Ion Engine Reliability as Affected by Corrosion of Materials

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Detailed corrosion information on 50- and 500-hr exposure tests of a number of ion engine structural metals in both cesium vapor and liquid is presented   The structural metals tested for corrosion included the 300 series stainless steels, Sicromo, and Inconel, as well as a titanium vanadium alloy   Tests on tantalum, tungsten, and a possible oxygen getter alloy were also run   Important aspects of the impurities study are the effects of oxygen in cesium on corrosion as well as on potential degradation of the ionizer   The most formidable problems associated with oxygen relate to the measurement of the oxygen level in cesium   Analytical methods used for oxygen in other alkali metals have not proved entirely satisfactory for cesium

Introduction

FOR optimum performance, an ion engine using a cesium propellant requires an ionizing structure which can continuously produce a beam of charged cesium particles of uniform density   The neutral portion of the effluxed cesium should be a small percentage of the total cesium flow   To obtain an ion engine system which is capable of continuous operation for periods of up to three years, prescribed and essentially fixed beam characteristics are necessary   Clogging of the porous ionizer or of the cesium liquid-vapor separator, or increased efflux of neutral particles, can be very detrimental to engine life or performance

To achieve the objective, we must be able to deliver pure cesium vapor to the ionizer   Impurities may have the effect of increasing or decreasing the ionizer pore size, thereby affecting the ionizing efficiency or flow characteristics   They may also, if carried in the vapor, poison the tungsten emitter surface   Such changes in the physical structure or of the surfaces of the ionizer may result in emission of neutral atoms as well as in excessive variations in engine thrust   A large neutral efflux is detrimental because of the charge-exchange phenomena between the neutrals and ions which occur near the accelerating structure; the positive particles can return to the structure and sputter the electrode

Changes in ion engine performance which may occur during extended operations can be caused by impurities that are either added to or were originally present in the cesium supply   The highest purity cesium metal contains certain metal impurities as well as oxygen in the form of oxides   Additional impurities can occur through transfer operations of the highly reactive cesium, by contamination from container materials which have not been thoroughly cleaned, and from corrosion or solubility of the container materials

In addition to the impurities considerations of the cesium supply, it is important that the materials of construction for an ion engine suffer no loss in structural integrity through corrosion   To determine the performance of such candidate materials of construction, the Hughes Aircraft Company has conducted a corrosion testing program

Test Results

The corrosion tests were static capsule tests   Candidate materials for the feed system were exposed to cesium liquid at 35°C for 4000 hr to simulate long-term storage, and to both cesium liquid and cesium vapor at 400°C for 50 and 500 hr to simulate feed system operation   Candidate materials of

construction for ionizers and surrounding high temperature structures were electrically heated to 980° and 1370°C while being held in cesium vapor at 265°C   The materials at both temperatures were exposed to cesium vapor for 50 and 500 hr

The methods used to evaluate corrosion were observation of weight change, spectrographic analysis of the cesium, metallographic examination, and testing of mechanical properties

Figure 1 shows weight changes of eight materials which were exposed in triplicate for four different exposure conditions   These were at 400°C for 50 hr in vapor, 50 hr in liquid, 500 hr in vapor, and 500 hr in liquid   The weight changes were relatively minor, with the largest change amounting to slightly more than 0 1 mg/cm^2 in a period of 500 hr   This is equivalent to a depth of 7×10^{-5} cm per year   It is thus evident that little metal was lost to affect the integrity of the construction material

Comparison of the 50- with the 500-hr exposures did not indicate a time-rate relationship with all materials   However, several trends are shown in Fig 1   The predominant pattern for all stainless steels (347, 316, and 302 which was sensitized) was weight gain when exposed to either liquid or vapor   Sicromo 2-½ steel, 6Al-4V titanium alloy, and copper lost weight

The behaviors of the Haynes 25 and the Inconel were more erratic   The former gained weight in the long term exposures, but lost weight in the shorter exposures   The Inconel gained weight when exposed to liquid, but lost weight when exposed to vapor   Some of these weight changes represent such small differences that they are at the limits of accuracy in weighing

According to the producer of the metal, the cesium used in these tests contained 200–300 ppm of oxygen, determined by the butyl bromide method   The oxygen is chemically combined with the cesium in the form of cesium compounds   It is our opinion that the oxygen content of the cesium plays a most important role in the reactions with other metals   The predominant reactions which result in attack of the metals and alloys tested are oxidation-reduction rather than solution of the metals in the cesium   The relative free energies of formation of cesium oxide and the oxides of the material under test predicts whether the latter will be oxidized or whether their oxides will be reduced by cesium   These free energy predictions must be used with caution because the exact compositions of the cesium oxides are not known with certainty and therefore the correct free energy is difficult to estimate   Although many investigators have assumed that any oxygen in cesium is present as the monoxide, this is not an established fact   It must also be kept in mind that the reaction rates are not indicated by the free energy values

It is known that oxides of cesium are relatively unstable when heated [1-3]   Published values for the decomposition temperature of Cs_2O range from 360°C[1] to approximately 700°C[2]   Other cesium oxides ranging in composition from Cs_2O_2 to Cs_7O
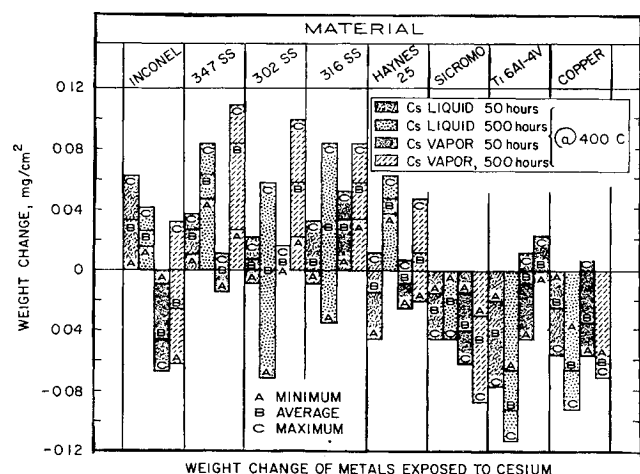
Fig 1   Chart of weight changes in eight materials exposed to cesium for four different conditions

Fig 3   Stainless steel (316) sample no 217 exposed to cesium liquid for 500 hr at 400 C   Etchant: Marbles reagent (original magnification 1000 ×; reduced 7% in reproduction)

also will be decomposed by heat and vacuum at relatively low temperatures

From the free energy of formation data, the elements tantalum, chromium, zirconium, molybdenum, tungsten, and titanium should be oxidized by cesium monoxide   Copper, however, would not be oxidized by cesium monoxide, but any copper oxide would be reduced to metallic copper by the cesium   The free energies of formation of the oxides of nickel, iron, manganese, and cobalt are so close to that of cesium monoxide as to preclude a precise prediction of the direction of reaction

From the foregoing considerations, it would appear that those metals which are oxidized by reaction with cesium oxide would gain weight   However, there is another important criterion to be considered: How well does the resultant oxide adhere to the base metal?   In the case of austenitic stainless steels it is well known that corrosion resistance in aqueous media is due to the tightly adhering surface oxide film (largely chromium oxide)   Therefore, the explanation for the weight gain for the stainless steels is apparent   Even though these materials gain weight, chromium was found in the cesium after exposure   This indicates that either the chromium oxide has some solubility in cesium or does not completely adhere to the base metal

Additional experimental evidence of oxidation of the stainless steels was found in metallographic examination   All 500 hr specimens were found to have a film 0 0002 in thick on their surfaces   Figure 2 is a photomicrograph of 302 stainless steel after exposure to cesium vapor, Fig 3 shows the

structure of 316 stainless after exposure to cesium liquid, and Fig 4 is 316 stainless after exposure to cesium vapor   Neither the magnitude of the weight gain nor the quantity of oxygen available in the cesium suggests that this layer is composed entirely of oxides of the elements present in stainless steel   Diffusion probably plays a part in the reaction, with the resultant film not following a stoichiometric relationship for the metal oxides

The loss of weight in the titanium alloy, despite the fact that it is a potent oxygen getter, is probably due to the sloughing off of the resultant oxide   This was confirmed by analysis of the cesium which consistently showed increases in titanium

Although use of refractory metals at boiler temperatures was not contemplated, tantalum tubes were used initially to enclose the test specimens   These tubes, which where heated in an inert atmosphere, failed catastrophically (see Figs 5 and 6)   Spectrographic analyses of cesium after exposure showed as much as 1% of tantalum (in elemental or compound form)   The disappointing performance of tantalum is also attributed to oxidation and it is entirely possible that its behavior would be satisfactory in an oxide-free cesium environment   The explanation for the embrittlement of the tantalum is that instead of forming a passive oxide film as did the stainless steels, the oxygen was readily dissolved and diffused through the metal

Indeed, tantalum and the refractory metals, tungsten and molybdenum, did successfully withstand 500-hr exposures
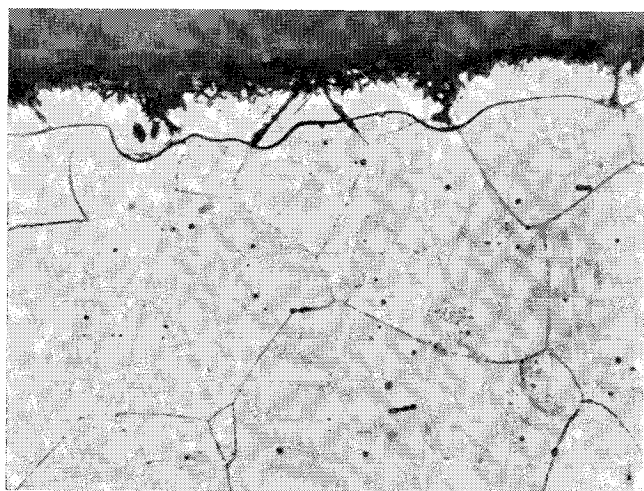

Fig 2   Steel (302) sample no 55 exposed to cesium vapor for 500 hr at 400°C   Etchant: Kallings (original magnification 1000 ×; reduced 7% in reproduction)
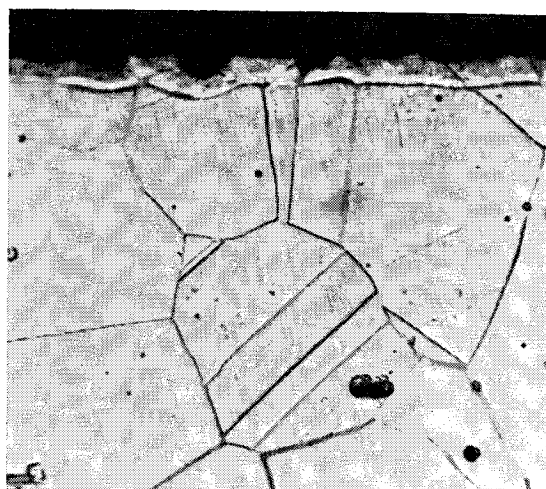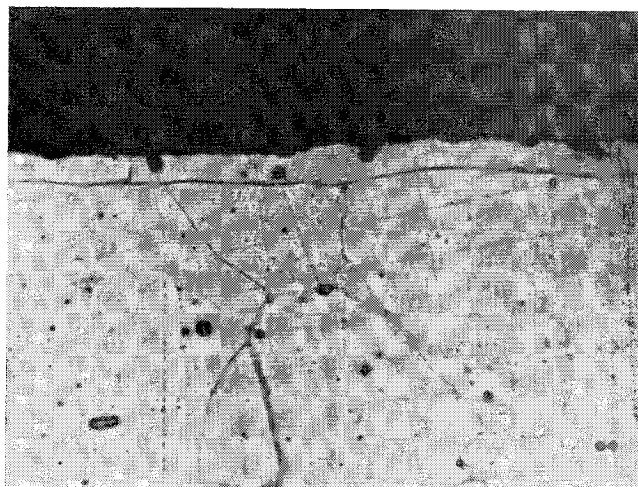

Fig 4   Stainless steel (316) sample no 214 exposed to cesium vapor for 500 hr at 400°C   Etchant: Marbles reagent (original magnification 1000 ×; reduced 7% in reproduction)
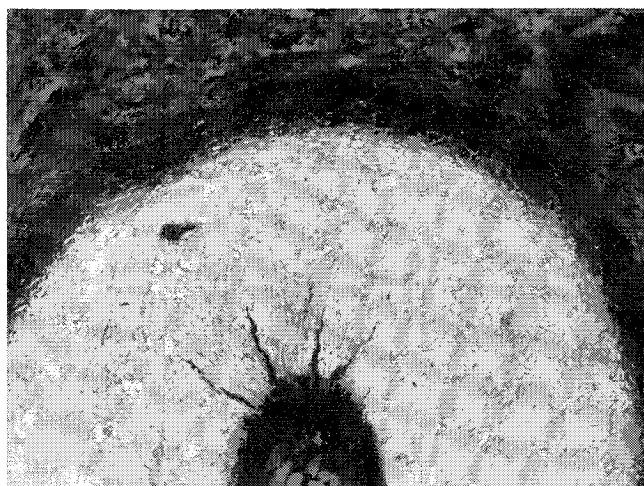
Fig 5 Tantalum tube exposed to cesium liquid for 500 hr at 400 C Etchant: HF + NH₄F (original magnification 100 ×; reduced 7% in reproduction)

at 980° and 1370°C in cesium vapor of low oxygen content The vapor was generated at a temperature of 265°C, giving a vapor pressure of less than 1 mm Hg At this lower temperature, little of the cesium monoxide present in the liquid would be expected to decompose The cesium vapor, therefore, was relatively pure compared to that generated at 400°C

Although not a part of the planned corrosion program, severe attack of molybdenum feed tubes operating at about 1000°C was observed in one accidentally contaminated ion engine In addition to corrosion of the tube, molybdenum was found deposited on the ionizer and the accelerating electrodes The mechanism for the corrosion and molybdenum transport appears to have been oxidation of the molybdenum, subsequent volatilization of the molybdenum oxide, and partial decomposition of the oxide on the hot ionizer

Except for the evidence that already has been presented, most of the attack of the metals and alloys was too minute to be detected metallographically The low alloy steel Sicromo 2-½, however, was decarburized to a depth of 0 002 in This is shown in Fig 7

The same materials that were exposed to the 400°C cesium environments were also exposed to cesium at 35°C for 4000 hr All materials lost an insignificant amount of weight and the stainless steels did not exhibit the film which was found on them when exposed to higher temperatures This indicates that the reaction rates are quite slow at the low temperatures

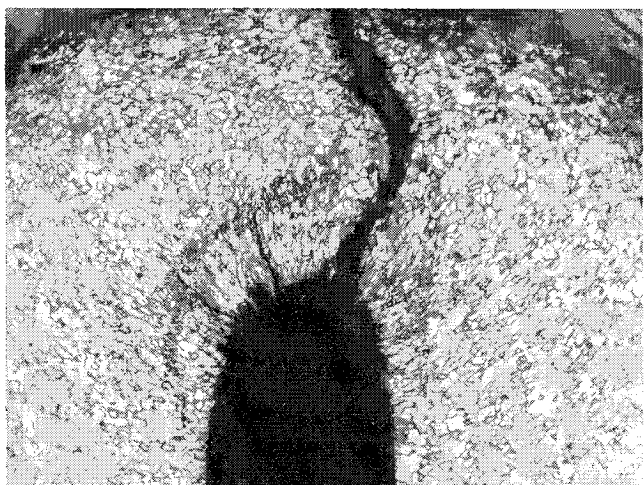Other materials exhibiting satisfactory corrosion resistance to the 400°C exposures were Nicrobraze alloy (AMS 4777),

Fig 6 Tantalum tube exposed to cesium liquid for 500 hr at 400°C Etchant HF + NH₄F (original magnification 100 ×; reduced 7% in reproduction)
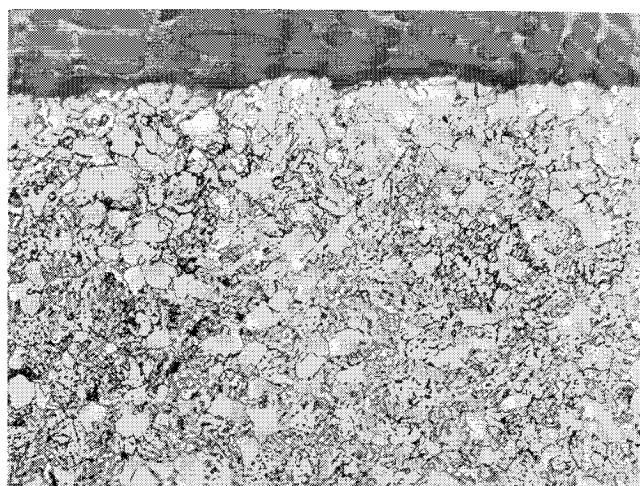

Fig 7 Sicromo sample no 186 exposed to cesium vapor for 500 hr at 400°C Etchant: 5% Nital (original magnification 300 ×; reduced 7% in reproduction)

molybdenum to 347 stainless steel joints brazed with Nicrobraze, and molybdenum to 347 stainless steel joints brazed with copper

A 50% titanium-50% zirconium alloy, tested to determine its effectiveness as a getter of oxygen, showed a higher weight gain than the stainless steels, thus demonstrating potential as a getter material for removing oxygen from cesium However, titanium was found in the cesium analysis indicating that the resultant oxide did not adhere completely to the alloy No zirconium was detected in the cesium

These tests did not determine true solubilities of elements in the cesium because the spectrographic analyses were semiquantitative, samples were not taken at the exposure temperature, and no attempt was made to determine whether the elements were present as elements or compounds In view of other evidence, it is quite likely that the impurities increase in the cesium took the form of compounds (oxides) Considering these limitations, the spectrographic analyses indicated the following relative constituents in cesium when exposed to alloys containing the elements shown in Table 1

Mechanical property data indicated no significant loss in properties or embrittlement of the feed system materials after exposure to cesium at 400°C

Conclusions

This study has indicated that for the 400°C temperature regime no severe restrictions are placed on this selection of materials exposed to cesium For the highest strength-to-weight ratios for 400°C exposures, the following classes of alloys are considered to offer the best potential: 1) precipitation hardening stainless steels, 2) precipitation hardening nickel base alloys, and 3) heat-treated low alloy steels

These conclusions are based on adequate performances of other alloys from these alloy systems Although titanium alloys suffered no degradation in this service, the degree of cesium contamination was sufficient to rule them out

However, for high operating temperature refractory metals, cesium containing oxygen is likely to impose serious problems This is true because the oxides of some of the refractory metals

Table 1 Relative solubility of elements in cesium from alloys containing these elements

Negligible	Very slight	Moderate	High
Copper	Chromium	Titanium	Tantalum
Manganese	Iron	Boron	
Nickel			
Cobalt			

are quite volatile at ionizer temperatures   As the refractory metals are oxidized, vaporization of their oxides will cause continuous erosion   Hence, the requirement for low oxygen-cesium appears to be mandatory

As we have emphasized, the corrosion resistance of metals and potential degradation of the ionizer is influenced by the oxygen content of the cesium   Unfortunately, adaptation of analytical methods used for determining oxygen in other alkali metals has not yet proved entirely satisfactory for cesium   Thus, it is difficult to evaluate fully the effect of oxygen concentration at this time

In conclusion, the most important problem with which we are faced in the use of cesium propellant for ion engines is the production and maintenance of high purity cesium with a low oxygen content

References

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Charged Aerosol Energy Converter

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The charged aerosol energy converter is an electrohydrodynamic unit which operates more efficiently than other electrohydrodynamic devices   By using charged aerosol particles in a dense gas the mobility is reduced so that slip velocities become negligible   A theoretical model is discussed and the solution of the equations indicates that constant gas velocity or constant thermodynamic state operation is possible   The experimental results show excellent agreement with the theoretical model, hence verifying the assumptions made   It is demonstrated both experimentally and theoretically that the only limitation to the generator is electric breakdown   At present the operation is confined to high velocity due to difficulties in producing the aerosol

Introduction

THE conversion of kinetic energy to electrical energy by making use of the retarding force exerted by an electric field on either ions or charged particles is an old concept[1] [2] which has recently been revived as a way of producing electricity in a system without moving parts

In one method under current investigation,[3] the particles are produced in an expansion through a supersonic nozzle into a vacuum chamber; thus, high kinetic energy is imparted to particles of very high mobility   The system, however, is not susceptible to staging, and coulomb beam spreading and space charge limitations are to be expected

In another method presently being investigated, the particles are immersed in a fluid, to which kinetic energy is imparted   For successful operation this requires negligible slip velocity of the particles as compared to the velocity of the carrier fluid   If ions are used, they may be suspended in an insulating liquid[4][5] resulting in very small mobilities This type of approach is very fruitful for high voltage generation, but high wall frictional losses reduce its capacity as a power source

Still another method,[6] which results in low slip velocity and frictional losses, is to increase particle size and suspend the particles in a gas   This method can result in high charge densities, and permits staging of several units   Since the kinetic energy of a gas can easily be obtained from an expansion originated by the addition of heat, it is possible to use this approach for the conversion of heat to electrical energy   This paper is devoted to the last approach just mentioned

Theoretical Model

Our theoretical model comprises a one-dimensional frictionless steady flow of aerosol through a nozzle whose shape is part of the problem   The aerosol particles are assumed uniform in size   Figure 1 depicts the situation: aerosol particles become charged instantaneously at a ground reference position x_1 and they give up their charge to a collector placed downstream at position x_2 The collector is connected through a load resistor R to ground   The space between the charging and collector planes constitutes the region where flow energy converts into electrical energy   Excellent but unnecessarily complicated theoretical analysis of the fundamental set of equations governing the conversion process has been made [7]–[9]   Here it is assumed at the start that the charged particles have negligible slip velocity (zero mobility) and that they do not affect the gas thermodynamically Under these assumptions, which later be seen to be justified from the experimental results, the general formulation of the problem is given by standard laws as follows:

$$\delta v A = \text{const} = M \qquad \text{(conservation of mass)} \qquad (1)$$