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MATERIALS RESEARCH LABORATORY

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REPORT

MRL-R-1139



CORROSION OF HIGH-DENSITY SINTERED TUNGSTEN ALLOYS

PART 1 : IMMERSION TESTING

J.J. Batten, I.G. McDonald, B.T. Moore and V.M. Silva

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ABSTRACT

Sintered tungsten alloys are candidate materials for certain Australian ammunition components, namely kinetic energy penetrators, because of their high density (about 19 g/cm^3). It is probable that a storage life of twenty years in an uncontrolled environment will be a requirement for this ammunition. Thus there is a need to determine the long-term storage capability of these alloys, in particular their capability to remain uncorroded during this period.

The corrosion behaviour of four candidate alloys has therefore been evaluated through weight loss measurements after total immersion in both distilled water and 5% sodium chloride solutions. The propensity of these alloys to corrode in a crevice situation was assessed in the sodium chloride solution. Some insight into the mechanism of corrosion was afforded by an examination of the surfaces after the tests using the SEM and through an analysis of the corrosion products.

Pure tungsten and all the alloys studied underwent corrosion during the tests, and in each case the rate of corrosion in sodium chloride solution was markedly less than that in distilled water. The rate in the crevice test was much the same as that obtained in the absence of crevices. A 95%W, 3.5%Ni, 1.5%Fe alloy was found to be the most corrosion resistant of the alloys under the above experimental conditions. Examination of the data shows that for each of the tests copper as an alloying element accelerates corrosion of tungsten alloys.

The mechanisms of corrosion included general dissolution, localized attack of the binder phase and tungsten grain loss, where the extent of each of these was dependent on the corrosion environment and alloy composition. In the presence of crevices, for the two alloys not containing copper, the main attack occurred in the creviced areas, while remote areas suffered little or no attack. Further, the corrosion products that accumulated adjacent to the creviced areas had a different composition from those on the remainder of the specimen. In contrast, for the two copper-containing alloys, the main attack occurred in areas remote from the creviced areas, and the chemical composition of the corrosion products on the specimens appeared to be uniform.

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POSTAL ADDRESS:

Director, Materials Research Laboratory
P.O. Box 50, Ascot Vale, Victoria 3032, Australia

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CORROSION OF HIGH-DENSITY SINTERED TUNGSTEN ALLOYS

PART 1 : IMMERSION TESTING

1. INTRODUCTION

Liquid-phase sintered tungsten alloys have been developed to provide a high-density material for applications such as counterweights, radiation shields and, of particular concern for this study, military penetrators. These latter alloys are composite materials containing 90 wt% or greater of tungsten, together with alloying additions. The tungsten appears as rounded grains (particles) surrounded by a binder (matrix) phase consisting of tungsten together with the alloying elements [1].

The resistance of pure tungsten to corrosion in normal environments is generally considered to be high [2], for it is stated that it suffers no attack from the atmosphere at room temperature, or from hot or cold water. On the other hand, the corrosion resistance of tungsten alloys (< 90%W) has been found to be somewhat lower than would be expected from the inertness of tungsten. Further, the corrosion resistance is affected adversely by non-metallic inclusions, and in some cases by the presence of micro-cracks [2].

Until recently, the corrosion of candidate high-density tungsten alloys ($\geq 90\%W$) for military penetrators had not been considered a problem. However, the unreliable performance of certain high-density penetrators due to deterioration during long-term storage under conditions of high humidity has caused a reassessment of the situation. Thus, for example, a 90%W, 7.5%Ni, 2.5%Cu alloy has been shown to readily corrode when exposed to air saturated with water vapour [3,4,5]. Similarly, it has been shown [6] that a tungsten alloy 97.1%W, 1.6%Ni, 0.7%Fe, 0.5%Cu, 0.1%Co also undergoes corrosion when exposed to an aqueous 5% solution of sodium chloride, with some dissolution of the tungsten grains together with localized attack of the binder phase.

Very little is known about the corrosion behaviour of tungsten in contact with other metals [7], such as the earlier-mentioned binder phase alloy consisting of tungsten plus alloying elements. Recent work by Aylott et al. [8], aimed towards filling this requirement, studied the galvanic effects between tungsten and two nickel alloys (70%Ni, 30%Cu and 50%Ni, 50%Fe) when immersed in a 1% sodium sulphate solution under

stagnant conditions at 25°C. This resulted in the tungsten/nickel-copper couple giving corrosion products at each electrode, with the tungsten being slightly more anodic. On the other hand, the tungsten/nickel-iron couple gave corrosion products on the nickel-iron only.

The present work is primarily aimed at giving an indication of the capability of the high-density sintered tungsten alloy used in the Australian Phalanx close-in weapon system to withstand a twenty year storage period under normal storage conditions and still be in an acceptable state for the Australian Defence Forces to use. Since the Australian Navy plans to use this particular tungsten alloy for the Phalanx system well into the future, the outcome of this investigation, and the implications for possible foreign sales, is of some significance. Three other candidate tungsten alloys (one from USA, two from UK) were also tested for comparative purposes.

The work described here is aimed at giving a better understanding of the chemistry of the corrosion reactions of these alloys. Part 2 will address the primary aim stated above, namely to ascertain the probable behaviour of these alloys during long-term storage under typical storage conditions.

2. EXPERIMENTAL

2.1 Materials

The selected sintered tungsten alloys were fabricated using powder metallurgy techniques in which a fine powder mix (initial particle sizes of approximately 5 μm [1]) was pre-compacted and liquid-phase sintered at about 1500°C. At this temperature the alloying elements melt and tungsten grain growth occurs. The final tungsten grain size depends upon sintering time and temperature as well as the initial powder size, but will typically be about 60 μm . Thus, in the final alloy systems, the material usually has a two phase composite structure of rounded tungsten grains in a binder phase consisting of tungsten together with the alloying elements [1,9].

From Table 1 it will be seen that the materials used in the present study contained 90 to 97 wt% of tungsten with alloying additives of nickel, iron, copper and cobalt. Electron probe micro-analysis (EPMA) of the as-formed binder phase in these penetrator materials revealed that their tungsten contents varied from 2.4 to 33.7% (see Table 1), and in one case the binder consisted of two phases. Pure tungsten (99.99 wt%) was also included in the testing programme to give base line data.

2.2 Measurement of the Extent of Corrosion

Immersion tests were conducted on cylindrical specimens of the above alloys in both distilled water and in a 5% sodium chloride solution, both solutions being unbuffered. The tests were conducted with the specimens resting on the bottom of the glass beakers containing the solution, while the beakers themselves were loosely covered with watch-glasses.

In order that this work could be compared directly with that of Levy and Chang [6], the length (l) to diameter (d) ratio of the cylinders was two to one. The diameters of the specimens used were: (AUS) 11.5, (US) 14.5, (UK(Fe)) 13, (UK(Cu)) 22 and (W) 9 mm. The corresponding volume of solution (v) in which these specimens were completely immersed (one specimen per beaker) was selected so that it was in proportion to the surface area of the specimen exposed. These volumes were 0.4, 0.5, 0.45, 1.2 and 0.2 litre respectively.

The above cylinders (except for AUS and W) were dry-machined from rod (25 to 30 mm initial diameter). All the specimens were polished with 240A and 600A silicon carbide paper, rinsed with distilled water, degreased in acetone, air dried, weighed and then exposed in duplicate to the prescribed test.

After the test period (usually seventy days), and prior to weighing, corrosion products were removed from the specimens. The samples were scrubbed with a tooth brush and warm tap water, ultrasonically cleaned in distilled water for ten minutes, rinsed in acetone and air dried. They were then weighed and average corrosion rates calculated. Corrosion products were analysed using standard techniques.

2.3 Determination of the Influence of Crevices on the Corrosion Reaction

The above tests were repeated, but in this case crevices were deliberately formed on the cylindrical specimens using synthetic rubber O-rings, where three rings were used per specimen (see Fig. 5). These rings were boiled in distilled water for one hour prior to being used (in accordance with ASTM Standards, Part 10, G48) to ensure the removal of water-soluble ingredients that might affect corrosion. In these tests two specimens were placed in each beaker, and the d, l, V values (see Section 2.2) were: (AUS) 11.5, 44, 1.2; (US) 25, 70, 4; (UK(Fe)) 28, 68, 4.5; (UK(Cu)) 29, 69, 5; (W) 9, 39, 0.8 (mm, mm, litre, respectively).

3. RESULTS AND DISCUSSION

3.1 Full Immersion Test: Distilled Water

3.1.1 Products formed during the test

Within fourteen days of exposure all the metals studied had formed visible corrosion products on their surfaces. Further, with the sample UK(Fe) an orange-brown deposit was visible in the area of contact with the glass beaker, indicative of some form of crevice-type corrosion or at least some crevice effect. As exposure continued, the reaction products became more voluminous.

Figure 1 shows that at the end of the test period each sample was covered by a thin film. Consequently, the weight loss measurements (Table 2) indicate that virtually all the corrosion products are accounted for by those in solution (except for UK(Cu) and W). The table also indicates that corrosion products accumulated under the samples UK(Fe) and W.

The compositions of all the corrosion products (Table 2), when compared with the composition of the binder (Table 1), indicate that both the binder phase and the primary tungsten grain phase have corroded. However, the very high percentage of tungsten in the products from US and UK(Cu) indicates that in these cases the attack on the tungsten grains has been extensive. Note also from Table 2 that iron was not detected in the solution from AUS but it was the main constituent of the deposit on its surface. Also, the pH of the final solutions ranged from 3.1 to 6.6 (originally 5.2).

3.1.2 Corrosion rate in distilled water

Table 2 indicates that the alloy AUS is the most corrosion resistant (i.e. lowest corrosion rate) of all the alloys tested in distilled water, followed by pure tungsten, then by the other alloy not containing copper (UK(Fe)) and the alloys containing copper (US, UK(Cu)) in decreasing order. Note that the corrosion rate for UK(Cu) is about one half of that for mild steel in sea water, thus indicating that it has a "low" corrosion resistance. The relative resistance to corrosion of AUS when compared against pure tungsten is also of interest.

3.1.3 Scanning Electron Microscope (SEM) examination of the corroded surfaces

Figure 2 consists of SEM micrographs of the surfaces of tungsten and the four tungsten alloys after full immersion in distilled water for seventy days and after the corrosion products have been removed; the interpretation of these micrographs is given in Table 3. From these it is clear that the mode of attack has varied between the various alloys. For AUS and UK(Fe) the primary tungsten particles have suffered little or no attack but some attack (still slight) is evident on the binder phase. On the other hand, for US and UK(Cu) extensive attack on the tungsten grains and the binder is evident and tungsten grain loss has occurred (i.e. grains cease to be bound).

From the above results the alloys may be broadly classified into two categories, based on the pattern of attack on the surface:

- (i) extensive attack for the alloys containing copper and
- (ii) slight attack for the alloys free of copper.

3.2 Full Immersion Test: In 5% Sodium Chloride Solution

3.2.1 Products formed during the test

For the alloys AUS and US, after fourteen days of exposure, corrosion products were visible in the area of contact with the glass - these were orange-brown and light brown respectively. For the alloy UK(Fe) a light brown deposit had formed on it and an orange-brown deposit under it.

Figure 3 shows that after the seventy day test period extensive, flocculent, light brown products (unlike those of the previous test) had formed on the samples AUS, US and UK(Fe), while a dull grey film had formed on UK(Cu). Pure tungsten was still in pristine condition. A similar trend existed for the deposits that formed in the area of

contact with the glass (Table 4). Further, for AUS and UK(Fe) the above flocculent corrosion products accounted for the greater proportion of the weight loss of the alloys (Table 4).

In this case, a comparison of the binder composition with that of the corrosion products (Tables 1 and 4) indicates that the main corrosive attack is occurring on the binder phase. From Table 4 it will also be seen that the composition of the corrosion products on the specimen surface and in solution are different (e.g. note the distribution of Fe and Cu). Also it will be seen that the pH of the final solutions ranged from 4.8 to 7.1 (originally 6.1).

3.2.2 Corrosion rate in 5% sodium chloride solution

Table 4 indicates that in this case pure tungsten is more corrosion resistant than the four alloys tested, followed by AUS and UK(Fe) (the copper-free alloys), and finally UK(Cu) and US (the copper-containing alloys) in order of decreasing corrosion resistance. An inhibiting effect of 5% sodium chloride solution is also evident (cf. Tables 2 and 4).

3.2.3 SEM examination of the corroded surfaces

Figure 4 consists of SEM micrographs of the surfaces of tungsten and the four tungsten alloys after full immersion in 5% sodium chloride solution for seventy days and after the corrosion products have been removed; these results are summarized in Table 3. Unlike the distilled-water results (also Table 3), for the alloys UK(Fe) and UK(Cu) it is predominantly the binder phase that is corroding, but for US both the binder and the tungsten grains have corroded. On the other hand, in both corrosive environments only light general corrosion occurred on the alloy AUS.

3.3 Full Immersion Tests with Crevices

The work of Levy and Chang [6], together with the present study, has indicated strongly that the presence of crevices does play a role in the course of the corrosion reaction of these alloys. This study was aimed at giving more detailed information about their effect.

3.3.1 Tests with crevices in distilled water

The initial experiments were carried out with the creviced specimens (see Section 2.3) fully immersed for seventy days and, in each case, the resulting corrosion rates were less than those without crevices. For example, with pure tungsten the corrosion rate dropped from 0.65 (Table 2) to 0.02 mil/yr in the presence of crevices. However, a similar effect was obtained when the O-rings that formed the crevices (both boiled and used previously, and not boiled) were placed on the bottom of the beaker containing distilled water and the pure tungsten samples (rather than around the samples). Thus, from the point of view of the influence of crevices, the results of this experiment are invalid. However, it is pertinent to the next section to mention that over a test period of twelve months, localized attack in the creviced areas was not observed for the two samples studied on the SEM, namely AUS and UK(Cu).

3.3.2 Tests with crevices in 5% sodium chloride solution

3.3.2.1 Corrosion products formed

Fourteen days after the start of this experiment, corrosion products were evident on the areas adjacent to the O-rings on AUS, US and UK(Fe); for UK(Cu), although no corrosion products were evident, there was a distinct smell of chlorine when the glass cover was removed from its beaker - this smell persisted for about sixty days.

Figures 5 and 6 are photographs of the samples after exposure times of seventy days and twelve months, respectively. Comparison of these with Figure 3 indicates that the corrosion behaviour (except for W) has been dramatically affected by the O-rings. For example, corrosion products have accumulated adjacent to the O-rings for AUS and UK(Fe) and their composition appears to have been affected. Further, for UK(Fe) there now appear to be two, quite distinct, corrosion products on the surface.

The chemical compositions of the above corrosion products are presented in Table 5. Comparison of these results with the non-creviced situation (Table 4) yields the following main points:

(a) For the solutions

- (i) For UK(Fe), the percentage of corrosion products in solution is significantly lower than that in the absence of crevices in sodium chloride solution.
- (ii) For US and UK(Fe), the chemical composition of the products is different from that in the absence of crevices in sodium chloride solution.

(b) For the specimens

- (i) For AUS and UK(Fe), there are two distinct products on the surface.
- (ii) For US and UK(Cu), the chemical composition of the products has altered.

With regard to the mechanism of attack, the amount of tungsten in the products indicates that, in general, both the binder phase and the primary tungsten grain phase have corroded. Finally, the tables indicate that the pH of the final solutions has not been significantly influenced by the O-rings.

3.3.2.2 Corrosion rate

Comparison of the results in Tables 4 and 5 indicates that in sodium chloride solution, the over-all corrosion rates have not been significantly influenced by the presence of creviced areas, and the trends in the rates associated with copper are still present. Note also that the corrosion rates have remained fairly constant throughout the extended test period.

3.3.2.3 SEM examination of the corroded surfaces

It has already been shown that the presence of crevices can affect the course of this reaction, i.e. the nature of the corrosion products and their location - in particular for AUS and UK(Fe) (the copper-free alloys). The following work is aimed at gaining some insight into the role of creviced surfaces on these alloys. To this end, the surfaces were examined in three areas using the SEM, namely under the O-ring, immediately adjacent to it, and an area some distance from it.

Figures 7 to 12 are SEM micrographs of the surfaces of the four tungsten alloys after full immersion in 5% sodium chloride solution for seventy days and/or twelve months in the presence of crevices, and after removal of the corrosion products. For each micrograph designated by "a", the left hand half is the area covered by the O-ring. Table 6 summarizes the results of this study.

In general, for the two copper-free alloys (AUS, UK(Fe)), the attack has primarily taken place in the area under the O-ring (indicative of differential aeration or crevice type corrosion), while the areas some distance from the O-ring have suffered little attack (this is particularly the case for the primary tungsten grain phase). On the other hand, for the two copper-containing alloys (US, UK(Cu)) the main attack has taken place away from the creviced areas.

4. GENERAL DISCUSSION

4.1 Corrosion Rate

- (a) This rate for the four alloys and pure tungsten is appreciable in distilled water and (except for pure tungsten) in 5% sodium chloride solution (see Tables 2 and 4).
- (b) Regardless of the nature of the corrosive environment, usually pure tungsten has the lowest corrosion rate and the alloys containing copper (US, UK(Cu)) have the highest (Tables 2 and 4).
- (c) In all cases, the rate is less in 5% sodium chloride solution than in distilled water.
- (d) The presence of crevices has no significant effect on the rate in sodium chloride solution.
- (e) In all environments the Australian alloy is the most corrosion resistant alloy and is even more corrosion resistant than pure tungsten in distilled water.

4.2 Corrosion Products in Solution

- (a) The percentage of products in solution:

Table 7 illustrates that this is dependent on the test environment.

(b) The chemical composition of products in solution:

(i) In distilled water

These consist predominantly of tungsten..

(ii) In 5% sodium chloride solution

Products in solution are as follows:

AUS, UK(Fe) - predominantly nickel

US - predominantly tungsten and nickel

UK(Cu) - equal proportions of nickel and tungsten

(iii) In 5% sodium chloride solution with crevices

Similar to (ii) above.

4.3 Corrosion Products on the Samples

- (a) In the absence of crevices, the composition of these products is influenced by the nature of the corrosive environment.**
- (b) The presence of crevices in 5% sodium chloride solution influenced the composition and location of these products. For example:**
 - (i) For AUS and UK(Fe), nickel-rich and iron-rich products formed on distinct areas of the surface.**
 - (ii) For US, the percentage of copper in these products is much less when crevices are present.**

4.4 Mode of Attack

- (a) In the absence of crevices in distilled water and in 5% sodium chloride solution:**
 - (i) For copper-containing alloys - both the binder phase and the primary tungsten grain phase are attacked; this attack may be severe on both phases, and tungsten grain loss has occurred.**
 - (ii) For copper-free alloys - attack has mainly been on the binder phase, it has not been severe, but has resulted in tungsten grains protruding above the binder phase.**

- (b) In the presence of crevices in 5% sodium chloride solution:
- (i) For copper-containing alloys - no crevice-type attack occurred.
 - (ii) For copper-free alloys - severe attack of the binder and tungsten grain phases occurred in the creviced areas, thus a crevice-type corrosion has occurred.

4.5 Comparison of our Results with Galvanic Corrosion Studies of Tungsten Coupled to Nickel Alloys

In the work of Aylott et al. [8], two nickel alloys (70%Ni, 30%Cu and 50%Ni, 50%Fe) were coupled to pure tungsten in a 1% sodium sulphate solution under stagnant conditions at 25°C. Initially the corrosion potentials of the uncoupled electrodes were measured, yielding the results:

W - 255 mV (SCE)
NiCu - 20 mV (SCE)

W - 225 mV (SCE)
NiFe - 550 mV (SCE)

Aylott et al. [8] showed that, when coupled in about equal areas, for the tungsten/nickel-copper system corrosion products are formed at each electrode, with the tungsten being predominantly anodic. On the other hand, for the tungsten/nickel-iron system, the nickel-iron alloy is anodic.

Translating these results to actual high-density sintered tungsten alloys in 5% sodium chloride solution, where the exposed area of the binder phase is much less than that of the primary tungsten grain phase, then the following results might be expected:

- (a) For the copper-containing alloys, the tungsten grain phase (anodic, large area) would cathodically protect the binder phase (small area), and the attack would be predominantly on the tungsten particles. Thus tungsten should be the major corrosion product in the sodium chloride solution with only a small amount of binder elements.
- (b) For the copper-free alloys in sodium chloride solution, the small area of anodic binder phase would be expected to suffer attack while the relatively large cathodic tungsten particle phase should be little affected. Thus the corrosion products could consist of nickel and iron, together with tungsten where this originates mainly from the attack on the binder phase.

The above predictions about the nature of the corrosion products in sodium chloride solution are not born out for the copper-containing alloys and only roughly born out for the copper-free alloys. This lack of agreement could be associated with the composition of the nickel alloys studied by Aylott et al. [8]. Those alloys were chosen to represent a close approximation to the alloy phases, but our work has shown that the binder phase normally contains appreciable amounts of tungsten (Table 1). It is predicted that this included tungsten in the binder phase would reduce the difference in potential between the binder phase and the primary tungsten grain phase. In general, this could mean that neither phase could completely cathodically protect the other, with a concomitant attack occurring on both phases and both yielding corrosion products, albeit to varying extents.

5. CONCLUSIONS

The work has yielded many unusual and unexpected features of the corrosion reaction of high-density sintered tungsten alloys ($\approx 90\% W$), and has resulted in a better understanding of the chemistry of the corrosion process. In general, the course of the reaction is profoundly influenced by the chemical composition of the binder phase, the nature of the corrosive environment, and the presence of crevices.

The results indicated that the binder phase and/or the primary tungsten grain phase may be attacked, often severely, and that tungsten grain loss may occur. If the binder phase is attacked more readily than the tungsten grains, penetration in those areas can exceed those calculated penetration rates based on weight loss data. This type of attack could result in loss of strength and ductility.

An implication from this work is that the tested tungsten alloys are likely to corrode at a significant rate if stored in uncontrolled environments where condensation is likely to occur. This could lead to long-term storage problems: this aspect of the work is the topic of Part 2.

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TABLE 1

Nominal Chemical Composition of the Alloys Used, and
Composition of the Binder Phase in the Penetrators

Nominal Composition of the Alloys Used

SOURCE	SYMBOL	COMPOSITION (wt%)				
		<u>W</u>	<u>Ni</u>	<u>Fe</u>	<u>Cu</u>	<u>Co</u>
Australia	AUS	95	3.5	1.5		
USA	US	97	1.6	0.7	0.5	0.1
UK	UK(Fe)	90	5	5		
	UK(Cu)	90	7.5		2.5	

Composition of the Binder Phase in the Penetrators

	<u>W</u>	<u>Ni</u>	<u>Fe</u>	<u>Cu</u>	<u>Co</u>
AUS	23	55	21		
US	13.8	47.6	19.0	16.3	3.3
UK(Fe)	23	38.7	38.3		
UK(Cu) Phase I	33.7	53.8		12.5	
Phase II	2.4	38.4		59.3	

TABLE 2

Results of Full Immersion Tests in Distilled
Water at Ambient Temperature for Seventy Days

Sample	Sample weight loss, amount accounted for in solution (mg)	Observation After the Test			Corrosion Rate mg cm ⁻² day ⁻¹ mil/yr*	
		Solution appearance, pH and analysis	Corrosion Products			
			On specimen surface	Deposited on beaker bottom under sample		
AUS (3.5 Ni, 1.5 Fe)	14, 14	Clear, pH=6.6 <u>Analysis(mg)</u> 5 Ni, 0 Fe, 9 W	Widespread, thin, non-uniform brown film <u>Analysis(%)</u> 18 Ni, 48 Fe, 34 W	None	0.027	0.2
US (1.6 Ni, 0.7 Fe, 0.5 Cu, 0.1 Co)	283, 281	Clear, pH=3.1 <u>Analysis(mg)</u> 11 Ni, 4 Fe, 2 Cu, 264 W	Extensive, uniform black film	None	0.255	1.9

TABLE 2 (continued)

Sample	Sample weight loss, amount accounted for in solution (mg)	Observation After the Test			Corrosion Rate	
		Solution appearance, pH and analysis	Corrosion Products		mg cm ⁻² day ⁻¹	mil/yr*
			On specimen surface	Deposited on beaker bottom under sample		
UK(Fe) (5 Ni, 5 Fe)	130, 134	Clear, pH=5.5 <u>Analysis(mg)</u> 14 Ni, 8 Fe, 112 W	Extensive, uniform black film. Pitting occurred on the ends of the sample	Moderate amount, orange-brown	0.147	1.1
UK(Cu) (7.5 Ni, 2.5 Cu)	660, 554	Clear, pH=5.1 <u>Analysis(mg)</u> 17 Ni, 3 Cu, 534 W	Extensive, uniform brown film	None	0.335	2.5
W	70, 41	Clear, pH=3.5 <u>Analysis(mg)</u> 41 W	Extensive, non-uniform, speckled dark grey film	Little, yellow	0.087	0.65

* For Comparison - the corrosion rate of mild steel in still sea water is 5 mil/yr

TABLE 3

State of the Surface of Tungsten Alloys after Full Immersion
in Either Distilled Water or Sodium Chloride Solution
at Ambient Temperature for Seventy Days

Sample	Corrosive Environment	
	Distilled Water	5% Sodium Chloride Solution
AUS	<p>A few polishing marks still evident on tungsten particles, but there has been some tungsten surface attack and binder attack.</p> <p>In summary, attack has been general with slightly more attack on the binder. Elemental ratio of corrosion products supports above interpretation.</p>	<p>A few polishing marks still evident on tungsten particles and the binder, but there has been some tungsten surface attack and binder attack.</p>
US	<p>No sign of polishing marks, both the surface of the tungsten particles and binder have been attacked. Binder has been more severely attacked and tungsten particles are standing proud. Tungsten grain loss has occurred. Thus, general dissolution and localized more severe attack on the binder have occurred. Elemental ratio supports this interpretation.</p>	
UK(Fe)	<p>Tungsten particles and binder have been attacked. Binder more severely attacked, leaving tungsten particles standing proud of the binder. Craze appearance of surface is due to some dried residual corrosion products (thin film) still on the surface. Elemental ratio supports this interpretation.</p>	<p>A few polishing marks still evident on the tungsten particles and the binder. Attack appears to be fairly general, but the elemental analysis of the corrosion products suggests that there has been localized attack on the binder.</p>
UK(Cu)	<p>No sign of polishing marks. Severe, selective attack on tungsten particles together with tungsten grain loss has occurred, leaving behind the honey-comb structure of the binder, i.e. the binder has been left relatively intact. There appears to have been grain boundary attack on some tungsten grains. Elemental ratio of the corrosion products indicates that some attack of binder has occurred.</p>	<p>No sign of polishing marks. Both the surface of the tungsten particles and binder have been attacked, leaving tungsten particles standing proud of the binder. This latter effect is partly obscured by residual corrosion products (white areas) still adhering to the binder. Some of these products are standing proud of the tungsten particles (these products contain chloride). The elemental ratio indicates that both tungsten particles and binder have been attacked.</p>
W	<p>General roughening of the surface.</p>	<p>Polishing marks still pronounced. Little attack on the surface.</p>

TABLE 4

Results of Full Immersion Tests in Sodium Chloride Solution
at Ambient Temperature for Seventy Days

Sample	Sample weight loss, amount accounted for in solution (mg)	Observation After the Test			Corrosion Rate	
		Solution appearance, pH and analysis	Corrosion Products		mg cm ⁻² day ⁻¹	mil/yr
			On specimen surface	Deposited on beaker bottom under sample		
AUS (3.5 Ni, 1.5 Fe)	21. 9	Faint yellow, pH=6.8 <u>Analysis(mg)</u> 7 Ni, 0 Fe, 2 W	Extensive, flocculent, light brown <u>Analysis(%)</u> 13 Ni, 52 Fe, 35 W	Moderate amount, orange-brown	0.022	0.2
US (1.6 Ni, 0.7 Fe, 0.5 Cu, 0.1 Co)	83. 49	Milky, pH=6.2 <u>Analysis(mg)</u> 17 Ni, 0 Fe, 2 Cu, 30 W	Extensive, flocculent, light brown <u>Analysis(%)</u> 3 Ni, 18 Fe, 17 Cu, 62 W	Extensive amount, covering base of beaker and under sample, light brown	0.067	0.5
UK(Fe) (5 Ni, 5 Fe)	25. 9	Yellow, pH=6.9 <u>Analysis(mg)</u> 7 Ni, 0 Fe, 2 W	Extensive, flocculent, light brown <u>Analysis(%)</u> 16 Ni, 66 Fe, 18 W	Moderate amount, orange-brown	0.027	0.2

TABLE 4 (continued)

Sample	Sample weight loss, amount accounted for in solution (mg)	Observation After the Test			Corrosion Rate	
		Solution appearance, pH and analysis	Corrosion Products		mg cm ⁻² day ⁻¹	mil/yr
			On specimen surface	Deposited on beaker bottom under sample		
UK(Cu) (7.5 Ni, 2.5 Cu)	120, 117	Faint green, pH=7.1 <u>Analysis(mg)</u> 53 Ni, 0 Cu, 64 W	Uniform dull grey film	Trace, aqua	0.040	0.3
W	2, 0	Clear, pH=4.8 <u>Analysis(mg)</u> 0 W	None	None	0.003	0.02

TABLE 5

Results of Full Immersion Tests in Sodium Chloride Solution
with Crevices at Ambient Temperature

TEST PERIOD FOR SAMPLES: (1) SEVENTY DAYS
(2) ONE YEAR

Sample	Sample weight loss, amount accounted for in solution (mg)	Observation After the Test		Corrosion Rate		
		Solution appearance, pH and analysis	Corrosion Products		mg cm ⁻² day ⁻¹	mil/yr
			On specimen surface	Deposited on beaker bottom under sample		
AUS (3.5 Ni, 1.5 Fe)	140, 40 (1)&(2)	(1) Clear (2) Clear (1) pH=7.5 (2) pH=7.7 <u>Analysis(mg)</u> (1)&(2) 30 Ni, 0 Fe, 10 W	(1) Extensive orange-brown deposit adjacent to O-rings and on one end. Extensive brown spots on remainder (2) Extensive orange-brown deposit adjacent to O-rings and on one end. Green film on remainder <u>Analysis(%)</u> (2) (a) Near O-rings 11 Ni, 59 Fe, 30 W (b) General surface 80 Ni, 10 Fe, 10 W	(1) None (2) None	(1)0.027 (2)0.013	(1)0.2 (2)0.1

TABLE 5 (continued)

Sample	Sample weight loss, amount accounted for in solution (mg)	Observation After the Test		Corrosion Rate		
		Solution appearance, pH and analysis	Corrosion Products		mg cm ⁻² day ⁻¹	mil/yr
			On specimen surface	Deposited on beaker bottom under sample		
US (1.6 Ni, 0.7 Fe, 0.5 Cu, 0.1 Co)	2220, 1373 (1)&(2)	(1) Clear (2) Clear (1) pH=6.5 (2) pH=6.9 <u>Analysis(mg)</u> (1)&(2) 551 Ni, 0 Fe, 7 Cu, 815 W	(1) Extensive light brown deposit (2) Much more extensive light yellow deposit on upper half of sample <u>Analysis(%)</u> (1)&(2) 5 Ni, 38 Fe, 2 Cu, 55 W	(1) Moderate amount, light brown (2) Large amount, light yellow. Green on remainder of bottom of tank	(1)0.054 (1)0.4 (2)0.080 (2)0.6	
UK(Fe) (5 Ni, 5 Fe)	640, 19 (1)&(2)	(1) Clear (2) Clear (1) pH=7.6 (2) pH=7.7 <u>Analysis(mg)</u> (1)&(2) 19 Ni, 0 Fe, 0 W	(1) Extensive orange-brown deposit near O-rings and on one end. Remainder covered with light brown deposit (2) More extensive orange-brown deposit near O-rings and on one end. Remainder covered with green film <u>Analysis(%)</u> (2) (a) Near O-rings 9 Ni, 74 Fe, 17 W (b) General surface 87 Ni, 8 Fe, 5 W	(1) None (2) Extensive orange-brown deposit	(1)0.027 (1)0.2 (2)0.013 (2)0.1	

TABLE 5 (continued)

Sample	Sample weight loss, amount accounted for in solution (mg)	Observation After the Test		Corrosion Rate		
		Solution appearance, pH and analysis	Corrosion Products		mg cm ⁻² day ⁻¹	mil/yr
			On specimen surface	Deposited on beaker bottom under sample		
UK(Cu) (7.5 Ni, 2.5 Cu)	1670, 1265 (1)&(2)	(1) Clear (No chlorine smell) (2) Aqua (1) pH=7.2 (2) pH=7.3 <u>Analysis(mg)</u> (1)&(2) 533 Ni, 0 Cu, 732 W	(1) Patches of aqua film (2) Uneven aqua film on most of sample <u>Analysis(%)</u> (2) 5 Ni, 4 Cu, 91 W	(1) None (2) Some, aqua	(1) 0.054 (2) 0.054	(1) 0.4 (2) 0.4
W	16, 6	(1) Clear (2) Clear (1) pH=4.5 (2) pH=4.2 <u>Analysis(mg)</u> 6 W	(1) None (2) None, metal has become dull	(1) None (2) None but general yellow deposit on bottom of beaker	(1) 0.003 (2) 0.004	(1) 0.02 (2) 0.03

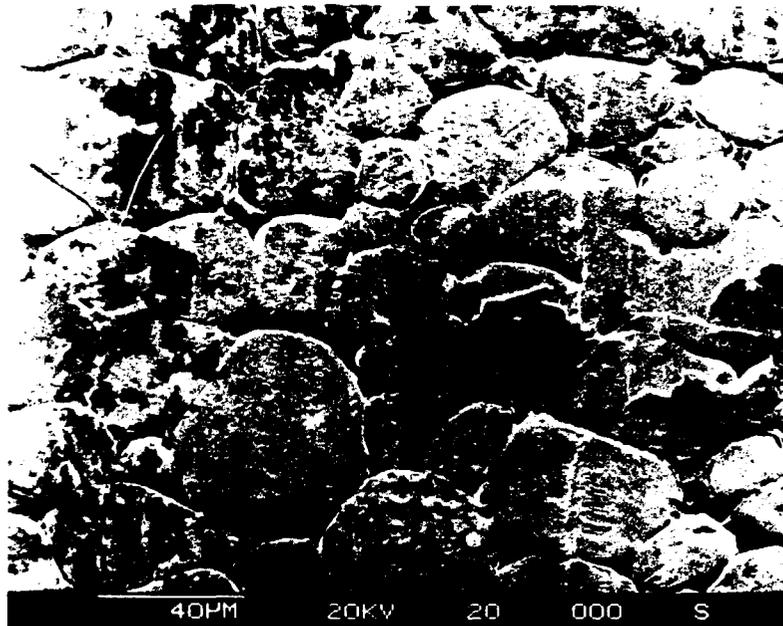
TABLE 6

State of the Surface of Tungsten Alloys after full Immersion in Sodium Chloride Solution in the Presence of Crevices

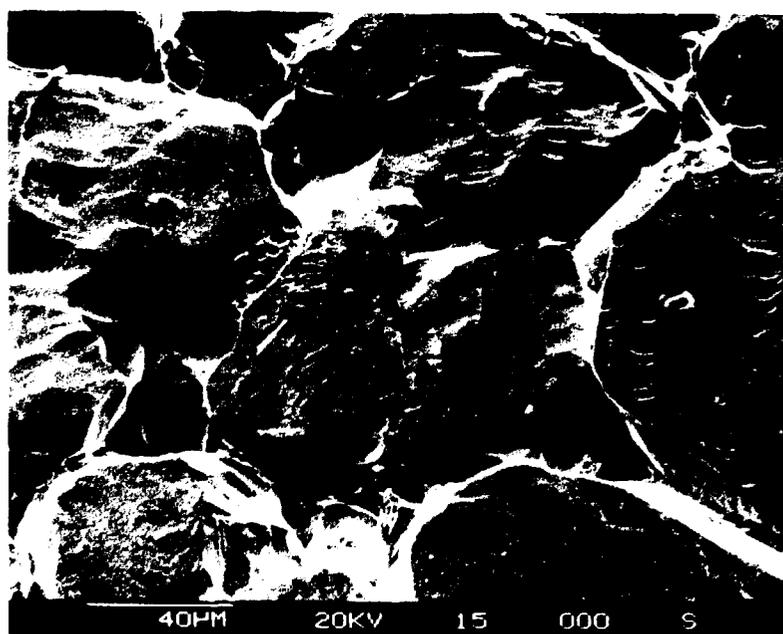
Corrosion System	Observation After the Test		
	Under O-ring	Immediately adjacent to O-ring	Away from O-ring
AUS, 70 day exposure (Fig. 7)	Some polishing marks still evident on tungsten particles, there has been some tungsten surface attack. Binder has been attacked (see inset).	Appears to have been some general attack.	Polishing marks still quite evident. Little attack, if any.
AUS, 12 month exposure (Fig. 8)	Both the surface of the tungsten particles and binder have been severely attacked. Tungsten particles could be standing proud of binder.	Appears to have been some general attack.	Polishing marks still quite evident on tungsten particles, hence little attack. Binder has been attacked.
US 12 month exposure (Fig. 9)	Some polishing marks still evident. Both the surface of the tungsten particles and binder lightly attacked.	Attacked more than under O-ring.	Severe attack on both tungsten particles and the binder.

TABLE 6 (continued)

Corrosion System	Observation After the Test		
	Under O-ring	Immediately adjacent to O-ring	Away from O-ring
UK(Fe) 12 month exposure (Fig. 10)	Both the surface of the tungsten particles and binder have been severely attacked.	Appears to have been some general attack.	Polishing marks still quite evident on tungsten particles, hence little attack. Binder has been attacked.
UK(Cu) 70 day exposure (Fig. 11)	Polishing marks still evident on tungsten particles and binder. There may have been slight general surface attack.	Some polishing marks are still apparent although attack has occurred.	No polishing marks on tungsten particles or binder. Both have been attacked. Tungsten particles are standing proud of binder.
UK(Cu) 12 month exposure (Fig. 12)	A few polishing marks still on tungsten particles but there has been tungsten surface attack. Binder has been attacked and tungsten particles could be standing proud of it.	Appear to have more polishing marks than under O-ring, and holes between tungsten particles.	Extensive attack on both tungsten particles and binder. Tungsten particles standing proud of binder.



(a)



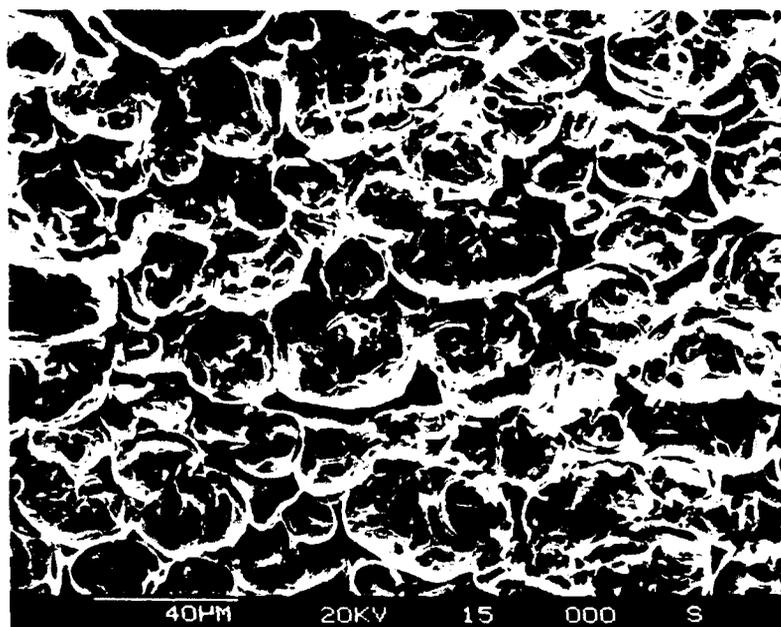
(b)

FIG. 2

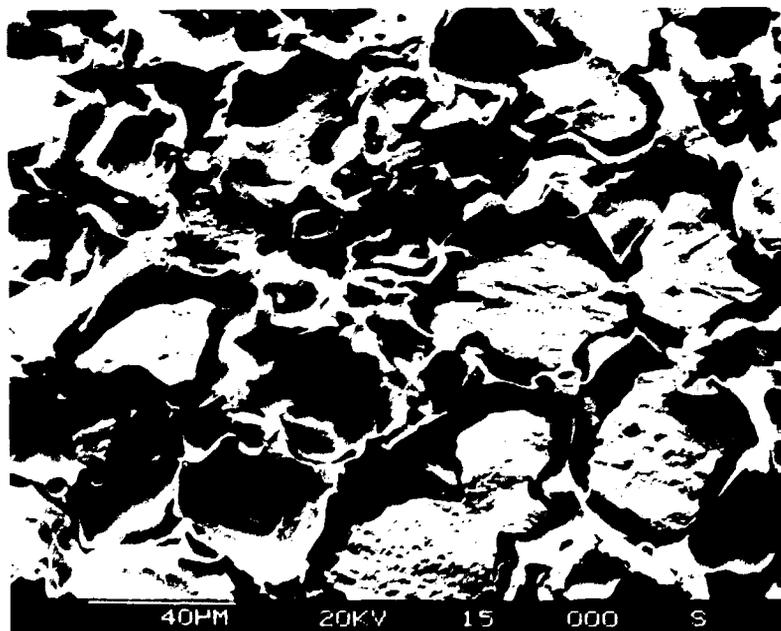
SEM micrographs of the surfaces of tungsten alloys and tungsten itself after full immersion in distilled water for seventy days and after removal of the corrosion products.

(x500)

Alloys	(a) AUS	(b) US
	(c) UK(Fe)	(d) UK(Cu)
	(e) W	



(c)



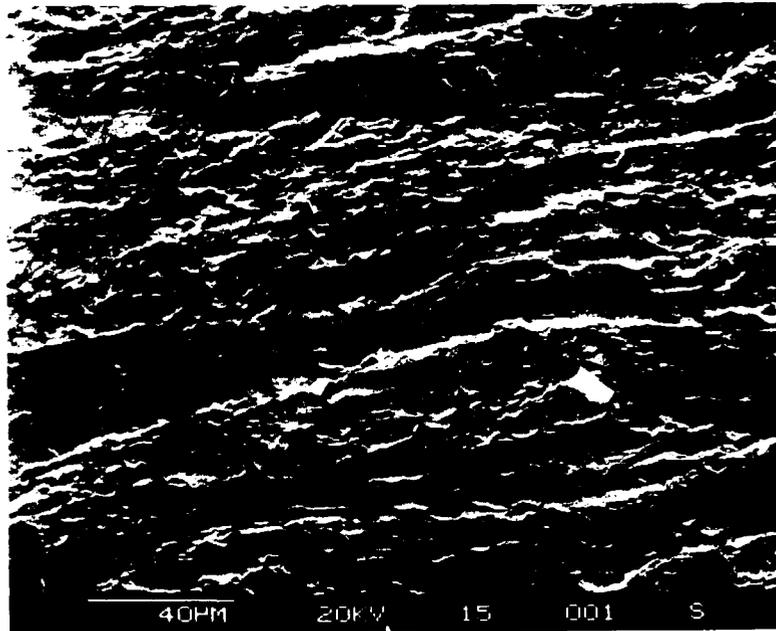
(d)

FIG. 2

SEM micrographs of the surfaces of tungsten alloys and tungsten itself after full immersion in distilled water for seventy days and after removal of the corrosion products.

(x500)

Alloys	(a) AUS	(b) US
	(c) UK(Fe)	(d) UK(Cu)
	(e) W	



(e)

FIG. 2
(this page)

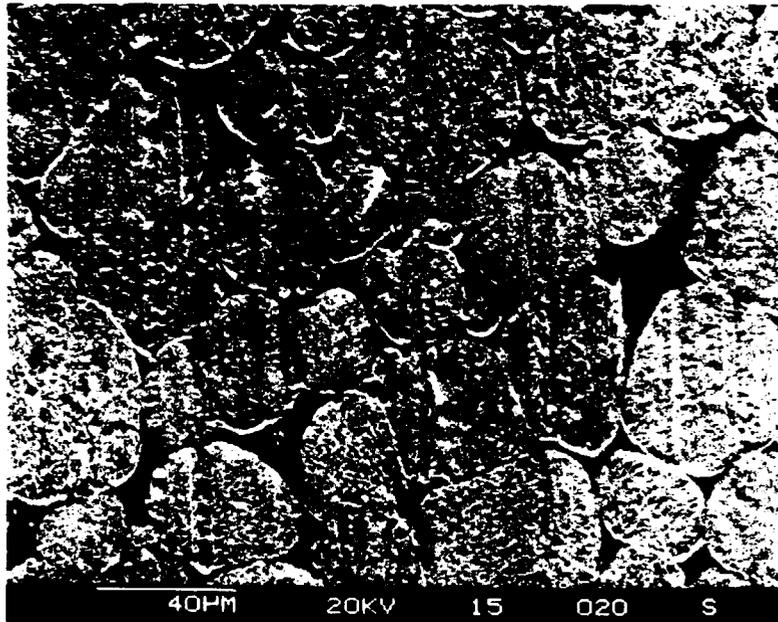
SEM micrographs of the surfaces of tungsten alloys and tungsten itself after full immersion in distilled water for seventy days and after removal of the corrosion products.

(x500)

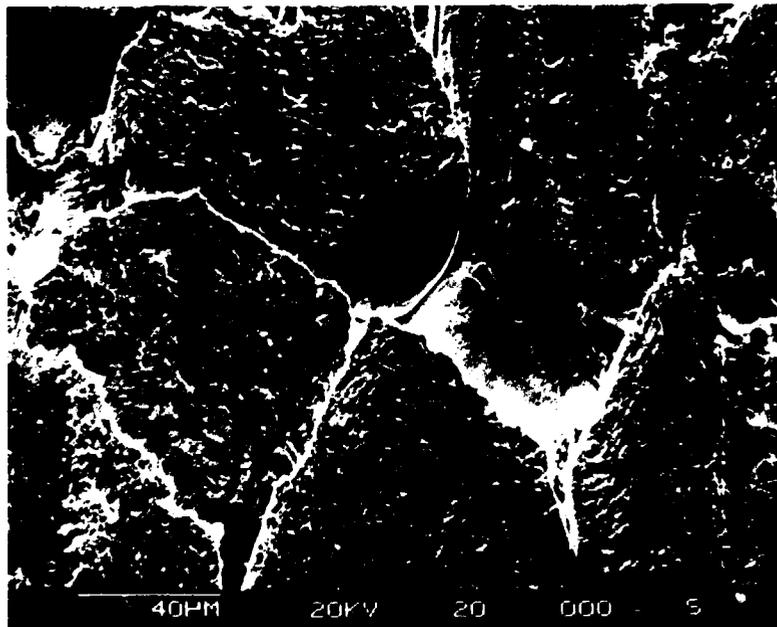
Alloys	(a) AUS	(b) US
	(c) UK(Fe)	(d) UK(C ₁)
	(e) W	

FIG. 3
(next page)

State of tungsten alloys and tungsten itself after full immersion in 5% sodium chloride solution for seventy days at ambient temperature.



(a)

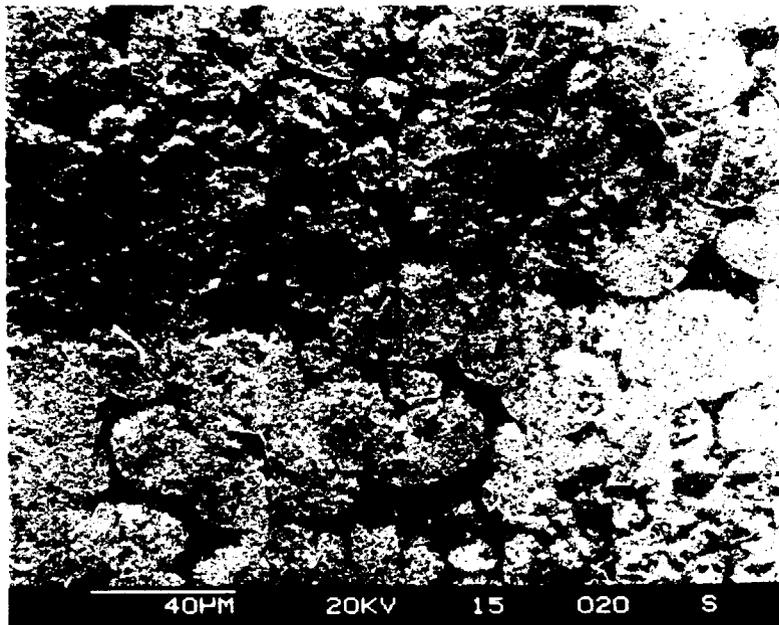


(b)

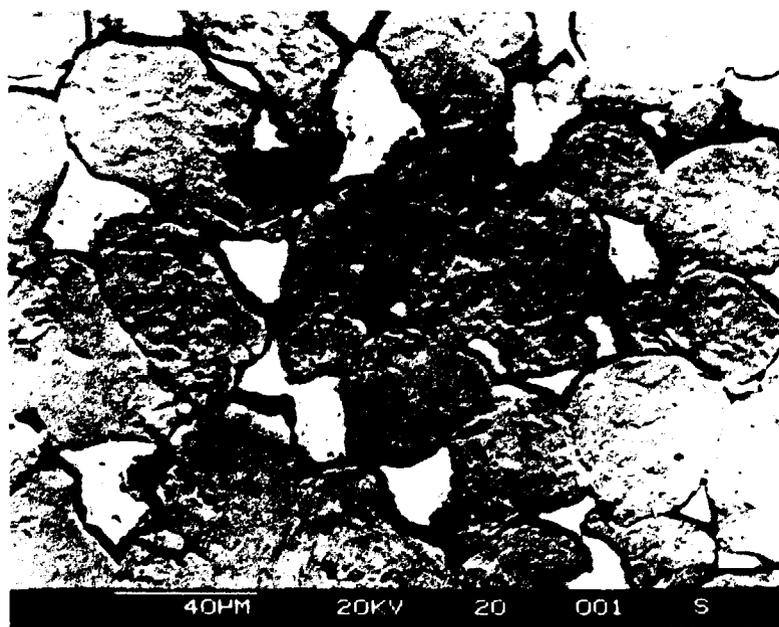
FIG. 4

SEM micrographs of the surfaces of tungsten alloys and tungsten itself after full immersion in 5% sodium chloride solution for seventy days. (x500)

Alloys	(a) AUS	(b) US
	(c) UK(Fe)	(d) UK(Cu)
	(e) W	



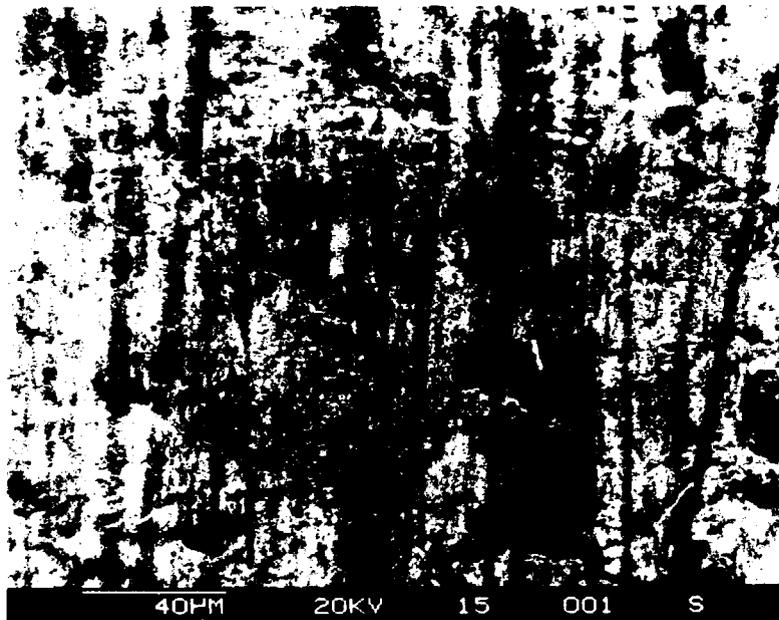
(c)



(d)

FIG. 4 SEM micrographs of the surfaces of tungsten alloys and tungsten itself after full immersion in 5% sodium chloride solution for seventy days. (x500)

Alloys	(a) AUS	(b) US
	(c) UK(Fe)	(d) UK(Cu)
	(e) W	



(e)

FIG. 4
(this page)

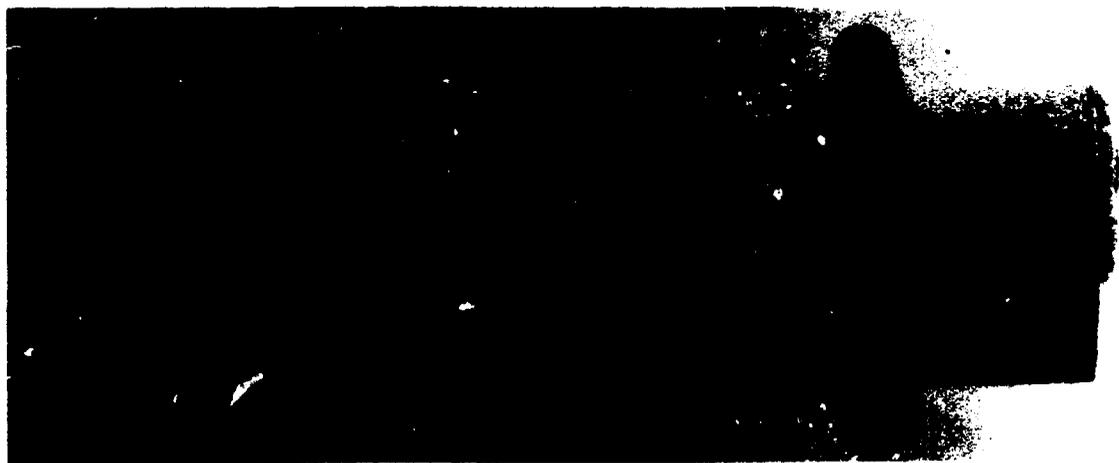
SEM micrographs of the surfaces of tungsten alloys and tungsten itself after full immersion in 5% sodium chloride solution for seventy days.

(x500)

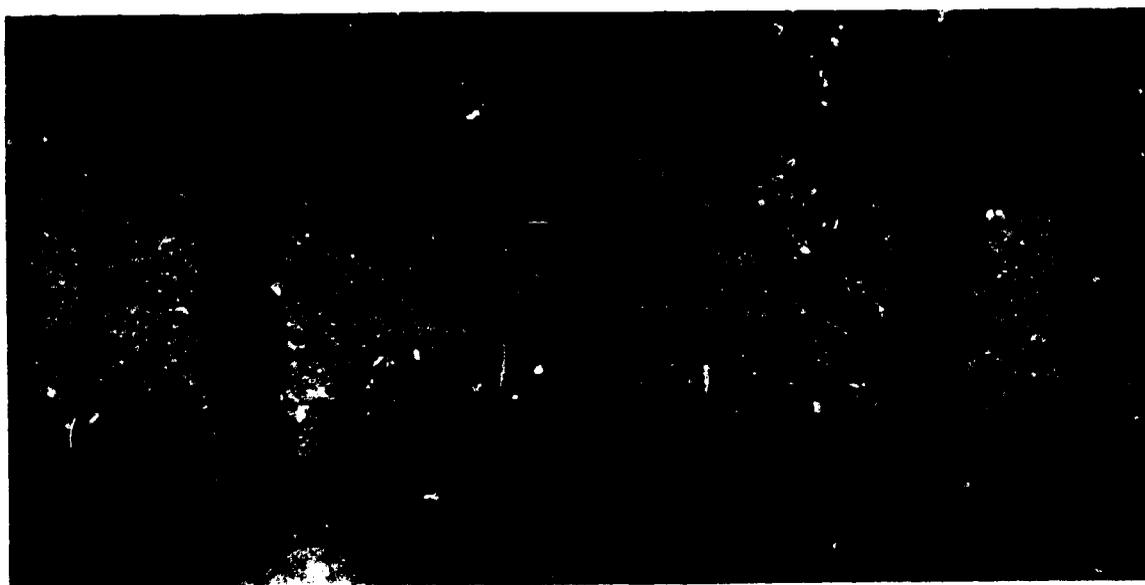
Alloys	(a) AUS	(b) US
	(c) UK(Fe)	(d) UK(Cu)
	(e) W	

FIG. 5
(next page)

State of tungsten alloys and tungsten itself after full immersion in 5% sodium chloride solution for seventy days at ambient temperature, in the presence of crevices.



(a)



(b)

FIG. 6 State of tungsten alloys after full immersion in sodium chloride solution for twelve months in the presence of crevices.

- | | |
|------------|------------|
| (a) AUS | (b) US |
| (c) UK(Fe) | (d) UK(Cu) |

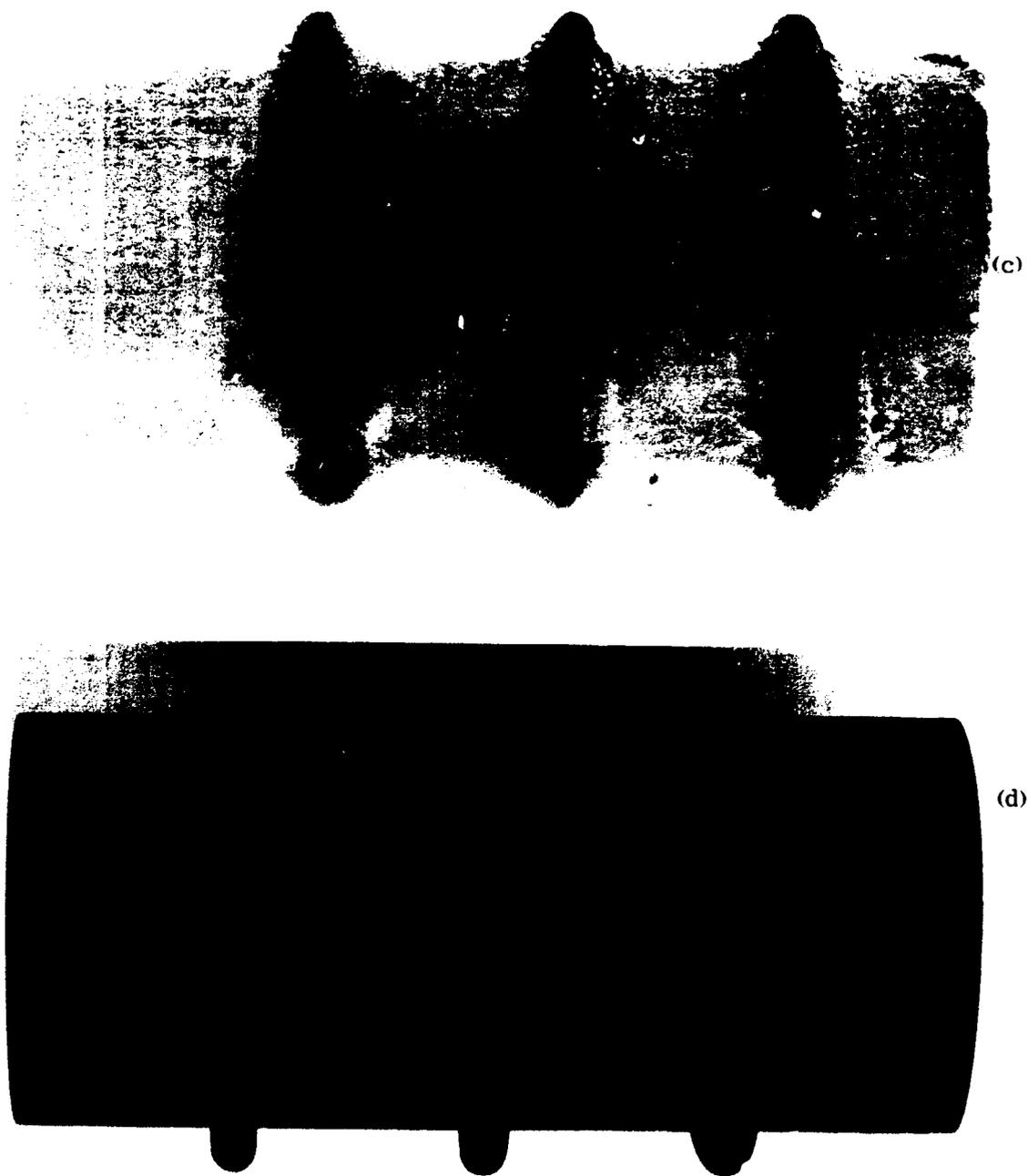


FIG. 6 State of tungsten alloys after full immersion in sodium chloride solution for twelve months in the presence of crevices.

- | | |
|------------|------------|
| (a) AUS | (b) US |
| (c) UK(Fe) | (d) UK(Cu) |



FIG. 7

SEM micrographs of the surface of the tungsten alloy AUS after full immersion in sodium chloride solution for seventy days in the presence of crevices.

- | | | |
|-----|---|--------|
| (a) | LHS of micrograph, area under the O-ring; RHS, area immediately adjacent to O-ring. | (x200) |
| | Inset, area under the O-ring. | (x500) |
| (b) | Area some distance from O-ring. | (x500) |



(a)



(b)

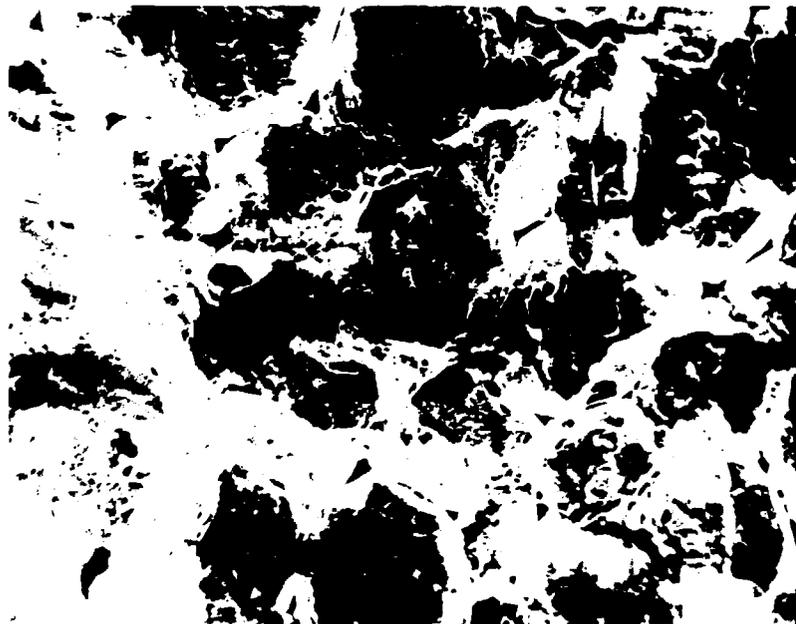
FIG. 8

SEM micrographs of the surface of the tungsten alloy AUS after full immersion in sodium chloride solution for twelve months in the presence of crevices.

- (a) LHS of micrograph, area under the O-ring; RHS, area immediately adjacent to O-ring. (x176)
Inset, area under the O-ring. (x440)
- (b) Area some distance from O-ring. (x440)



(a)



(b)

FIG. 9

SEM micrographs of the surface of the tungsten alloy US after full immersion in sodium chloride solution for twelve months in the presence of crevices.

- | | | |
|-----|---|--------|
| (a) | LHS of micrograph, area under the O-ring; RHS, area immediately adjacent to O-ring. | (x72) |
| | Inset, area under the O-ring. | (x144) |
| (b) | Area some distance from O-ring. | (x144) |



(a)



(b)

FIG. 10

SEM micrographs of the surface of the tungsten alloy UK(Fe) after full immersion in sodium chloride solution for twelve months in the presence of crevices.

- (a) LHS of micrograph, area under the O-ring; RHS, area immediately adjacent to O-ring. (x144)
 Inset, area under the O-ring. (x360)
- (b) Area some distance from O-ring. (x360)



(a)



(b)

FIG. 11

SEM micrographs of the surface of the tungsten alloy UK(Cu) after full immersion in sodium chloride solution for seventy days in the presence of crevices.

- (a) LHS of micrograph, area under the O-ring; RHS, area immediately adjacent to O-ring. (x136)
Inset, area under the O-ring. (x340)
- (b) Area some distance from O-ring. (x340)



(a)



(b)

FIG. 12

SEM micrographs of the surface of the tungsten alloy UK(Cu) after full immersion in sodium chloride solution for twelve months in the presence of crevices.

- | | | |
|-----|--|------------------|
| (a) | LHS of micrograph, area under the O-ring; RHS, area immediately adjacent to O-ring.
Inset, area under the O-ring. | (x152)
(x390) |
| (b) | Area some distance from O-ring. | (x390) |

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TITLE

Corrosion of high-density sintered tungsten alloys
Part 1 : Immersion testing

AUTHOR(S)

J.J. Batten
I.G. McDonald
B.T. Moore
V.M. Silva

CORPORATE AUTHOR

Materials Research Laboratory
Defence Science & Technology Organisation
PO Box 50,
Ascot Vale, Victoria 3032

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ABSTRACT

Sintered tungsten alloys are candidate materials for certain Australian ammunition components, namely kinetic energy penetrators, because of their high density (about 19 g/cm³). It is probable that a storage life of twenty years in an uncontrolled environment will be a requirement for this ammunition. Thus there is a need to determine the long-term storage capability of these alloys, in particular their capability to remain uncorroded during this period.

The corrosion behaviour of four candidate alloys has therefore been evaluated through weight loss measurements after total immersion in both distilled water and 5% sodium chloride solutions. The propensity of these alloys to corrode in a crevice situation was assessed in the sodium chloride solution. Some insight into the mechanism of corrosion was afforded by an examination of the surfaces after the tests using the SEM and through an analysis of the corrosion products.