

# Stress-corrosion studies on materials used for surgical implants\*

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## SYNOPSIS

Samples of Vitallium (a cobalt-chromium alloy), 316L stainless steel, and titanium T318 were subjected to the boiling magnesium chloride test so that their susceptibility to stress-corrosion cracking could be determined, and their behaviour under service conditions was then assessed.

Stress-corrosion cracking was confined to the stainless-steel samples, while gross pitting was detected in the samples of forged Vitallium. It was concluded that the use of stainless steel should be avoided for long-term surgical implants. Surface imperfections on the stainless steel are generally the cause of pitting, from which stress-corrosion cracks are sometimes propagated.

## SAMEVATTING

Monsters van Vitallium ('n kobalt-chroomlegering), vlekvrystaal 316L, en titaan T318 is aan die toets met kokende magnesiumchloried onderwerp om hul vatbaarheid vir spanning-korrosiebarste te bepaal waarna hul gedrag onder gebruikstoestande geëvalueer is.

Spanning-korrosiebarste was beperk tot die vlekvrystaalmonsters terwyl ernstige invreting waargeneem is in die monsters van gesmede Vitallium. Daar is besluit dat die gebruik van vlekvrystaal vermy moet word vir langdurige chirurgiese inplantings. Oppervlakkoute op die vlekvrystaal is gewoonlik die oorsaak van invreting waaruit spanning-korrosiebarste soms ontstaan.

## Introduction

A small but definite incidence of failure<sup>1, 2</sup> of orthopaedic implants has led metallurgists and surgeons to suggest stress-corrosion cracking (S.C.C.) as the cause of the failure. However, there is by no means agreement on this matter, some workers<sup>3-5</sup> finding no evidence of S.C.C. while others<sup>6-8</sup> report failures due to it.

It is believed<sup>9-11</sup> that a clearer picture of the situation could be obtained if all failures were subjected to metallurgical investigation. The object of the research reported here was to clarify the position to some degree.

## Stress-Corrosion Cracking

The first recognized case of S.C.C. was in the late 1800s at the time of the monsoon in India and Burma. The 'season-cracking' of brass cartridge cases was noticed when they were exposed to a moist atmosphere in the presence of ammonia (probably a product of the natural degradation of vegetation). The cure was a stress-relief anneal of the cartridge cases, which were cold-pressed, thereby removing residual stresses. Interest in the problem died down until 'caustic embrittlement' of steel boilers became a problem. The stresses experienced at the rivets of the boilers exceeded the elastic limit of the steel, and alkalis introduced into the water to minimize corrosion collected in the crevices between the rivets and plates until the concentration of alkali induced S.C.C. With the use of all-welded boilers and improved methods of water treatment, the problem has been minimized, although it sometimes still appears in tanks used to store concentrated alkalis.

Today, the problem appears in a wide variety of systems, including intergranular stress-corrosion of

high-strength aluminium alloys in aqueous sodium chloride solutions, transgranular stress-corrosion of titanium alloys in aqueous halide solutions, transcrystalline cracking of magnesium alloys in NaCl-H<sub>2</sub>O<sub>2</sub>-H<sub>2</sub>O solutions, transcrystalline stress-corrosion of austenitic stainless steel in chloride, hydroxide, and bromide solutions, and stress-corrosion of mild steel in nitrate and hydroxide media.

Stress-corrosion has been defined as 'the spontaneous failure by cracking of a metal under combined action of high stress and corrosion'<sup>2, 12</sup> and 'the rupture of metal, taking the form of cracks that may occur under the conjoint influence of a corrosive environment and applied or residual stresses'<sup>13</sup>. The phenomenon includes corrosion-assisted brittle fracture and stress-assisted corrosion, where metal physics, microstructure, and electrochemistry combine to produce rapid penetration along a trans- or inter-crystalline path. A description that is favoured is thus: susceptibility of a metal or alloy to stress-corrosion implies greater deterioration in the mechanical properties of the material through the simultaneous action of static stress and exposure to a corrosive environment than would occur by the separate but additive effects of these agencies.

## Testing for S.C.C.<sup>14</sup>

The purpose of all stress-corrosion testing is to be able to predict the susceptibility of an alloy to this mode of failure in a particular environment. The specific aim of a comprehensive project on S.C.C. of materials used for surgical implants would be to determine the resistance to S.C.C. of an actual or simulated structure in its anticipated service conditions of low temperature, relatively low chloride concentration, and limited period of static tensile loading. However, this would entail testing over extended periods of time, and the project reported here was limited to the following:

\*This paper is an abridged version of a dissertation that won one of the Institute's student awards for 1975.

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- (a) a determination of the susceptibility to S.C.C. of three biometals,
- (b) a prediction of the effect of changes in environment, and
- (c) a prediction of the effect of changes in level of the applied stress.

Whether the predictions mentioned would be of a quantitative or qualitative nature would depend to a large extent on the nature and the number of results obtained.

Since the compositions of the alloys used in surgical implants are specified in ASTM Specifications and British Standards, the available materials are limited. The following three materials, which are all available commercially, were chosen for the tests: AISI type 316L stainless steel, Vitallium, and titanium T318. The metallurgical treatment undergone by a particular alloy can effect its properties to a marked extent but, since the alloys in surgical implants would be used in the 'solution-treated' condition (no heat treatment is possible in an operating theatre), it was felt that such differences would not affect the test procedure adopted.

AISI type 316 L is an austenitic stainless steel of extremely low carbon content. It is non-magnetic and non-hardenable by heat treatment, but it hardens readily during cold work. If this material is to be used for surgical implants, it is usually annealed at 1050°C to remove the effects of any cold work that might have resulted from its manufacture.

Vitallium is a cobalt-chromium alloy of low carbon content having a yield stress that compares favourably with that of stainless steel. The cast alloy has excellent abrasion resistance, but its fatigue limit is rather low, which makes it unsuited to applications where cyclic stresses are common. Wrought Vitallium was developed to overcome the disadvantage of the cast alloy, and its fatigue limit is much higher than that of its cast counterpart.

T318 is a titanium-aluminium-vanadium alloy that has excellent mechanical qualities, and its fatigue endurance limit is expected to be adequate although little work has been done on this aspect of the alloy. An important consideration is that titanium has a strength-to-density ratio much closer to that of bone than has stainless steel or Vitallium.

The design of test specimens<sup>3</sup> is a subject open to much discussion, and there are many theories and suggestions as to the techniques that should be adopted. The recommendations of ASTM Sub-Committee G 0106, at present engaged in preparing comprehensive analyses of the common S.C.C. test specimens and recommended practices for their use, are still eagerly awaited.

The type of stressing<sup>15</sup> to be used in the present tests was not easy to select. Dead-weight loading might be applicable to the shafts of hip prostheses, whilst, in the case of residual stresses after forming and misalignment, constant deflection stress is more applicable. Stresses would never be static in the human body, and no portion of any prosthesis would ever be under a constant tensile stress. In addition, the effects of alternating load on S.C.C. is a complex and little-understood problem. The tests used in this project involved constant static tensile

stress mainly because these represent the most severe conditions that could occur.

For most tests, the proper selection of the corroding agent is vital. In tests on metals for surgical implants, solution composition, temperature, oxygen pressure, hydrodynamics, pH and level of impurity should be those corresponding to body conditions.

Laboratory tests that yield dependable results for one alloy may not yield dependable results for another, even if both alloys are of the same basic metal. Accelerated tests always require calibration against service conditions. The essential function of an accelerated S.C.C. test is to provide a rapid test for the comparison of alloys or for quality control. Corroding agents should contain the specific iron responsible for S.C.C. of the type of alloy but should produce a minimum of general corrosion.

The 3.5 per cent NaCl Alternate Immersion Test, ASTM B192-44T, has been declared obsolete, and is at present under review. In any case, it was considered that this test would not provide any additional information to that provided by the proposed tests.<sup>1</sup> The Boiling Magnesium Chloride Test, which provides the most aggressive conditions for S.C.C. induced by ions, was one of the proposed tests. A.S.T.M. Sub-Committee G.0106 has prepared an advance specification relating to this test in view of its universal acceptance as a dependable accelerated test.

### Experimental Method and Results

The three alloys were subjected to the boiling magnesium chloride test as a test of their susceptibility to S.C.C. Those that were found to be susceptible were then tested *in vitro* in an environment that simulated body conditions. As neither of these tests was entirely satisfactory the three selected alloys were then tested by a modified version of the magnesium chloride test.

### Boiling Magnesium Chloride Tests

The susceptibility of AISI type 316L stainless steel to S.C.C. in chloride media is a problem that has been investigated many times, and only brief verification of this was required. However, the incidence of S.C.C. in Vitallium and titanium T318 had not been studied to any great extent, and accelerated tests in boiling magnesium chloride were therefore undertaken. A sample of cast and lightly cold-worked type 304 stainless steel was tested in the same manner to serve as a basis for comparison.

Small test specimens (40 mm by 5 mm by 5 mm) of solution-annealed 316L stainless steel and cast and wrought Vitallium alloys were machined accurately, and the surface was polished to a 400 water-paper finish in accordance with the suggestions of Colangelo and Greene<sup>16</sup>.

The clamp used to stress the test pieces is shown in Fig. 1. It was made of mild steel, and rubber insulator pads were needed to insulate the sample to avoid cathodic protection of the biometals and possible prevention of S.C.C. The three-point loading system used brought the outermost surface fibres of the sample into

tension, with the area opposite the bolt having the highest stress. This stress was calculated by

$$\sigma = \frac{6Ety}{L^2},$$

where  $\sigma$ =tensile stress,  $E$ =Young's modulus,  $t$ =thickness of sample,  $y$ = maximum deflection, and  $L$ =distance between supports. By tightening or loosening the bolt-nut combination, the stress could be varied at will.

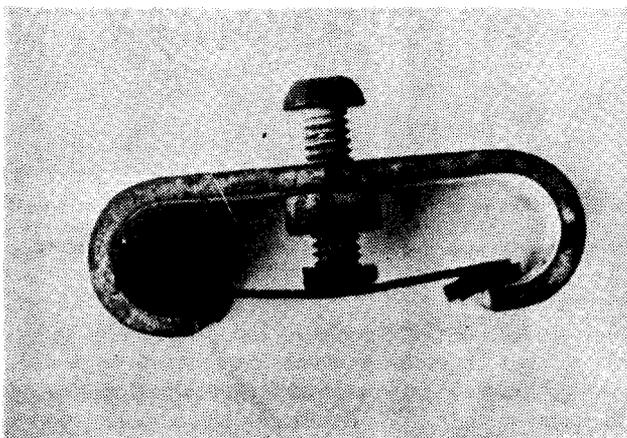


Fig. 1—Jig used for the stressing of specimens, showing the rubber insulation in position

Since titanium T318 was obtainable only in the form of orthopaedic screws and 0,83 mm and 1,5 mm wire, it could not be tested by this method. Commercial-purity titanium samples were therefore stressed in the same manner as the biometals to give some indication of the propensity to failure by S.C.C. of titanium.

The Pyrex test vessel used for these tests is shown in Fig. 2. The container was heated on an electric hot-plate and the boiling solution was refluxed continually with a finger type of condenser. On being heated, the magnesium chloride dissolves in its own water of hydration, and the salt boiled at 152°C. This compares well with the 154°C suggested by ASTM. The temperature of the boiling salt solution was automatically controlled by the thermostatic hot-plate temperature controller. Variations of only 2°C were registered over a three-hour period.

The sample was loaded in the jig and stressed to the desired level by tightening of the nut. Thorough washing in trichlorethylene to remove all oil and grease, air drying, and immersion in boiling water were used to clean the specimens.

The temperature of the boiling solution was raised to 150°C and the clamp placed in the solution carefully. Boiling ceased momentarily but recommenced in a few moments. The reflux condenser was replaced, and the time at which the test was started was noted. Every half-hour the clamp was removed and quenched in cold water. The surface of the sample was examined under a hand lens for surface cracks, and was then replaced in the solution. Depending on the alloy under test, periods of between 4 and 72 hours were used for testing.

After failure, the samples were removed and examined under a low-power microscope, and any surface cracks

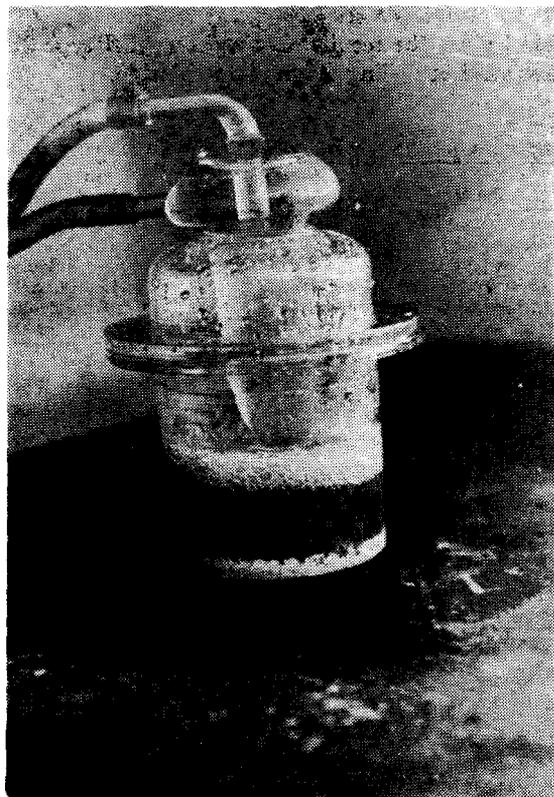


Fig. 2—Pyrex container used in the boiling magnesium chloride tests, with the finger-type reflux condenser in position

were noted and marked. Dye-penetrant was used to show up the cracks on the surface. The cracked samples were mounted in plastic, prepared metallographically, and examined microscopically in both the etched and un-etched conditions so that the crack morphology could be determined.

All the samples were tested at the same temperature but at different stress levels so that the effect of stress on time-to-failure could be determined.

A brief test was conducted on small twisted wire loops (Fig. 3) of all the biometals immersed in boiling magnesium chloride. The loops were removed every half hour, studied under a hand lens, and re-immersed until failure occurred.



Fig. 3—Two of the wire loops submitted to the boiling magnesium chloride tests

*Results for Stainless Steel*

Table I gives the results obtained on AISI type 316L stainless steel in boiling magnesium chloride.

TABLE I  
RESULTS OF ACCELERATED TESTS ON STAINLESS STEEL

No.	Material	Stress MPa	$\sigma_{0.2}$ %	Time h	Remarks
1	Solutionized 316L	197	95	19	Broken
2	Solutionized 316L	124	60	27	Cracked
3	Cold-worked 316L	720	95	5	Broken
4	Cold-worked 316L	455	60	12	Cracked
	Cold-worked 304	645	98	4.5	Broken
	316L wire loops	—	—	7	Cracked

Fig. 4 shows the cracks in one of the samples before etching, the jagged surface and branching cracks being indicative of stress-corrosion cracks in stainless steel. The fracture surface also showed these small branching cracks. After etching, all the cracks were confirmed as transcrystalline. In sample 4, one crack was generally transgranular, but a small section appeared to be intergranular (Fig. 5). The explanation for this, as given by Edelenau<sup>17</sup>, is that such cracks can result from the coalescence of numerous short transgranular cracks across the grain boundaries.

A microscopic study of the surface of the test plate failed to reveal the presence of pits, which might have initiated the cracks. Hoar<sup>13</sup> is of the opinion that the visible pits that develop on stainless steel exposed to chloride ions are saucers, and hence do not act as stress raisers initiating mechanical failures. Fontana and



Fig. 4—Transgranular cracks in sample 1 (solutionized 316L stainless steel) after the boiling magnesium chloride test (electrolytic oxalic,  $\times 240$ )

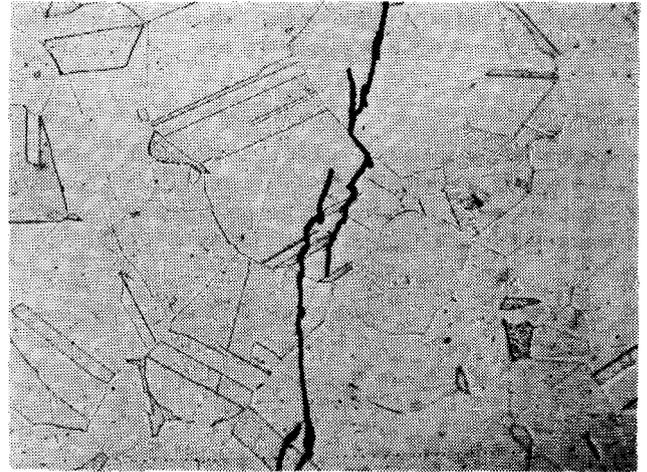


Fig. 5—Cracks in sample 4 (cold-worked 316L stainless steel) after the boiling magnesium chloride test; one of the cracks at the centre is intergranular and the other is transcrystalline (electrolytic oxalic,  $\times 450$ )

Greene<sup>18</sup> believe that breaks in the passive film or enriched layer on stainless steel, brought on by tensile stress, allow more rapid corrosion at localized regions on the metal surface. The outermost fibres of the plates were stressed appreciably, and hence any brittle surface film would have been ruptured.

Close examination of the coiled wire loops revealed the presence of cracks extending from the outer edge towards the inner edge. A polished section of a loop is shown in Fig. 6, and the importance of pits in the initiation of S.C.C. is obvious. Although the samples of wire and plate were all of 316L stainless steel, a range of chemical composition is allowed within the specification, and the role of pitting in the nucleation of S.C.C. may well be a function of the chemistry of the alloy. For instance, molybdenum has a beneficial effect in increasing the resistance of the passive film to pitting in chlorides.<sup>19</sup>

The susceptibility of austenitic stainless steel to chloride S.C.C. has been shown to be strongly influenced

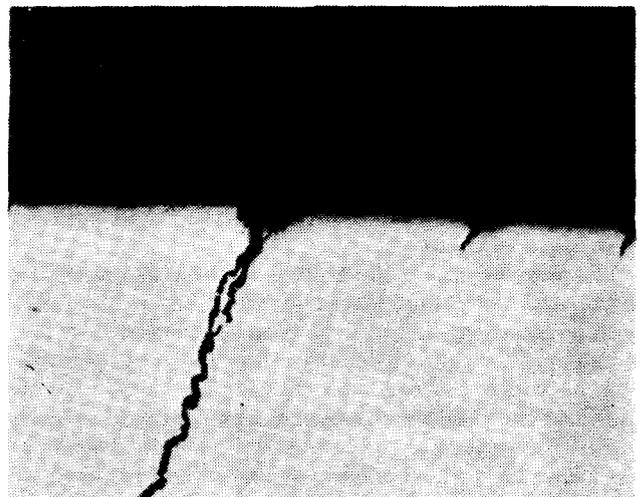


Fig. 6—A polished section of a stainless-steel loop that had been submitted to the boiling magnesium chloride test, showing cracks originating from the base of pits (unetched,  $\times 200$ )

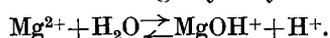
by chemical composition, even to the levels of carbon and nitrogen present<sup>13</sup>. This is due to the effects of stacking-fault energy and co-planar dislocation arrays (both affected by interstitialcies on the area of new surface created by slip-steps during deformation. Stress-corrosion can be avoided by providing lattices without stacking faults and facilitating easy cross-slip on widely separated planes.

The surface of the 316L wire was markedly pitted after the test exposure period. The sites of these pits appear to have been influenced to some extent by surface scratches on the wire that were caused by the die surface in the cold-drawing operation used in its manufacture. This is in accordance with the preliminary results of Rentler and Greene<sup>20</sup>, who believe that corrosion and mechanical failure in fine orthopaedic wires are attributable to surface imperfections such as crevices, pits, and scratches.

Although surface cracks were noted in sample 1 after four hours, catastrophic failure occurred only after 19 hours. Since the metal was stressed to approximately 0,2 per cent proof stress, the rate of crack propagation would initially have been large. However, the test method was of the constant deflection type and, once cracking had released the tensile stress in the outermost fibres of the plate, the induced stress at the crack tip fell to a much lower level. A decrease in the stress level increases the time to cracking, and there appears to be a minimum stress level below which no cracking occurs within a specific environment at a specific temperature.<sup>18</sup> Cracks were initiated in sample 4 within 5 hours, but the sample still failed to break through within 24 hours; perhaps the stress acting on the crack was below the minimum threshold for the environmental conditions.

Sub-microscopic corrosion tunnels can develop by anodic action within minutes on a stressed austenitic stainless-steel surface exposed to boiling magnesium chloride<sup>21</sup>, most probably at sites caused by the emergence of dislocation arrays. These sites may form only at a threshold strain. Hoar<sup>13</sup> believes that the corresponding stress is 0,1 per cent proof stress. Since the samples were stressed to almost 0,2 per cent proof stress in these tests, no slow-step process was retarding crack growth.

The effects of increased solution acidity on S.C.C. were not studied in the present tests. Crack initiation periods are shorter in solutions of lower pH because the rate of hydrogen evolution in corrosion pits or tunnels is facilitated by the acidity of the bulk solution. The effective acidity of solution within a stress-corrosion crack depends on the activity coefficient of the hydrogen ion, as well as on the quantity of hydrogen ions formed by anodic reactions. While the activity coefficient is not available for hot concentrated chloride solutions, it is large and increases with increasing tendency of the cation to undergo hydrolysis via



The period of crack initiation during normal testing in boiling magnesium chloride (more acidic than other chlorides) is small, while the larger value of the activity coefficient in this medium leads to accelerated rates of crack propagation<sup>22</sup>. A complicating feature is oxygen

solubility, the presence of dissolved oxygen or other oxidizing species being critical to the cracking of austenitic stainless steels in chloride solution; if the oxygen is removed, cracking will not occur. Oxygen is readily available in boiling magnesium chloride solutions, and hence the cathodic process is not likely to be the rate-controlling step.

The cold-worked samples (3 and 4), when stressed to the same level of stress as the solution-treated plates (1 and 2), failed in a much shorter time owing no doubt to the pernicious combination of residual and applied stress. Of critical importance is the influence of tensile strain rate upon the exchange current density of the material corroding in the crack. Since constant deflection testing was used, the parameter of strain rate was maintained constant, permitting direct comparison of the test results.

#### Results for Vitallium

Both cast and wrought Vitallium were tested over prolonged periods in chloride media at high stress levels, but no failure of any sample was recorded. Table II lists the tests undertaken.

TABLE II  
RESULTS OF ACCELERATED TESTS ON VITALLIUM

No.	Material	Stress MPa	$\sigma_{0.2}$ %	Time h	Remarks
1	Cast alloy	425	95	72	No failure
2	Cast alloy	269	60	72	No failure
3	Wrought alloy	819	95	72	Pitted—no cracks
4	Wrought alloy	517	60	72	Pitted—no cracks
	Wire loops	—	—	100	Pitted

After the test, the surface of the wrought alloy was pitted, and microscopic examination of the surface confirmed the presence of gross pitting. The pitting appeared to be localized to regions of carbide segregation. (Fig. 7).

After the small wire coils had been subjected to the test for 100 hours, they were pitted and roughened. Microscopic examination revealed that the pitting was

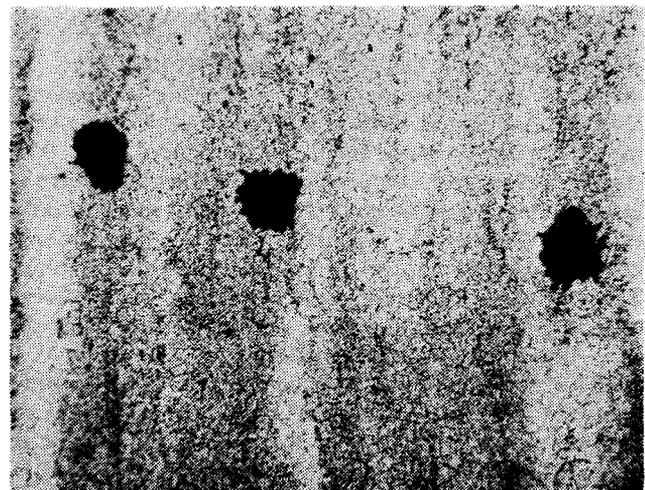


Fig. 7—Pits on a Vitallium plate that had been submitted to the boiling magnesium chloride test, showing how carbon-rich areas appear to be more prone to pitting (HCl, HNO<sub>3</sub>, acetic acid, × 180)

uniform and did not lead to cracks. The dye-penetrant also failed to reveal cracks.

The apparent immunity of cobalt-base alloys to S.C.C. was expected from the lack of reports in the literature of failures of this material in aqueous chloride solutions. These cobalt-base alloys are generally used for their excellent creep resistance and mechanical properties at elevated temperatures, and were first used in surgery after 1937, but many problems associated with the production process were encountered. Low ductility, blow-holes, and carbon spots were often found in the castings. Since implants are often of complex shape and the material has to be cast by the 'lost-wax' process, these are still problems.

Research by Sury<sup>4</sup> into the problem of S.C.C. in both the cast (Protosul-2) and forged (Protosul-10) alloys failed to reveal any susceptibility of either material to S.C.C. He believes that the total insensitivity of the alloys to S.C.C. is to be expected since the alloy is similar to the high-chromium nickel-based alloys that show excellent resistance to this type of corrosion. An adequate explanation of this apparent resistance to S.C.C. must be made with due consideration to the physical metallurgy of the material, as well as to the basic principles underlying S.C.C.

The conclusion from the present tests was that cast and wrought Vitallium alloys do not undergo S.C.C. in boiling magnesium chloride within a period of 100 hours. Hence, chloride-induced S.C.C. of Vitallium alloys is highly unlikely in the human body.

#### Results for Titanium T318

No failures of any titanium sample were noted in the course of these experiments. Table III gives details of the tests undertaken

TABLE III  
RESULTS OF ACCELERATED TESTS ON TITANIUM

No.	Material	Stress MPa	$\sigma_{0.2}$ %	Time h	Remarks
1	Commercially pure titanium	425	95	72	No failure
2	Commercially pure titanium	269	60	72	No failure
	Wire loops	—	—	72	No failure
	Deformed screw	—	—	72	No failure

Sanderson and Scully<sup>23</sup> investigated the S.C.C. of titanium and titanium alloys in boiling magnesium chloride, and found that all the alloys were susceptible to S.C.C. but titanium metal was immune. They concluded that pitting is a prerequisite to cracking, which is largely intercrystalline, and that pits form preferentially along the stressed and roughened edges of the plates as a result of defects in the passive oxide film. Titanium T318 appeared to be the most susceptible of the alloys tested, prior grain-boundary segregation resulting in slow intergranular anodic dissolution. Co-planar dislocation arrays, similar to those in FCC metals, were found in the high-aluminium alloys, which tends to indicate a susceptibility to transcrystalline cracking. Criticism of the use of time-to-failure as the inverse measure of the susceptibility of titanium alloys to S.C.C. was made by Cocks *et al.*<sup>24</sup>, who maintain that only a portion of the total time corresponds to true S.C.C., the rest being attributable to film breakdown or

pit initiation. Bucknall<sup>25</sup> believes that titanium is immune to S.C.C. in seawater and in boiling magnesium chloride, and Gray<sup>26</sup> concludes that hot salt cracking of titanium is more likely to be hydrogen embrittlement than S.C.C.

The total absence of failure in the present specimens is not difficult to explain. The surface of all the samples was polished, and sufficient time for the formation of passive films was allowed prior to testing, so that pitting was unlikely. Since T318 is not readily available in plate form, a bent screw and the loops were used. The stress level in either case is not known, but it was not considerable. However, the lack of pits does tend to exclude the possibility of S.C.C. in titanium alloys.

#### In Vitro Tests

As the testing of any biomaterial should be undertaken in an environment that simulates body conditions as closely as possible, the apparatus was designed with this in mind. It was evident, however, that the conditions in the human body are relatively mild as far as corrosivity is concerned, and hence very extended exposure time would be required. This was impossible in the project undertaken.

An overall view of the apparatus is shown in Fig. 8. The two specimen containers were placed in series since the material under investigation was the same in either tube, and no contamination would take place. The composition of the solution was the same as that used by Hoar and Myers<sup>27</sup> (Table IV).

TABLE IV  
COMPOSITION OF SOLUTION USED FOR IN VITRO TEST

Compound	Quantity, g/l
Sodium chloride (NaCl)	8,0
Potassium chloride (KCl)	0,40
Magnesium chloride (MgCl <sub>2</sub> )	0,10
Calcium chloride (CaCl <sub>2</sub> )	0,14
Sodium bicarbonate (NaHCO <sub>3</sub> )	0,35
'D' Glucose	1,00
Chloride content as Cl	6,38
Approximate pH	6,05

The solution was heated to  $37 \pm 0,5^\circ\text{C}$  in two glass coils in an oil-immersion tank, the aeration tank being exposed to the air to allow its cooling to compensate for the continuous heating of the solution in the thermostatically controlled oil-bath. The gas distributor (size 4) and the thermometer were both located in the aeration tank, which was raised to adjust the head of solution in the specimen containers. Medical-purity oxygen was bubbled slowly and continuously into the solution during the test periods. It was calculated that this solution would become saturated with oxygen after one hour, and hence the solution was passed through a by-pass short-circuiting the aeration tank. The throttling clamp on the by-pass was used to reduce the volumetric flow rate of solution through this section as the pump delivered 5,6 l/min, giving an approximate linear flow rate over the wire samples of 8,3 cm/s. This was obviously far too high to simulate body conditions and was reduced to 1,3 cm/s by use of the throttle.

A lever system was used to stress the wire in tension. The load was obtained by hanging weights from the hooks at points spaced at 5 cm intervals along the beam, and hence the exact moment on the right-hand side of

TABLE V  
STRESS ON WIRE SAMPLES

Dia. of wire mm	Mass kg	Stress at various distances from pivot, MPa								
		10 cm	15 cm	20 cm	25 cm	30 cm	35 cm	40 cm	45 cm	50 cm
1 mm	3,18	183	224	264	303	343	383	422	462	502
	4,55	218	275	331	389	446	502	559	615	674
0,83 mm	3,18	266	325	383	440	497	555	612	671	728
	4,55	316	399	481	564	647	728	811	893	978

the beam could be calculated. This moment was balanced by the force on the wire acting 5 cm from the point of balance. The moment caused by friction at the fulcrum was negligibly small since the two contacting surfaces were polished with 1000 water-paper to reduce friction. Table V gives the range of stresses that were applied during the series of tests on wire samples of various gauges.

Only the materials that had shown a tendency to pitting or S.C.C. in the accelerated tests were tested in this series, i.e., stainless steel. Because of the limited time available, the duration of testing was limited to 600 hours. Even under the severe stresses imposed upon the alloy (approximately 95 per cent of  $\sigma_{0.2}$  in all cases), the combination of low temperature and low chloride content did not produce cracking of the samples. These tests were hence discontinued and a new test procedure adopted.

The wire samples were cut into 20 cm lengths and passed through the two rubber corks at the ends of the specimen containers. The ends of the wire were passed through holes drilled transversely through securing bolts at the top and bottom of the vessel. By tightening nuts on either side of the wire, the wire was clamped above and below the container. The upper bolt was part of the lever used for supplying the force, and the lower was hooked into two cup-hooks at the base of the stressing-frame. Hooks were then placed at required positions along the lever and loaded with the weight selected. The flow rate of solution through the specimen containers was adjusted to the required level by use of the throttle. The temperature of the solution was noted regularly throughout the test. The oxygen flow rate was adjusted at the start of the test and maintained constant, and the wires were all examined under a low-power microscope after the test.

No failure was recorded in any of these tests, and microscopic examination confirmed the absence of pitting or cracking. One sample showed a small defect, located at the point where the wire passed into the rubber cork, and this site of localized corrosion was attributed to crevice attack. The limited duration of these tests is one of the obvious reasons for the lack of positive experimental results. AISI type 316L stainless steel is fairly resistant to S.C.C. and, as the chloride content of the solution used was 6 g/l, long exposure would be necessary before failure occurred. In addition, the flow rate of human body fluids is not constant over an implant and tends to be quasi-viscous. Thus, the test undertaken does not give any definite indication of the tendency to S.C.C. failure of orthopaedic implants under service conditions. Extensive *in vivo* studies are necessary to determine the performance of stainless steel in the human body.

### Modified Magnesium Chloride Tests

The boiling magnesium chloride test indicated the extreme conditions under which S.C.C. would take place, while the *in vitro* tests obviously required very extended test periods for acceptable results to be obtained. A compromise between the two limits had thus to be found. The magnesium chloride test bears no relationship to conditions prevailing in the human body, while the *in vitro* tests cannot be used for rapid prediction of behaviour. No other standard test procedures were readily available, and a new test was therefore devised.

It was recognized that four factors had to be considered: temperature, chloride content of the medium, hydrodynamic conditions, and availability of oxygen. Because it is believed that S.C.C. of stainless steel is unlikely below 80°C, a temperature of 80°C was selected. However, the heating coils used in the oil-immersion tank had stagnant regions that tended to boil and fill the system with steam, which reduced the maximum temperature obtainable to about 77°C.

The chloride content of the solution determines time to failure, and 1100 g/l was selected as the initial chloride concentration. This was subsequently lowered to 600 g/l for further tests. Because the flowrate of body fluids surrounding implants is generally very slow, semi-stagnant conditions were chosen. The test apparatus caused some convection currents to flow, and the migration of the solution simulated the quasi-viscous flow of human fluids.

The form of oxygen available in physiological fluids is an aspect neglected by some researchers. Oxygen is not present as gaseous molecular oxygen dissolved in solution nor as atomic absorbed oxygen, but as a chelate known as oxy-haemoglobin. The ligand field strength of this compound is very high, and oxygen is not readily available for electrochemical reactions at the metal surface. Thus, simple contact of the solution with the atmosphere was selected as the source of oxygen.

The apparatus that was used is shown in Fig. 9. The stressing rig used was the same as that in the *in vitro* tests. The flow rate of the heating water circulated through the system was 5,7 l/m, and hence the temperature obtained inside the specimen container was  $76 \pm 1,5^\circ\text{C}$ , measured with a thermometer situated in the vessel alongside the wire. The solution that lay above or below the jacketed portions of the vessels was obviously colder than the central portion and caused slow convection currents to occur. These were easily detectable with potassium permanganate crystals. An air trap had to be incorporated into the system to prevent steam from filling the pump and causing stagnation of the solution.

The procedure adopted was identical to that used in the *in vitro* tests. However, failures of the biomaterials occurred, and the composition of the solution was

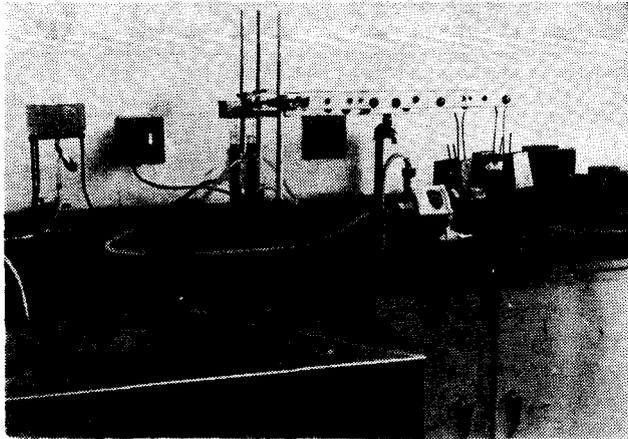


Fig. 8—The general layout of stressing levers and solution containers for the in vitro tests (the thermostatic immersion bath is in the foreground)

altered to 600 g of chloride ions per litre.

#### Results for Stainless Steel

Table VI gives the results of this series of tests on type 316L stainless-steel wire.

TABLE VI  
RESULTS OF MODIFIED MAGNESIUM CHLORIDE TESTS ON STAINLESS STEEL

No.	Stress MPa	Proof stress %	Cl <sup>-</sup> concn g/l	Time h	Remarks
1	485	95	1100	110	—
2	485	95	1100	193	—
3	485	95	600	374	—
4	485	95	600	416	Linear Pitting
5	485	95	300	600	No failure
6	485	95	300	600	No failure

From the results obtained, it is apparent that the chloride content is an important determinant of the time-to-failure of this alloy. No failures of stainless-steel wire were noted in the test using a chloride ion concentration of 300 g/l within the 600 hour test period. This result gives some idea of the resistance to S.C.C. of 316L at temperatures below 80°C.

Microscopic examination of the corrosion test samples, indicated that the majority of the cracks could be attributed to some surface defect, mostly pits (Fig. 10). The role of surface imperfections, noted by Rentle and Greene<sup>20</sup>, is once again exemplified. Avoidance of these surface defects would reduce the occurrence of failures most drastically. This is an area where liaison with the manufacturer could lead to marked improvements.

The wire samples tested in magnesium chloride slurry failed in a much shorter period than those tested in the more dilute solution. However, the mode of failure as noted in the metallographic examination was the same in both cases. The increased chloride ion content enabled pitting of the wire to take place sooner, and hence the crack initiation step of the process was shortened. The effects of chloride ion content on the crack propagation rate is generally regarded as negligible under the conditions of very high stress used in this research. This is probably due to the slip-arrest stages being the rate-controlling step. Dislocation pile-up occurs

fairly readily in highly stressed stainless steel owing to this material's marked propensity to work-harden. At lower stress levels, the rate of crack propagation may be reduced because slip-arrest may be retarded by chemical means, e.g., anodic dissolution-repassivation cycling<sup>13</sup>.

No cracks were detected after an exposure of 600 hours in the solution having a chloride ion concentration

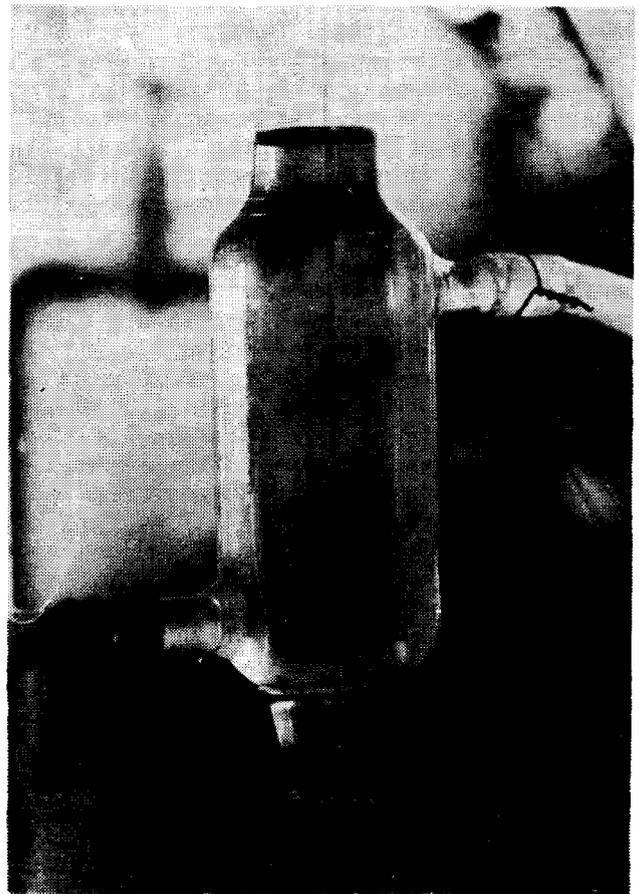


Fig. 9—Close-up of the specimen container used in the modified boiling magnesium chloride tests (the solution is placed in the inner tube while heating water is circulated in the outer jacket)

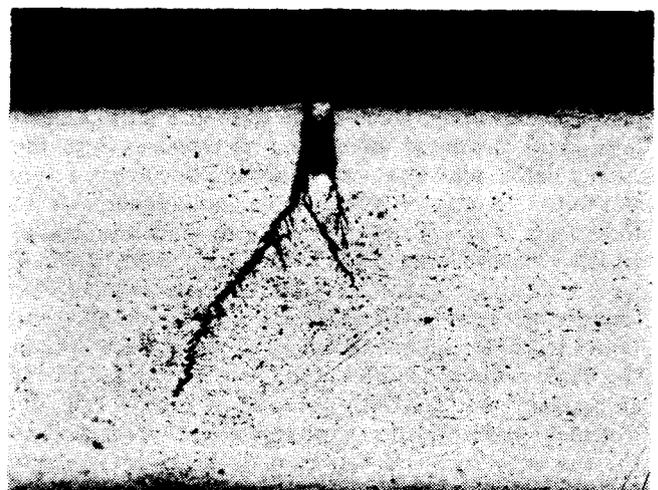


Fig. 10—Crack associated with a surface pit in 316L stainless steel that had been submitted to the modified boiling magnesium chloride test ( $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\times 120$ )

of 300 g/l. The relationship between time-to-failure and chloride content may thus be non-linear, which makes extrapolation to other concentrations of chloride impossible. Hence, no accurate estimation of the minimum time-to-cracking of 316L stainless steel in the human body can be given. Since the tests were conducted at higher temperatures than those in the human body, extrapolation of the results is complicated further. The combination of residual stress, high constant tensile stress, a chloride concentration that is 50 to 200 times that *in vivo*, and a significantly higher temperature obviously results in exceedingly severe conditions.

It is thus concluded that S.C.C. of 316L stainless-steel orthopaedic implants requires a long exposure time. While joint replacements are expected to last as long as possible, some implants, e.g. Kuntsher nails, Steinman pins, osteotomy plates, may be removed once they have served their purpose. The mechanical properties of austenitic stainless steel are vastly superior to those of cast Vitallium-type alloys but equal to those of forged Vitallium alloys. Stainless steel is far less expensive than the cobalt-base superalloys, and the manufacturing methods used are easier. For applications where the mechanical properties of the alloy are of prime importance, and where removal of the implant within 12 to 18 months is a standard procedure, stainless steel offers decided advantages over cobalt-chromium alloys. For purposes where the corrosion resistance of the implant is an important consideration, such as in hip, elbow, or knee prostheses, the apparent inertness of the cobalt-base alloys is an overriding advantage.

The use of a scanning electron microscope enables entire fracture surfaces to be examined at very high magnification at one viewing, since great depth-of-field is possible. Fractographs can be examined to determine the nature and morphology of a fracture, evidence of slip, role of surface defects, and surface corrosion products.

The stainless-steel wire under the electron microscope showed both ductile and brittle portions. The brittle portion was, in most cases, covered by corrosion product, which appeared in all cases to be an oxide. The amount of corrosion product present seems to indicate that cracking took place long before fracture. A passive metal such as stainless steel shows little corrosion in neutral chlorides. The ideas of 'wedging' by solid corrosion product have been advanced by Hoar<sup>13</sup> and Fontana and Greene<sup>18</sup>. It is likely that Cr<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> are both formed, although the volume of product obtained makes X-ray analysis very difficult.

One sample showed very interesting pits on the wire surface below the fracture (Fig. 11). The pits are localized to one region and may have been initiated by small surface inhomogenities. This severe pitting took place after 416 hours in the 600 g/l chloride ion solution, and it can be concluded that pitting is a time-dependent phenomenon and may require surface defects to initiate it. It is noteworthy that the pitting appears to have led ultimately to fracture. Small crystallographic cracks in the corrosion product at the base of a pit appear to be associated with S.C.C. at the base of the pit.

Conclusions regarding the depth of a crack that is

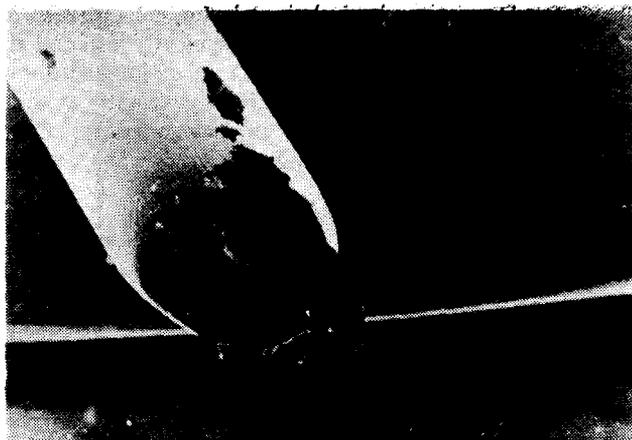


Fig. 11—The fracture surface of stainless-steel wire that had been submitted to the modified boiling magnesium chloride test, showing longitudinal pits in the wire, which may have led to premature fracture ( $\times 38$ )

required before catastrophic failure takes place are difficult to obtain direct from the fractographs. Fig. 12 shows the detail of the region where the brittle-ductile transition occurs. Since the crack reduces the cross-sectional area of the wire, the area of free surface created determines the point at which ductile fracture occurs. It was calculated that any crack that reduces the area of the wire used from 0,785 mm<sup>2</sup> to 0,602 mm<sup>2</sup> would lead to ductile failure. Many small cracks would be able to achieve this reduction sooner than a single large crack, where crack propagation is controlled largely by electrochemical phenomena.

#### Results for Vitallium

No failure or evidence of pitting was recorded after 600 hours of testing, and the tests on this material were therefore discontinued.

Pitting of the wrought alloy plate in boiling magnesium chloride was noted after long exposure, but a far longer exposure in solution at 77°C had no effect. This seems to indicate that pitting of wrought Vitallium alloys is possible only at temperatures above 100°C or after an exceptional exposure time. As the activation energy

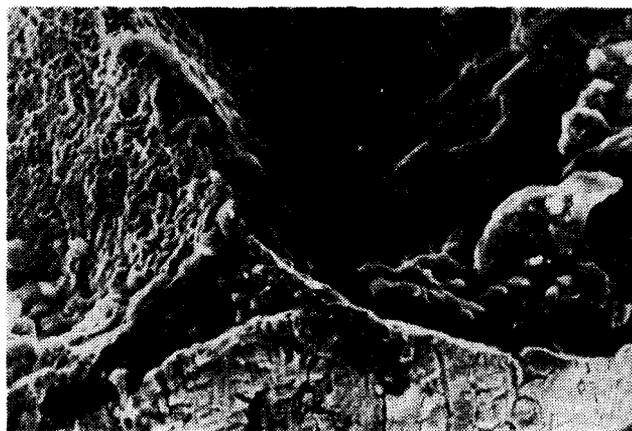


Fig. 12—Ductile-brittle transition region in stainless-steel wire that had been submitted to the modified boiling magnesium chloride test; corrosion product covers the brittle region, and the microscopic voids in the ductile region are visible

necessary for pitting depends largely upon temperature, the pitting process seems to be chemically controlled. The pitting noted on many Vitallium orthopaedic implants has been induced primarily by crevice attack. Some other reactant present in physiological fluids, perhaps an organic acid, might catalyse the pitting reaction.

### Discussion

ASTM type 316L stainless steel is known to be susceptible to S.C.C. in chloride media. The necessary conditions of a minimum stress of  $0.1 \sigma_{0.2}$  and a minimum chloride content (in oxygenated solutions) of 10 p.p.m. are both possible in the human body<sup>18</sup>. Constant tensile stresses were not possible, but residual stresses, which have a pronounced effect, are usually present to some extent.

Vitallium alloys are not susceptible to chloride S.C.C. but generally have poor mechanical properties because of the complicated manufacturing processes required, and sometimes also contain defects in their structure. The wrought alloys are susceptible to pitting.

Titanium T318 appears immune to S.C.C. and pitting in dilute chloride media, but is too weak for many applications.

Fixation devices, which are not designed to bear weight but are used as adjuncts by holding bone fragments in the proper position during healing, may be left in the body or removed at the surgeon's discretion. If the device is sure to be removed, stainless steel is the obvious choice of material provided it is in the solution-annealed condition. Wrought Vitallium or titanium alloy should be used if the implant is not to be removed.

Prostheses, which permanently replace part of the body, should be made of a Vitallium-type alloy. For applications in which resistance to wear may be of importance, cast Vitallium would be preferable; for load-bearing, wrought Vitallium is ideal. However, the cobalt-base alloys are expensive and difficult to produce with the high degree of control that is necessary.

The manufacture of an austenitic stainless steel that would have the mechanical properties and corrosion resistance of type 316L while having resistance to S.C.C. has been attempted. An extensive study undertaken by Loginow and Bates<sup>28</sup> showed that nickel and carbon improve the S.C.C. resistance of annealed steels, that nickel and silicon increase the resistance of cold-worked steel, and that nitrogen, phosphorus, and molybdenum decrease the resistance in all steels. The study resulted in the formulation of a steel (18Cr 18Ni 2Si 0.06C) with low phosphorus and molybdenum that had a decidedly improved resistance to S.C.C. Its physical and mechanical properties are similar to those of 316L stainless steel. This alloy would be ideal for orthopaedic applications, but extensive clinical and laboratory testing is still required before it can be used.

There are many other materials that are also suitable (e.g., Incoloy 825, Uddeholm 250UV, Sandvik 2RK65), but the recommendations of the ASTM Sub-Committee on Surgical Implants indicates that uniformity of material is desirable, and any new material may therefore meet with opposition. Closer quality control of the wrought cobalt-base alloys and improved manufacturing

techniques for the cast cobalt-base alloys would solve the problem of suitability of material.

### Acknowledgements

Grateful acknowledgement is made to the following, who assisted the authors in various ways: L. Solomon; Ms S. E. Gross and G. Goulding; Messrs N. C. Webb, A. Xoseka, T. Utter, and R. Retief; and Escom.

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## NIM reports

The following reports are available free of charge from the National Institute for Metallurgy, Private Bag 7, Auckland Park, 2006 South Africa.

### Report no. 84

*Leaching tests on the copper sulphide mineral valleriite from Palabora Mining Company — a preliminary report.* (22nd Dec., 1966; re-issued Jun. 1976).

A large number of exploratory leaching tests on pure valleriite from Palabora Mining Company are described. It was established that the mineral does not respond well to conventional reagents, other than oxidizing ores in acid or alkaline medium; of these, ferric ion is an effective lixiviant.

A number of recommendations for future work are made.

### Report no. 157

*Results of tests to obtain pure Valleriite* (17th Apr., 1967; re-issued Jun. 1976).

Attempts to obtain pure valleriite from valleriite-rich samples failed because of the tendency of this mineral to slime and to break within valleriite grains rather than on boundaries. The result was that many chats are present in all the fractions coarse enough for magnetic and density separations. These phenomena may also be important in the treatment plant at Phalaborwa.

Pure valleriite for analysis and testwork could be obtained only by hand-picking from exceptionally rich samples.

### Report no. 1222

*The liquid-liquid extraction of zinc from zinc chloride solutions by the use of di-2-ethyl hexyl phosphoric acid.* (5th Mar., 1971; re-issued Aug. 1976).

The conversion of zinc chloride to zinc sulphate represents a step in a process developed to recover zinc from spent pickle liquor. This has been accomplished by the extraction of zinc by a 25 per cent solution of di-2-ethyl hexyl phosphoric acid in paraffin.

Equilibrium results are given both for simple shake-out tests and for batch countercurrent shake-out tests with re-use of solvent.

It was established that a chloride solution containing 15 grams of zinc per litre can be treated at a phase ratio (organic to aqueous) of 15 to give a 90 per cent recovery of zinc.

### Report no. 1513

*The upgrading of chromite ore from Moreesburg.* (10th Jan., 1973; re-issued Jun. 1976).

An account is given of attempts to improve the chromium-to-iron ratio in a chromite ore by the removal of the iron-rich metallic phase resulting from partial reduction of the ore.

Gravity separation, rusting, ferrous-ferric leaching, and magnetic separation were all tried, and the leach was found to be the only method offering any hope of success. However, further investigation is required.

### Report no. 1619

*Reduction of the chromium in ilmenite concentrates.* (10th Feb., 1974; re-issued Jun. 1976).

Methods for the reduction of chromium in ilmenite concentrates were explored cursorily as a way of obtaining information on the mode of occurrence of the chromium and the use of these methods in practice.

A lift-type induced-roll magnetic separator gave a concentrate of 0,08 per cent  $\text{Cr}_2\text{O}_3$  from a feed of 0,11 per cent  $\text{Cr}_2\text{O}_3$ .

Electrostatic separation of screen-sized material gave a moderate reduction of  $\text{Cr}_2\text{O}_3$  content in some tests, but the results were very variable and insufficient work was done to establish the true potential of the process.

Heating of the ilmenite prior to magnetic separation gave a variety of results, depending on the conditions of heating. When the ilmenite was heated to 600°C under reducing conditions and then separated by a Frantz Isodynamic separator, a fraction having a  $\text{Cr}_2\text{O}_3$  content of 0,06 per cent was obtained.

Flotation of a feed having a  $\text{Cr}_2\text{O}_3$  content of 0,24 per cent produced an average  $\text{Cr}_2\text{O}_3$  grade of 0,18 per cent when Armac C was used as the collector.

In the tests employing flotation, electrostatic separation, or thermal treatment prior to magnetic separation, ilmenite free from  $\text{Cr}_2\text{O}_3$  was never obtained. This makes it unlikely that all the chromium is present as discrete grains of chromite and suggests the possibility that at least part of the chromium is closely associated with the ilmenite.

Products of 0,06 per cent  $\text{Cr}_2\text{O}_3$  were obtained in two of the tests involving thermal pretreatment and this figure is tentatively regarded as the lowest  $\text{Cr}_2\text{O}_3$  content obtainable by a concentration process that does not include grinding of the ilmenite.

Because only a limited amount of work was done on the lift-type induced roll separator, electrostatic separation, flotation, and magnetic separation after thermal treatment, there is a possibility that results slightly better than those recorded in this report can be obtained in the course of further work on these methods.

### Report no. 1660

*An economic assessment of the production of high-grade fluorspar pellets.* (8th Aug., 1974; re-issued Jun. 1976).

A preliminary analysis of probable production costs indicated that South Africa should be able to produce high-grade fluorspar pellets for export at a competitive cost.

Pelletizing tests have shown that pellets of 95 per cent effective  $\text{CaF}_2$ , with 0,5 per cent sodium silicate as a binder, can be economically produced for export to the U.S.A. and to Western Europe. These exports could earn R4,44 million per annum on the U.S. Market or R4,33 million per annum in Western Europe.

Any reduction of the effective  $\text{CaF}_2$  content to below 95 per cent would allow for the higher recovery of  $\text{CaF}_2$  and an increase in production, but net returns would be only slightly improved. (Continued on page iv)