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Dissolution amounts of nickel, chromium and iron from SUS 304, 316 and 444 stainless steels in sodium chloride solutions

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The release of nickel and chromium from stainless steels by sweat, is often responsible for allergic contact dermatitis. The amounts of metal released from stainless steels were in trace amounts, because corrosion resistance was excellent. However, measurement of dissolution amounts is difficult, and if these amounts are not known, the improvement and development of stainless steels with excellent resistance to NaCl solution is difficult. In this work, trace dissolution amounts from the main components of stainless steels which can cause an allergy were investigated. SUS 304, 316 and 444 stainless steels were used in this test. The test solutions used were 0.9 (isotonic sodium chloride solution), 1, 3, 5 and 10 wt% NaCl solutions. Nickel,chromium and iron ions in the test solutions were rapidly determined by stripping voltammetry. The detection limits of Ni(II), Cr(VI) and Fe(III) ions in 1 wt% NaCl solution were 1.0, 0.1 and 0.5 ng cm^{-3}, respectively, with standard deviations of five tests at 5 ng cm^{-3} Ni(II), Cr(VI) and Fe(III) ions, of 6.4%, 1.8% and 2.2%, respectively. Generally, the amounts of the metals dissolved increased in direct proportion to the immersion, in the range 30–60 days for nickel, 30–90 days for chromium and 30–120 days for iron. The dissolution amounts of nickel from SUS 304 and 316 stainless steels increased rapidly over 60 days, while that of chromium increased rapidly over 90 days, in isotonic sodium chloride solution. The ratio of the three dissolved metal ions was not consistent with the composition of the specimens. The ratio of dissolved nickel in SUS 304 and 316 stainless steels was larger than that in the specimen, and dissolved preferentially. The dissolution ratio of chromium and iron in SUS 444 stainless steel approximately agreed with the composition of the specimen.

1. Introduction

Metal allergy has often been discussed in recent newspapers and magazines. Typical metal ions involved are well-known: nickel and chromium ions. Metals from metal products which are in contact with the skin are dissolved in sweat. When these metal ions invade the skin, antibodies are generated by the lymph cells. The antibodies then react to the metal ions and eczema is produced on the skin [1]. Stainless steels are used for jewellery, wrist watches, joint-replacement parts, etc. The release of nickel and chromium from stainless steels, or nickel from pure nickel and nickel-plated metals is often responsible for allergic contact dermatitis, especially among women. The nickel content in stainless steel thus has been regulated in the stainless steels that contain nickel and chromium, which is used in the production of the wrist watches in Denmark and Germany. It is likely that other countries will also have to make adjustments. Corrosion and corrosion resistance in various kinds of stainless steels have been studied by using electrochemistry. However, the release of nickel and chromium from stainless steel is not well known.

We are of the opinion that contact with the skin and the concentration of salt in sweat are major factors affecting the dissolution. The test solution used isotonic sodium chloride solution (0.9 wt% NaCl) and 1–10 wt% NaCl aqueous solutions as test concentrations of isotonic NaCl solution. The amounts of nickel, chromium and iron dissolved from stainless steels in the test solutions were determined by the stripping voltammetry method.

2. Experimental procedure

2.1. Samples and test solutions

SUS 304 is widely used because its sensitivity to stress corrosion cracking is excellent for chloride ions. SUS

316, which has a corrosion resistance better than that of SUS 304, is also used. SUS 444 has received attention as a potential material for use in medicine, because it does not contain nickel, and its corrosion resistance is excellent in stainless steels. The compositions of the JIS standard [2] are shown in Table I.

The test solutions used were 0.9 (isotonic sodium chloride solution), 1, 3, 5, 10 wt % NaCl aqueous solutions.

2.2. Procedure

The exposed area of the test specimens used was 2 cm × 2 cm (thickness 0.5 mm). One side of each specimen was sealed with a teflon adhesive tape. The exposed plane was polished with emery paper (2000 grade) before testing. The specimen was placed in 100 cm^3 test solution in Erlenmeyer flask with plug, and the test solutions were maintained at 310 K. After a set period, the specimen was removed, and the metal concentration in the solution was determined by stripping voltammetry.

A Trace Lab 50 system voltammetric analyser (Radiometer) was used in connection with an MDE 150 hanging mercury drop electrode. Anodic stripping voltammetry in the differential-pulse mode was used. The determination conditions were controlled by a personal computer (NEC, PC-9821), and metal ions were determined from the voltage–current curves.

2.2.1. Determination of Ni(II) ions [3]

Using a pipette, 1–5 cm^3 test solution was transferred into a 10 cm^3 measuring flask. The pH was adjusted to pH 9 by the addition of 2 cm^3 1 mol dm^{-3} NH_4OH–1 mol dm^{-3} NH_4Cl buffer solution. The 2 cm^3 0.0535 mol dm^{-3} dimethylglyoxime ethanol solution was added and the contents were made up to 10 cm^3 with distilled water. This solution transferred into the measurement cell, and purged with nitrogen gas for 3 min. The pre-concentration potential (− 700 mV versus Ag.AgCl) was applied to a fresh mercury drop while the solution was being stirred for 3 min. Following the pre-concentration period, the stirring was stopped and after 10 s, the voltammogram was recorded by applying a negative-going differential pulse scan (with a scan rate of 50 mV s^{-1} and an amplitude of 50 mV). The scan was terminated at − 1300 mV versus Ag.AgCl.

TABLE I Chemical compositions (wt %) of the stainless steels

Composition	SUS 304	SUS 316	SUS 444
C	$\leqslant 0.08$	$\leqslant 0.08$	$\leqslant 0.025$
Si	$\leqslant 1.00$	$\leqslant 1.00$	$\leqslant 1.00$
Mn	$\leqslant 2.00$	$\leqslant 2.00$	$\leqslant 1.00$
P	$\leqslant 0.045$	$\leqslant 0.045$	$\leqslant 0.04$
S	$\leqslant 0.03$	$\leqslant 0.03$	$\leqslant 0.03$
Ni	8–10.5	10–14	–
Cr	18–20	16–18	17–20
Mo	–	2–3	1.75–2.5
N	–	–	$\leqslant 0.025$

2.2.2. Determination of Cr(VI) ions [4]

Again, 1–5 cm^3 test solution was transferred by pipette into a 10 cm^3 measuring flask. The pH was adjusted to pH 6 by addition of 2 cm^3 0.0315 mol dm^{-3} piperazin-N,N′-*bis* (2-ethane sulphonic acid) disodium (PIPES) solution and sodium tartaric buffer solution. Then 2 cm^3 *N*′-nitroso-*N*-phenylhydroxylamine ammonium (cupferron) solution was added and the volume made up to 10 cm^3 with distilled water. This solution was transferred into the measurement cell, and purged with nitrogen gas for 5 min. The pre-concentration potential (− 625 mV versus Ag.AgCl) was applied to a fresh mercury drop while the solution was stirred for 1 min. Following the pre-concentration period, stirring was stopped and after 10 s, the voltammogram was recorded by applying a negative-going differential pulse scan (with a scan rate of 50 mV s^{-1} and an amplitude of 50 mV). The scan was terminated at − 1250 mV versus Ag.AgCl.

2.2.3. Determination of iron (III) ions [5]

After transferring 1–5 cm^3 test solution by pipette into a 10 cm^3 measuring flask, the pH was adjusted to pH 7 by addition of 2 cm^3 9×10^{-3} mol dm^{-3} PIPES and 2-[4-(2-Hydroxyethyl)-1-piperazinyl]-ethane sulphonic acid and ammonia buffer solution. Then 2 cm^3 2×10^{-5} mol dm^{-3} α-nitroso-β-naphtol solution was added and the volume made up to 10 cm^3 with distilled water. This solution transferred into the measurement cell, and purged with nitrogen gas for 5 min. The pre-concentration potential (− 200 mV versus Ag.AgCl) was applied to a fresh mercury drop while the solution was stirred for 1 min. Following the pre-concentration period, stirring was stopped and after 10 s the voltammogram was recorded by applying a negative-going differential pulse scan (with a scan rate of 50 mV s^{-1} and an amplitude of 50 mV). The scan was terminated at − 600 mV versus Ag.AgCl.

3. Results and discussion

The detection limits in 1 wt % NaCl solution were 1.0 ng cm^{-3} (Ni(II) ion), 0.10 ng cm^{-3} (Cr(VI) ion) and 0.50 ng cm^{-3} (Fe(III) ion) in the above determination methods, respectively. The relative standard deviations of five measurements using 5 ng cm^{-3} metal ions were 6.4% (Ni(II) ion), 1.8% (Cr(VI) ion) and 2.2% (Fe(III) ion).

The orders of the dissolution amounts of nickel, chromium and iron from stainless steels in NaCl solutions are shown in Table II. The dissolution amounts of nickel from SUS 304 and 316 in isotopic NaCl solution are shown in Fig. 1. Prior to 60 days immersion, the dissolution amounts of nickel from SUS 316 in which the nickel content was larger in comparison with that of 304 were smaller. After 90 days immersion, the dissolution amounts of both stainless steels were the same. Sweat becomes more concentrated on the skin in the summer season and in hot places as water evaporates. Therefore, dissolution amounts

TABLE II Orders of dissolution amounts of nickel, chromium and iron from stainless steels in NaCl solutions

Immersion (days)	SUS 304			SUS 316			SUS 444	
	Ni	Cr	Fe	Ni	Cr	Fe	Cr	Fe
30	10 > 3 > 1 = 0.9 > 5	10 = 5 = 3 = 1 = 0.9	3 > 5 > 10 > 1 > 0.9	10 = 5 = 3 = 1 = 0.9	10 > 1 = 5 = 3 = 0.9	10 > 5 > 3 > 0.9 > 1	10 > 0.9 > 1 = 3 > 5	10 = 5 = 3 = 1 = 0.9
60	10 > 3 > 0.9 > 5 > 1	10 > 0.9 > 3 = 1 > 5	5 > 3 > 10 > 0.9 > 1	10 > 3 > 0.9 > 5 > 1	10 > 0.9 = 5 = 3 = 1	10 > 3 > 5 > 0.9 > 1	10 > 3 > 1 = 0.9 > 5	10 > 3 > 5 > 0.9 > 1
90	10 > 5 > 3 > 0.9 > 1	10 > 0.9 > 1 > 3 > 5	10 > 5 > 3 > 0.9 > 1	10 > 3 > 0.9 > 5 > 1	10 > 1 > 0.9 > 3 > 5	10 > 5 > 3 > 0.9 > 1	10 > 0.9 > 3 > 1 > 5	10 > 5 > 3 > 0.9 > 1

were measured in 1, 3, 5 and 10 wt % NaCl solutions. The amounts of nickel dissolved from SUS 304 and 316 stainless steels in 1, 3, 5 and 10 wt % NaCl solutions are shown in Figs 2 and 3. The dissolution amounts of nickel from both stainless steels increased with the number of immersion days, and there was a sharp increase after 60 days. The amounts of nickel dissolved were about ten times those of chromium and iron, as described below.

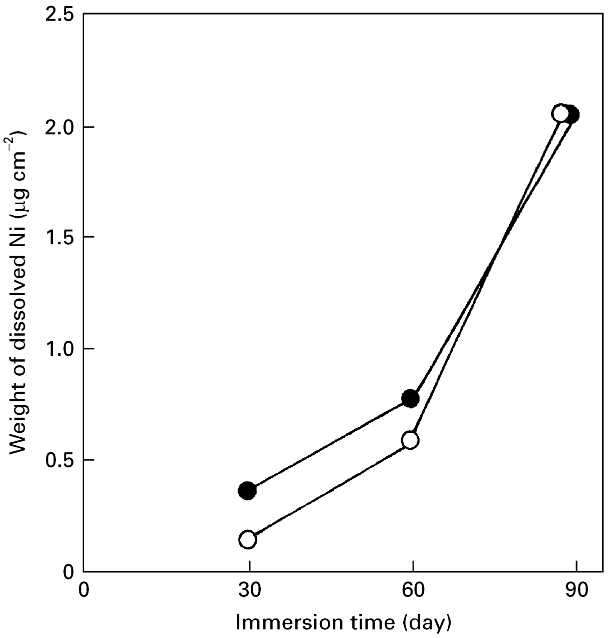

Figure 1 Effect of immersion time on the weight of dissolved nickel for (●) SUS 304 and (○) 316 stainless steels in a isotonic sodium chloride solution.

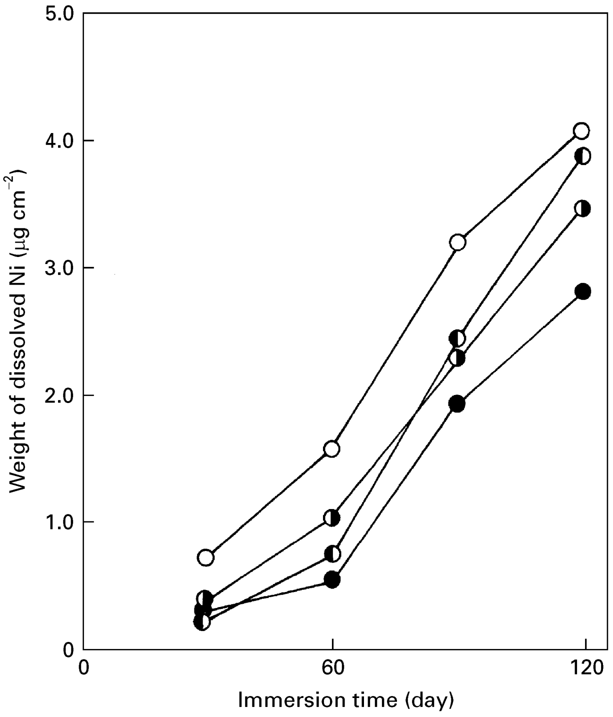

Figure 2 Effect of immersion time on the weight of dissolved nickel for SUS 304 stainless steel in sodium chloride solutions: (●) 1 wt %, (◑) 3 wt %, (◐) 5 wt %, (○) 10 wt %.

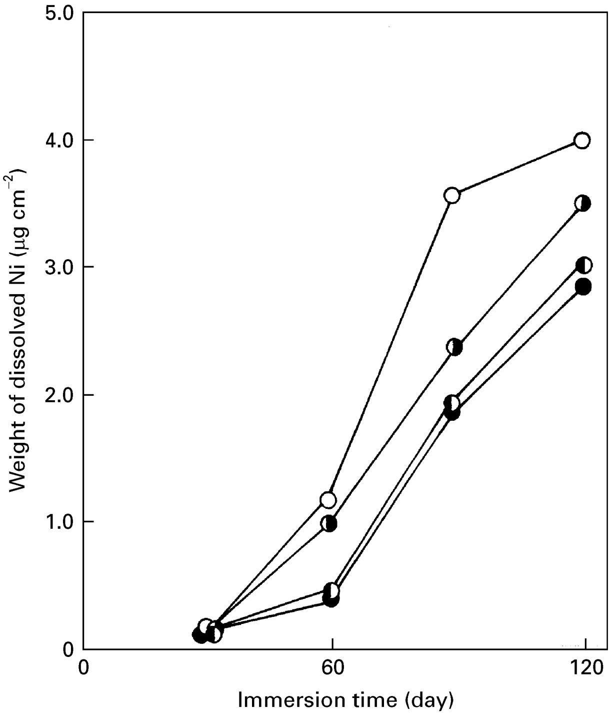

Figure 3 Effect of immersion times on the weight of dissolved nickel for SUS 316 stainless steel in sodium chloride solutions. For key, see Fig. 2.

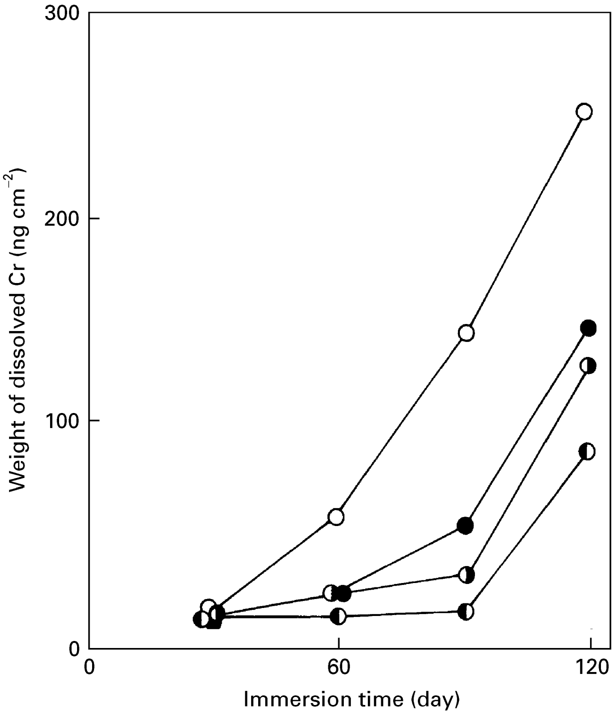

Figure 5 Effect of immersion time on the weight of dissolved chromium for SUS 304 stainless steel in sodium chloride solutions. For key, see Fig. 2.

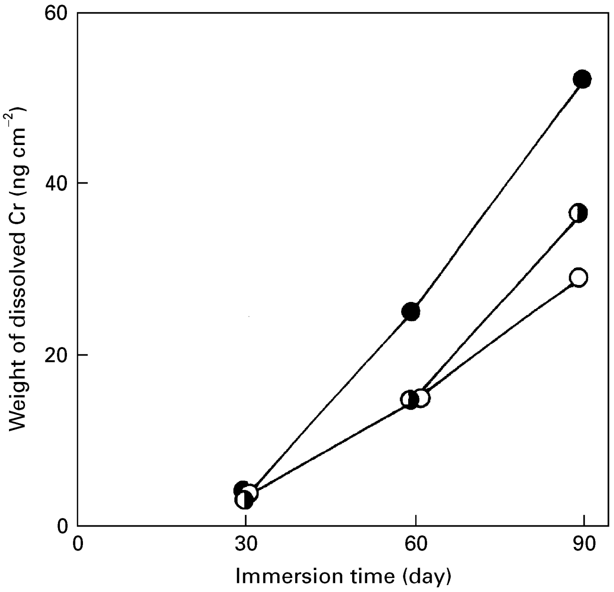

Figure 4 Effect of immersion time on the weight of dissolved chromium for SUS (●) 304, (○) 316 and (◑) 444 stainless steels in a isotonic sodium chloride solution.

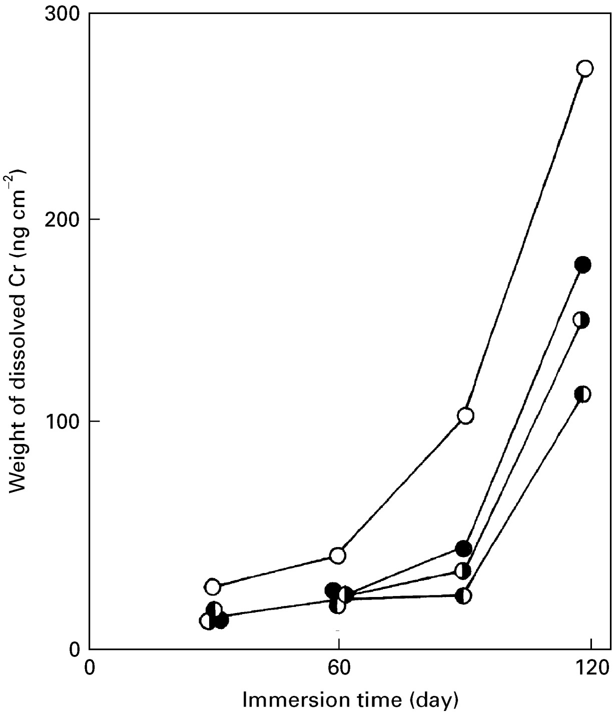

Figure 6 Effect of immersion time on the weight of dissolved chromium for SUS 316 stainless steel in sodium chloride solutions. For key, see Fig. 2.

The dissolved chromium ion was hexa-valent and it was concluded that the dissolved Cr^{3+} and Cr^{3+} ions were oxidized by oxygen dissolved in the test solution because the immersion time was long. The dissolution amounts of chromium from SUS 304, 316 and 444 stainless steels in isotopic NaCl solutions are shown in Fig. 4. The orders of the dissolution amounts of chromium were SUS 304 = 316 = 444 at 30 days immersion, 304 > 316 = 444 at 60 days immersion, and 304 > 444 > 316 stainless steels at 90 days immersion. The amounts of chromium dissolved from SUS 304 and 316 stainless steels increased in proportion to the number of immersion days. Figs 5–7 show the amounts of chromium dissolved from SUS 304, 316 and 444 stainless steels in 1, 3, 5 and 10 wt % NaCl aqueous solutions. In the case of SUS 444, dissolution amounts in 1–5 wt % NaCl solutions increased in proportion to the immersion time in the

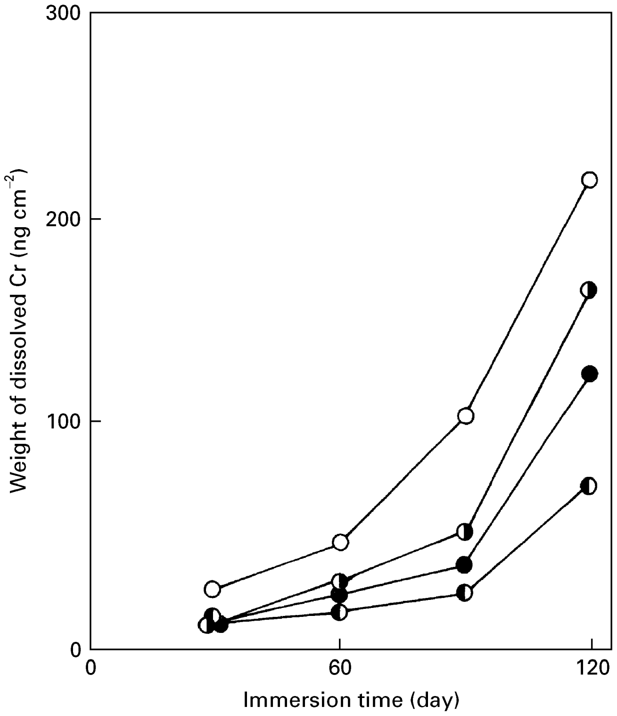

Figure 7 Effect of immersion time on the weight of dissolved chromium for SUS 444 stainless steel in sodium chloride solutions. For key, see Fig. 2.

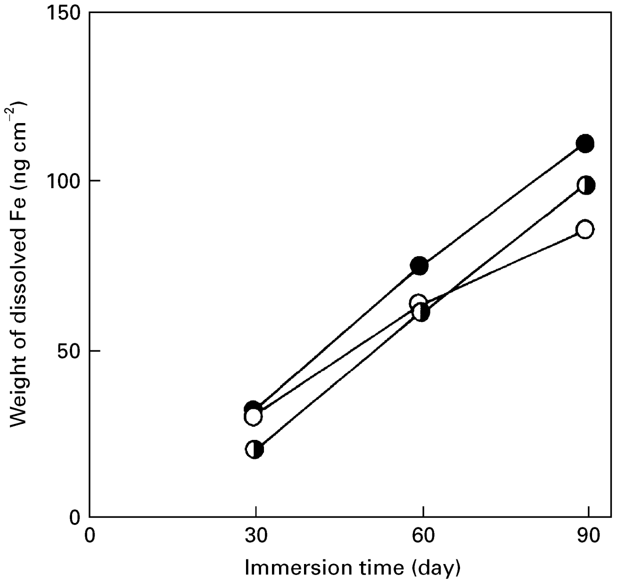

Figure 8 Effect of immersion time on the weight of dissolved iron for SUS (●) 304, (○) 316 and (◑) 444 stainless steels in a isotonic sodium chloride solution.

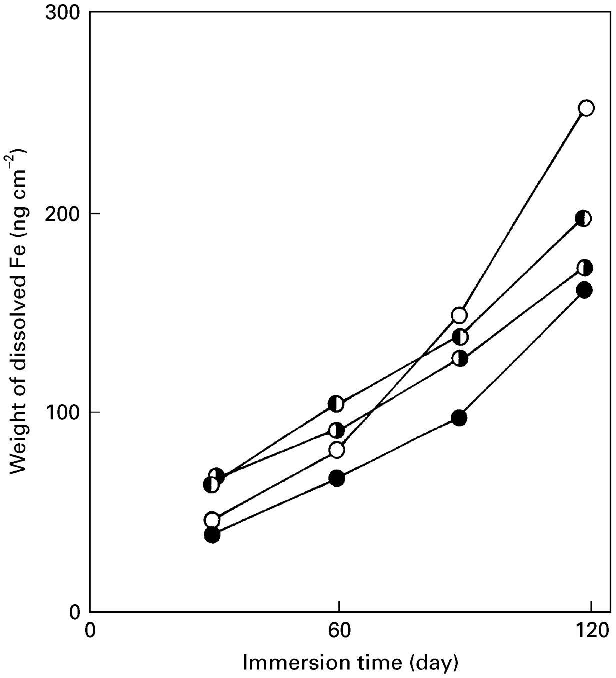

Figure 9 Effect of immersion time on the weight of dissolved iron for SUS 304 stainless steel in sodium chloride solutions. For key, see Fig. 2.

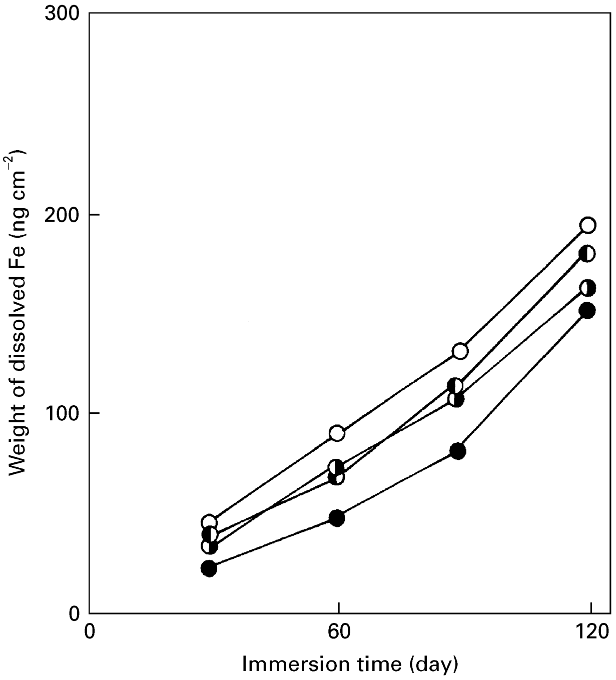

Figure 10 Effect of immersion time on the weight of dissolved chromium for SUS 316 stainless steel in sodium chloride solutions. For key see Fig. 2.

range 30–90 days. After 90 days, the dissolution amounts increased sharply.

Fig. 8 shows the dissolution amounts of iron from SUS 304, 316 and 444 stainless steel in isotopic NaCl solution. The orders of the dissolution amounts of iron were SUS 304 = 316 > 444 at 30 days immersion, 304 > 316 = 444 at 60 days immersion and 304 > 444 > 316 at 90 days immersion. The amounts of iron dissolved from either stainless steel was proportional to the immersion time. Figs 9–11 show the dissolution amounts of iron from SUS 304, 316 and 444 stainless steels in 1, 3, 5 and 10 wt % NaCl aqueous solutions. For SUS 304 stainless steel, the amounts dissolved in 1–5 wt % NaCl solutions increased in proportion to the immersion time in the range 30–90 days. In the case of SUS 316 stainless steel, the dissolution amounts showed a similar tendency in the range from 30–90 days. For SUS 444 stainless steel, the dissolution amounts showed similar tendency in 1, 3, 5 and 10 wt % NaCl solution in the range from

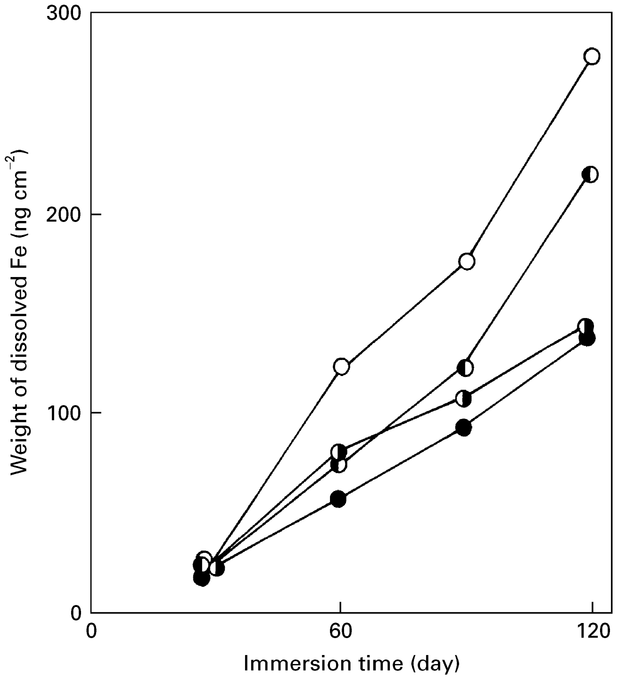

Figure 11 Effect of immersion time on the weight of dissolved chromium for SUS 444 stainless steel in sodium chloride solutions. For key see Fig. 2.

TABLE III Ratio of dissolution amounts (wt %) in isotonic sodium chloride solution

Immersion days	SUS 304			SUS 316			SUS 444	
	Ni	Cr	Fe	Ni	Cr	Fe	Cr	Fe
30	86.1	1.8	12.1	76.8	2.7	20.5	13.8	86.2
60	87.9	3.6	8.5	88.0	2.3	9.7	19.5	80.5
90	92.7	2.3	5.0	94.7	1.4	3.9	27.3	72.7

30–120 days.The amounts dissolved in 1 wt % NaCl solutions increased in proportion to the immersion time in the range from 30–120 days.

The ratio of metals dissolved from stainless steels in isotopic NaCl solution is shown in Table III. At the present time, nickel, chromium and iron were dissolved; all other components were neglected. The amounts of each metal dissolved were not the same proportion to the substrate composition ratio. In the case of SUS 304 and 316 stainless steels, the ratios of chromium and iron are larger than that of nickel, the dissolution amounts being decreased compared with that of nickel. Nickel was dissolved preferentially after 90 days immersion. The dissolution proportions of nickel from SUS 304 and 316 increased and that of iron was decreased with increasing immersion time, whereas that of chromium from SUS 316 increased with increasing immersion time. The dissolution proportion of chromium from SUS 444 increased and that of iron decreased with increasing immersion time, but for 316 stainless steel, the dissolution proportion of chromium decreased with increased immersion time. The proportion was smaller after 30 days immersion and larger after 90 days immersion than the substrate composition ratio. It was considered that the dissolved metals were from the passivation film on the substrate.

4. Conclusion

The dissolution amounts of nickel, chromium and iron from SUS 304, 316 and 444 in isotopic and 1–10 wt % NaCl solutions could be determined by stripping voltammetry. In general, the dissolution amounts of the metals increased to proportion after 30–60 days (Ni), 30–90 days (Cr), and 30–120 days (Fe) immersion. The dissolution ratios of nickel in SUS 304 and 316 were larger compared with the substrate composition ratio, and those of chromium were smaller. The dissolution amounts of chromium and iron from SUS 444 stainless steel showed a similar tendency. The dissolved amounts of each metal were not in the same proportion as the substrate composition ratio. It was considered that the dissolved metals were from the passivation film on the substrate.

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