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FROM THE ORTHOP. CLINIC, UNIVERSITY OF LUND
(CHIEF PROF. G. WIBERG) *AND THE DEPARTMENT OF MEDICAL PHYSICS* (HEAD ASS. PROF. P. PETERSEN) *OF THE INSTITUTE OF PHYSIOLOGY, LUND* (CHIEF PROF. G. KAHLSON)

EXPERIMENTAL INVESTIGATION OF CORROSION OF STAINLESS STEELS USED IN BONE SURGERY

BY

HANS EMNÉUS

EJNAR MUNKSGAARD
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INTRODUCTION

A stainless steel may be "noble" enough for some purposes in certain chemical environments. On introduction of a new component to the material or the environment, however, the relative nobility of the metal may prove insufficient, and the steel can then no longer be regarded as stainless for its purpose.

An attack of various corroding agents on stainless steel may result in:

1. General surface corrosion
2. Pitting
3. Intergranular corrosion
4. Crevice corrosion
5. Contact or galvanic corrosion
6. Stress corrosion

As a rule, the chromium-nickel-steels of 18-8-type do not undergo general corrosion in chloride solution at pH 5—8. Intergranular corrosion can only occur on material, which has been sensitized at 500—800° C. There is always a risk of stress corrosion in the presence of both chlorides and oxygen, provided that the stainless steel is in a state of tension. At such a low temperature as 40° C and at such a concentration of NaCl as in body fluids the risk is probably negligible. The other condition, tension, is present, for example, in cerclage (residual tension), where the tension is of sufficient order. Since the first condition for stress corrosion — high chloride concentration and high temperature — is not present, this type of corrosion can be excluded in surgical practice (BERG — personal comm.).

As far as *surgical appliances* are concerned, three types of corrosion must be considered: pitting, crevice corrosion and galvanic corrosion. It should be emphasized once more that surgical cold working, e. g. twisting and cutting of wires (cerclage) of chromium-nickel-steel and chromium-nickel-molybdenum-steel is a causal factor of pitting and crevice corrosion. (See EMNÉUS 1960.)

ENVIRONMENTS

The environments of a stainless steel appliance are important. Highly concentrated solution of electrolytes favour corrosion. Chlorides are, broadly speaking, the strongest corrosives of these. Other anions (e. g. ureates, lactates, sulphates, phosphates, oxalates, gluconates and fatty acid salts) occur in such low concentrations in living tissue and have such a relatively slight accelerating effect on corrosion, that their effect is negligible compared with that of the aggressive chlorides (FINK & SMATKO 1948). In damaged biological tissue the pH probably varies relatively much. The pH of recently damaged tissue may be 5.3—5.6, after which it rises to 7.35 during healing (FERGUSON 1959).

UHLIG (1948) has shown pitting to be most pronounced between pH 5 and pH 9 in chloride solutions. There is little difference in the corrosive effect of a chloride solution at pH 5 and pH 7 (see diagram 1). This is in line with the investigations of FINK & SMATKO (1948). They found no difference between the destructive effects of physiological saline, ordinary serum, serum acidified to pH 5—pH 5.5 with the KH_2PO_4, serum containing sulphonamide and serum inoculated with staphylococcus aureus.[1]

Stainless steels tend to become passive, *i. e.* to be covered with a film of chromium oxides and entrapped oxygen, in the presence of oxygen, *e. g.* in oxygen-containing solutions. Such a film offers considerable protection against most corrosive

[1] Observe that phosphate and amines are inhibitors of pitting under certain conditions (remark of the author).

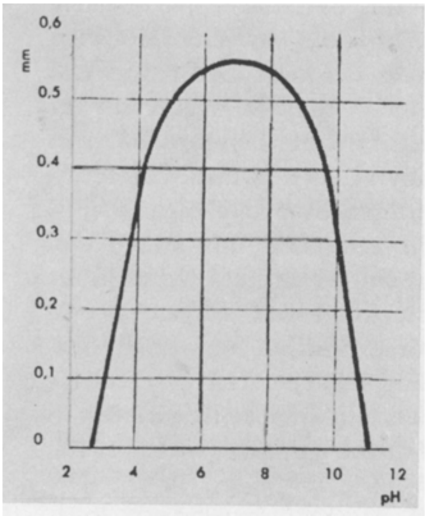

Diagram 1.

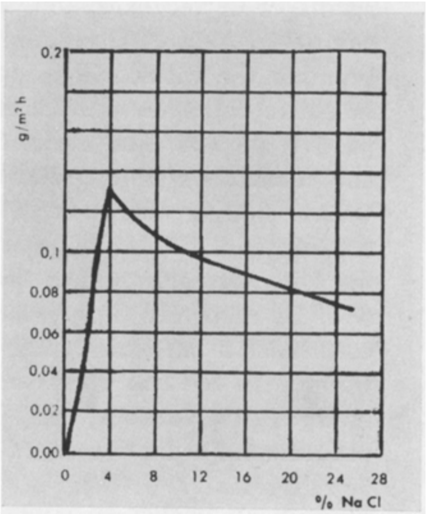

Diagram 2.

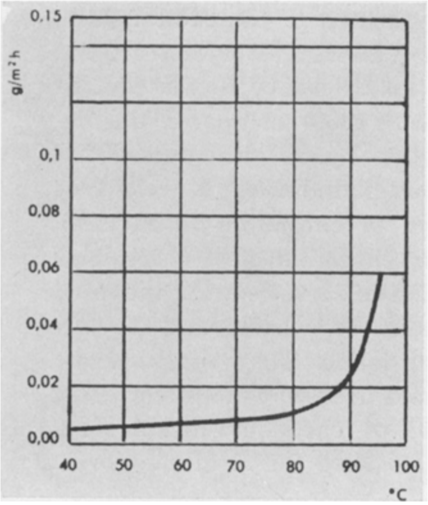

Diagram 3.

Diagram 1. Influence of pH on the depth of pitting in 18-8-steel in NaCl.

Uhlig 1948

Diagram 2. Influence of concentration of NaCl on pitting in 18-8-steel.

Uhlig 1948

Diagram 3. Influence of temperature on pitting in 18-8-steel in 1 % NaCl.

Uhlig 1948

agents, with the exception, however, of halides, particularly chlorides. If a passive film is attacked by chlorides, for example, the attack will be punctate, the individual points will be active or anodic and be extremely small in relation to the passive surface. The current density will therefore be high and corrosion will progress rapidly at such points. The result will be pitting corrosion. The presence of oxidising agents, *e. g.* oxygen, in the solution will accelerate this attack still more by depolarization of the cathode. Therefore living tissue with its relatively high chloride content and oxygen content constitutes a particularly stimulating medium for pitting. Sea-water with NaCl in a concentration of 3 per cent is certainly more aggressive than living tissue, and the aggressiveness is proportional to the concentration of the chloride (UHLIG 1948). See diagram 2.

PREVIOUS INVESTIGATIONS

Studies of previous surgical alloys and elements used during the 1920ies and 1930ies in the manufacture of surgical appliances have been surveyed by HENSCHEN & GERLACH (1934), HJÖRDIS JÖRGENSEN (1941) and VENABLE & STUCK (1947). These surveys are, however, of less relevance to the present investigation. JONES & LIEBERMAN (1936) compared the behaviour of chromium-vanadium steel and chromium-nickel steel in physiological saline. They found loss of weight of chromium-vanadium steel but not of chromium-nickel steel. VENABLE & STUCK (1947) compared chromium steel, chromium-nickel steel (18-8) and vitallium. The samples were mounted in the form of plates with screws in screw-holes, and the corrosive medium was physiological saline. They analyzed the electrolytes after 3 weeks and found them to contain corrosion products of chromium steel and of chromium-nickel steel, respectively. No corrosion products were found in the corrosive medium around vitallium.

FINK & SMATKO (1948) compared the losses in weight in physiological saline and serum of chromium-nickel steel, chromium-nickel-molybdenum steel and vitallium and found the loss of weight to the smallest for chromium-nickel steel (AISI 302).[1]

CLARK & HICKMAN (1953) studied the corrosion tendency of conventional surgical alloys by measuring the so-called back-EMF. From the back-EMF it is, however, difficult to obtain detailed information about the behaviour of the alloys after they have been cold worked, or about the weaknesses they may have when used for special purposes. BOWDEN, WILLIAMSSON & LAING (1955) studied changes occurring during application of an appliance and found a transfer of substance from the tool (screw-driver) to the screw-head. They also mentioned the deformation of the screw-head. But they did not investigate these two effects of "cold working" separately. EMNÉUS & PETERSEN (1958) studied the effect of cold working of annealed 18-8 wire, as judged by measurements of the potentials.

A fairly thorough search of the literature failed to reveal any investigation in which the corrosive conditions were studied experimentally *in vitro* with respect to the entire situation prevailing on insertion of different types of appliances (screw, plates and wires).

VENABLE & STUCK (1947) as well as FINK & SMATKO (1948) were unable to ascertain under what conditions and where corrosion occurred. In addition, it is difficult to accept the results of FINK & SMATKO, who found corrosion of vitallium to be more common than that of 18-8 steels.

Experimental investigations have been made of the reaction of the tissue around various metal implants, generally around single implants. (VENABLE & STUCK 1937, HJ. JÖRGENSEN

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[1] Sometimes the passive surface is intact despite strongly corrosive environments. This may be due to the surface treatment of the material, to chance, to variation in the composition of the material, and to the mechanical stress being only relatively slight. Under such favourable circumstances AISI 302 may be resistant even under conditions in which vitallium, for example, is attacked. But it should be emphasized that this is very rare.

1941, BOTHE & DAVENPORT 1940, LEVENTHAL 1951, VOIGT & SEYFART 1955 and CLARK & HICKMAN 1958) and around appliances, such as plate and screws used in osteosynthesis (HUDACK 1940, KEY 1941 and 1946, BLUNT, HUDACK & MURRAY 1952 and JERGESEN 1955) or around metals worked in some other way (LAING *et al.* 1955 and 1958 and EMNÉUS & STENRAM 1960). The investigations suggest that corrosion is liable to occur at the points of contact between the same or different kinds of metals (possibly crevice or galvanic corrosion)[1] (BLUNT, HARDOCK, MURRAY 1952, JERGESEN 1955 and EMNÉUS & STENRAM 1960). In addition, the site at which the metal has been surgically cold worked also favours corrosion (LAING *et al.* 1958 and EMNÉUS & PETERSEN 1958).

There is every reason to consider the corrosion problem mainly from a biological standpoint. In the choice of material for technical constructions to be used in salt water the manufacturer can often select a material which is not fully resistant and which can be protected by means of cathodic protection, *i. e.* making the metal a cathode in a D. C. circuit. The cathodic material is then not attacked. This is in principle what occurs when iron is covered with or connected to zinc. Zinc is less noble than iron, and therefore it becomes the anode and the iron the cathode. Zinc-plated surfaces are therefore not attacked until the zinc has been consumed. In technical constructions a continuous supply of metal ions from the construction to the environment is, as a rule, less important as long as the attack is not punctate or sufficient to jeopardize the strength of the construction.

Technical problems arising from exposure of a construction to salt water can be solved by using high alloyed Cr-Ni-Mo-steel and by giving the construction a shape and surface tending to minimize the effect of corrosion. This is, however, only sometimes possible in the design of surgical appliances.

When the surgeon has inserted the nails and/or applied the cerclage wires or plates with screws, it is not possible to treat

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[1] Remark of the author.

the surface of the inserted construction, which must therefore remain unchanged in the corrosive environments. Neither can he arrange any cathodic protection. *Nor can he tolerate resolution of more than minute amounts of metal ions because of their irritating action.*

PERSONAL INVESTIGATION

Methods and Material

PETERSEN & EMNÉUS (1960) showed that their modification of the ferroxyl test is particularly suitable for qualitative studies of corrosion of surgical appliances.[1] PIER & SCHWENK (1960) studied pitting on 18-8-steel with the ferroxyl test. EMNÉUS (1960) inserted metal implants into chickens. Three months later the implants were removed and studied for corrosion by the ferroxyl test. He found fair agreement between the amount of iron pigment in the tissue and the results of subsequent ferroxyl test of the steel implants. He also found that the ferroxyl test placed higher demands on the metal than biological tests. In addition EMNÉUS & PETERSEN showed that the ferroxyl test can demonstrate corrosion, even of cobalt and nickel alloys. EMNÉUS (1960) compared the reaction of the tissue, as demonstrated by an accumulation of metal pigments, with the ferroxyl test of cobalt alloys and found some agreement, though the cobalt alloys appeared to be resistant to the otherwise provocative effect of ferroxyl test.

In order to check to what extent the result of the ferroxyl test varies with the salt solution (concentration of NaCl) to which the test objects were exposed, the following experiments were performed.

0.9 mm annealed 18-8 wire (832 M) of the type used for cerclage was cut into 600 pieces about 1 cm long. The cutting process, which is a type of cold working, deforms the ends of these 1 cm long pieces. The ends are then liable to undergo

[1] All experiments were begun at 40° C and proceeded at room temperature, note diagram 3.

corrosion because the passive surface layer is destroyed or damaged there. There is hardly any transfer of the metal from the pliers to the wire, though metal from the wire may be transferred to the pliers. The 600 pieces of wire were divided into 6 groups of 100 each and deposited in three concentrations of NaCl and in 2 concentrations of indicators ($K_3(Fe\,CN)_6$) 2 per cent and 0.2 per cent respectively — Table 1.

TABLE 1.

Concentration of NaCl	Concentration of $KFeCN_6$	Cut ends with indication of corrosion
0,45 %	0,2 %	92/200
0,90 %	0,2 %	99/200
3,0 %	0,2 %	109/200
0,45 %	2,0 %	120/200
0,90 %	2,0 %	127/200
3,0 %	2,0 %	150/200

It is clear from the table that the tendency to corrosion increased with increasing concentration of the NaCl from 0.45 % up to 3 per cent. It was decided to use 0.9 per cent NaCl.

Comparative tests were made with 0.9 % NaCl solution and human plasma and dog plasma. The effect of plasma is more difficult to judge owing to deposition of protein and fat on the wire specimens, but despite this it was obvious that the tendency to corrosion was greater in 0.9 % NaCl solution than in plasma.

2 mm 18-8 wire used for the test was almost always severely damaged or deformed when cut into pieces, and practically all the pieces showed corrosion when deposited in 0.9 % NaCl solution, but only 75 per cent of those placed in plasma.

Since the values obtained in most of the experiments described below were relative, is was decided to limit the experiment to 0.9 % NaCl solution.

To summarize, the ferroxyl test is provocative, as pointed out previously by PETERSEN & EMNÉUS (1960) and KUTZELNIGG

(1960). This provocative effect increases with the concentration of the indicator. A chloride ion concentration corresponding to 0.9 per cent NaCl is slightly higher than that in the body, but was used for all experiments. EMNÉUS (1960) showed that the ferroxyl test in 0.9 per cent NaCl gives results agreeing well with biological tests and that NaCl could at any rate be used for the purpose under consideration. Plasma is perhaps less aggressive than 0.9 per cent NaCl, but it has several disadvantages if it is to be used in a qualitative corrosion test such as the ferroxyl test. When comparing the corrosion tendency of stainless steels for surgical appliances, it is quite justified to place higher demands on such metals than might be required by living tissue.

EXPERIMENTS WITH COLD WORKING OF ANNEALED STAINLESS STEEL WIRE OF 3 QUALITIES

Cerclage-wire used in Sweden usually consists of stainless steel wire of 18-8 type. This quality is called 2R2 (Sandviken) and 832 M (Avesta). When cold worked, as when used for cerclage, the twisted segment becomes harder than the eye (EMNÉUS & PETERSEN 1958). In addition the passive layer will be damaged at the free cut ends.

Modern appliances for osteosynthesis material of steel is usually made of FST, FMB or AISI 316 (Table 2) if manufactured in England or America. If manufactured in Sweden, they will be made of 453 S and 832 SV or even sometimes of chromium steel. FMB and AISI 316 correspond approximately to Avesta 832 SK, FST of Sandviken 2R2 or Avesta 832 M.

AISI 317 and Avesta 832 SL were not placed on the market until some years ago.

In the experiments 12.5 cm long electropolished wires 1 mm in diameter and of the three qualities 2R2, 832 SK and 832 SL were twisted a definite number of turns in a special apparatus, the stress in the wire increasing per number of turns (see Fig. 1).

TABLE 2.

	C	Cr	Ni	Mo	Fe
FST[1], AISI 303[4], *2R2*[2] and *832 M*[3]	0,05—0,10	17,5—18	8—9,5	—	Bal.
832 SV[3]	0,05	17,5	10,0	1,5	,,
FMB[1], AISI 316[4], *832 SK*[3]	0,05—0,08	17,5—18	8—11	2,7	,,
453 S[3]	0,08	26	5	1,5	,,
AISI 317[4]	0,05—0,08	17,5	14	3,7	,,
832 SL[3]	0,05	17,5	14—15	4,5	,,

[1] Firth-Vickers, Great Britain
[2] Sandvikens Jernverks AB, Sweden
[3] Avesta Jernverks AB, Sweden
[4] American Iron and Steel Institute specifications.

Table 2 gives the approximate compositions of some representative chromium-nickel and chromium-nickel-molybdenum steels. Steels of these types may be represented in surgical appliances used in Sweden today.

The steel qualities used in the present investigation are italicized.

For this experiment 50 pieces of cerclage wire of the three different qualities each, were turned 4 times, and 100 pieces of wire of each quality were cut off with pliers. The twisted pieces of cerclage wire were removed from the apparatus before they were cut off. In order to prevent corrosion of the cut ends, the latter were painted with cellulose lacquer. The hundred 1 cm long pieces referred to above were studied for corrosion at the cut ends.

Twenty-five pieces of twisted wire and 50 pieces of wire cut from every quality were deposited in ferroxyl-gel with an indicator concentration of 0.2 per cent. The other series of 25 and 50 pieces, respectively, were deposited in ferroxyl-gel with an indicator concentration of 2 per cent. They were studied for corrosion after 24 hours. See Table 3 and Figs. 2 a, 2 b, 2 c and 2 d.

In clinical work the cerclage wire must be twisted at least 4 times and, if it should be twisted as tightly as possible, which

TABLE 3.

Quality	Concentration of electrolyte	Concentration of indicator	Twisted parts with indication of corrosion	Cut ends with indication of corrosion
2R2	0,90% NaCl	0,2%	24/25	34/100
2R2	,,	2,0%	24/25	26/100
832 SK	,,	0,2%	24/25	53/100
832 SK	,,	2,0%	25/25	62/100
832 SL	,,	0,2%	0/25	14/100
832 SL	,,	2,0%	0/25	11/100

TABLE 4.

Quality	Concentration of electrolyte	Concentration of indicator	Number of twists	Twisted parts with indication of corrosion
2R2	0,90% NaCl	2,0%	3	25/25
832 SK	,,	,,	3	24/25
832 SL	,,	,,	6	0/25

in the specially devised apparatus used in the present investigation, was 6 times for a length of 12.5 cm. If twisted 7—8 times the wire "telescopes" or breaks.

The experiment was extended to include tests with a reduction of the requirements placed on 2R2 and 832 SK in that the (25 pieces) wire was twisted only three times (Fig. 2 b). 25 pieces of 832 SL were twisted 6 times (Fig. 2 d). As before, the free ends were painted with lacquer. The experiment was otherwise the same as before (Table 4).

Results

Judging from the ferroxyl test, 1 mm wire of 2R2 and 832 SK does not tolerate the stress involved by cerclage. 832 SL, on the other hand, tolerates almost maximal working of this type. Cutting with the pliers, however, caused corrosion in the free ends of 832 SL, though only occasionally.

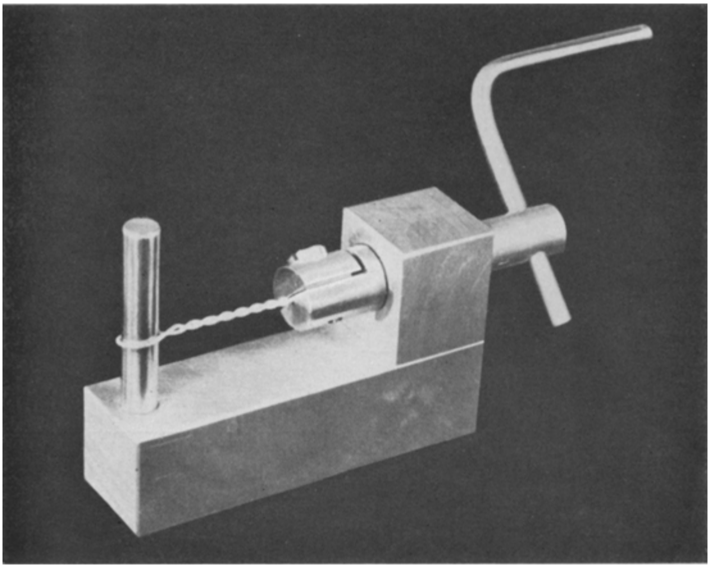

Fig. 1. Apparatus for twisting wires.

Each type of wire used for the experiment was always taken from the same coil. The experiments were repeated several times with the same quality of wire from the same supplier, but from different coils. The experiments referred to above were carried out on electropolished wire. 832 SL wire with a pickled and passivated surface was found to possess the same resistance as electropolished 832 SL. A large number of coils of 832 SK and SL-wires of the same dimensions were tested, and the properties were found to be constant except on one occasion. On that occasion a distinct reduction of the resistance to corrosion was found for one coil of 1 mm SL-wire. The wires did not tolerate 5—6 turns and showed an increased tendency to corrosion at the free cut ends. Check-examination of the wire by the suppliers revealed that the Mo-content was too low. Preliminary investigation has shown that the minimal Mo-content acceptable is 4.2—4.5 (BERG & HENRIKSSON

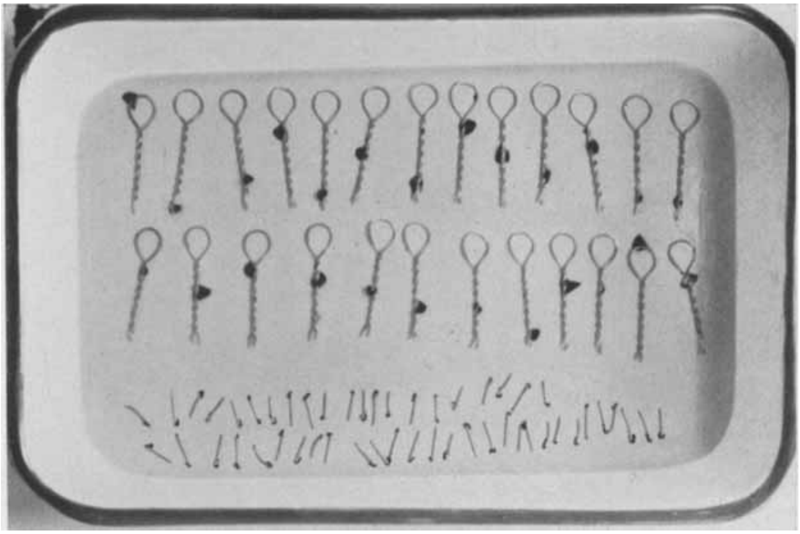

Fig. 2 a. 832 SK, 4 turns, indicator conc. 0.2 %.

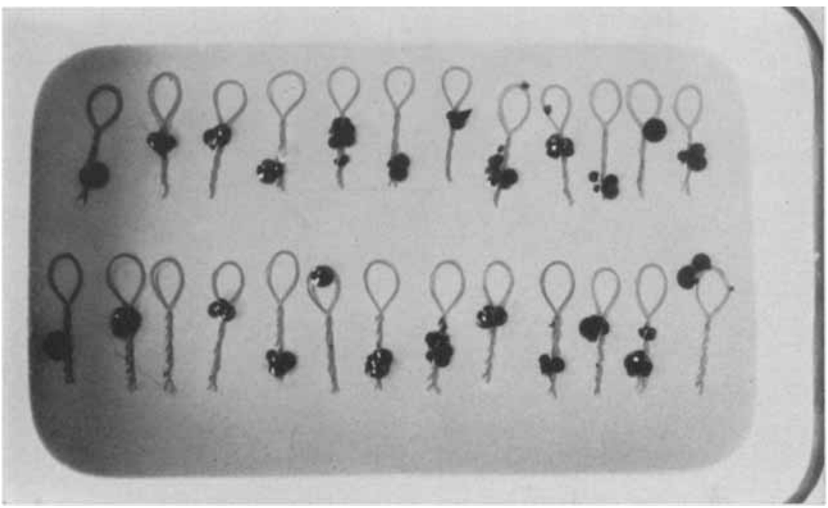

Fig. 2 b. 832 SK, 3 turns, indicator conc. 2 %.

Fig. 2. Twisted wires (cerclage) after exposure to ferroxyl gel for 24 hours.

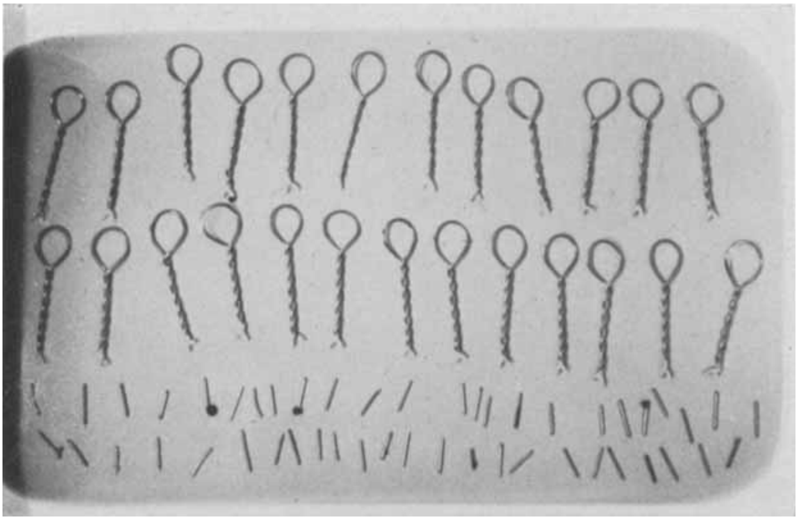

Fig. 2 c. 832 SL, 4 turns, indicator conc. 2 %.

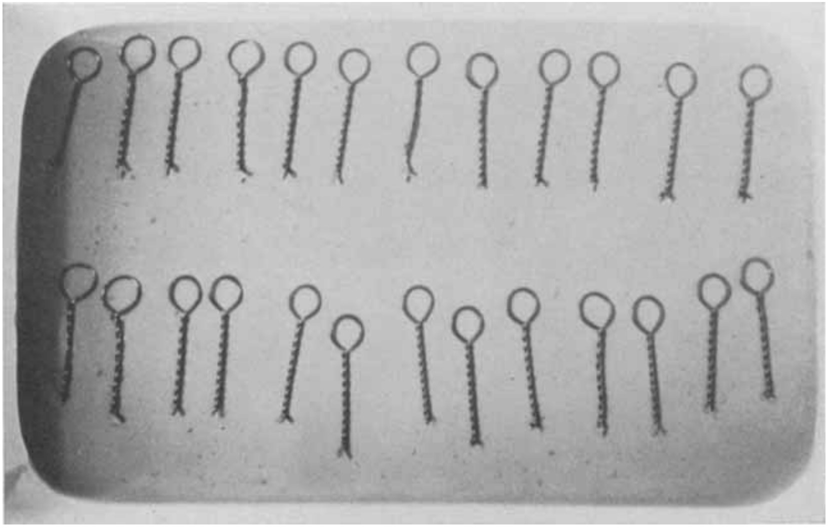

Fig. 2 d. 832 SL, 6 turns, indicator conc. 2 %.

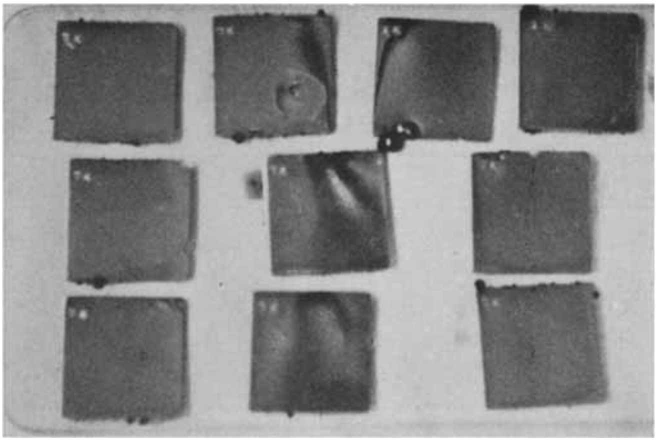

Fig. 3. Polished plates of 832 SK after exposure to ferroxyl gel (conc. of indicator 2 %) for 24 hours. Note the relatively large bubbles on edges of third plate in top row and second in second row (Plates 3 and 6 in Table 5 B).

personal communication). In the case in question it was 4.13. This experiment clearly illustrates the value of the ferroxyl test of checking the resistance of alloys to corrosion.

EXPERIMENTS WITH 1 MM STAINLESS STEEL SHEETS OF 3 QUALITIES

Square plates (35 mm × 35 mm) (average weight 9.5 g) were stamped out of 1 mm annealed stainless steel sheets. The cut edges were carefully ground to remove deposits and any surface damage. The surface and the edges were polished mechanically. In one corner one or two letters were stamped. A total of 60 square plates were made, 20 of 832 M, 20 of 832 SK and 20 of 832 SL.

After the plates had been washed in soda and benzene, 10 of each quality were weighed separately, after which they were placed in ferroxyl gel with 2 per cent indicator. Plates of 832 M soon showed a reaction along their edges, and this reac-

TABLE 5

A

Loss of weight 832 M			
First 24 hours		Second 24 hours	
1. 0,0042	6. 0,0056	1. 0,0059	6. 0,0057
2. 0,0094	7. 0,0058	2. 0,0078	7. 0,0070
3. 0,0047	8. 0,0076	3. 0,0053	8. 0,0077
4. 0,0058	9. 0,0059	4. 0,0042	9. 0,0059
5. 0,0046	10. 0,0047	5. 0,0036	10. 0,0062

B

Loss of weight 832 SK			
First 24 hours		Second 24 hours	
1. 0,0004	6. *0,0011*	1. 0,0002	6. 0,0001
2. 0,0005	7. 0,0001	2. 0,0002	7. 0,0001
3. *0,0018*	8. 0,0003	3. 0,0003	8. 0,0017
4. 0,0004	9. 0,0002	4. 0,0005	9. 0,0002
5. 0,0004	10. 0,0003	5. 0,0001	10. 0,0002

C

Loss of weight 832 SL			
First 24 hours		Second 24 hours	
1. 0,0005	6. 0,0000	1. 0,0000	6. 0,0000
2. 0,0000	7. 0,0000	2. 0,0000	7. 0,0002
3. 0,0000	8. 0,0000	3. 0,0004	8. 0,0001
4. 0,0002	9. 0,0002	4. 0,0000	9. 0,0000
5. 0,0000	10. 0,0003	5. 0,0001	10. 0,0002

tion increased during the course of 1 day to assume considerable dimensions. The 832 SK plates showed a reaction along the edges of a number of plates (see Fig. 3), 832 SL on the other hand showed only very slight edge corrosion, and then only in one plate. After 24 hours the plates were removed from the gel and cleaned in soda and in benzene and weighed again. They were then re-exposed to ferroxyl gel for 24 hours and re-weighed (Table 5).

It is clear from Fig. 3 that the losses in weight varied with the intensity of the colour. The entire 832 M series showed large blue bubbles, and weight losses of 4—9 mgr. 832 SK showed such bubbles in 2 plates (Nos. 3 and 6). This is also apparent from Fig. 3.

832 SL, on the other hand, hardly showed any colour. A small blue patch on plate 10 might correspond to a weight loss of 0.0003. A weight loss of 0.0003 is insignificant.

It might be objected that these considerable losses of weight of 832 M and 832 SK do not correctly reflect the rate of corrosion in 0.9 NaCl.

The ferroxyl test is provocative and it is not possible to form any quantitative opinion of the rate of corrosion except by comparing the three qualities.

EXPERIMENTAL SURFACE DAMAGE

1) In an attempt to elucidate the risks involved by stamping of letters and by unintentional surface damage liable to occur during operations or when handling appliances in a department of surgery, the following experiment was performed.

2 plates 25 × 190 mm with a mechanically polished surface were manufactured from 832 M and 832 SK respectively, 30 letters (M for 832 M and SK for 832 SK) were stamped on each plate and underneath these letters 60 deep stabs were made in 2 rows with surgical screwdrivers of two sorts (Stille-Werner no. 18987 and Stille-Werner 6832—3). On exposure to ferroxyl gel with 2 per cent indicator only a small attack was

TABLE 6.

Type of tool used	832 M		832 SK		832 SL	
	Number of holes with gross indication of corrosion	Number of holes with microscopic indication of corrosion	Number of holes with gross indication of corrosion	Number of holes with microscopic indication of corrosion	Number of holes with gross indication of corrosion	Number of holes with microscopic indication of corrosion
2,8 mm High speed steel drill (AB Malcus)	18/40	7/40	4/40	7/40	0/40	0/40
2,8 mm Carbon steel drill (Stille Werner 18707)	3/40	3/40	2/40	4/40	0/40	0/40
2,8 mm Vitallium drill (Austenal Inc. Stille Werner 6803—4)	15/40	6/40	3/40	2/40	0/40	1/40
Screw driver of chromium vanadium steel	0	0	0	0	0	0
Surgical screw driver (Stille Werner 18 — 18987)	0	0	0	1/10	0	0
	Total 52/120		Total 22/120		Total 1/120	

Microscopic means Magn. × 5.

seen in one M on 832 M (Fig. 4). LAING (1959) feared that corrosion would occur under these circumstances.

2) 10 × 3 plates (35 × 35 mm) of 832 M, 832 SK and 832 SL respectively, were exposed to a standard effect of 3 types of drills namely 2.8 mm high speed steel drill (AB Malcus, Halmstad), 2.8 mm nickel plated carbon steel drill (Stille 18707) and 2.8 mm vitallium drill (Austenal Inc. Stille-Werner 6803-4).

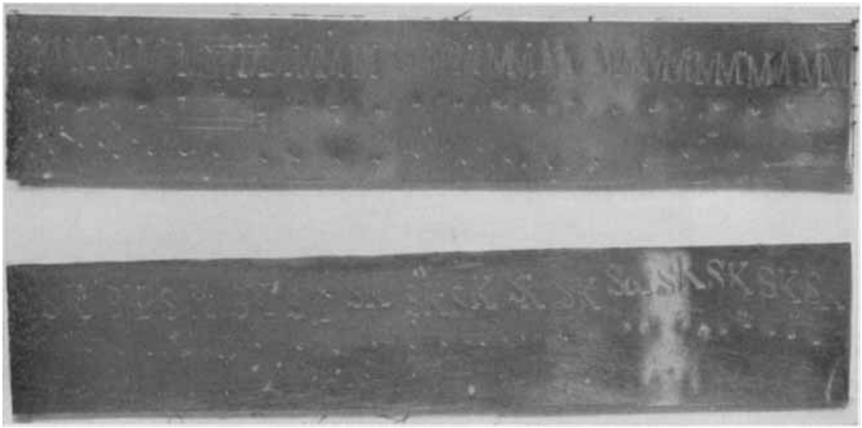

Fig. 4. Letters were stamped on one plate of 832 M (upper) and one of 832 SK. Exposure for one hour to ferroxyl gel revealed no gross corrosion in the stamped letters.

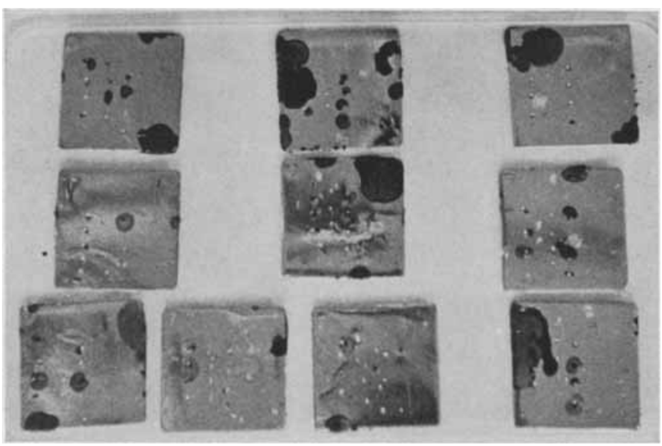

Fig. 5. Ten plates of 832 M with the surface damaged by drills and screw driver scratches. The appearence of the plates is dominated by edge corrosion but corrosion is also seen in the drilled cavities.

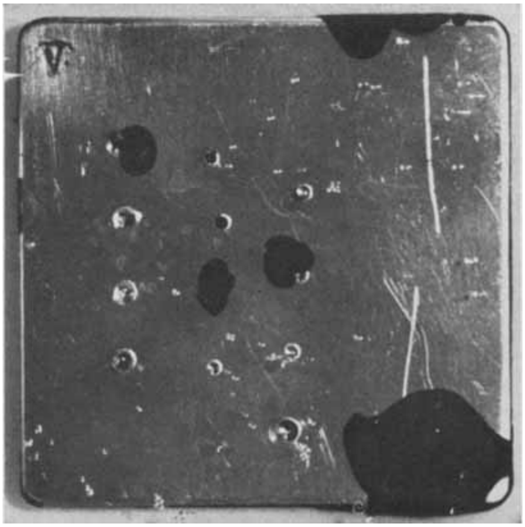

Fig. 6 a. 832 M with marked corrosion in several cavities.

Fig. 6 b. 832 SK with marked corrosion in 2 cavities.

Fig. 6. Plates damaged by drills of high speed steel (left row), carbon steel (middle row) and vitallium (right row).

Fig. 6 c. 832 SL with slight corrosion in one cavity.

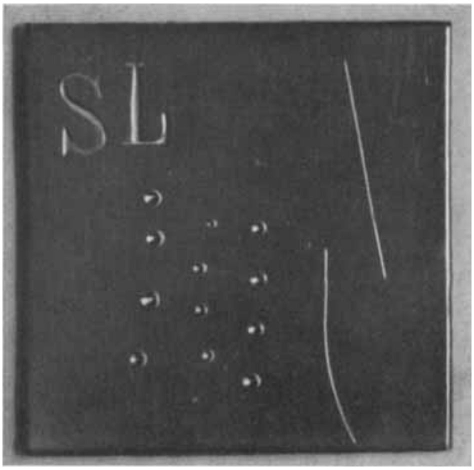

Fig. 6 d. 832 SL without corrosion in any cavity.

The drills were fastened in the usual way in a stationary electric workshop drill. The design of the experiment was such that the drill was allowed to fall against the plate from a height of 2 mm with a load of 4 Kgf while the drill was rotating slowly. The drill was in contact with the plate for 2 seconds.

On each plate 4 cavities were cut with each type of drill and one scratch with a screw driver made of chromium-vanadium steel and one with a surgical screwdriver (Stille-Werner nr 18987). A total of 120 cavities were drilled and 20 scratches were made on each quality of steel. (Figs. 6 a, b, c and d).

Steel shavings were removed by compressed air. The plates were then exposed to ferroxyl gel with 2 per cent indicator.

Result

A reaction in some of the drill cavities appeared after a short while and was distinct after 1 hour.

The reaction first increased steadily and then ceased to increase after 24 hours.

The results were noted after 24 hours and are apparent from Table 6. Of the ten 832 M plates, all showed corrosion in at least one cavity, Fig. 5. Of 832 SK plates three showed no corrosion and of the 832 SL plates, nine showed no corrosion in any of the 12 cavities. Figs. 5 and 6 illustrate the experiment.

Comments

The experiment showed that stamping of letters or figures hardly ever causes corrosion of 18-8 steel. Accidental surface damage with surgical instruments caused corrosion of ordinary 18-8 steel (832 M) when the surface damage was serious, such as drilled cavities. Screw driver scratches did not appear to enhance corrosion. 832 SK, which is of the same composition as FMB-steel and AISI 316, may sometimes corrode, if the surface damage is deep. 832 SL usually tolerates even such deep surface damage without corrosion.

TABLE 7.

A.

Quality 2R2	Mo/Fe	Ni/Fe	Cr/Fe
1.	0,008	0,117	0,103
2.	0,016	0,143	0,174
3.	0,009	0,123	0,092
4.	0,014	0,142	0,185
5.	0,010	0,117	0,094
6.	0,014	0,112	0,147
7.	0,011	0,130	0,120
8.	0,015	0,135	0,150
9.	0,009	0,078	0,135
10.	0,010	0,107	0,180
Mixture of corrosion products from several wires	0,010	0,116	0,091

B.

Quality 832 SK	Mo/Fe	Ni/Fe	Cr/Fe
1.	0,009	0,169	0,105
2.	0,008	0,168	0,137
3.	0,011	0,197	0,291
4.	0,019	0,232	0,189
5.	0,013	0,180	0,087
6.	0,011	0,166	0,281
7.	0,015	0,164	0,416
8.	0,008	0,161	0,207
9.	0,009	0,072	0,144
10.	0,009	0,147	0,288
Mixture of corrosion products from several wires	0,012	0,162	0,186

Composition of the corrosion product

As protoplasm poisons Fe^{+2}, Cr^{+3}, Ni^{+2} and Mo^{+6} are not equal. Fe can hardly be considered severely toxic. That Cr^{+3} and Ni^{+2} are much more toxic is beyond doubt.

The artificial corrosion product obtained in the ferroxyl test of chromium-nickel steel and chromium nickel molybdenum steel can be readily collected and anlyzed. Fe and nickel give a deposit with $K_3(FeCN)_6$. Chromium, on the other hand, gives no precipitate but a green colour, which remains in solution.

The content of 10 artificial corrosion bubbles from 18-9 steel 2R2 and 10 from 17.5-11-2.7 steel 832 SK was analyzed roentgenspectrographically by fil. lic. J. Baecklund of Avesta Jernverks AB (Table 7).

Table 7 gives the X-ray intensity of Mo, Ni and Cr in relation to Fe. Because Fe also occurs in the $FeCN_6$ radical of the artificial corrosion product the intensity of Mo, Ni and Cr is certainly too low compared with a real corrosion product. It would hardly be fully justified to draw conclusions about corrosion in living tissue from these analyses of the artificial corrosion products in the ferroxyl test. In the ferroxyl test the products of corrosion contain nickel in roughly the same proportion as does the original alloy.

EXPERIMENT WITH CREVICES (1.)

In all surgical cases where screws and plates, screws and flanges or nuts and bolts are used, crevices may occur. Technically, crevices imply a risk of stagnation of electrolytes and concentration of electrolytic products present. Further, a reduction of the oxygen concentration may occur in the crevice. This probably holds also for metal appliances deposited in human living tissue.

A few preliminary experiments were performed first. The 10 plates of 838 M, 832 SK and 832 SL each, which were used for studying surface damage caused by drill and chisel

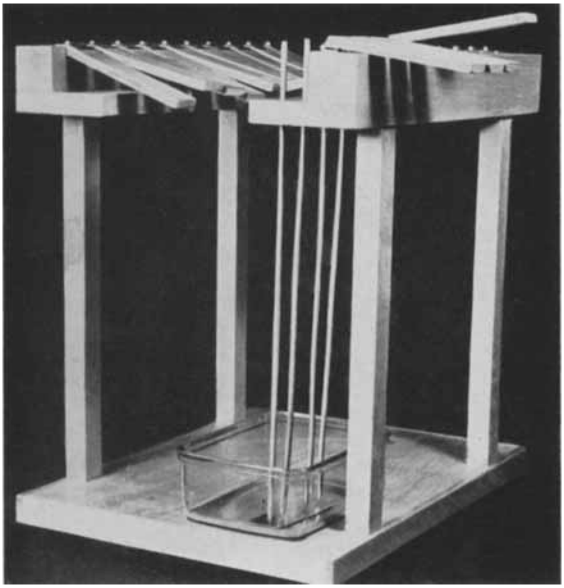

Fig. 7. Frame used for the experiments with crevices between ends of rods and surface of plates.

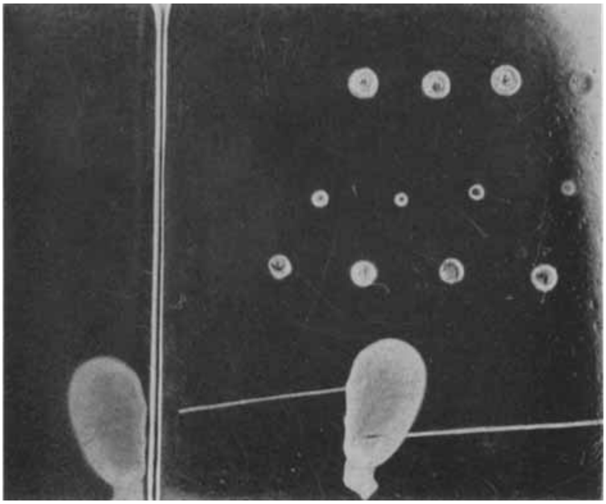

Fig. 8. Corrosive areas between superimposed plates of 832 M.

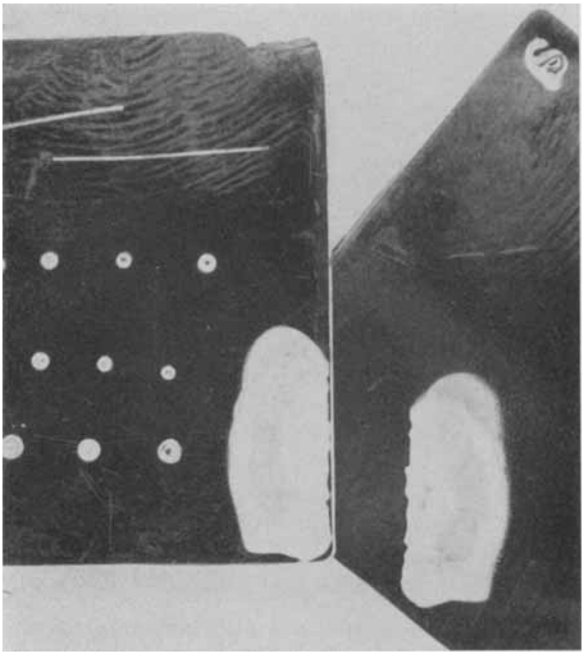

Fig. 9. Corrosive areas between superimposed plates of 832 SK.

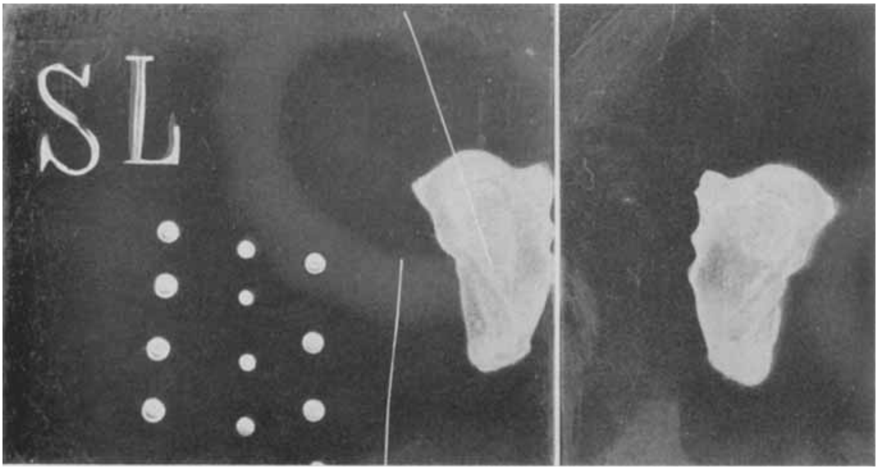

Fig. 10. Corrosive areas between superimposed plates of 832 SL.

scratches were placed in the liquid gel (0.9 % NaCl and 2 % indicator), one on the other, so that the gel could fill the crevices before the next plate was deposited. Undamaged surfaces were placed against damaged surfaces. In addition the plates were placed like roof tiles over one another.

After a day (24 hours) Turnbull blue was seen to ooze from the crevices of 832 M, but not from those of SK and SL. The experiment was continued for a week. Then abundant corrosion bubbles were seen in several crevices of 832 M and in crevices of 832 SK, but not of 832 SL.

Plates of 832 M were held together firmly by Turnbull blue. This also applied, though to a less extent, to two plates of 832 SK and SL. Between 10 plates there are 9 crevices, 832 M showed deep corrosion in 5 of the crevices (Fig. 8). 832 SK showed a deep area of corrosion between plates 6 and 7 (Fig. 9). 832 SL likewise showed a large, but superficial, area of corrosion between plates 4 and 5 (Fig. 10). The corrosion areas were mirror pictures of one another as is apparent from the illustrations.

Exactly the same experiments were carried out on 10 plates with intact surfaces of polished plates of 832 SK and of SL. This time the experiment was continued for 2 days. Then corrosion areas were seen in 4 crevices of 9 in 832 SK and in one of 9 in 832 SL. In the last case the corrosion was situated between the third plate and the fourth.

Comments

In this experiment the ferroxyl test was used, not to demonstrate corrosion by colour indication but provoke corrosion. It soon produced large and readily demonstrable damages. Such severe damage as that observed in the latter experiment was not seen in any of the other experiments with ferroxyl test on polished surfaces of chromium-nickel or chromium-nickel-molybdenum steel. This might be an illustration of crevice corrosion.

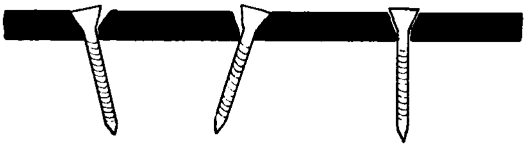

Fig. 11.

EXPERIMENT WITH CREVICES (2.)

When fractures are fixed with plates and screws there will always be crevices between the head of the screw and the plate (see Fig. 11).

A method for studying crevices of this type was devised. In a frame of the type shown in Fig. 7 20 rods can be placed against plates of the same alloy. The plates are placed in a vessel containing ferroxyl gel (2 % indicator). The rods can be loaded via a lever and be pressed against the plates with any desired moderate pressure.

A series of experiments were performed to compare the three alloys 832 M, 832 SK and 832 SL (see Table 2). The alloys were tested as rods, 4 mm in diameter and 300 mm long with a weight of 28 gram. These rods were made of annealed wire from the same coil and were thus probably of the same batch. One end of the rod was ground flat and the other ground to a fine point. The ends were then surface treated by pickling and passivation in HNO_3.

Results

The results are apparent from Figs. 12—14.

832 M 1 A. Tip against plate produces corrosion at two sites. (The corrosion at site of rod 4 is due to edge corrosion and is not located at the tip of the rod.) Fig. 12 a.

1 B. Ground plane end against plate produces strong corrosion at 9 sites. Fig. 12 b.

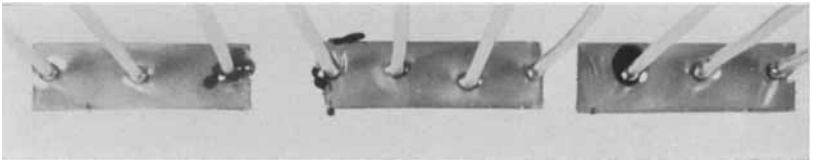

Fig. 12 a. Pointed rods resting on plates as seen from above. Rods and plates of 832 M. Note edge corrosion in the middle plate.

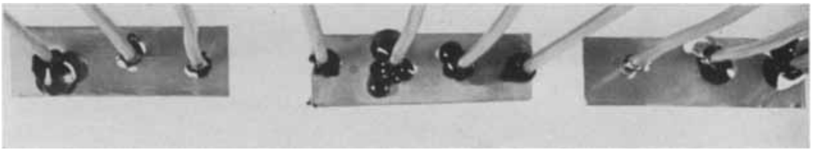

Fig. 12 b. As in fig. 12 a, but ends of rods ground plane.

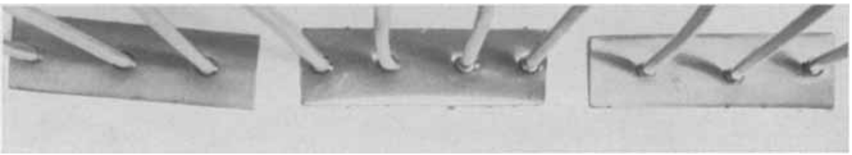

Fig. 13 a. Pointed rods resting on plates. Rods and plates of 832 SK.

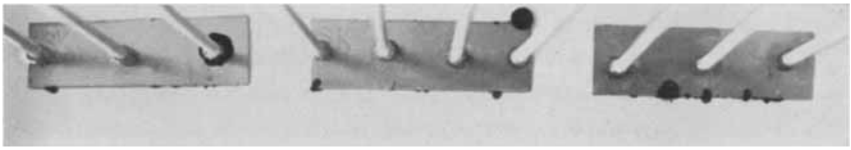

Fig. 13 b. As in fig. 13 a, but ends of rods ground plane.

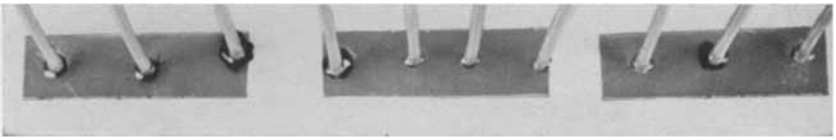

Fig. 13 c. As in fig. 13 b, but rods loaded with 500 g.

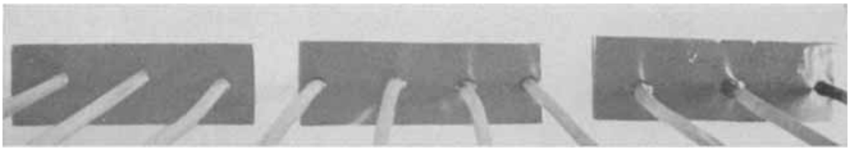

Fig. 14 a. Pointed rods resting on plates. Rods and plates of 832 SL.

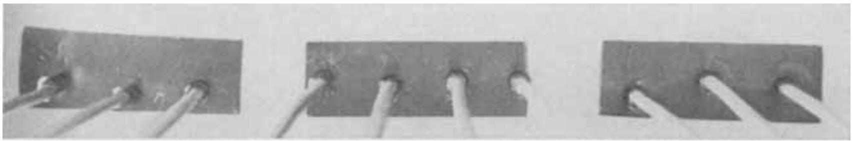

Fig. 14 b. As in fig. 14 a, but ends of rods ground plane.

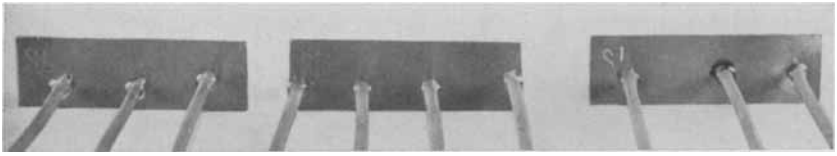

Fig. 14 c. As in 14 b but rods loaded with 500 g.

832 SK 2 A. Tip against plate causes no corrosion. Fig. 13 a.

2 B. Ground plane end against plate causes strong corrosion at site of one contact. Several sites of corrosion along the edge of the plates. Fig. 13 b.

832 SL 3 A. Pointed end against plate causes no corrosion. Fig. 14 a.

3 B. Ground plane end against plate cause no corrosion. Fig. 14 b.

After the rods had been reground and resharpened they were loaded with 500 g and thus pressed against a new series of plates[1] with a 20-fold force. The rods weighed about 28 g.

[1] All plates in each quality were made of the same sheet.

832 SK 2 C. Pointed end against plate causes no corrosion.
2 D. Ground plane end against plate causes severe corrosion at 3 points of contact. Fig. 13 c.

832 SL 3 C. Pointed end against plate causes no corrosion.
3 D. Ground plane end against plate causes severe corrosion at one point of contact. See Fig. 14 c.

All photographs were taken after the test had been allowed to proceed for 12 hours, but incipient corrosion could be detected within 5—10 minutes.

After 1 hour it was always possible to predict what the results would be after 12 hours. Figs. 15—17 illustrate corrosive areas after experiment I A and I B.

When a metal plate is fixed by screws, the surfaces of the plates and the screws are pressed against one another with considerable force. The design of the present experiments was not such as to ascertain whether this pressure favours corrosion or whether corrosion is due entirely to the crevice between the surfaces. "Spot" contact with the tip of the rods, however, appeared to favour corrosion less than contact between two plane surfaces. The sharp points of the rods loaded with 500 g produced no signs of corrosion of 832 SK or SL. Judging from experiments with loaded plane-bottomed rods, the interspace between the bottom of the rod and the supporting surface will possibly decrease with increasing load of the rod, and it is known that the risk of corrosion increases as the crevice becomes very small.

No attempts were made to ascertain the effect of the last turn or so, when a screw is screwed tight, on the surface of the threading and head of the screw or on the surface of the plate through which it is screwed.

Comments

It is clear that 832 M was unable to satisfy the requirements placed upon it by the experimental conditions.

832 SK was evidently sensitive to small crevices and, like 832 M, failed to stand the present test.

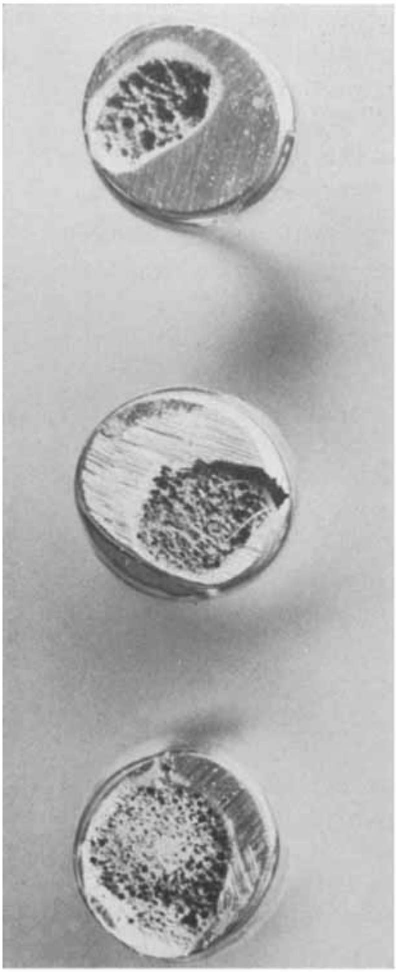

Fig. 15.

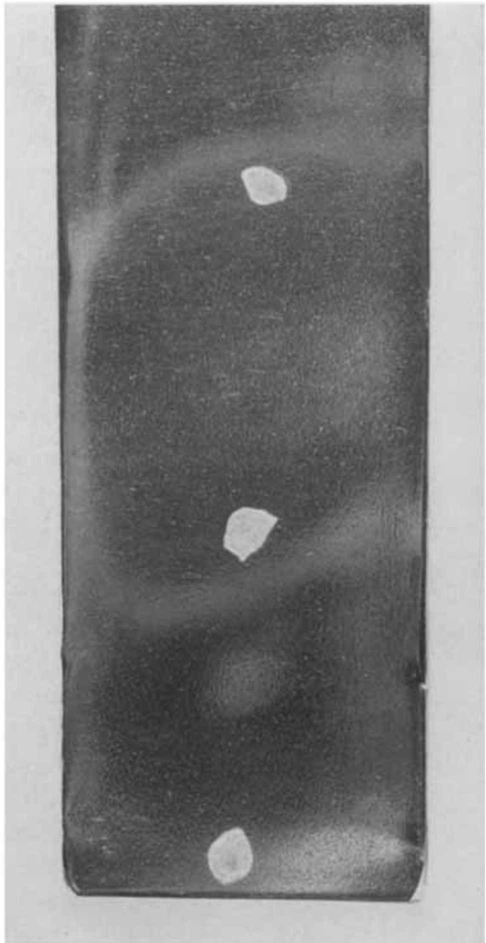

Fig 16.

Fig. 15. Corrosive areas on plane ends of rods of 832 M after exposure to ferroxyl gel in the way seen in fig. 12 b. (× 5).

Fig. 16. Corrosive areas in plate of 832 M on which rods in fig. 15 had been placed.

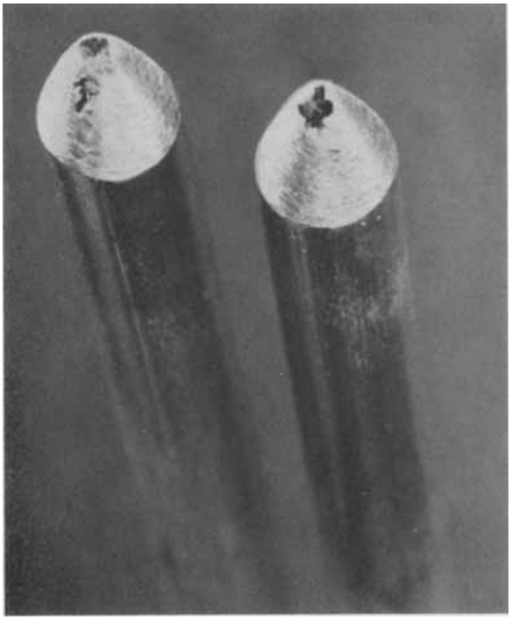

Fig. 17. Corrosive areas on pointed ends of rods of 832 M after exposure to ferroxyl gel in the way shown in fig. 12 a. (X 5).

832 SL was superior to the other two alloys, but crevice corrosion was nevertheless noted in one sample.

Although it is too early to say in what measure the present experimental findings apply to plates sunk and screwed in human bone, and with due reservation for the provocative nature of the ferroxyl test, it would appear that 832 SL best fills the requirements for orthopaedic surgery.

EXPERIMENTS WITH CONTACT BETWEEN DIFFERENT ALLOYS AND ELEMENTS

Handbooks on corrosion are liable to give the less critical reader the impression that so-called stainless steel alloys can be used in combination with vitallium, for example, in metal contact: all are in the same groups in the galvanic series (37—45). Table 8.

But it should be pointed out that chromium steel (12—18 %) cannot be regarded as passive in the presence of chlorides. Even austenitic chromium-nickel-steel and high-alloyed chromium steel (23—30 %) can lose its passiveness in crevices and in points or spots that have been cold worked. If a chromium-nickel-molybdenum steel loses its passiveness, it will be assignable to group 14—23 (Table 8), and in relation to vitallium, it will show a potential fall that might be 600—700 millivolts with anodic corrosion of the steel as a consequence. Corrosion of a small spot in steel by combination with vitallium might give a high current density. Vitallium in its property of a cathode suffers no loss of substance.

The combination of chromium steel (12—18 %) and 18-8 in chloride environments is *per se* unadvisable because chromium steel does not tolerate this electrolyte (KALLING & LILJEKVIST 1948). On combination of 18-8 with 18-8-2.5 the aggregate as a whole will have the same weakness as its weakest link, namely 18-8 steel.

In industry problems of this type can be solved in different ways such as by cathodic protection or by addition of inhibitors. In surgery, however, there is only one way open: to minimize the dissolution of heavy ions into the living tissue.

Although it is a commonplace that different alloys should not be used in direct contact in surgery, occasional combinations of such alloys will always occur and particularly with the ever increasing number of alloys becoming available.

In Sweden at least 4 different alloys of stainless steel type must be considered (Table 2). Besides vitallium another cobalt alloy (vitallium-like), namely neutrilium and also titanium in the form of the pure element, has appeared on the market.

Unintentional combination of different stainless steel alloys will give the aggregate the properties of the weakest component. If the weakest component is chromium steel (12—18 %) the aggregate will not be anti-corrosive at all in chloride environments.

TABLE 8.

Galvanic series for different metals and alloys.

Electrod potential measured in saltwater against saturated calomel electrod ranging from —1,51 for magnesium alloys to +0,33 for platinum.

1. Magnesium alloys
2. Zinc
3. Galvanized steel and iron

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4. Aluminium, pure, and Al without copper
5. Aluminium of compound type with anodic coating
6. Cadmium alloys
7. Aluminium with copper

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8. Carbon steel
9. Steel with an addition of copper
10. Cast iron
11. Chromium steel 4—6 % Cr, active
12. *Chromium steel 12—30 % Cr, active*
13. Ni alloyed cast iron

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14. *18—8 stainless steel, active*
15. *18—8 stainless steel with 3 % Mo, active*
16. Tinman's solder (lead + tin)
17. Lead
18. Tin
19. Muntz metal
20. Manganese bronze
21. Tolrin bronze
22. Marine bronze
23. Phosphor-bronze

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24. Nickel, active
25. Inconel (80 % Ni, 5 % Fe, 15 % Cr), active
26. Titanium, active
27. 80—20 Ni-Cr alloy
28. Brass
29. Admiralty brass
30. Aluminium brass
31. Tombac
32. Nickel silver
33. Copper
34. Copper-nickel alloy
35. Siliceous bronze
36. Monel metal

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37. Silver solder
38. Nickel, passive
39. Inconel, passive
40. 80—20 Ni-Cr alloy, passive
41. *Chromium steel (12—18 % Cr), passive*
42. *18—8 stainless steel, passive*
43. *Chromium steel (23—30 % Cr), passive*
44. *18—8 stainless steel with 3 % Mo, passive*
45. *Vitallium*

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46. Graphite
47. Amalgam
48. Quicksilver
49. Gold
50. *Titanium, passive*
51. Platinum

In combinations with direct contact of stainless steel and vitallium the steel will be the anode. This is what also happens when stainless steel and titanium are in direct contact.

On unintentional combination of vitallium and titanium,

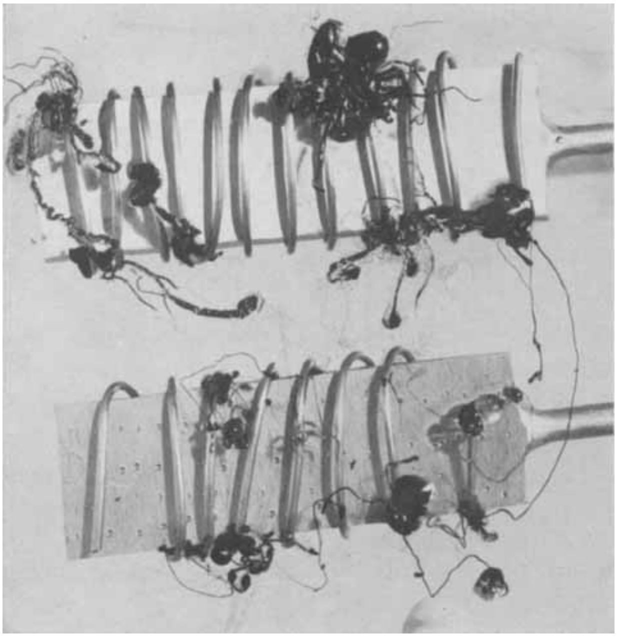

Fig. 18. 832 M wire wound round vitallium plate and exposed to ferroxyl gel for 24 hours. Observe massive corrosion.

vitallium will be the anode and vitallium will lose substance, if the passive layer is not intact. It is not likely that titanium can be activated in 1 % chloride environments.

Experiments

1. Electropolished 1 mm wire of 2R2 was wound round vitallium plates: 12 times round one plate and 6 times around the other. There were thus a total of 48 and 24 points of contact respectively. The plates were then placed in ferroxyl gel (2 % indicator) and after 3—4 minutes Turnbull blue began to ooze from a number of the points of contact between the wire and the plate. After 1 hour Turnbull blue was abundant (Fig. 18).

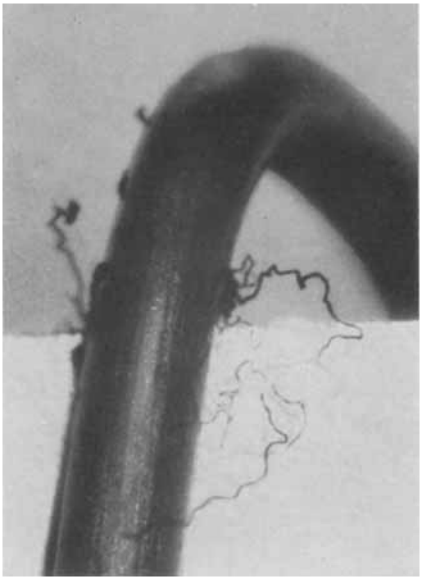

Fig. 19. 832 SK wire wound round vitallium plate and exposed to ferroxyl gel for 24 hours. Magn. × 20. Note rel. slight corrosion.

2. The experiment was repeated with the same vitallium plates and 1 mm, electropolished 832 SK. In the beginning no sign of any reaction could be demonstrated, but after 1 hour small spots of blue could be recognized with the naked eye. On examination under the microscope a blue colour was seen at several of the points of contact (see Fig. 19). After 1 day faint but gross blue spots were seen. Under the microscope such spots were seen at all points of contact (Fig. 19). The experiment was extended to include cutting off the wire with pliers under the surface of the gel, and then signs of corrosion soon appeared at the cut surface. These ends became intensely blue within 1 hour.

3. The experiment was repeated with 832 SL. No macroscopic or microscopic signs of corrosion appeared within 1 day (Fig. 20). When the wire was cut in lengths as in previous experiment marked corrosion occurred within 1 hour.

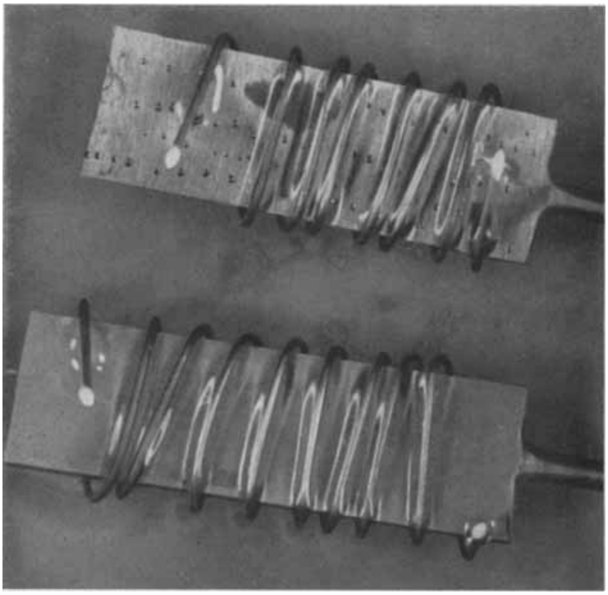

Fig. 20. 832 SL wire wound round vitallium plates and exposed to ferroxyl gel for 24 hours. No corrosion indicated.

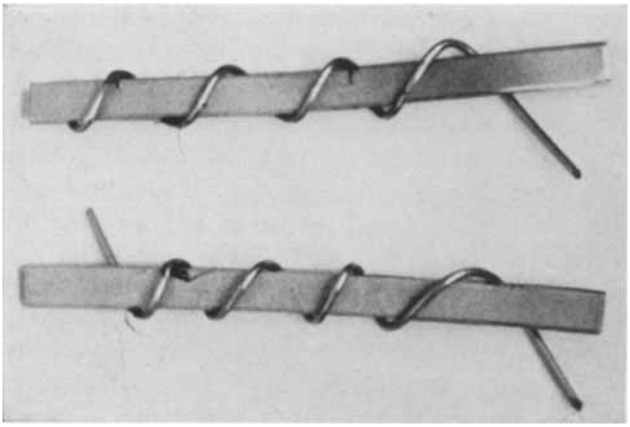

Fig. 21. 832 SK wire wound round rectangular titanium rods. Corrosion only slight.

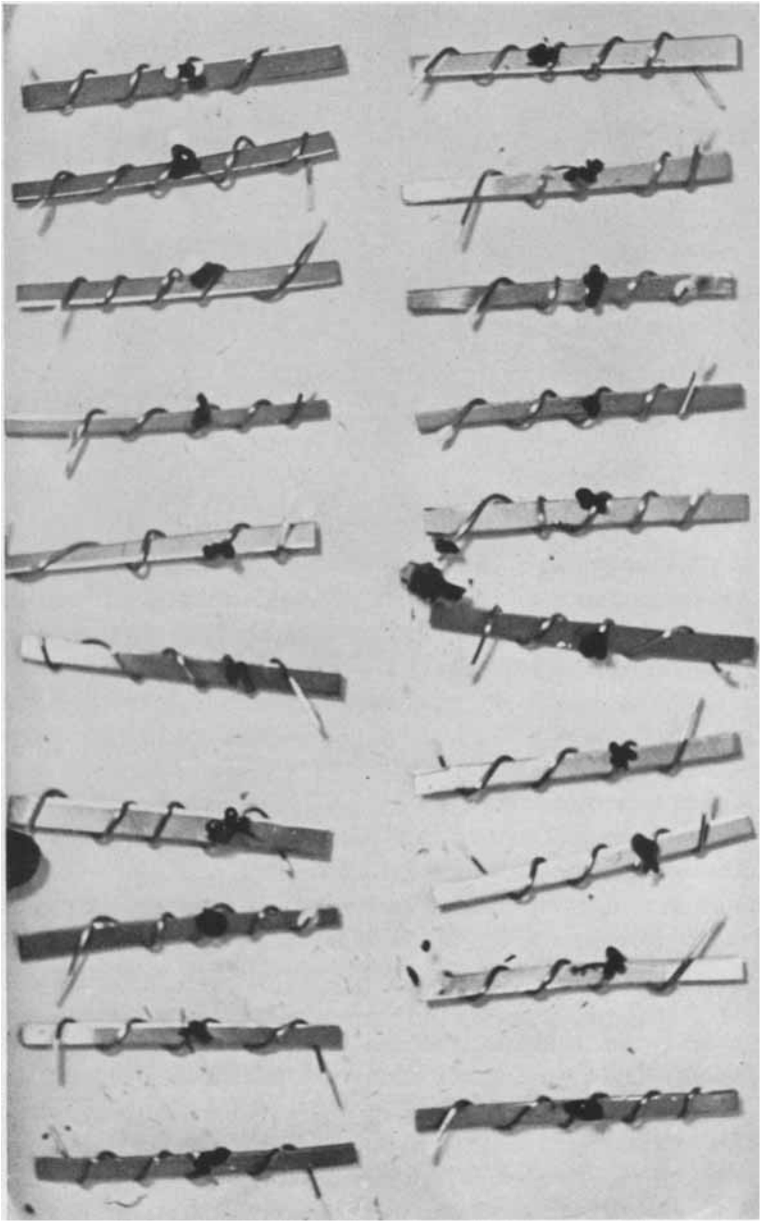

Fig. 22. 832 SK wound round rectangular titanium rods. The wire was divided roughly in its middle without taking it out of the gel. Note constant gross corrosion in the cut ends. This picture was taken 2 hours after the wire was divided.

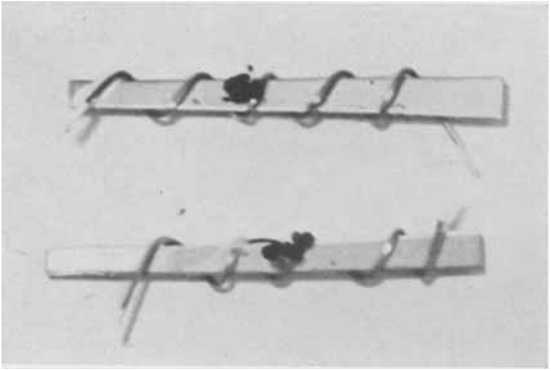

Fig. 23. Enlargement of first two samples illustrated in fig. 22.

4. 1 mm polished 2R2 was wound 4 turns around 20 titanium square rods, thus 16 points of contact between each rod and the wire, with a minimum of 320 points of contact between the wire and all the rods. The rods were then deposited in ferroxyl gel. After 30 minutes many sites of contact showed signs of corrosion. After 1 day a large number of the sites of contact showed corrosion. Only one of the 20 samples showed no such corrosion.

5. Same experiment as in 4, but now with 832 SK. After 30 minutes several points of contact showed corrosion. On examination under the microscope practically all points of contact showed corrosion (Fig. 21). When the wires were cut under the surface of the gel, all the cut surfaces showed corrosion within 2 hours (Figs. 22 and 23).

Exactly the same experiment was performed with 832 SL, but now the results were different. No corrosion was seen within 30 minutes. After 24 hours gross corrosion was seen at one site and microscopic corrosion at 4. When the wires were cut under the surface of the gel, all showed corrosion within 2 hours — almost the same picture as in the experiment with 832 SK (Fig. 22).

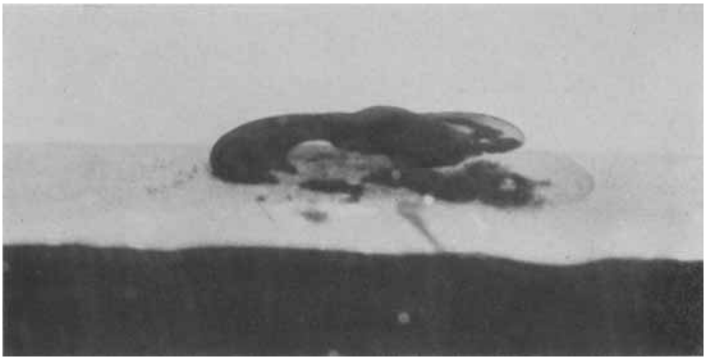

Fig. 24. Corrosion in a vitallium plate around which titanium wire had been wound, the corrosion was due to a flaw in the plate. Magn. × 20.

Comments

These experiments which can only be regarded as preliminary, but they nevertheless show that under some experimental conditions annealed wire of 832 SL quality is so passive that if it is absolutely intact it does not corrode on direct contact with vitallium and titanium. The slightest damage such as on cold working can, however, activate even this steel with galvanic corrosion as a result.

Steel of type 832 SK might occasionally retain its passiveness, but even the slight cold working, *e. g.* cutting with pliers, or crevices can occur and activate the steel.

WHAT ARE THE RISKS OF UNINTENTIONAL USE OF VITALLIUM AND TITANIUM IN COMBINATION?

According to the standard electrode potential series, vitallium will be the anode and titanium the cathode. Thus, vitallium should be able to undergo corrosion, if its passive surface is broken and the vitallium is active.

A number of experiments have been made with direct contact between titanium and vitallium. Series of vitallium screws

(Austenal Inc.) were inserted in wooden blocks and titanium wire was wound tightly around the screws. Despite the numerous crevices between the turns of the wire and the screws no corrosion of vitallium was demonstrable within a week.

Similar experiments were carried out with titanium wire wound around vitallium plates. The surface of one plate had been damaged by drilling 120 cavities. On one occasion one small spot of corrosion was demonstrated after 3 days in one vitallium plate (Fig. 24). The corrosion was seen at a site of a flaw in the plate but not in any drill cavity. The corrosion product was analysed x-ray-spectrographically (Baecklund) and was found to contain Co, Cr and Mo.

Comments

Judging from the experiments, it seems that hard vitallium has a very passive surface and that even on contact with titanium it corrodes only exceptionally. LAING *et al.* suggested that there might be a risk of corrosion of vitallium screws screwed with steel screw drivers owing to transfer of metal from the latter to the screws. Judging from experiences with the strong passiveness of hard vitallium even on contact with titanium, it may be questioned whether there really is any risk of corrosion of vitallium under these circumstances.

If the tools are made of steel, any particles torn from them will, of course, go into solution, but since they will be an anode in relation to a vitallium screw, for example, and because of their smallness, they will be rapidly dissolved (Fig. 28). Why the cathodically protected vitallium should corrode under such circumstances when it tolerates a cleft in contact with titanium is difficult to understand.

PETERSEN & EMNÉUS (1960) pointed out that corrosion (local action) could not be produced experimentally with hard vitallium made by Austenal Inc.

On one occasion hard vitallium in direct contact with titanium showed signs of corrosion in the ferroxyl gel test (see above) (Fig. 24).

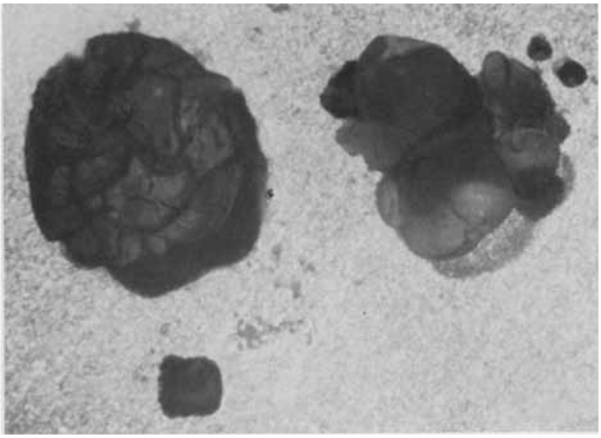

Fig. 25. Plate made of cobalt alloy of approx. the same composition as vitallium and placed in ferroxyl gel (2 % indicator) without any previous treatment whatsoever. Note slight corrosion. Magn. × 20.

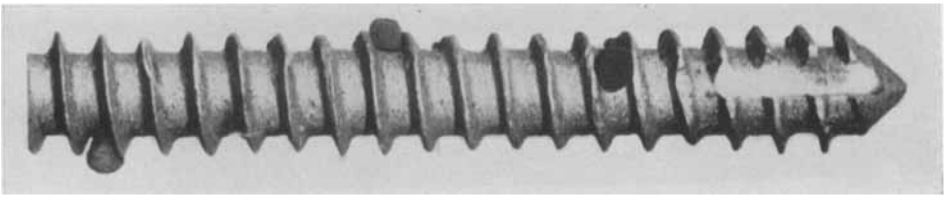

Fig. 26. Screw of same alloy as plate in fig. 25. Note corrosion though screw was brand new placed in ferroxyl gel with 2 % indicator. Magn. × 5.

It should be observed that the manufacture of vitallium is a complicated process (as pointed out by VENABLE in 1948). Not all manufactures can produce a really homogeneous material. Austenal Inc., however, appear to have overcome these difficulties.

Attempts have been made in Sweden to manufacture Co alloys of stellite type resembling vitallium, and specimens have been sent to the department of Med. Physics in Lund for testing for medical use.

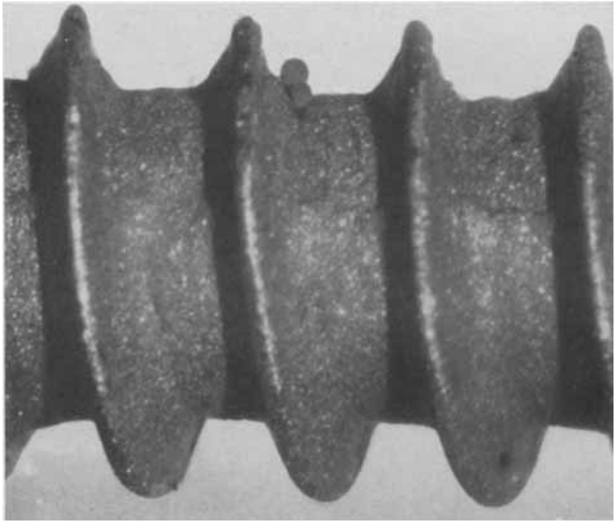

Fig. 27. As in fig. 26 but ferroxyl gel cointained only 0.2 % indicator. Magn. × 20.

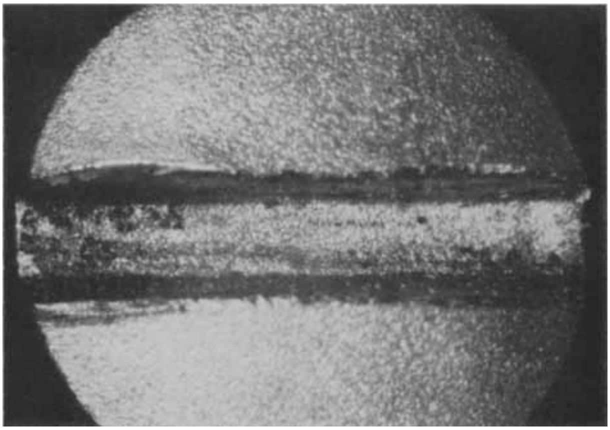

Fig. 28. Vitallium screw screwed in wooden block with driver of chromium vanadium steel. After exposure to ferroxyl gel, the transfer is demonstrable within a few minutes. (Dark colour in the picture.)

The plates were measured for hardness and studied for corrosion in the ferroxyl gel test. The hardness varied from 17 to 34 Rc (Rockwell C).

In the ferroxyl test punctate corrosion occurred within 24 hours (Figs. 25, 26 and 27).

The variation in the hardness was sufficient to suspect structural differences in one and the same plate, so that local elements could arise. This was also confirmed by the ferroxyl test.

During the last months an improved domestic stellite has been tested at the Department of Med. Physics. It appears that this quality is less corrosive than the quality tested in the present investigation.

It may thus be concluded that reliable stellite plates can only be caste by highly specialized manufacturers.

SUMMARY

The risks of corrosion under some conditions resembling those of surgery have been studied with the aid of the ferroxyl test. Under the experimental conditions it appears that:

1. Cold working (cerclage) of
   a) 2R2 and 832 SK involves a serious risk of corrosion
   b) 832 SL will tolerate twisting but less well cutting with pliers.
2. a) Slight surface damage (screw driver scratches) and stamping of letters involves no risk in either quality.
   b) Deep surfaces damage (drill cavities) involves a serious risk in 832 M, a moderate risk in 832 SK and practically no risk in 832 SL.
3. Crevices involve
   a) a serious risk in 832 M
   b) a moderate risk in 832 SK
   c) a slight risk in 832 SL.
4. Contact with vitallium involves a
   a) serious risk of gross corrosion in 2R2
   b) serious risk of minute corrosion in 832 SK
   c) serious risk of gross corrosion in 832 SK and 832 SL, if the steel is severely cold worked, as it sometimes is in bone surgery.
5. Contact with titanium involves the same risks for the three steel qualities as those stated under 4 (vitallium).
6. Vitallium ought to stand contact with titanium except under very unfavourable conditions.

It appears that chromium-nickel-molybdenum steel with a content of 17.5 % Cr, 14 % Ni and 4.5 % Mo is superior to steel with 17.5 % Cr, 11 % Ni and 2.7 % Mo under the experimental conditions used.

CLINICAL CONSIDERATIONS

It is more difficult to assess the chemical effect of plates, screws, pins and wires in the human body than to judge the effect of metal implants in experimental animals or in vitro. In the first place it is necessary to rule out all effects of surgical technical procedures and infection.

When this is done the mechanical effect of a foreign body must be considered.

Comparison of the degree of chemical effect with that of mechanical requires detailed records.

When large appliances are used, it would appear that the mechanial component of the cause of the reaction is greater than the chemical. A Kuentscher nail in the femur must, of course, imply a severe mechanical effect just as will a MacLaughlin nail with a plate.

General clinical experience has, however, shown that the benefit obtained by these applications is so considerable compared with conservative methods that they more than outweigh the risk of infection and mechanical or chemical irritation.

Since the mechanical factor has been accepted as unavoidable in bone and joint surgery, the chemical component has come to the foreground in recent years, although it may be a factor of less importance.

In the 1930ies and 1940ies the chemical component was brought under fair control by the introduction of high alloyed chromium-nickel steel of so-called 18-8-type (LANGE 1926, JONES & LIEBERMAN 1936, HUDOCK 1940, SHERMAN 1940, KEY 1941). The still better qualities of chromium-nickel-molybdenum steel were shown by SHERMAN (1940) and KEY (1941).

The stellites, particularly vitallium, were introduced by

VENABLE & STUCK (1937, 1947). Despite attempts in USA (1947) and in Great Britain (1956) to limit the selection of types of steel for osteosynthetic purposes to chromium-nickel-molybdenum steel (AISI 316 and FMB), it has been found that even this type of steel shows corrosion spots after it has been in the body for some time (ZAPFFE 1955, SCALES 1955, SCALES & ZAREK 1955, HICKS 1958, SCALES *et al.* 1959, COHEN *et al.* 1959).

Vitallium is so inert that SCALES & ZAREK (1955) and SCALES *et al.* 1959 concluded that they never found any corrosion spots in any vitallium implants that had been in the human body.

At the Department of Orthopaedic Surgery in Lund all cases in which surgical implants have been removed are receiving special attention. Special notes are made of the clinical course, histological findings of biopsy specimens and the results of physical and chemical investigations of the extracted implants, which includes

1. Gross inspection
2. Examination with magnet
3. Roentgen-spectrographic analysis
4. Microscopical examination
5. Corrosion test (ferroxyl test).

A clinical investigation, as mentioned above, does not yield such reliable information as do experimental studies because it is hardly possible to judge the reaction of the tissue around the entire nail or plate, except, of course, at autopsy. Investigation must be limited to examination of a piece of tissue from the region where the surgeon has found the tissue reaction to be most intense. In addition in a clinical investigation it is difficult to assess how much of the tissue reaction is due to mechanical irritation and how much to chemical.

Since many sorts of alloys are used, any collection must be relatively large to permit comparisons. The material hitherto collected at the department is not yet large enough to permit comparisons with any degree of certainty. The results will be published later.

On one point, however, the data obtained are of special interest namely indications of corrosion by the ferroxyl test. The information obtainable by this test will be apparent from a few examples given below.

INTERPRETATION OF FERROXYL TEST PERFORMED ON EXTRACTED SURGICAL IMPLANTS

It is known from metallurgic experience that chromium-nickel-molybdenum steel is passive in 0.9 per cent sodium chloride at a temperature of about 40° C provided it is not exposed to additional corrosion-promoting factors. A Rush-pin approaches the ideal in the absence of supervening corrosion promoting factors, see Fig. 29.

A Sven Johansson nail possesses similar though not quite so satisfactory properties. It is, however, subjected to somewhat greater stress and cold working on insertion[1] and also to metallic transfer from the guide wire in the central canal, see Figs. 30 a and b.

A Kuentscher nail has the same properties as the Sven Johansson nail but on insertion it is subjected to a fair degree of cold working and particularly the U-shaped femoral nail can be damaged quite a lot by the guiding pin. Figs. 31 and 32.

The classical plate with screws is exposed to three corrosion promoting factors: severe cold working of the screw heads, transfer of metal from the screw driver to the screw and last but probably not least the crevice between the plate and the screw heads, see Figs. 33 a, b, c and d.

Attention has been drawn to the transfer of metal from tools to plates and screws by Laing *et al.* (1955, 1958 and 1959). Figs. 28 and 30. In the present investigation the ferroxyl test was also used to study the transfer of metal from the guide in the central canal of three and four winged collum nails made of vitallium. As previously mentioned, if only

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[1] It is obvious that removal of a surgical appliance can damage it. This might cause corrosion as well as damage on insertion and must be born in mind when judging the ferroxyl test after extraction of an appliance.

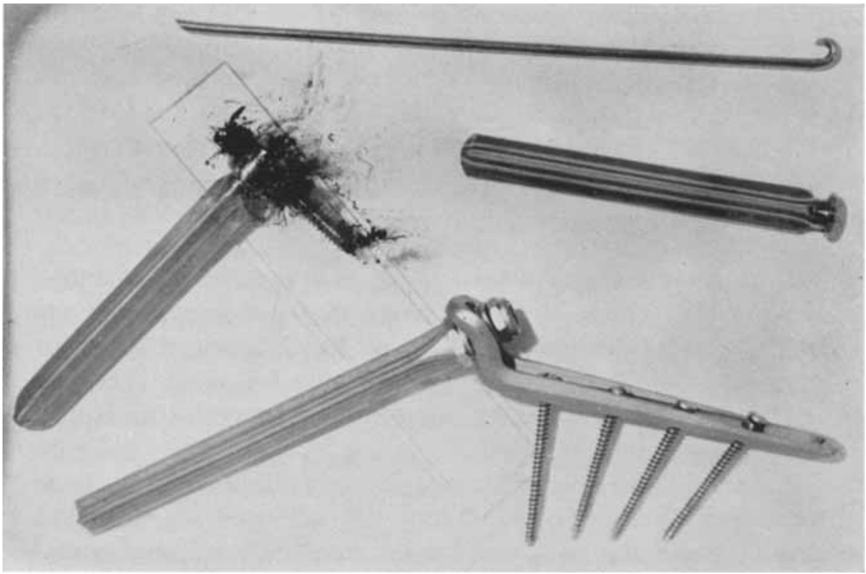

Fig. 29. Ferroxyl test (indicator concentration 2 per cent) of Sven Johansson nail, Mc Laughlin nail and plate, Aronson nail and Rush pin. Photograph taken 2 hours after beginning of test. Only the Aronson nail shows corrosion.

Sven Johansson-nail: Analysis: Cr 17.5 %, Ni 14 % and Mo 4.5 % (Avesta 832 SL). Clinical: The nail was extracted two weeks after insertion because it had projected through the femoral head. The nail was removed with an extractor of conventional type.

Mc Laughlin-nail of vitallium without signs of corrosion or transfer of metal from the tool to the nail. Clinical: Nail and plate removed three months after insertion because the fracture had healed but the nail threatened to project through the cranial part of the femoral head. Extraction revealed a large abscess under fascia lata. There were no clinical signs of infection and the surgeon was surprised by the finding. The entire plate was covered with oedematous purulent granulation tissue. Culture of the discharge gave no growth. Pathologist's report: oedematous granulation tissue with abundant Turnbull positive pigment.

Aronson-nail: Analysis: Cr 25 %, Ni 5 % and Mo 1.5 %. Clinical: Nail removed 4 years after insertion after the fracture had healed because patient had moderate tenderness and pain over the head of the nail. The nail was difficult to remove because the screw was tightly fixed in the canal through the nail. Removal of the screw thus implied a considerable amount of cold working on the screw head. Ferroxyl test showed severe

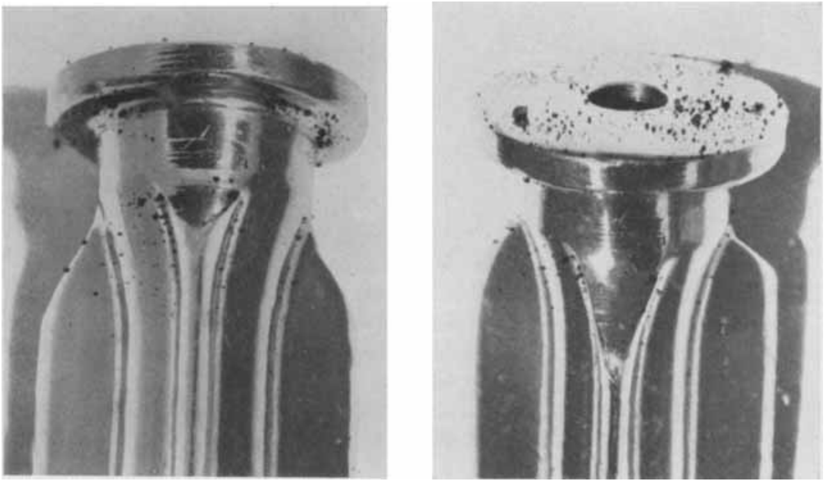

Fig. 30 a + b. Detailed view of head of Sven Johansson-nail in Fig. 29 (X 5) 24 hours after beginning of test. The black dots on the nail are in reality blue. They might be due to transfer of metal from the extractor and possibly persistant from transfer on insertion.

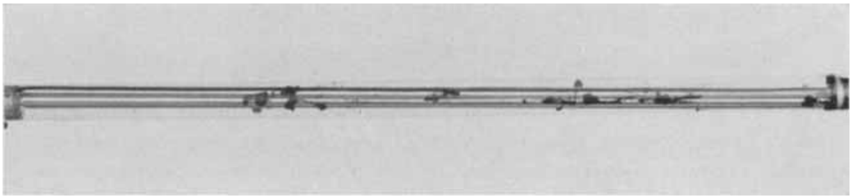

Fig. 31. Ferroxyl test of Kuentscher's nail in glass tube. Indicator concentration 2 %. Photograph taken 2 hours after beginning of test. Nail analysis: 18 % Cr, 8 % Ni and 1.5 % Mo rest Fe. Clinical: Nail removed 7 months after insertion, when femoral fracture in 18 year old female had healed. Corrosion at base in extraction eye, along the bridge of the nail and the edges of the U-channel as well as severe corrosion in the inside of the U-channel.

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corrosion of the screw head (effect of cold working) and of the canal of the screw (crevice corrosion).

Rush-pin: Analysis: Cr 18 %, Ni 10 % and Mo 2.5 %. Clinical: The nail was removed three months after insertion after fracture had healed. It was removed for prophylactic reasons. No indication of corrosion.

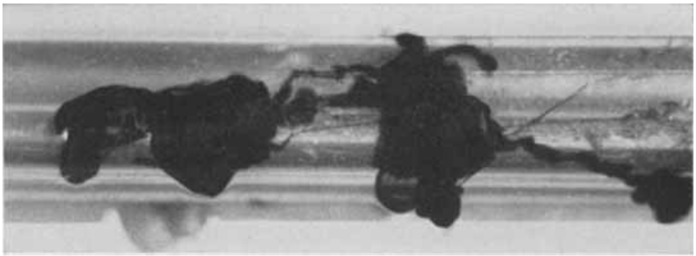

Fig. 32. Detail (× 10) of a part of Fig. 31 where corrosion in the channel was strongest.

Cause of corrosion: 1) Unsatisfactory composition of the alloy (low Mo-content).
2) Cold working of nail on insertion.
3) Transfer of metal from guide to nail.

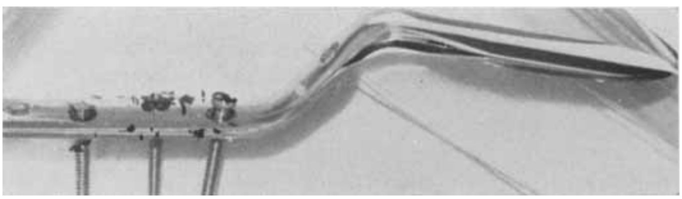

Fig. 33 a. Blount's plate in ferroxyl gel. Indicator concentration 2 %. Photograph taken 2 hours after beginning of test. Analysis not performed by author. Zimmer SMo stainless steel which is usually to be understood as 18 % Cr, 8—11 % Ni, 2.5—2.7 % Mo. Clinical: Plate removed 3 months after insertion as internal fixation of Mc Murray osteotomy after collum pseudarthrosis. Corrosion along edge of plate where the surface is severely damaged is several places. Entire plate covered by small surface scratches without corrosion. Abundant corrosion of screw hole. Note: the nail blade shows no corrosion.

moderate or slight, such deposits will soon be dissolved by the body fluid, especially if the nail has been in living tissue for a long time. This is supported by the fact that the "central canal test" is often negative. In those cases where the test is positive one might imagine that the transfer was severe or

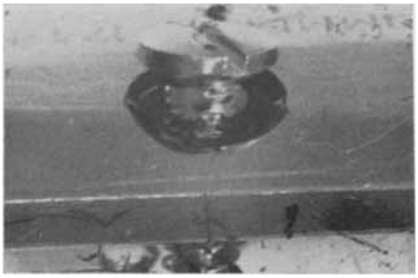

Fig. 33 b. This screw head (× 5) was deformed by the screw driver but shows hardly any corrosion. The screw hole, however, shows corrosion. The colours seen to ooze from underneath the plate around the screw come from the screw hole. This may be an example of crevice corrosion. In one of the larger areas damaged on the edge of the plate some corrosion is seen. No corrosion is seen in the stamped letters and figures.

Fig. 33 c. Detail of middle screw (× 5). Edges of plates severely damaged and corroded. Screw head shows hardly any corrosion. Abundant corrosion in screw hole.

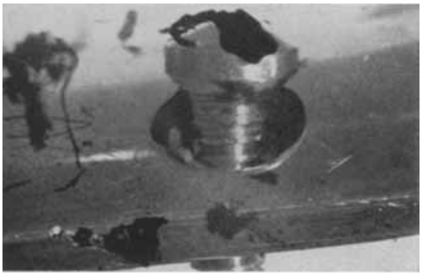

Fig. 33 d. Detail of uppermost screw in plate (× 5). Severe surface damage on edge with corrosion. Screw head markedly corroded. This may be an example of the total effect of the transfer of metal from a tool to the screw and of cold working.

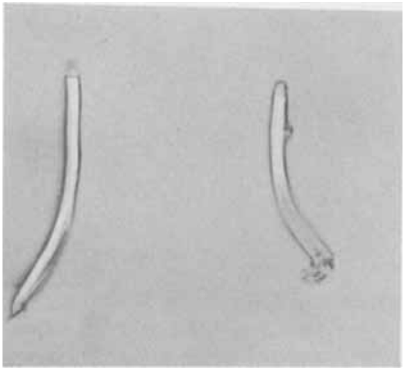

Fig. 34 a. Negative "central canal test" from collum nail made of vitallium. Central canal was cleared with a wooden ear pin. The diameter of the wooden ear pin was slightly less than that of the canal. Gel was poured into the canal and after it had set, it was pressed out with a similar ear pin. If the test is negative or only weakly positive it can be pressed out as a single coherent worm. It will of cause be somewhat compressed and not so long as the entire nail. Any persistant gel can be readily expelled with the wooden pin. If the wooden pin is then rolled over white filter paper any traces of Turnbull blue will become apparent.

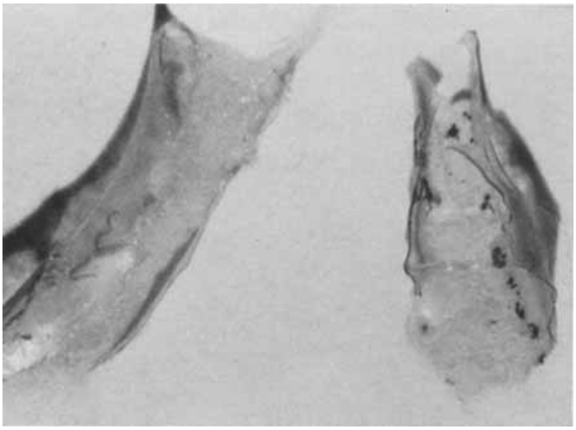

Fig. 34 b. Positive "central canal test" (× 10). If the test as in this case is positive the gel will not always be expelled as a single worm but in fragments due to the gel adhering to the wall of the central canal where

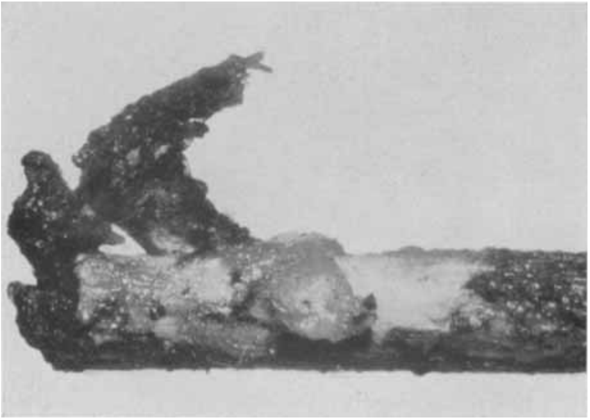

Fig. 34 c. The strongly positive central canal test from a collum nail of vitallium (× 10). The dark coloured gel attached to the ear pin is intensely blue. This large amount of Turnbull blue probably indicates transfer of metal from the guide that had been used. In this case it was difficult to pass through the earpin to clean the canal before the test.

that part of the transfer had persisted as rust in the canal. This deposit may possibly be one of the main sources of the iron pigment seen in granulation tissue around the heads of femoral nails made of vitallium (EMNÉUS 1957).

A negative, a slightly positive and a strongly positive "central canal test" are illustrated in Figs. 34 a, b and c.

If two different metals or alloys are in contact with crevices as *e. g.* plate screw there is great risk of corrosion of the metal which is less noble (*i. e.* anode in the element).

This gives rise to a genuine galvanic corrosion.

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the small deposits are located. The dark coloured patches in the ary gel to the right may represent metal transferred from the guide. It is possible though less likely that they may be due to rests from the manufacturing of the nail or iron in the vitallium. A further possibility is that it might be iron from decomposed haemoglobin. It can be broken down to ionized form. An accumulation of blood could be sealed in the central canal and there broken down to inorganic form but this sounds less likely.

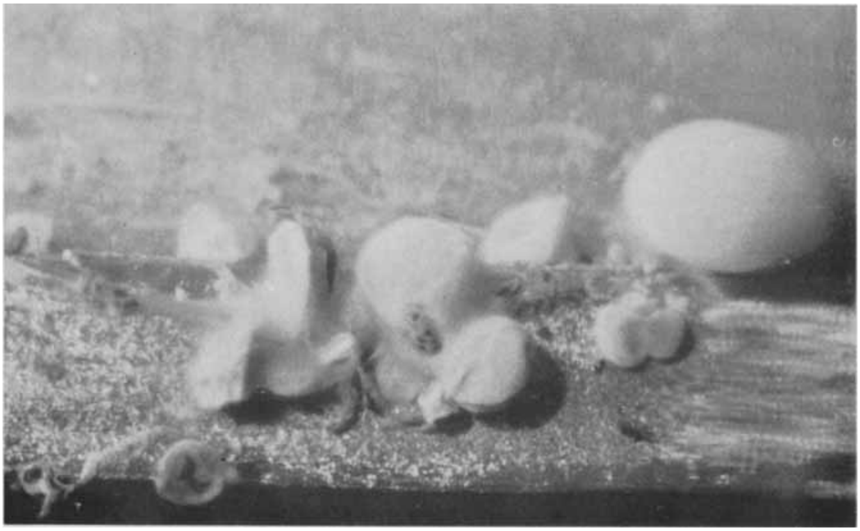

Fig. 35. Detail of Whright's plate of vitallium from angle between the nail blade and the screw blade (× 20). The photo was taken 24 hours after the beginning of the test. Clinical: Before insertion of the plate the latter had been heated and the angle increased from 80 to 130 degrees. The plate had been bent at that place represented by the picture. The plate had been used to fix a McMurray osteotomy. The plate was removed 8 weeks later because of dislocation of the osteotomy. The ferroxyl test indicates corrosion at the site where the plate had been bent. The bubbles are dark brown. Roentgen-spectrographic analysis of the artificial corrosion products showed Co, Cr, and Mo with predominance of Co.

Transfer of tool steel to the vitallium will likewise give rise to such a galvanic element. In such cases rapid dissolution of the steel alone may be expected (Fig. 28).

Stellites (Co-Cr) are present in vitallium and neutrillium. Vitallium is very resistant to corrosion. VENABLE & STUCK claimed this alloy as superior as early as 1937 and proved it in 1947. The reason why this has not generally been accepted might be explained in the following way. A Rush-pin made of chromium-nickel-molybdenum steel is almost as good as vitallium as far as corrosion is concerned. This may perhaps also

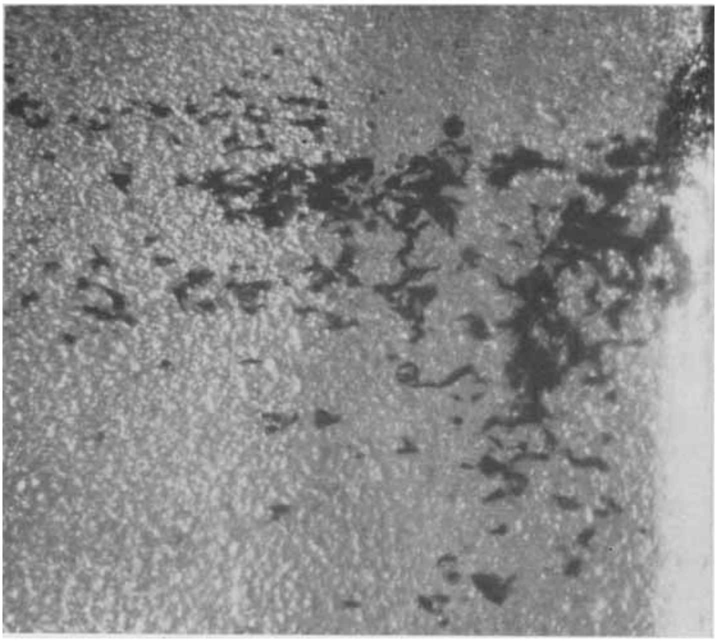

Fig. 36. Detail of plate adjacent to the angle of the same plate as in fig. 35 (× 20). In order to bend the plate to desired angle the plate might have been gripped with a pair of tongs in this place. The dark-coloured areas in the photograph are in reality intense blue. The iron demonstrated probably represents material transferred from these tools.

hold for a Sven Johansson nail. In addition, other properties of this steel may be preferable compared with vitallium.

However, in association with cold working and crevices in appliances such as a Blount's plate (Fig. 33), or Aronson-nail (Fig. 29), the weak point of the steel with respect to corrosion will become apparent. In spite of the fact that LAING (1959), for example, pointed out that vitallium might also be suspectible to crevice corrosion clinical experience (ZAREK & SCALES 1955, SCALES 1956 and SCALES *et al.* 1959) suggests that in this very respect it is superior. In large appliances consisting of a number of details, stellites appear to be superior to chromium-nickel-molybdenum steel as far as corrosion is concerned.

On one occasion the ferroxyl test showed corrosion of a vitallium plate made of Austenal. Figs. 35 and 36. In that case the surgeon had heated the plate and bent it for a special purpose. It is obvious that the manufacturer's guarantee cannot hold for material worked in this way. This example is only given to show that the ferroxyl test will also show corrosion of cobalt alloys.

The so-called microcorrosion of vitallium and pure titanium made probable by FERGUSON, LAING & HODGE 1960, EMNÉUS & STENRAM 1960 and EMNÉUS, STENRAM & BAECKLUND 1960 is still obscure and its clinical significance cannot be judged.

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