. But more than in case of Huey testing electrochemical procedures performed in a very acid-specific equipment and electronic periphery are a matter needing high experience and endurance for reproduction and qualification of the results. These methods are appropriate to be applied in research, not in industrial acceptance testing.

The swing to corrosion in lower concentrated, non-boiling nitric acid or its acidic solutions helps to relax the laboratory handling problems and ensures by addition of chromium (VI) ions that tests are performed nearly potentiostatically at even higher potentials than Huey testing, which brings us by chance closer to the conditions of the nuclear reprocessing environments. Under these conditions short-term tests are able to differ between steels of different quality. Long-term tests give results to compare and to relate the measured corrosion rate to the free corrosion potential. For the CrNi-steel, DIN W.Nr. 1.4306 in versions n, s, s(ESU) the dependency of long-term corrosion rate on free corrosion potential was an exponential one. It enables us to give - in case that the effective corrosion potential is known - much more than a vague forecast of steel corrosion behavior in nitric acid of different concentrations, temperatures and oxidizing ion additions.

6. ACKNOWLEDGEMENTS

Thanks are due to Mr. H. v. Berg and Mr. E. Pott for experimental work and evaluation.

7. REFERENCES

- /1/ Standard Huey Test
ASTM Standard A 262-86(1986)
DIN 50921 (1984)
Euronorm 121-72 (Dec. 1972)
Stahl-Eisen-Prüfblatt 1870 (1979)

- /2/ R. Kraft, S. Leistikow, E. Pott
Ergebnisse der korrosionschemischen Prüfung des nach dem Elektroschlacke-Umschmelzverfahren hergestellten Werkstoffs Nr. 1.4306 (X2CrNi 19 11) in Salpetersäure
KfK 3878 (November 1985)
- /3/ R. Simon
Elektrochemische Korrosionsuntersuchungen an austenitischen CrNi-Stählen in Salpetersäure mit und ohne Metallionen-Zusätzen
KfK 4372 (April 1988)
- /4/ S. Leistikow, R. Simon
Comparative Corrosion Tests of Different CrNi Stainless Steels AISI Type 304 L by ASTM Standard Practice and an Electrochemical Method in Azeotropic Nitric Acid
Proc. Intern. Conf. on Localized Corrosion
Orlando, Florida, USA, June 1-5, 1987
to be published
- /5/ G. Schanz, S. Leistikow
24 h-Korrosionsversuche mit elektrochemischen Potentialmessungen am CrNi-Stahl DIN W.Nr. 1.4306 in 7 molarer Salpetersäure unter Zusatz oxidierender Metallionen bei 90°C
KfK 4594 (July 1989)
- /6/ M. Okubo et al.
Demonstration Tests on Corrosion Resistance of Equipments for Spent Fuel Reprocessing Process
Intern. Conf. on Nuclear Fuel Reprocessing and Waste Management "Recod 87"
Paris, France, August 23-27, 1987
Vol. 3 (1987) 1181-1188

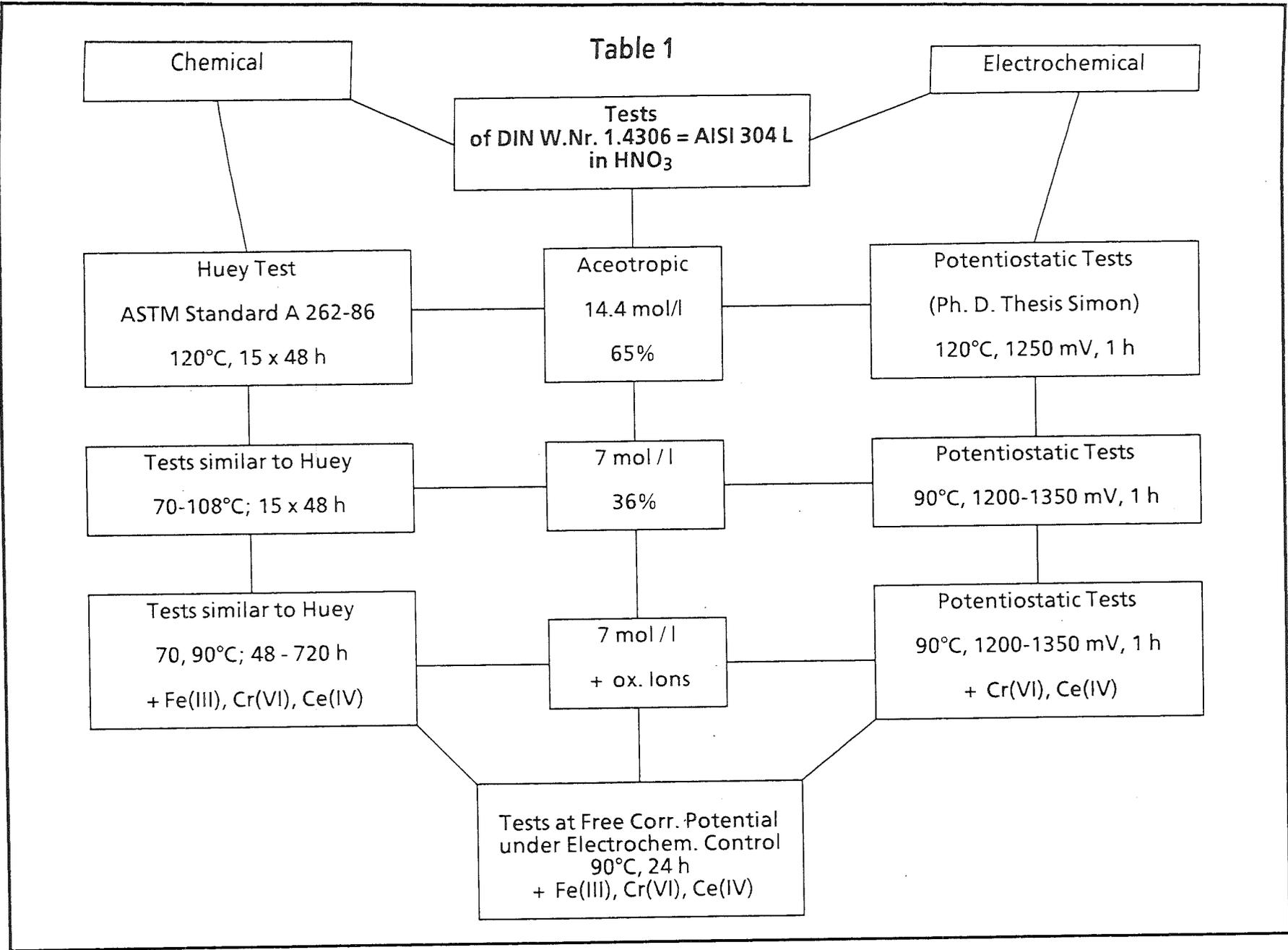


Table 2 Chemical Composition of the Different Austenitic CrNi Stainless Steels DIN W.Nr. 1.4306 = AISI Type 304 L

Werkstoff DIN W.Nr.	Chem. Composition (w%)							
	C	Si	Mn	P	S	Cr	Mo	Ni
1.4306 n	0.024	0.60	1.44	0.025	0.003	18.00	0.17	10.23
1.4306 s	0.015	0.02	1.7	0.022	0.007	19.11	0.02	12.5
1.4306 s (ESU)	0.007	0.02	1.59	0.022	0.005	19.13	-	12.40

Table 3 Redox Potential of Nitric Acid and Nitric Acid Containing Cr(VI)- and Ce(IV)-Ions, Free Corrosion Potential of Various Austenitic CrNi Steels DIN W.Nr. 1.4306 = AISI Type 304L and Resulting Long-Term Corrosion Rate

Acid		Ox. Species		Temperature [°C]	Fr. Corr. Potential [mV]	Redox Potential [mV]	Long-Term Corr. Rate of Steels [mm/a]
(mol/l)	Comp.	g/l	Metal Ions				
7	HNO ₃	-	-	90	970 - 1060	1320	0,004 - 0,009
14,4	HNO ₃	-	-	90	~ 1100	1380	0,02
14,4	HNO ₃	-	-	120	1100 - 1150	1410	0,1 - 0,3
7	HNO ₃	0,5	Cr(VI)	90	1225	1425	0,92 - 4,13
6	HNO ₃	6	Cr(VI)	70	1270	1440	0,7 - 3,7*)
7	HNO ₃	2	Ce(IV)	90	1300	1650	to be measured

*) Short-Term Test of 48 h duration

Table 4 Empirical Function to Approximate the Redox Potential of 7 molar Nitric Acid in Dependency on Cr(VI)-Ion Additions and Temperature

$$RX(\delta, C_{Cr(VI)}) = 1365 + \frac{2}{3}\delta + (50,5 - \frac{1}{4}\delta) \lg(2C_{Cr(VI)})$$

(RX in mV_H; δ in °C, C_{Cr(VI)} in g/l)

Examples of Calculation

C _{Cr(VI)}	(g/l)	0,005	0,05	0,5	6
RX [mV _H]	90°C	1369	1397	1425	1455
	70°C	1346	1379	1412	1447
	50°C	1322	1360	1398	1439
	30°C	1299	1342	1385	1431

Table 5 Nitric Acid Corrosion of Various CrNi Steels DIN W.Nr. 1.4306 = AISI Type 304 L

(7 m HNO₃, 0.5 g Cr(VI)/l, 90°C, 15 x 48 = 720 h)

- Consumption of Cr(VI) during each test period (48 h)

Calculated as difference between the initial (500 mg/l) and the measured final content in the test solution.

Exposure Period No.	Normal Quality (n)		Special Quality (s)		Special (ESU) Quality (s(ESU))	
	(mg/l)	(%)	(mg/l)	(%)	(mg/l)	(%)
1.	231	46	193	39	87	17
2.	410	82	324	65	148	30
3.	439	88	438	88	170	34
4.-15.(*)	467	93	461	92	252	50

- Calculated decrease of the redox potential of the test solution

	(mg/l)	(mV)	(mg/l)	(mV)	(mg/l)	(mV)
1.	231	8	193	6	87	2
2.	410	21	324	13	148	4
3.	439	25	438	25	170	5
4.-15.(*)	467	33	461	31	252	9

* Average values originating from 24 experimental results of each material quality

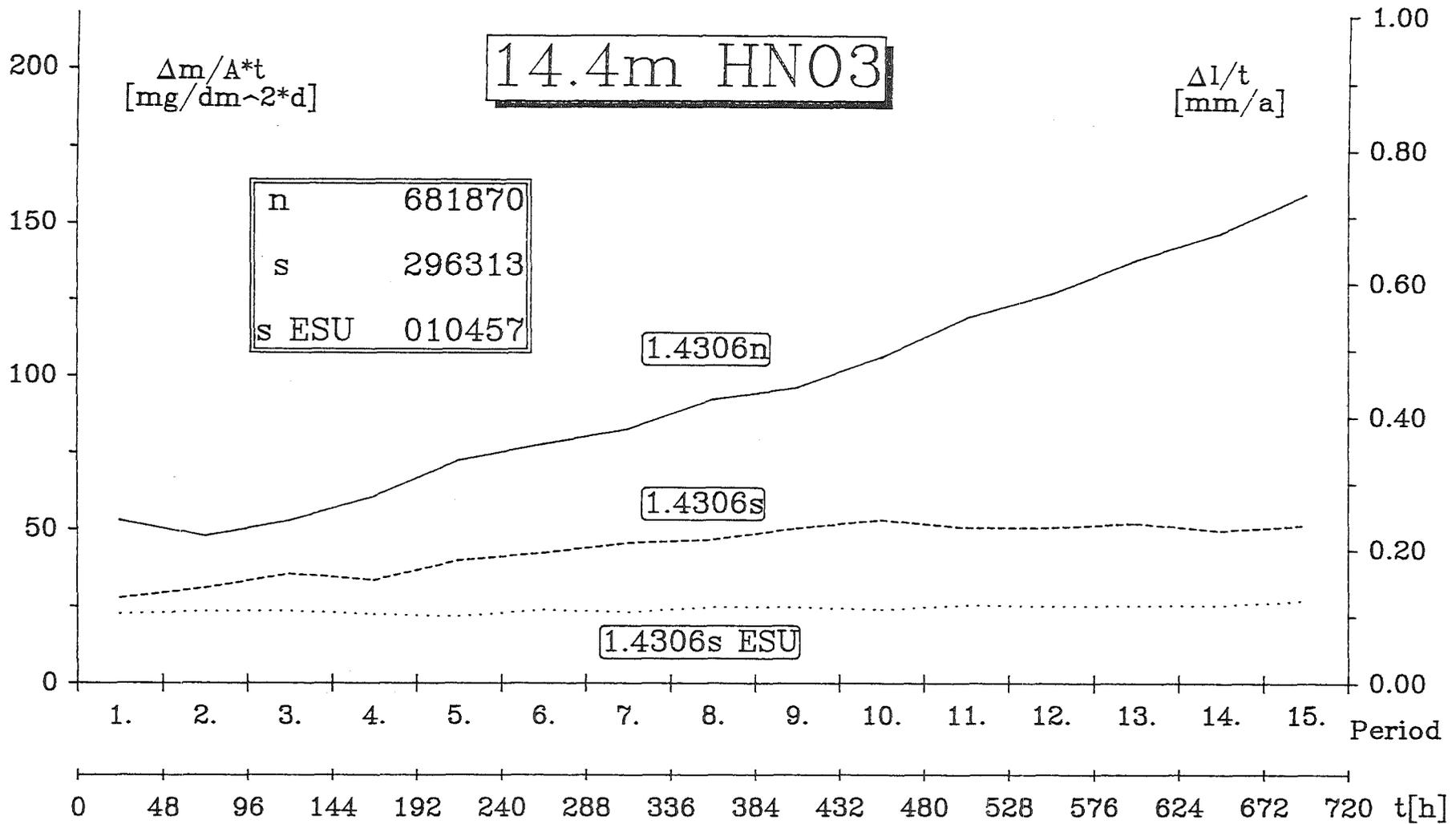


Fig. 1
 Comparison of Nitric Acid Corrosion of Various CrNi Stainless Steels
 DIN W.Nr. 1.4306 = AISI Type 304 L during ASTM Standard Huey Testing
 (c(HNO₃)=14.4mol/l, 120°C, 15x48=720h)

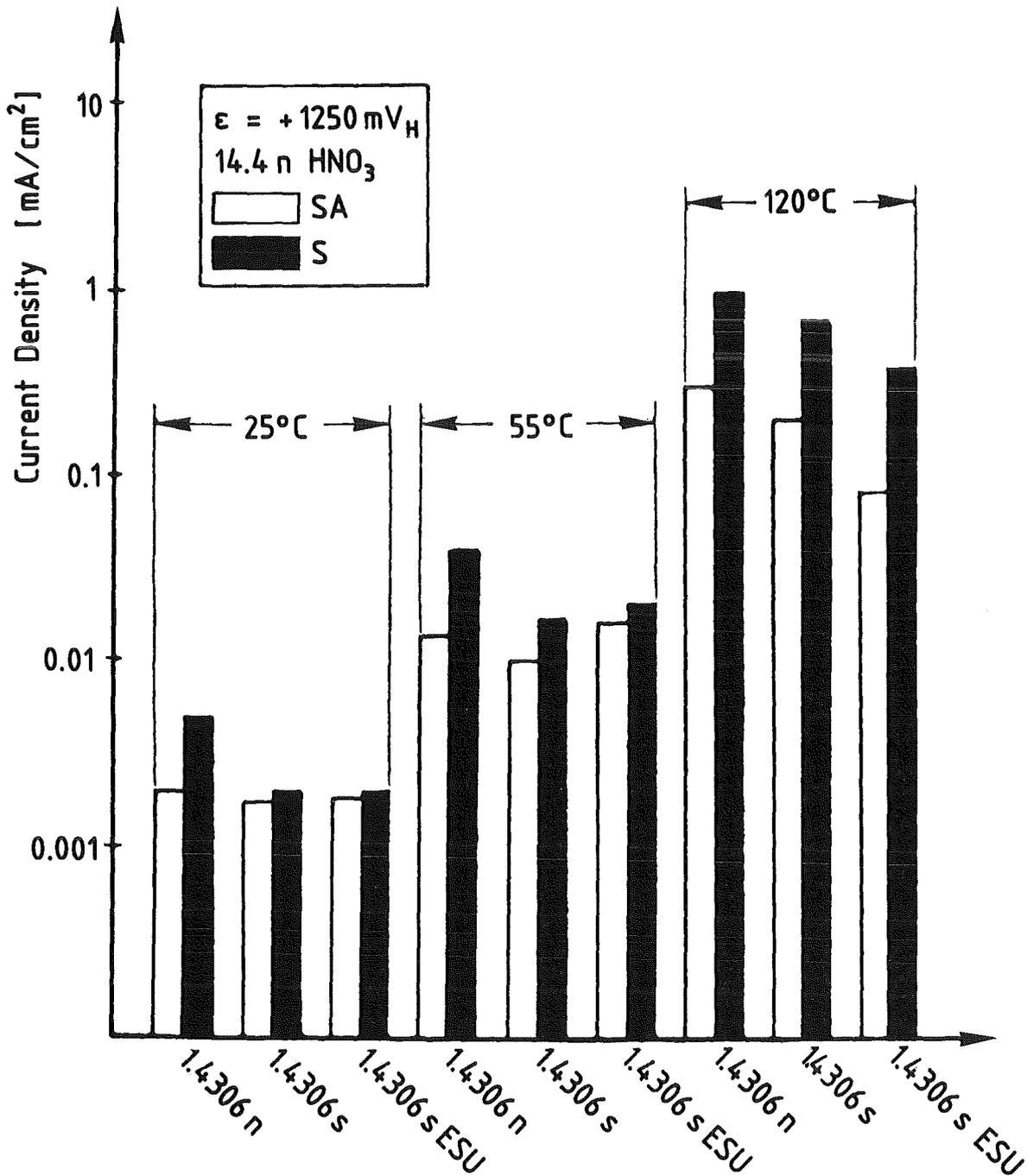


Fig. 2 Potentiostatic Experiments Testing Various CrNi Steels DIN W.Nr. 1.4306 = AISI Type 304L in Nitric Acid ($c(\text{HNO}_3) = 14.4 \text{ mol/l}$) Current Density as Function of Steel Composition n, s, s(ESU), Heat Treatment (SA=Solution Annealed, S=Sensitized) and Nitric Acid Temperature (25, 55, 120°C) (nach Simon /3/)

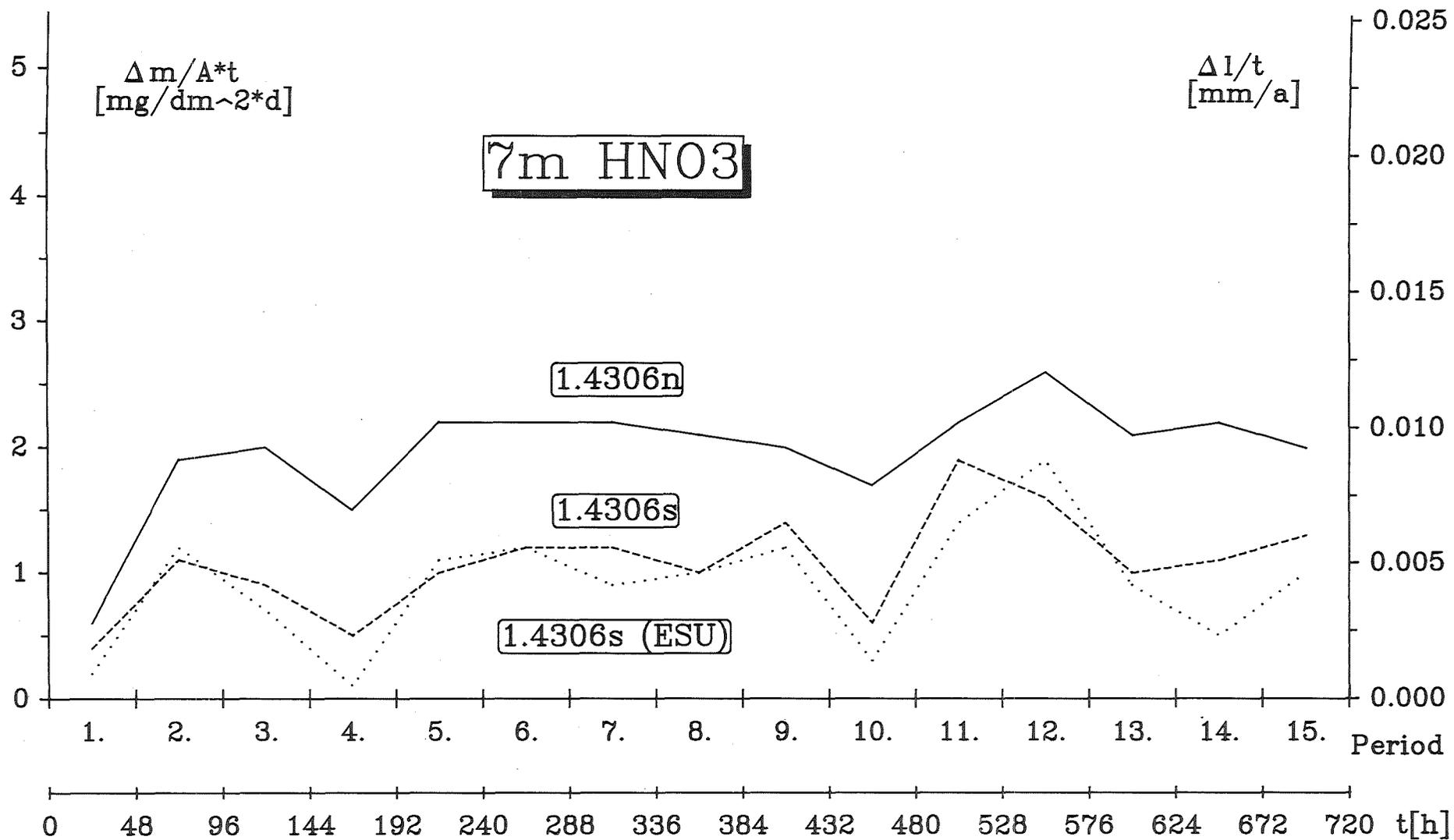
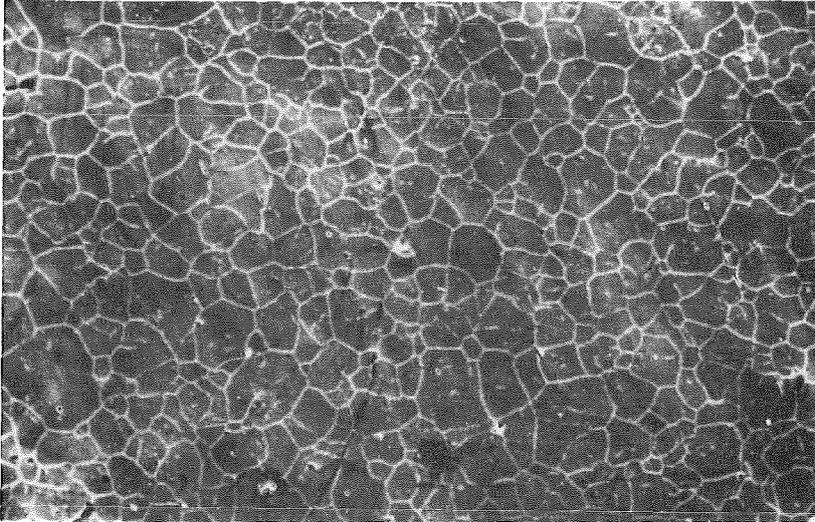


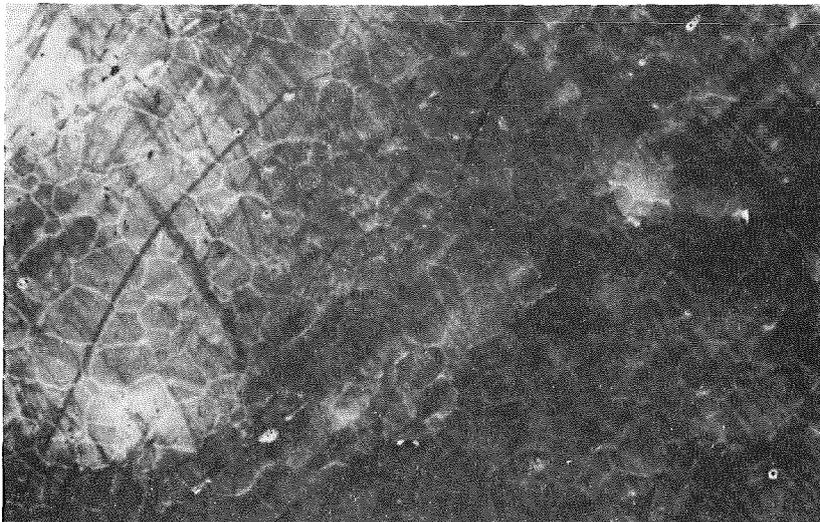
Fig. 3

Corrosion Tests of Various Solution Annealed CrNi Steels
 DIN W.Nr. 1.4306 = AISI Type 304 L in Nitric Acid ($c(\text{HNO}_3)=7\text{mol/l}$)
 90°C , $15 \times 48 = 720\text{h}$

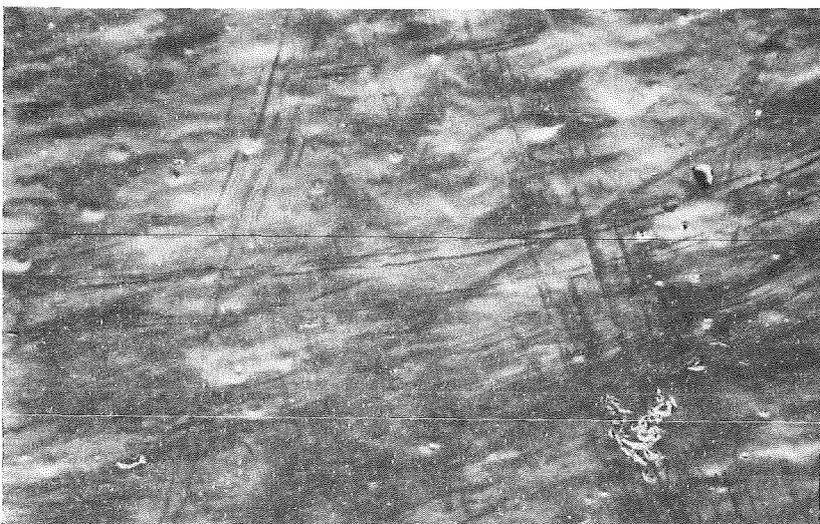




W.Nr. 1.4306n



W.Nr. 1.4306s



W.Nr. 1.4306s (ESU)

Fig. 4 Surface Micrographs (SEM) of Different Solution Annealed CrNi Steels DIN W.Nr. 1.4306 = AISI Type 304L after Corrosion in 36% Nitric Acid ($c(\text{HNO}_3) = 7 \text{ mol/l}$), 90°C , $15 \times 48 = 720\text{h}$

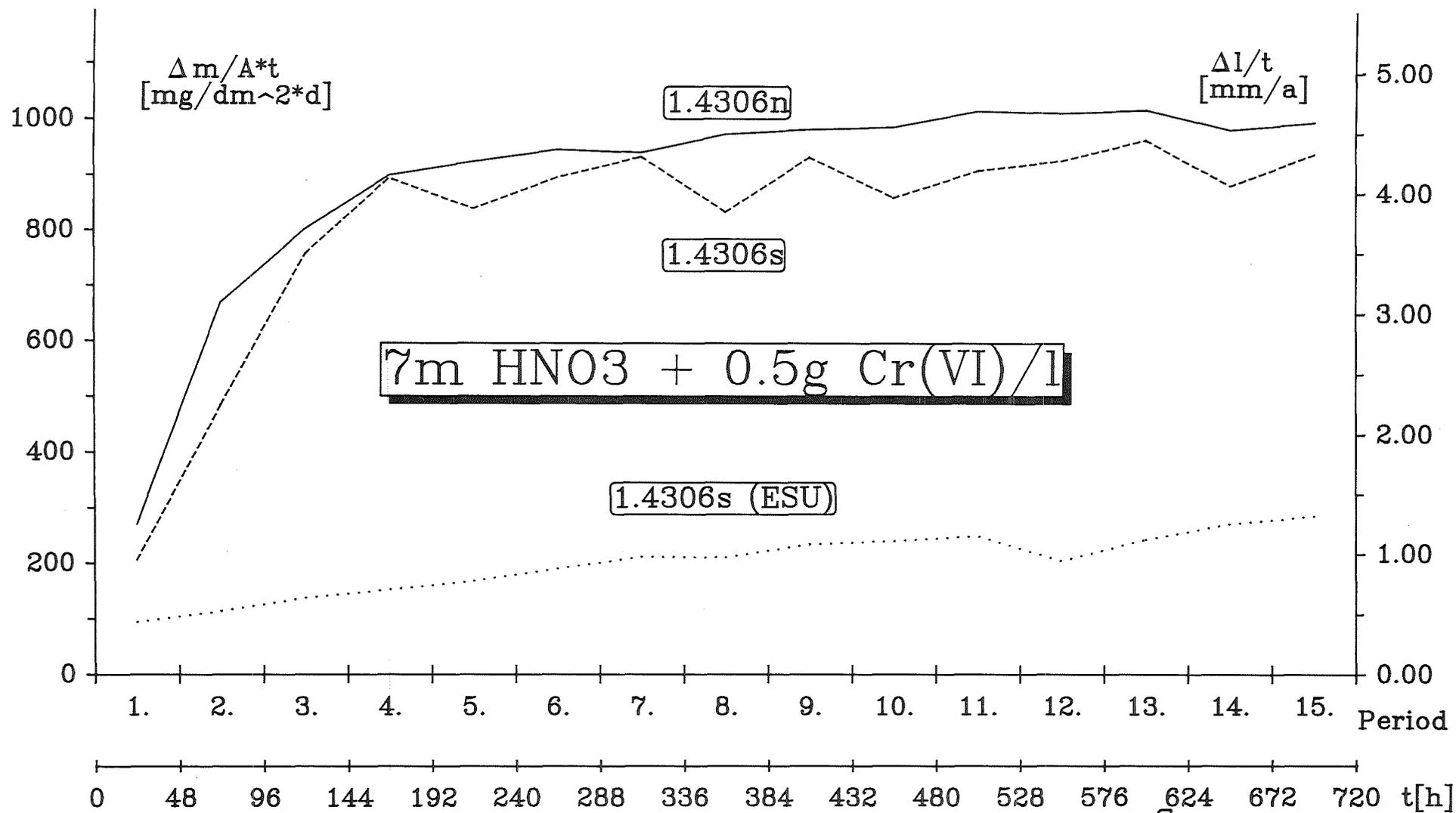


Fig. 5
 Corrosion Tests of Various Solution Annealed CrNi Steels
 DIN W.Nr. 1.4306 = AISI Type 304 L in Nitric Acid (c(HNO₃)=7mol/l)
 Containing 0.5g Cr(VI)/l, 90°C, 15x48=720h



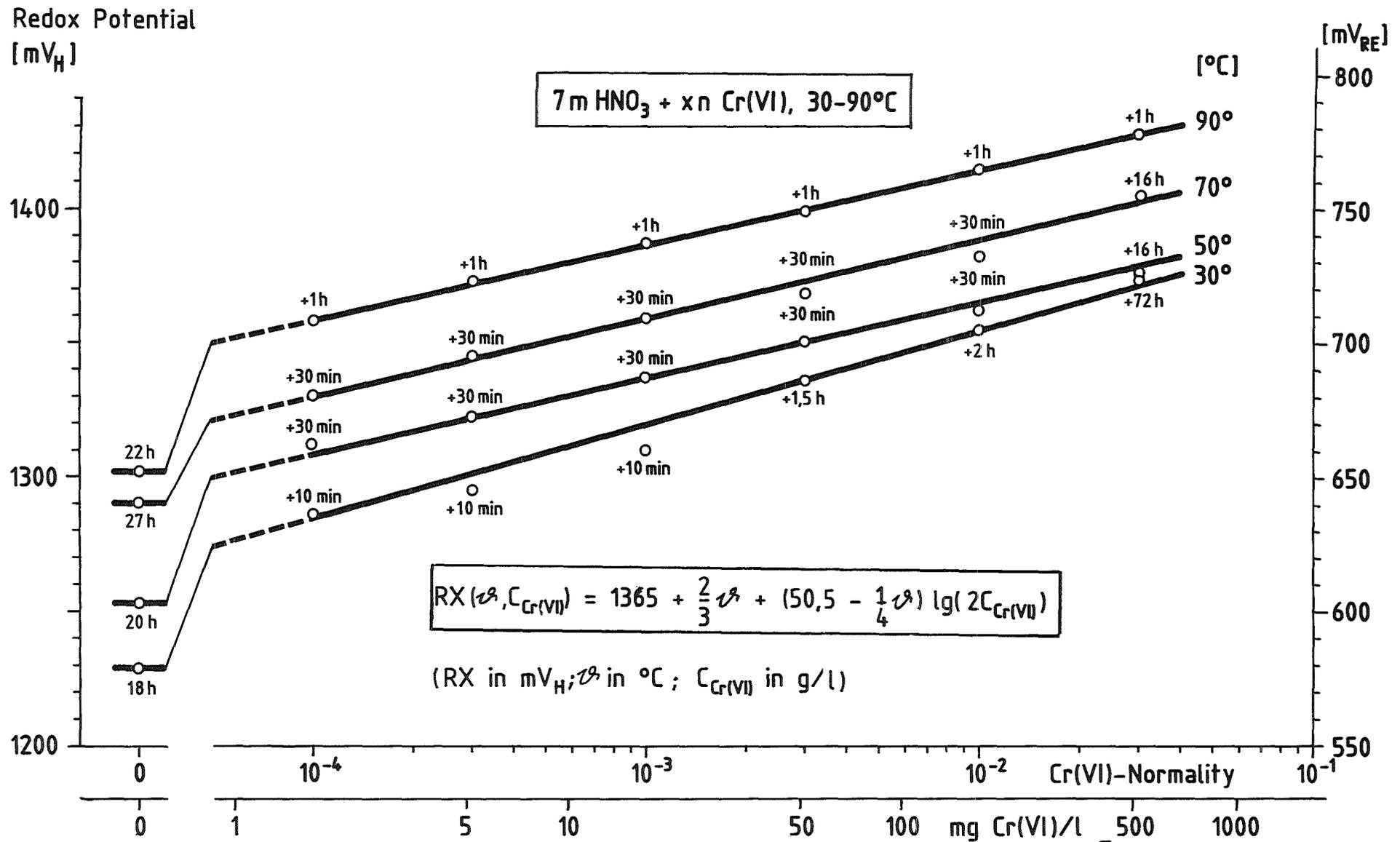


Fig. 6 Redox Potential of 36% HNO₃ (c(HNO₃) = 7 mol/l) as Function of Cr(VI) Content and Temperature (30-90°C)
Numbers indicating time of measurement

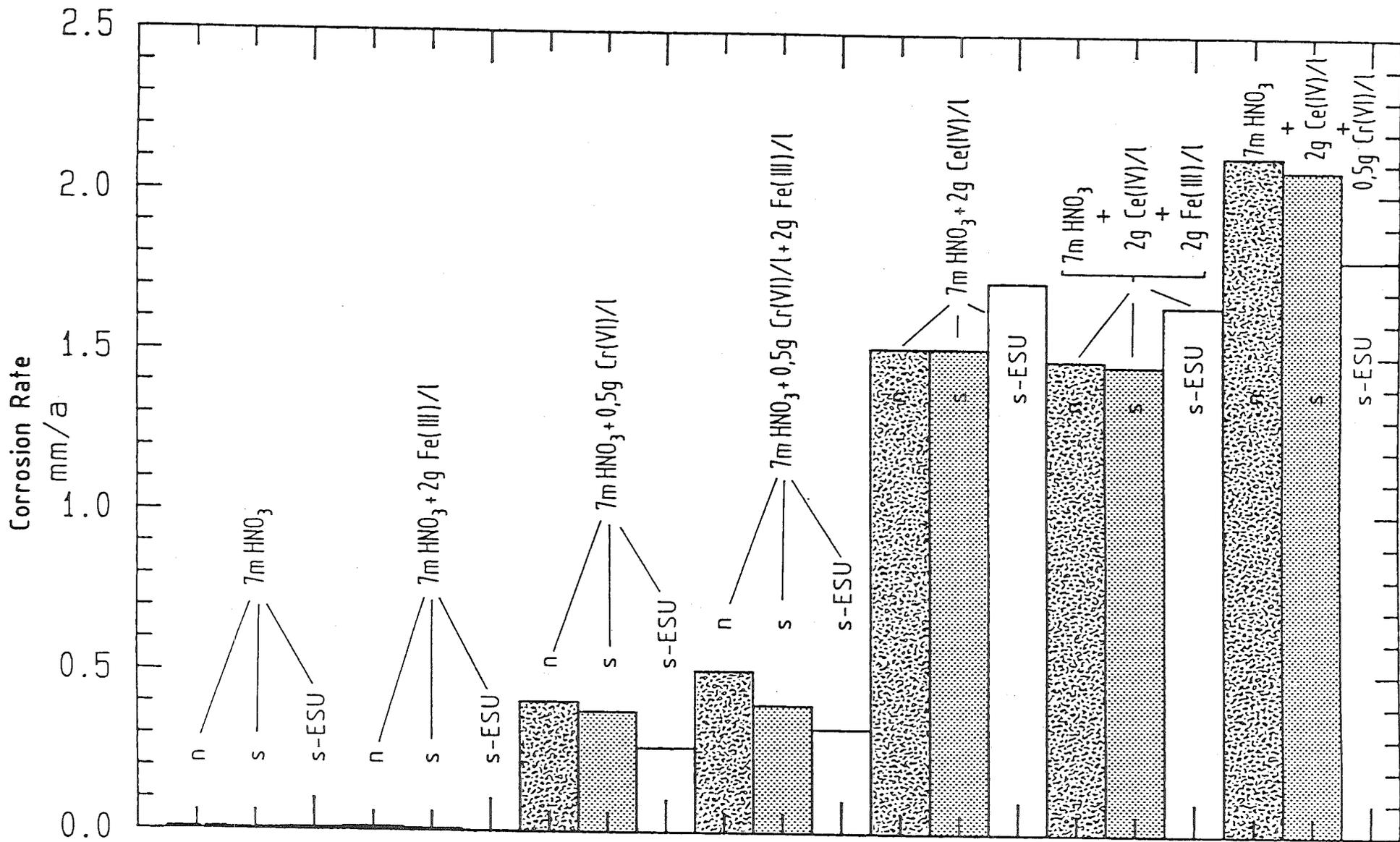
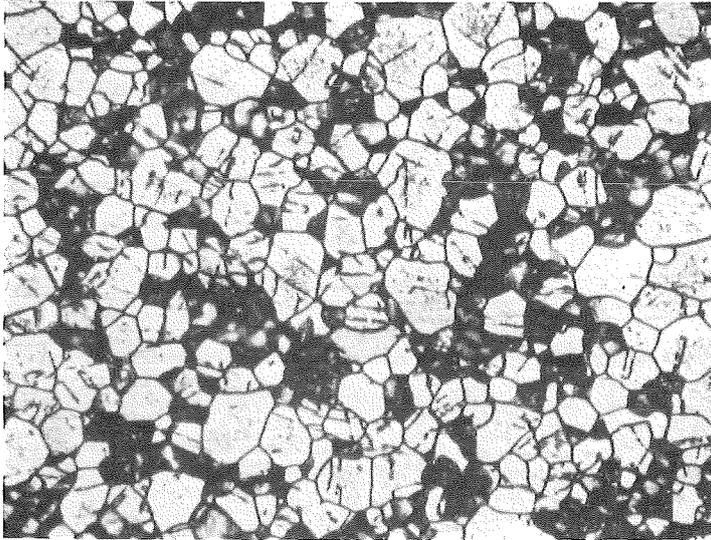
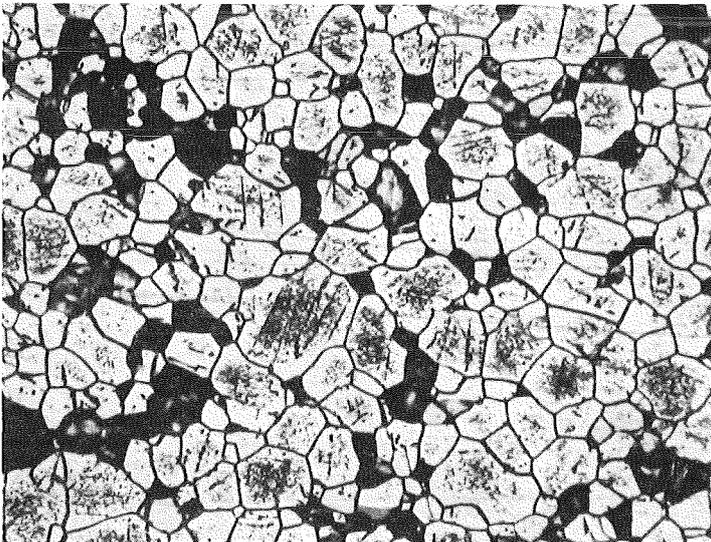


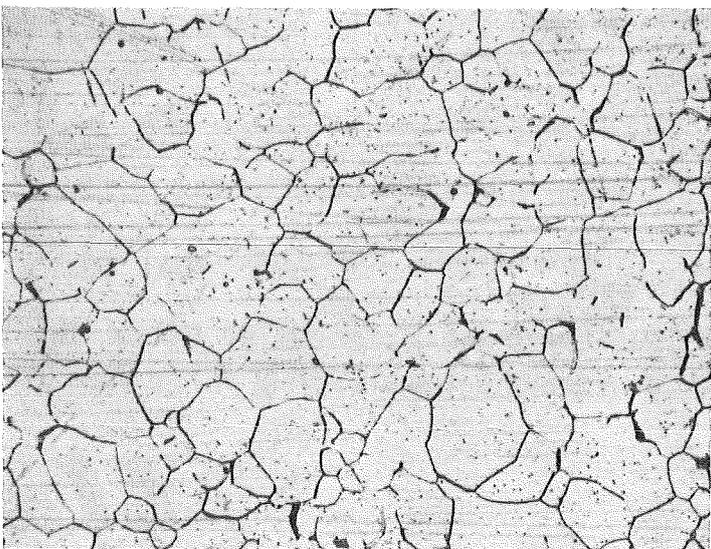
Fig. 7 Metal Loss by Corrosion at Free Corrosion Potential of Various Solution Annealed CrNi Steels
 DIN W.Nr. 1.4306 = AISI Type 304 L in 36% Nitric Acid ($c(\text{HNO}_3) = 7 \text{ mol/l}$) and 36% Nitric Acid Solutions
 Containing Fe(III)-, Cr(VI)- and Ce(IV)-Ion Additions (90°C, 24 h)



W.Nr. 1.4306 n



W.Nr. 1.4306 s



W.Nr. 1.4306 s (ESU)

— 100 μm

Fig. 8 Surface Micrographs of Different Solution Annealed CrNi Steels DIN W.Nr. 1.4306 = AISI Type 304L after Corrosion in 36% Nitric Acid ($c(\text{HNO}_3) = 7 \text{ mol/l}$) Containing 0,5g Cr(VI)/l, 90°C, 70 h

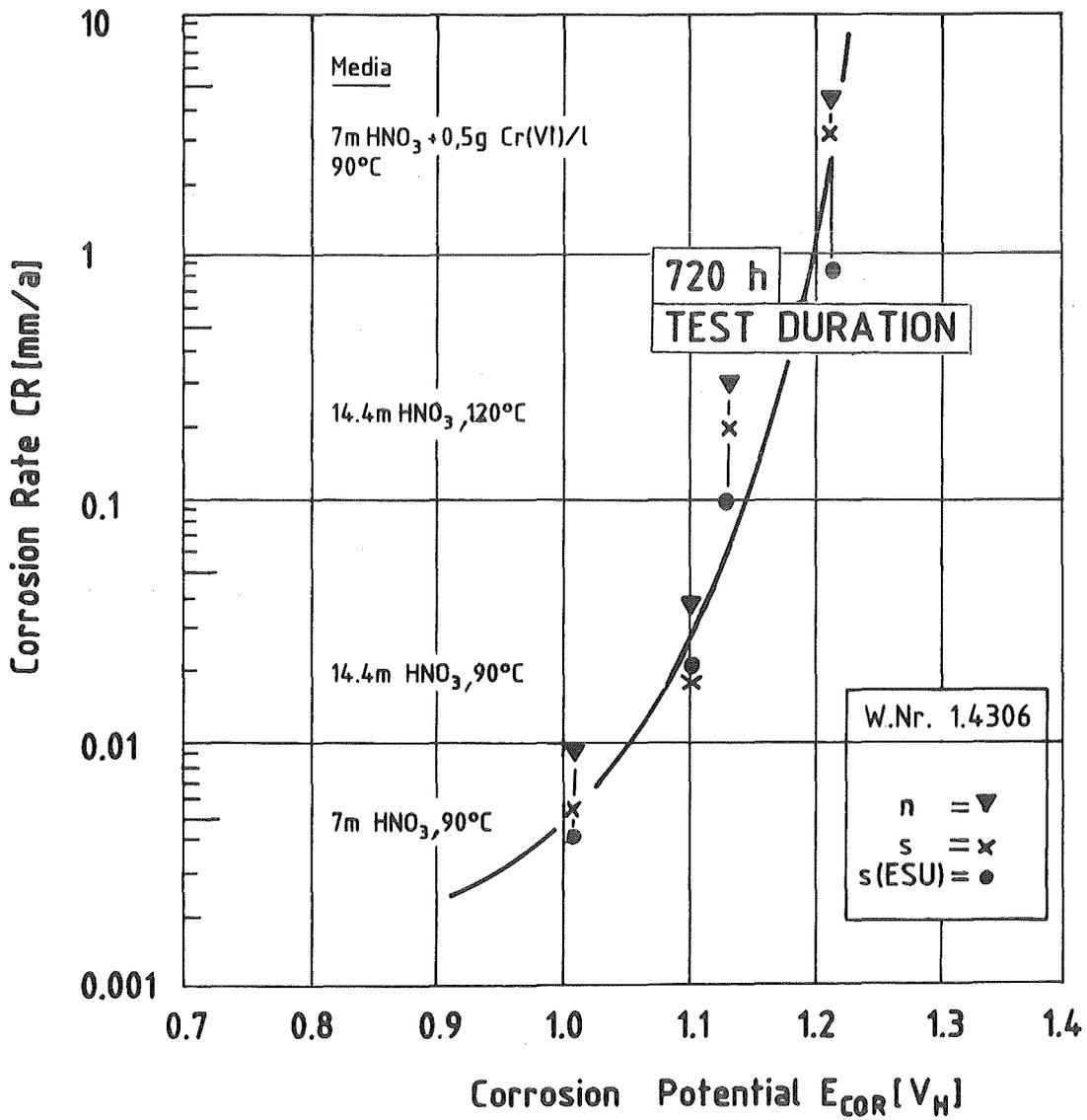


Fig. 9 Corrosion Rate versus Corrosion Potential of DIN W. Nr. 1.4306 = AISI Type 304L in Versions n,s,s(ESU) in Nitric Acid Media