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CORROSION PROBLEMS IN Ti/KClO$_4$ LOADED DEVICES WHEN SUBJECTED TO HUMIDITY ENVIRONMENTS*

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ABSTRACT

A piston motor/igniter loaded with a Ti/KClO$_4$ pyrotechnic and sealed with a silicone adhesive exhibited serious corrosion problems during aging. Five 24-hour thermal cycles between room temperature and 71°C at 90% relative humidity resulted in extensive surface corrosion of the Kovar pins and severe stress corrosion cracking of the Kovar pins in the vicinity of the bridgewire weld. No corrosion or cracking of the Nichrome bridgewire was observed. Similar results were observed after 60 days at 50% and 90% relative humidity at room temperature. Tests at ambient relative humidity and room temperature caused limited surface corrosion and no observable cracking.

It was determined that these problems resulted from the combined presence of chlorine containing contaminants and atmospheric moisture Chlorine was detected in both the surface corrosion product and the corrosion product in the subsurface cracks. The absence of reaction and/or morphological alteration of the Ti/KClO$_4$ at the pyrotechnic interface with the Kovar indicated the pyrotechnic was not involved in the corrosion reaction, and, hence, the chlorine was present in the surface contamination on the Kovar pins. The aging tests clearly indicate that external moisture was involved in the corrosion reaction. Calculation and experimentation have shown the silicone adhesive used to seal these devices to be permeable to water vapor, and the moisture conditions inside the devices equilibrated with external conditions within a few hours.

It was concluded that the corrosion and cracking could be solved by eliminating the source of moisture by hermetically sealing the devices. Tests of hermetically sealed units have confirmed this conclusion.

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INTRODUCTION

Titanium/potassium perchlorate ($Ti/KClO_4$) loaded pyrotechnic devices have been in use at Sandia National Laboratories for more than ten years. Typical applications have included igniters, piston motors, and valve actuators. These devices have long lifetimes (in excess of 20 years) and high reliability requirements associated with them. Such requirements place stringent demands on the material properties with one of the most important being the compatibility of the various materials used in a design. Corrosion of such critical areas as the electrode pins, bridgewire and weld interfaces cannot be tolerated and maintain the design requirements.

BACKGROUND

No compatibility problems were observed in $Ti/KClO_4$ loaded devices in screening, short term aging or long term aging tests until three years ago. At that time severe corrosion of the electrode pins and bridgewire was observed soon after manufacture of the first production lot of a valve actuator. Corrosion of these materials was observed within 30 days after production of the first lot. Numerous papers have been written concerning the causes of, mechanisms of, and solutions to this corrosion problem (refs. 1-7). In summary, the corrosion problem resulted from a combination of three factors.

1. Residual moisture in the $Ti/KClO_4$ powder.
2. Contamination of the electrode pins and bridgewire surfaces.
3. Insufficient passivation of the electrode pins and bridgewires.

All three factors were necessary to cause the corrosion problem. By minimizing the moisture and contamination levels and increasing the passivation thickness, the corrosion problem in this actuator was eliminated. Production was reinstated with no recurrence of the corrosion problem.

To show the effect of moisture on the corrosion mechanism, a non-corroded lot of this actuator was chosen for a humidity aging study. Half of the units had a 0.0125 cm hole drilled through the output closure disk, while the other half remained hermetically sealed. Equal numbers of each half were placed in desiccated, 50 percent and 92 percent relative humidity environments at ambient temperature. Several units were opened and examined to determine the extent of corrosion after six months aging. No corrosion above background was encountered in any of the hermetically sealed units or the drilled units that were aged in the desiccated environment. Extensive corrosion of the electrode pins (over 75 percent of the surface area) was observed for the drilled units aged in the 50 percent and 92 percent relative humidity environments. Only isolated areas of bridgewire corrosion were observed; this was to be expected as the Nichrome bridgewire was more corrosion resistant than the electrode pin material (50/50 iron-nickel alloy). This particular study has a direct bearing on corrosion problems encountered in two other component designs, a thermal battery igniter and a piston motor.

The above corrosion problems resulted in concern about possible problems in other Ti/$KClO_4$ pyrotechnic devices where moisture, contamination and passivation factors were not controlled. Of particular concern were an igniter and piston motor that have been in production since 1968. Soon after starting to screen for corrosion problems in other Ti/$KClO_4$ devices, a production lot of igniters was found to have severe corrosion of the electrode pins just prior to insertion into the next assembly. In addition, a severe humidity test of the piston motor design resulted in numerous open circuits when a bridgewire continuity test was performed. Subsequently, these units were examined to determine the cause of failure.

IGNITER CORROSION

Figure 1 shows the configuration of the igniter. Its primary function is as an ignition source in thermal battery applications. Table 1 lists the materials used in the igniter design.

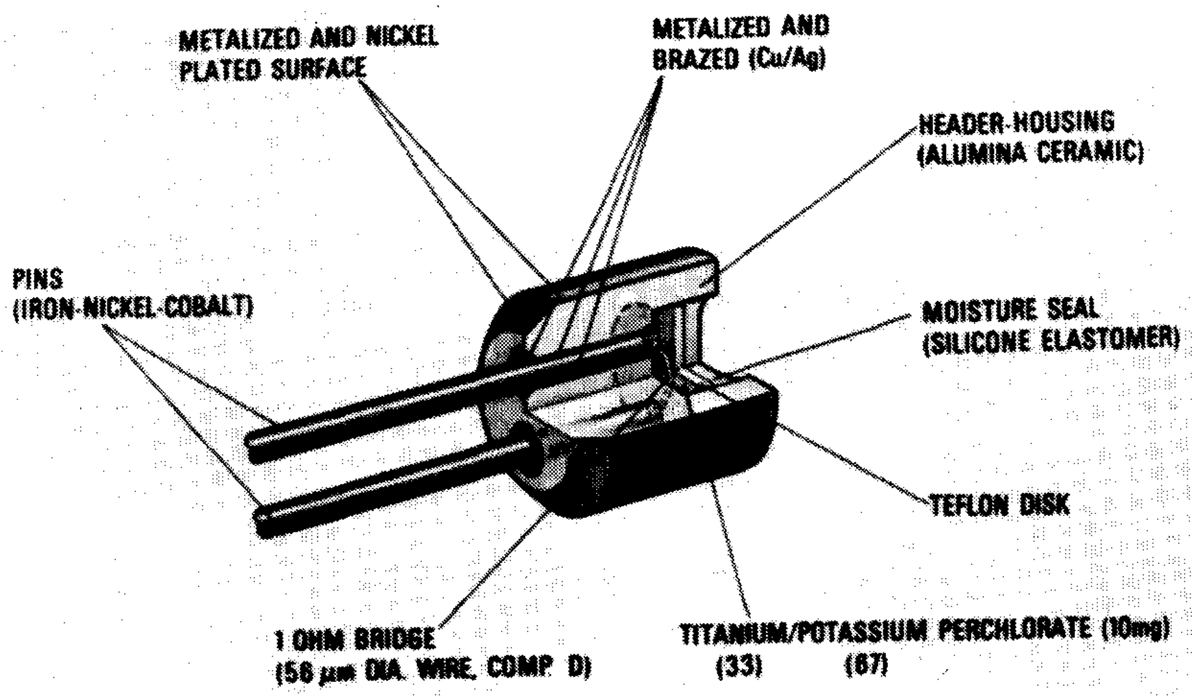


Fig. 1. Cutaway view showing design of igniter

TABLE 1

Materials used in the igniter

Header	Alumina Ceramic
Braze	Silver
Metallizing	Molybdenum/Manganese
Electrode Pin	Kovar
Bridgewire	Nichrome (Composition D)
Pyrotechnic	$Ti/KClO_4$ (33/67)
Output Seal	Silicone Elastomer (RTV-630)

Optical and scanning electron microscopy (SEM) of the previously mentioned lot of igniters revealed nearly 100 percent corrosion of the electrode pin surfaces as shown in Figure 2. In nearly half the units, the bridgewire was detached from the electrode pin at the weld interface. Evidence of pin corrosion in the weld area was apparent (Figure 3). No corrosion of the bridgewire was observed except for an isolated area near the weld. Energy dispersive x-ray analysis ($Z \geq 11$) of the pin corrosion product revealed major concentrations of the Kovar pin constituents with minor concentrations of chlorine.

Examination of the pyrotechnic powder interface in contact with the electrode pins revealed no morphological alteration of the potassium perchlorate ($KClO_4$) when compared to the bulk powder away from the pins as shown in Figure 4. This is contrast to the previous observations with the $Ti/KClO_4$ valve actuator where morphological alteration of the $KClO_4$ was observed whenever corrosion was present (ref. 4) Based on this observation, it was concluded that the pyrotechnic blend, and in particular the $KClO_4$, was not playing a primary role in the corrosion mechanism of the igniter.

Further evaluation of other production lots of the igniter produced prior to this lot revealed levels of corrosion ranging from none in some lots to the occurrence of small, isolated corroded areas in other lots. No corrosion of the weld areas was apparent. Except for one bridgewire where a single area of corrosion was found, no bridgewire corrosion was observed. Figures 5 and 6 are typical SEM photomicrographs of the pins and bridgewires from these production lots.

Evaluation of ten year old igniters that were installed within thermal batteries revealed a pattern of corrosion. Igniters from certain production lots were found to have corroded electrode pin surfaces while other igniter lots examined from thermal batteries were free of corrosion.

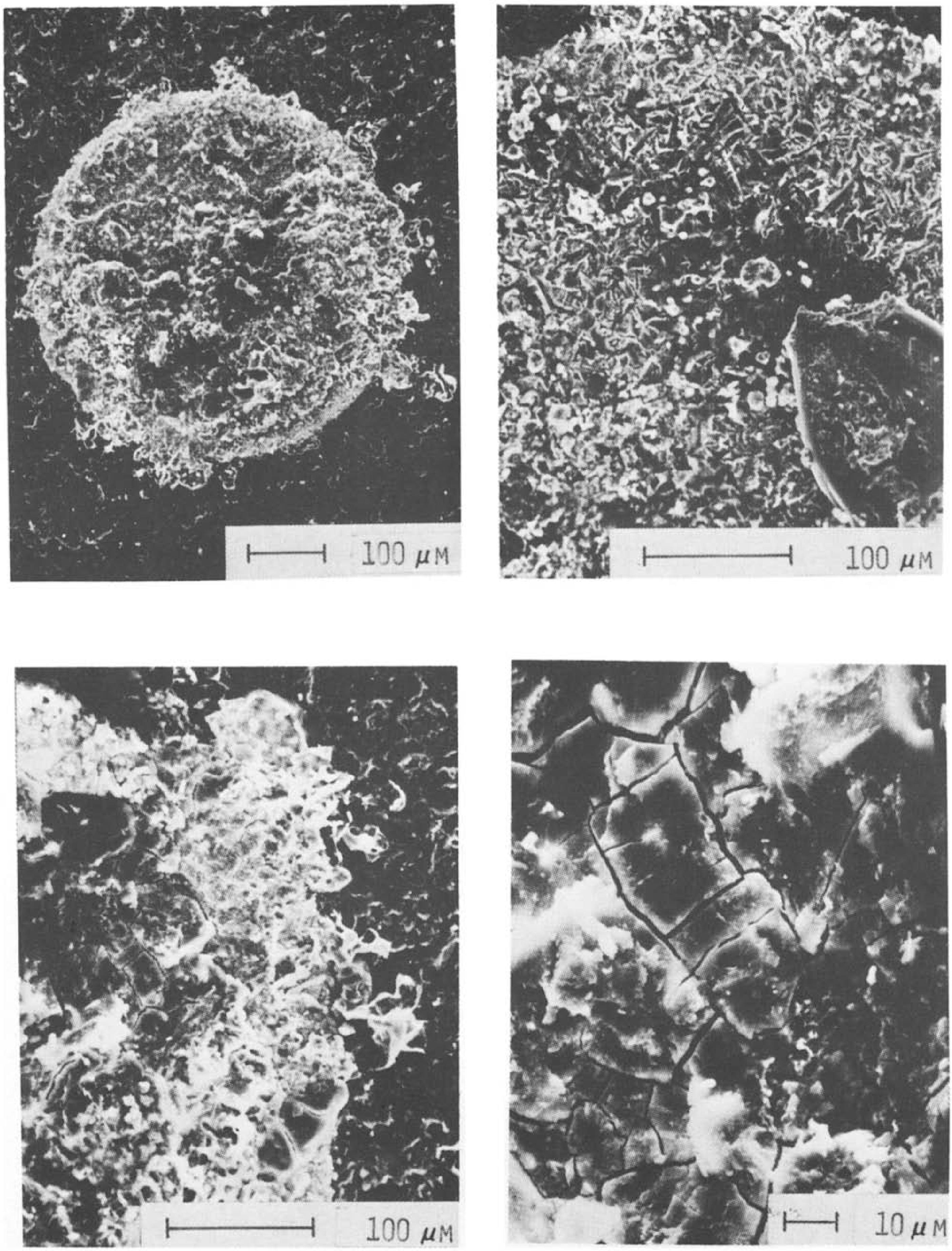


Fig. 2. SEM of electrode pins from corroded igniter lot

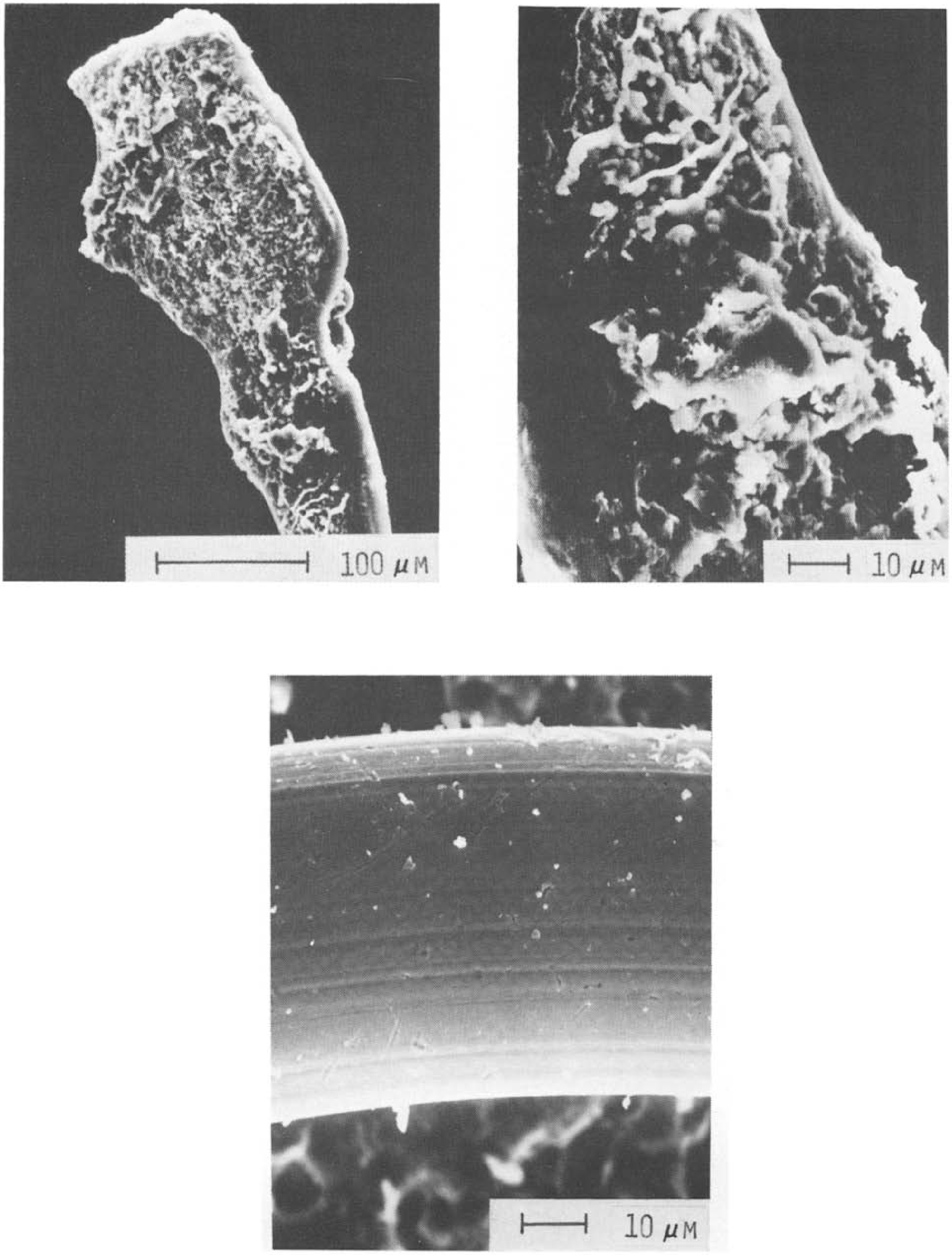
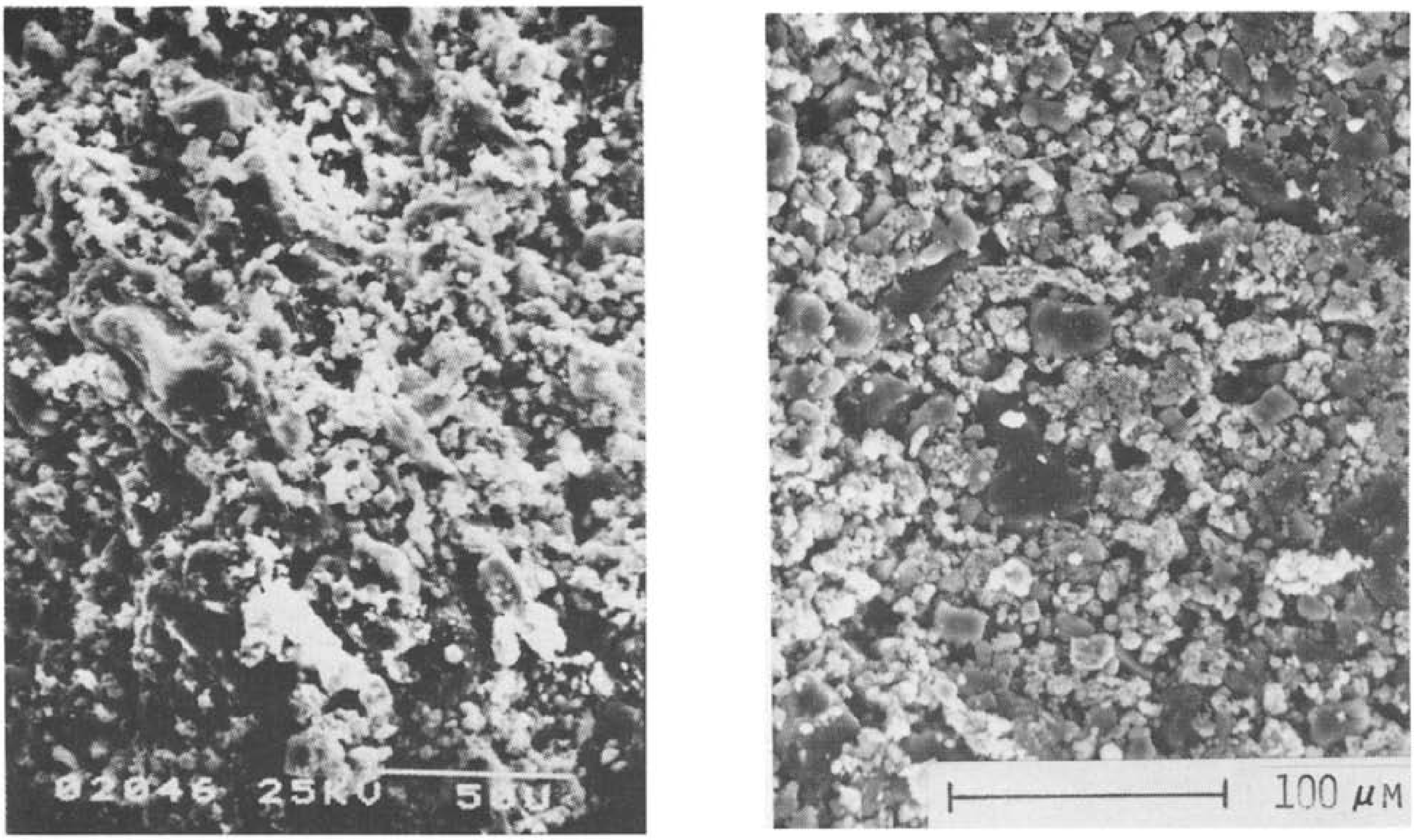
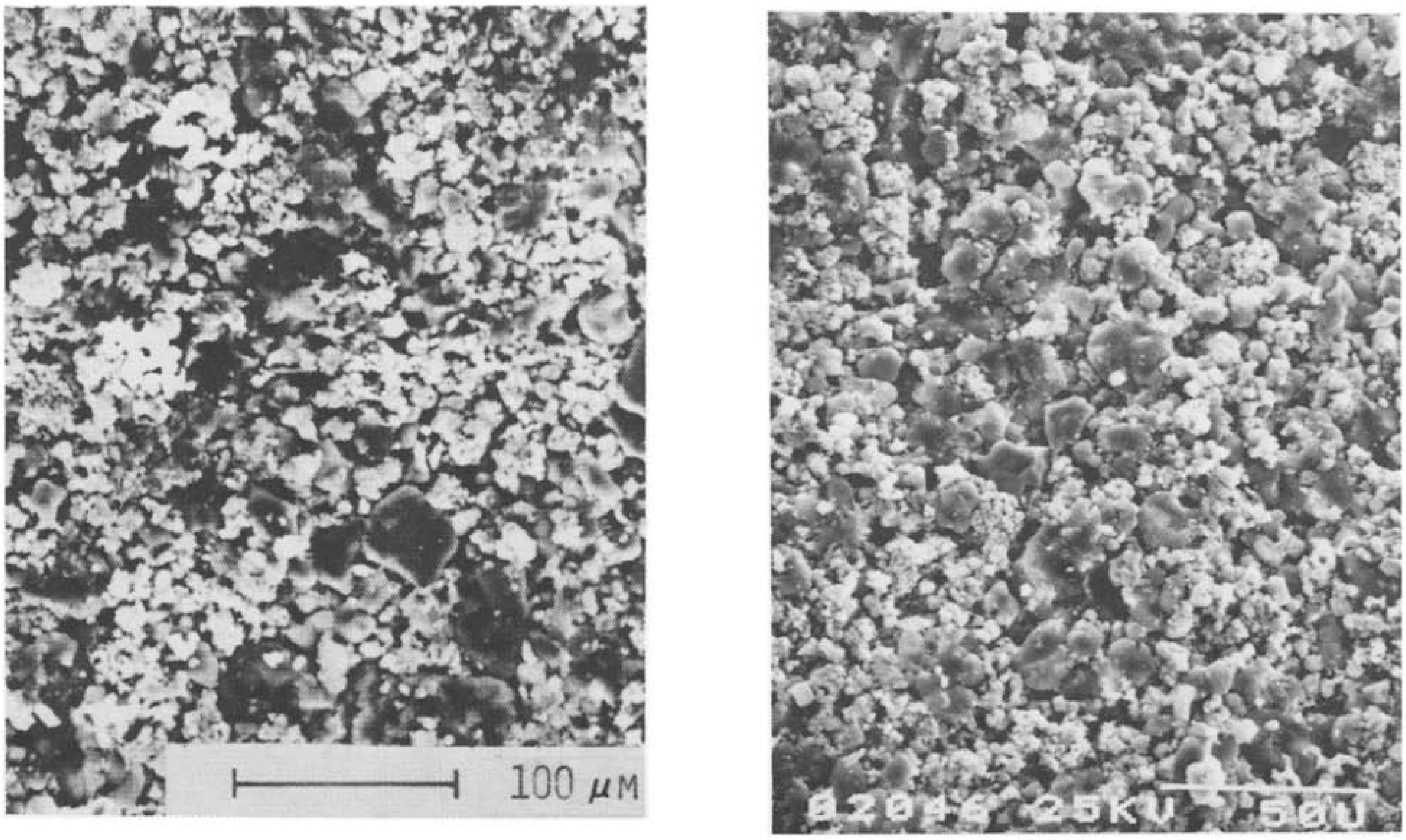


Fig. 3. SEM of bridgewire and weld interface from corroded igniter lot.

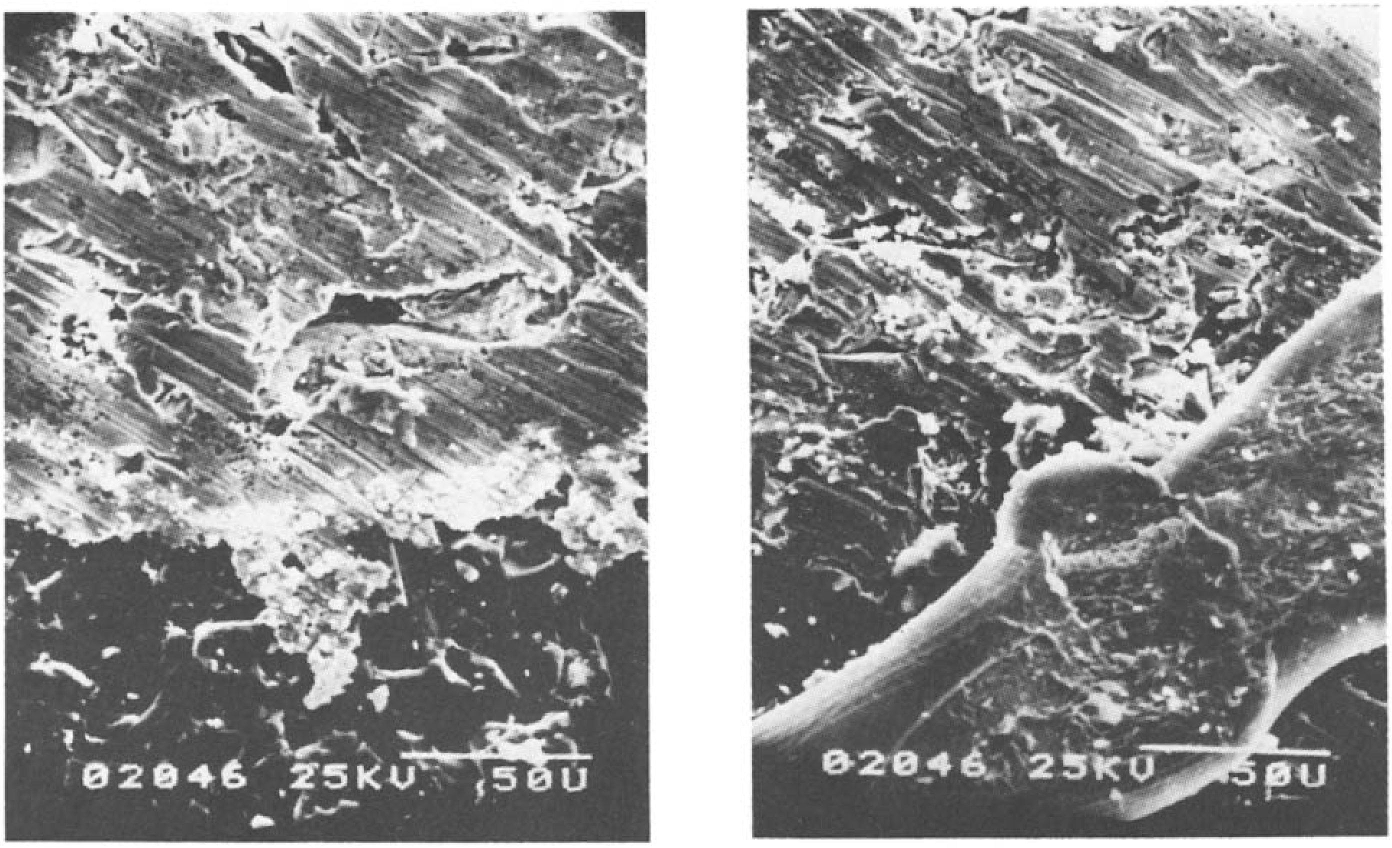


Pin Interface



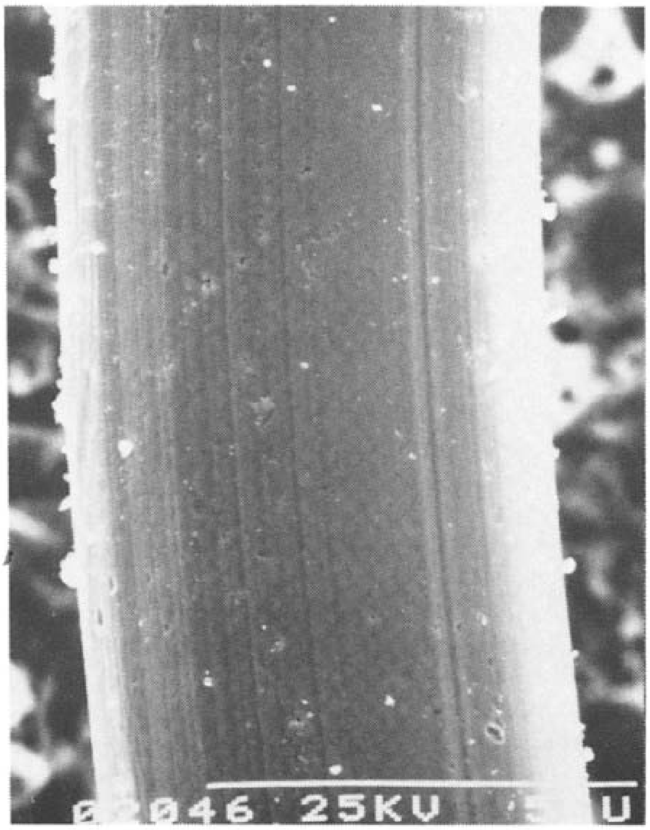
Bulk

Fig. 4. SEM of Ti/$KClO_4$ powder from corroded igniter lot (bulk and pin interface).



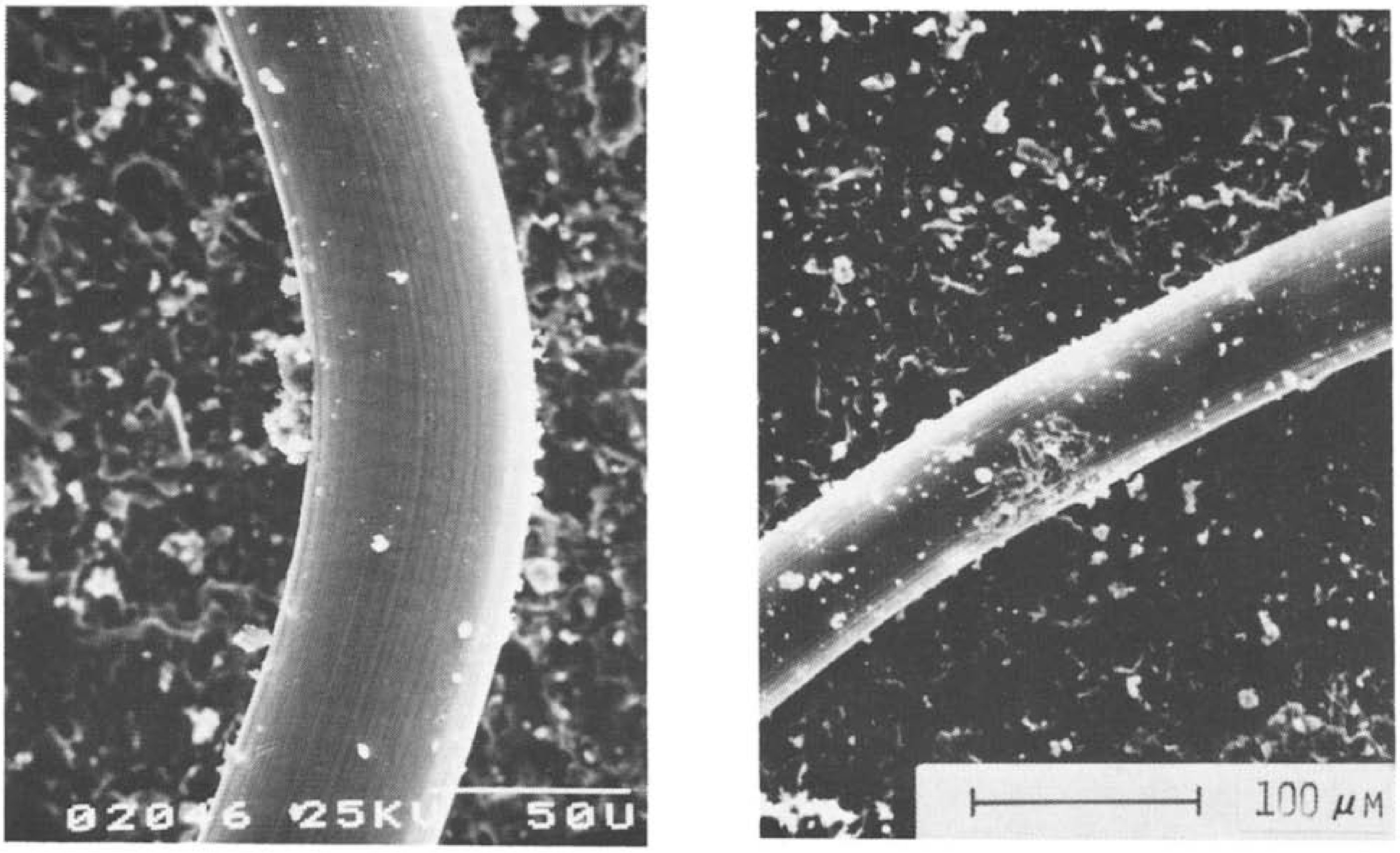
Electrode Pin

Electrode Pin/Weld Area



Bridgewire

Fig. 5. SEM of electrode pins and bridgewire from a non-corroded igniter lot.



Bridgewire

Electrode Pin

Fig. 6. SEM of electrode pins and bridgewire from a partially corroded igniter lot.

Based upon these observations no consistent pattern of corrosion was apparent which would indicate a compatibility problem. Where present, the degree of corrosion was variable from lot to lot. These observations were independent of whether the igniter had been installed in the thermal battery or not.

An additional study was implemented where a group of igniters were aged at ambient temperature and 33%, 50%, and 75% relative humidities. Within 60 days, evidence of electrode pin corrosion for the 50% and 75% relative humidity aged units was apparent. The degree of corrosion was greater in the 75% than in the 50% relative humidity aged units. The corrosion was similar to that in the previous corroded igniters, but not as extensive. Igniters aged at 33% relative humidity were similar to units examined at the start of this program.

PISTON MOTOR CORROSION

The piston motor is in many respects similar to the thermal battery igniter. The header design, materials, manufacturer, processing, and pyrotechnic are similar. The piston motor, shown in Figure 7, is a smaller version of the igniter. The design is considered to have a nonhermetic seal.

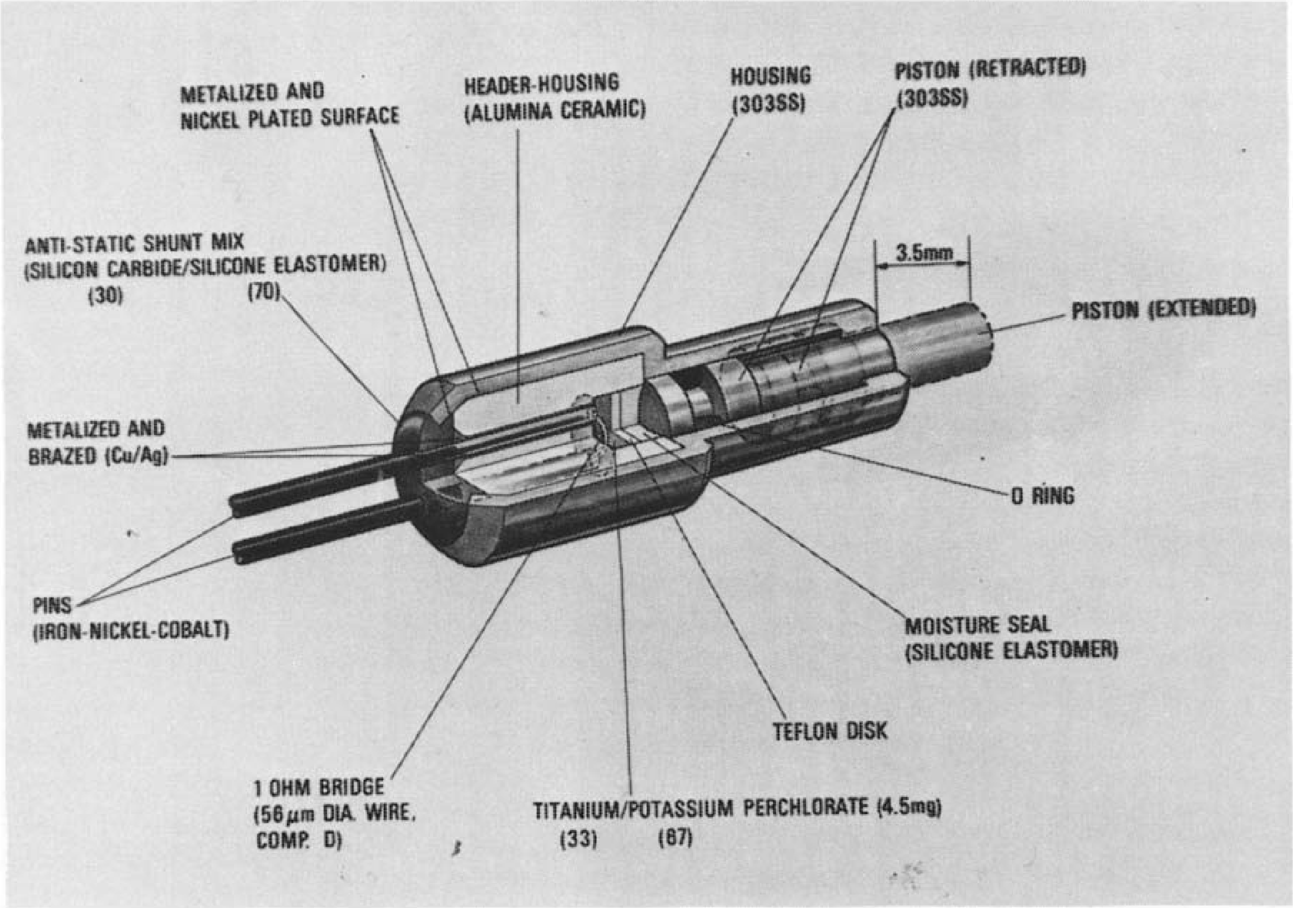


Fig. 7. Cutaway view showing design of piston motor.

Previous evaluations of this device from early lots (nearly eight years old) revealed the presence of minor corrosion. Such corrosion was best described as small isolated areas of corrosion most often associated with contamination on the electrode pin surface. Such contaminants included S^{-2}, Cl^{-}, and Si^{+4} containing materials. The observed corrosion was similar in extent to that found on unloaded header assemblies. No potential corrosion or failure of the weld was observed. Likewise no corrosion of the bridgewire was observed

The original design applications of the piston motor, including the ones examined for corrosion, did not require the use of the component in a high humidity environment. However, a recent application of this device required a severe humidity test cycle as shown in Figure 8. Measurement of the bridgewire resistance after humidity testing revealed values significantly above the 1.0 ± 0.1 ohm specification for the circuit. In many cases, an open circuit was indicated

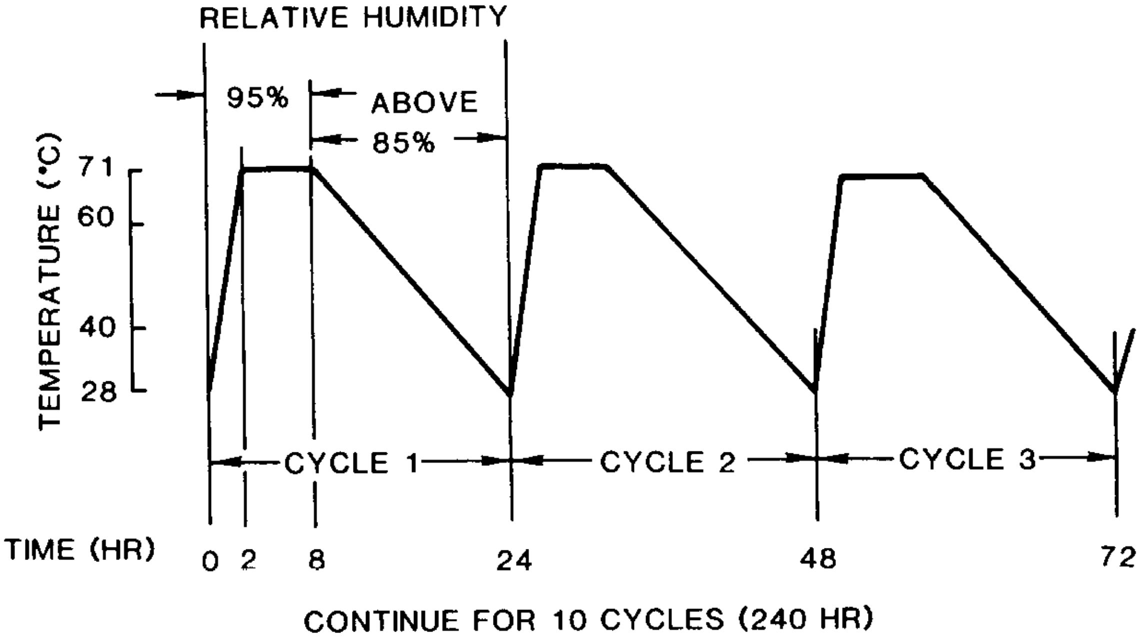
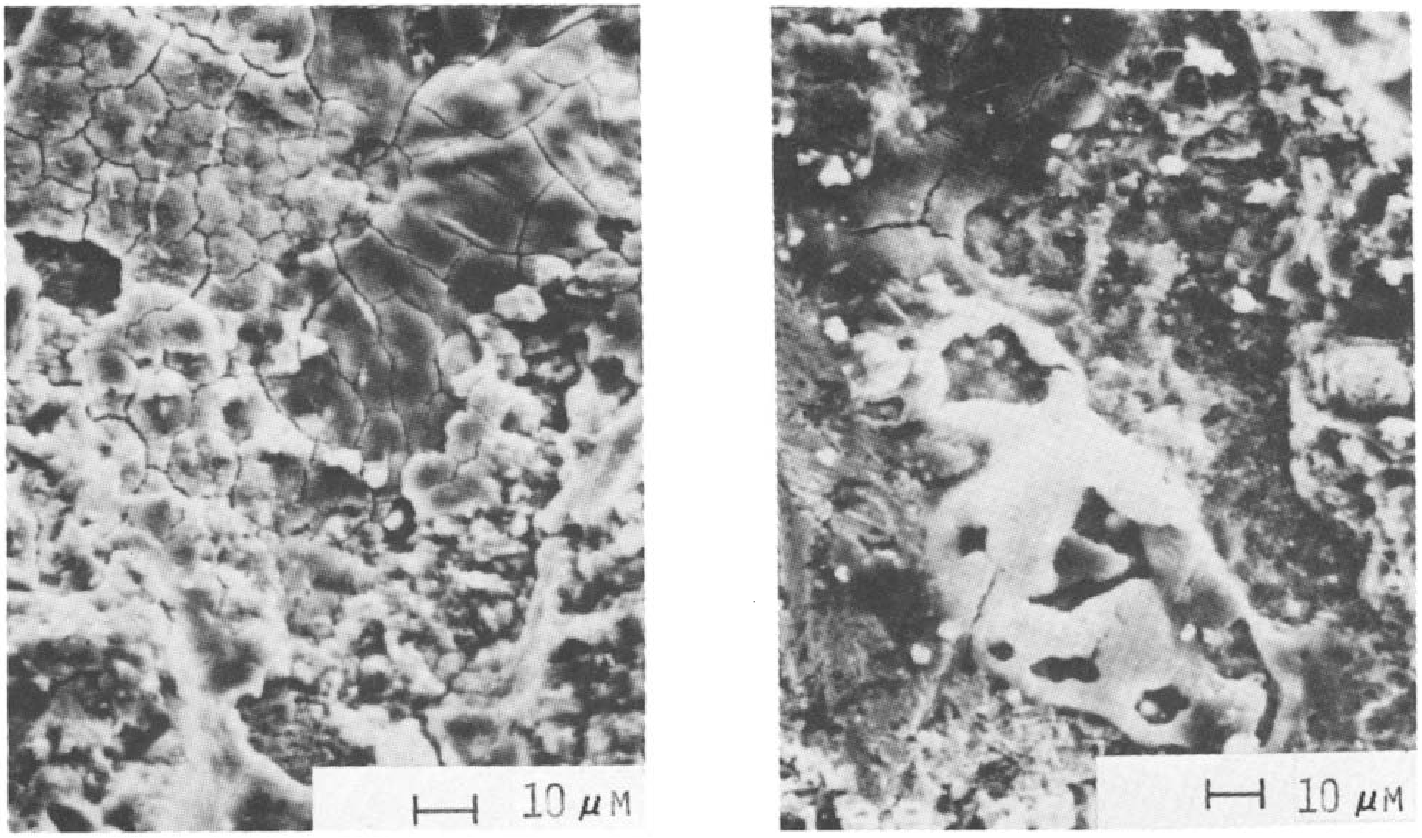


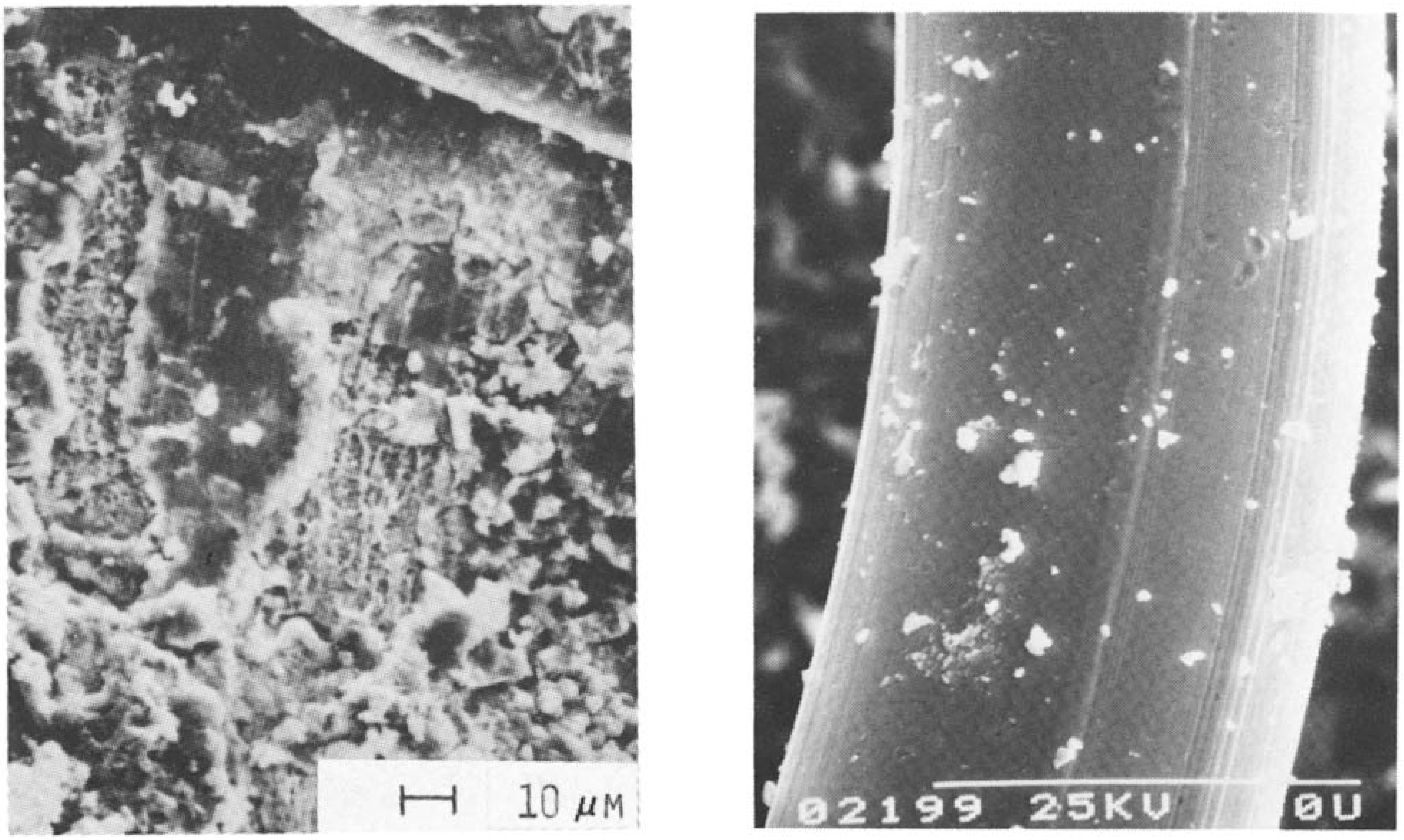
Fig. 8. The humidity cycle used for the piston motor

Disassembly and evaluation of the header revealed massive corrosion of the electrode pins (Figure 9). Nearly all of the surface was corroded. Either one or both of the bridgewire/pin welds were detached at the weld interface in one-half of the units evaluated. Optical and SEM examinations revealed similar corrosion of the electrode pins and weld areas as previously found for the thermal battery igniter. No bridgewire corrosion was observed. Similar units subjected to the same thermal cycle but without the humidity environment were found not to be corroded.



Electrode Pin

Electrode Pin



Electrode Pin

Bridgewire

Fig. 9. SEM of electrode pins and bridgewire from piston motors exposed to humidity cycle.

Additional lots of early piston motors when subjected to the same humidity cycle but removed at different times showed similar corrosion to have taken place at all time intervals. The degree of corrosion present increased with the number of cycles. Again no corrosion was observed on units which were thermally cycled only. Examination of the Ti/$KClO_4$ powder interface did not reveal any morphological alteration of the $KClO_4$, again indicating that the pyrotechnic was not playing a primary role in the corrosion mechanism.

Corroded and uncorroded units were sectioned through the pins and weld area to determine the depth of the corrosion and also to determine the mechanism of the bridgewire/pin separation. Figure 10 shows examples of these sectioned units. The corrosion was over 100 µm deep, and sharp cracking of the Kovar pin was observed proceeding around the weld effected area. Energy dispersive x-ray analysis ($Z \geq 11$) revealed the presence of chlorine in the surface corrosion product and also in the corrosion product within the cracks, even at the crack tip. Eventually this cracking coalesced and resulted in separation of the weld area from the pin. No surface corrosion or cracking was observed on those units previously identified as uncorroded.

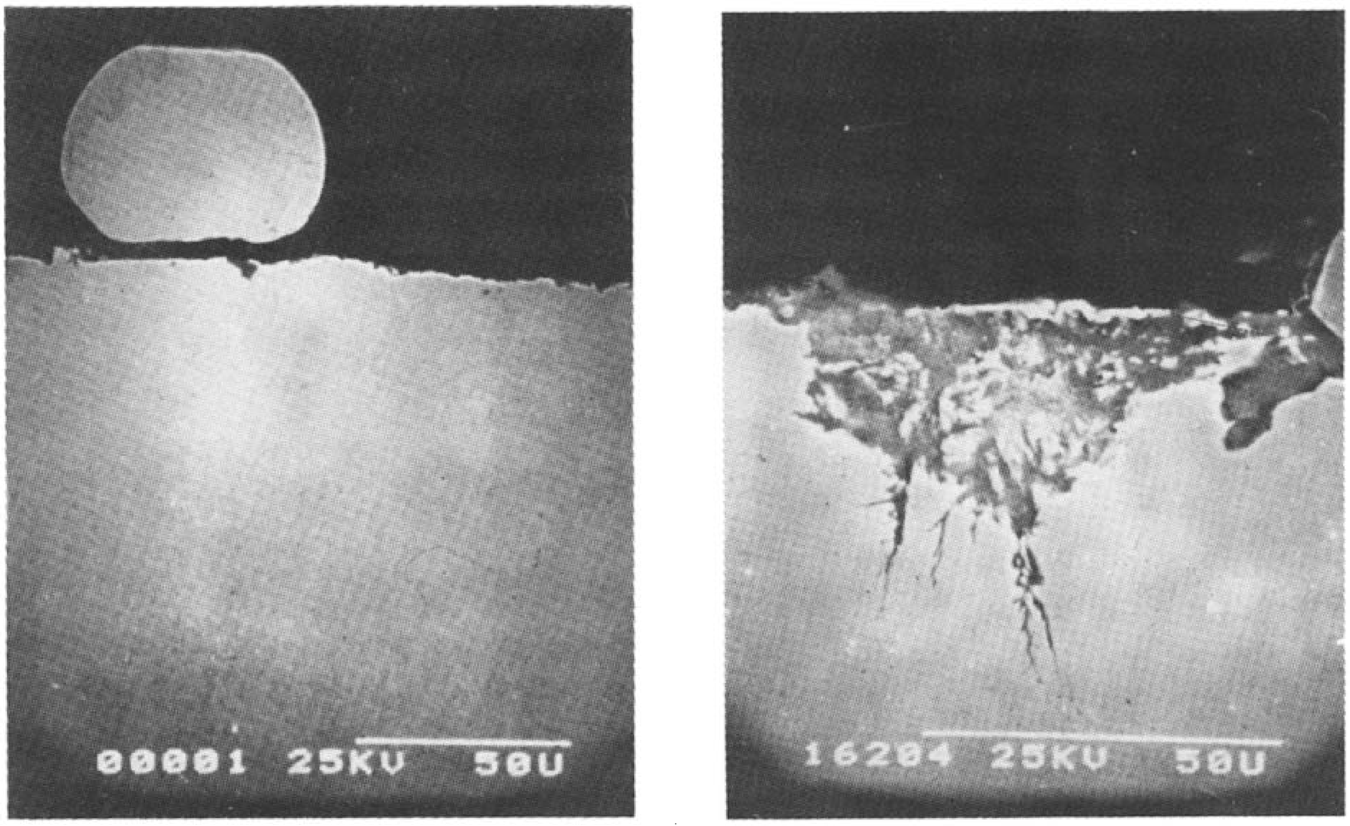
DISCUSSION OF RESULTS

Neither the igniter nor the piston motor was hermetically sealed, which means that they were inherently permeable to atmospheric gases, most notably water vapor. A silicone elastomer adhesive sealed the output end of the igniter, whereas, a silicone "O" ring and a silicone elastomer sealed the output and connector ends, respectively, of the piston motor. Silicone based polymers have exhibited high permeation rates to atmospheric gases and water vapor (ref. 8). Typical values for some of these materials are listed in Table 2 (refs. 9-11).

Table 2
Permeabilities of some organic materials

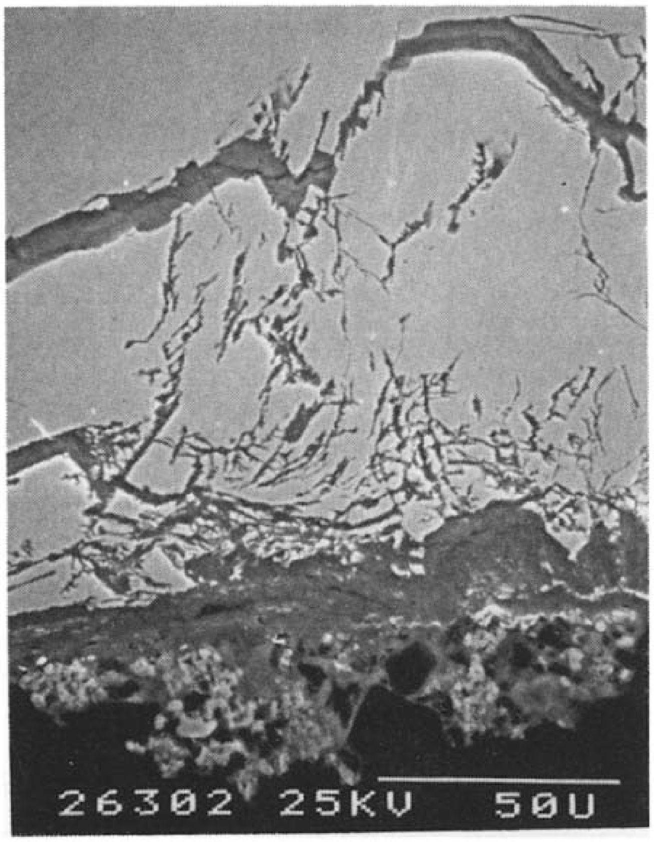
RTV Silicones	2.7 to $7.2 \times 10^{-7*}$
Epoxy	1.5×10^{-7}
Teflon	8.4×10^{-11}
Polysulfide (Thiokol)	4.9×10^{-8}
Kel-F/Teflon	3.6×10^{-10}

$^{*}cm^{3}(STP)s^{-1}cm^{-1}torr^{-1}$



Thermal Cycle - No stress corrosion cracking

Humidity Cycle - Showing Chloride assisted stress corrosion cracking



Humidity Cycle

Fig. 10. SEM of cross-sectioned header pins from piston motor (thermal and humidity cycled).

Calculations by Perkins (ref. 8) using the component dimension and permeability data have shown that near equilibrium conditions between the external and internal environments can be achieved in short periods of time, usually less than eight hours.

Placing these devices with their silicone seals in humidity tests was in many ways analogous to the experiment where a 0.0125 cm hole was drilled in the closure disks of the valve actuator. The extent of corrosion was similar.

The variation of the corrosion observed between lots of the igniters was really a function of their storage environments prior to the next assembly rather than any inherent difference between the lots. After manufacture the igniters were placed in nondesiccated bags, packaged and shipped to the thermal battery manufacturer. There they were unpacked and stored undesiccated in open atmospheres that had the potential for the presence of high humidity. Once installed in the thermal battery assembly, the high humidity environment was eliminated as a result of the highly desiccated nature of this assembly. If corrosion had started, it then ceased due to elimination of the moisture environment in this next assembly. The variation in corrosion depended upon storage time between manufacture and next assembly and the ambient humidity conditions during that time.

The piston motor which shows significant corrosion in all lots subjected to the severe humidity/temperature cycle was not originally hermetically sealed in the next assembly. As a result, the device was constantly exposed to humidity which permeated the silicone seal and affected the internal environment. The corrosion in these units, therefore, continued to increase with time. The separation of the bridgewire weld was the result of stress corrosion cracking of the Kovar. Weirick (ref. 12) has previously shown the susceptibility of this alloy to chloride assisted stress corrosion cracking in a humid environment. The above was similar. The source of the stress could be the residual stresses in the Kovar pins as a result of the welding process as evidenced by the fact that the cracking proceeds around the weld affected area. The source of the chlorine was surface contamination not cleaned from the units which has been observed on unloaded units. It was not from a reaction of the $KClO_4$.

A design change was necessary to eliminate the corrosion and stress corrosion cracking problems in the piston motor. A hermetically sealed version was designed and built for application with a humidity requirement. In units where the leak rate was less than 10^{-8} atm cc/sec, either no corrosion or minimal corrosion was observed when subjected to the humid environment. Significant to extensive corrosion was present in those units that had leak rates in excess of 10^{-8} atm cc/sec.

Hermetically sealing the igniter was not possible due to design requirements. A simple change in the packaging, shipping, and storage procedures was implemented such that the units were constantly under desiccation before assembly into the dry thermal battery unit. As a precaution, the same was implemented for the piston motors. Examination of units stored in this manner has shown no corrosion.

CONCLUSION

1. The source of the corrosion in both the igniter and piston motor was chlorine containing contamination combined with a high moisture environment.
2. The pyrotechnic $Ti/KClO_4$ was not involved in the corrosion problem of the igniter or piston motor.
3. In the absence of a high moisture environment corrosion was minimal or absent.
4. The corrosion was virtually eliminated from the igniters by implementing desiccated packing, shipping, and storage procedures
5. The piston motor was redesigned to provide a hermetic seal which has been found to eliminate the corrosion problem.

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