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CORROSION RESISTANCE OF VARIOUS CERAMICS AND CERMETS TO LIQUID METALS

W. H. Cook

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

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METALLURGY DIVISION

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ABSTRACT

The procedures used for the corrosion screening testing of ceramics and cermets in liquid lithium, sodium, and lead are discussed briefly. The results of such tests on various ceramics and cermets exposed for 100 hr to the liquid metals at 1500°F are given. These include various borides, carbides, nitrides, oxides, and silicides for the ceramics. The major part of the cermet screening corrosion tests reported are on tungsten carbide- and titanium carbide-base cermets. Some present and future uses for corrosion resistant ceramics and cermets are outlined.

INTRODUCTION

The primary purpose of this report is to present the corrosion trends of various ceramics and cermets in liquid lithium, sodium, and lead. These data are taken from exploratory or screening corrosion tests.[1] The secondary purpose is to describe briefly the equipment and methods used in this type of corrosion testing.

There are numerous applications in which ceramics or cermets are useful in liquid-metal systems. There are applications in which corrosion resistant, refractory ceramic electrical insulators are required.[2,3] As the temperatures have increased in actual and designed systems using liquid-metal heat-transfer media, current refractory metals and alloys have proven partially or wholly inadequate for some applications. These materials have a tendency to solid-phase bond or gall when used for high-temperature valves or bearings. The normally inert and refractory nature of the ceramics and cermets have made them attractive as materials

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[1] Most of these tests were made in the 1954–1955 period on samples that were readily available.

[2] C. B. Jackson (ed.), Liquid-Metal Handbook, Sodium-NaK Supplement, p. 345, Washington, D. C.: Department of the Navy (July 1, 1955).

[3] L. R. McCreight, "Ceramics for Nuclear Power Applications," Industrial Engineering Chemistry 46, 187 (Jan., 1954).

to resist such actions. For such applications as valves and bearings, cermets are favored over the ceramics because they are less brittle.

To find ceramics and cermets to meet the requirements of liquid-metal systems, the usual approach, used here and elsewhere, was to turn to the current stocks of the ceramic and metallurgical industries. Previous corrosion tests[4] in alkali liquid metals have demonstrated that the common ceramics, glasses or glass-bonded ceramics, would not meet the requirements. Taking advantage of this previous work, very pure, crystalline, commercial refractory ceramics and cermets were sought for these liquid-metal corrosion tests.

PROCEDURE

Specimens

If possible, a sample was always divided into two parts for each test to provide control and test specimens. The usual nominal dimensions of the test specimen were 1/4 x 1/4 x 1/2 in.

Tests and Equipment

The screening corrosion tests of the ceramics and cermets were direct adaptations of some of the methods and equipment developed for corrosion testing metals for similar purposes.[5]

The ideal test would consist of two components, the specimen and test medium. However, exposing the refractory and relatively brittle ceramics and cermets to the liquid metals involved too many complex fabrication problems to make two-component systems practical in these exploratory tests. Three-component tests were used as necessary concessions to these problems. In these tests the third component, the container, was Inconel (nominal composition 77% Ni–15% Cr–7% Fe) for the liquid sodium and ingot iron (99.50% Fe) for the liquid lithium or lead tests. Since these container materials had shown relative inertness to these

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[4] R. C. Lyon (ed.), Liquid-Metals Handbook, 2d ed., pp. 152, 156, 157, NAVEXOS P-733 (Rev.), Washington, D. C.: Department of the Navy (June, 1952).

[5] D. C. Vreeland, E. E. Hoffman, and W. D. Manly, "Corrosion Tests for Liquid Metals, Fused Salts at High Temperatures," Nucleonics **11**(11), 36–39 (November, 1953).

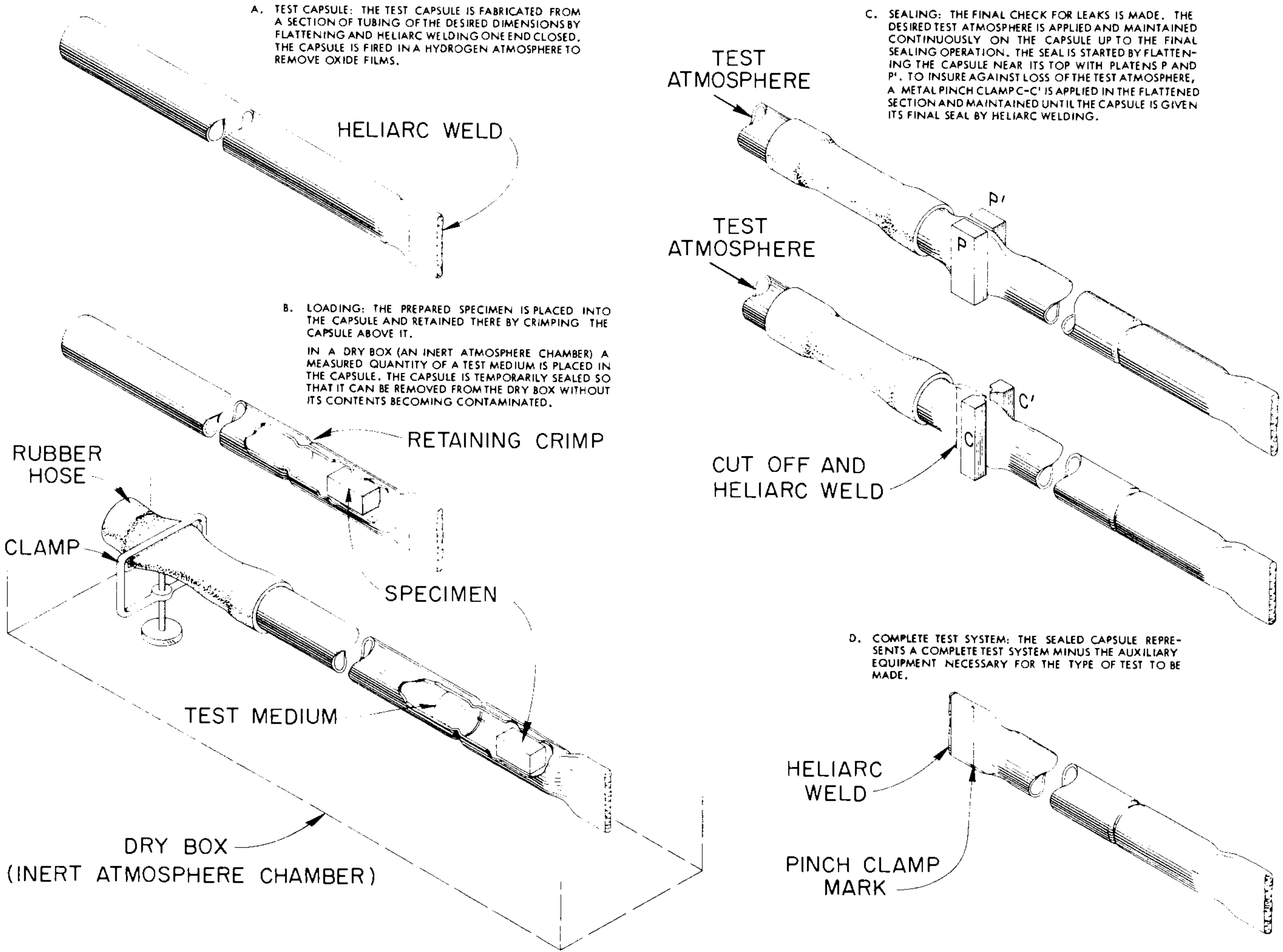
media, the desirable two-component test conditions were approached. Figure 1 outlines the standard corrosion test assembly procedure for such a test. The end in which the specimen was confined (Fig. 1b) will, for orientation purposes, always be referred to as the bottom of the test capsule

The test medium was loaded into the capsule in a dry box (inert-atmosphere chamber) to keep its contaminants at a minimum. The medium was added in its solid form as a carefully weighed quantity. This quantity was determined as that necessary to fill 35% of the volume of the capsule (1/2 in. o.d. x 0.035 in. thick wall x 10 in. long) at test temperature. The atmosphere for these tests was normally a vacuum of 1.0×10^{-4} mm Hg (at room temperature); occasionally, a pure inert gas (helium or argon) was used.

The tests were classified as static or dynamic. In the static test there was no movement of the medium and specimen relative to each other. In this test, the capsule as shown in Fig. 1d was placed into a furnace and held isothermally at 1500°F for 100 hr. Usually, in these tests, the capsules were sealed in a protective container of stainless steel.

The dynamic test used was a simple one in which the test capsule was placed in a seesaw (tilting) furnace as shown in Fig. 2a. Temperature control of the furnace was based on the temperature indications of thermocouple, TC_F, in the hot zone. To measure test-temperature conditions, thermocouples were spot welded to the test containers; so, the temperatures recorded were those of the outer container wall rather than the liquid metal. Unless otherwise stated these walls were 0.035 in. thick. The movements of the seesaw furnace, the liquid metal, and test specimen are shown in Fig. 2a and the temperatures corresponding to these movements are shown in Fig. 2b. The hot- and cold-zone temperatures were 1500 and 1150°F, respectively.

A six-furnace seesaw unit is shown in Fig. 3a. The unit was operated at one cycle per minute with a maximum angle of tilt of 45 deg with the horizontal. The thermocouple leads from the hot and cold zones were connected to a switching box through the thermocouple panel. The hot or cold zone of each test capsule could be monitored by means of the switching box and a continuous recorder (Fig. 3b). In all other ways each seesaw furnace was independent of the others. Each furnace was physically separate and had its own power supply and temperature controller.



A. TEST CAPSULE: THE TEST CAPSULE IS FABRICATED FROM A SECTION OF TUBING OF THE DESIRED DIMENSIONS BY FLATTENING AND HELIARC WELDING ONE END CLOSED. THE CAPSULE IS FIRED IN A HYDROGEN ATMOSPHERE TO REMOVE OXIDE FILMS.

B. LOADING: THE PREPARED SPECIMEN IS PLACED INTO THE CAPSULE AND RETAINED THERE BY CRIMPING THE CAPSULE ABOVE IT.

IN A DRY BOX (AN INERT ATMOSPHERE CHAMBER) A MEASURED QUANTITY OF A TEST MEDIUM IS PLACED IN THE CAPSULE. THE CAPSULE IS TEMPORARILY SEALED SO THAT IT CAN BE REMOVED FROM THE DRY BOX WITHOUT ITS CONTENTS BECOMING CONTAMINATED.

C. SEALING: THE FINAL CHECK FOR LEAKS IS MADE. THE DESIRED TEST ATMOSPHERE IS APPLIED AND MAINTAINED CONTINUOUSLY ON THE CAPSULE UP TO THE FINAL SEALING OPERATION. THE SEAL IS STARTED BY FLATTENING THE CAPSULE NEAR ITS TOP WITH PLATENS P AND P'. TO INSURE AGAINST LOSS OF THE TEST ATMOSPHERE, A METAL PINCH CLAMP C-C' IS APPLIED IN THE FLATTENED SECTION AND MAINTAINED UNTIL THE CAPSULE IS GIVEN ITS FINAL SEAL BY HELIARC WELDING.

D. COMPLETE TEST SYSTEM: THE SEALED CAPSULE REPRESENTS A COMPLETE TEST SYSTEM MINUS THE AUXILIARY EQUIPMENT NECESSARY FOR THE TYPE OF TEST TO BE MADE.

NOTE: IF IT IS NECESSARY STEPS B,C,AND D CAN BE PERFORMED IN THE DRY BOX; FOR EXAMPLE, THE WELDING OF Ti, Zr, Mo, ETC.

Fig. 1. Standard Corrosion Test Assembly Procedure.

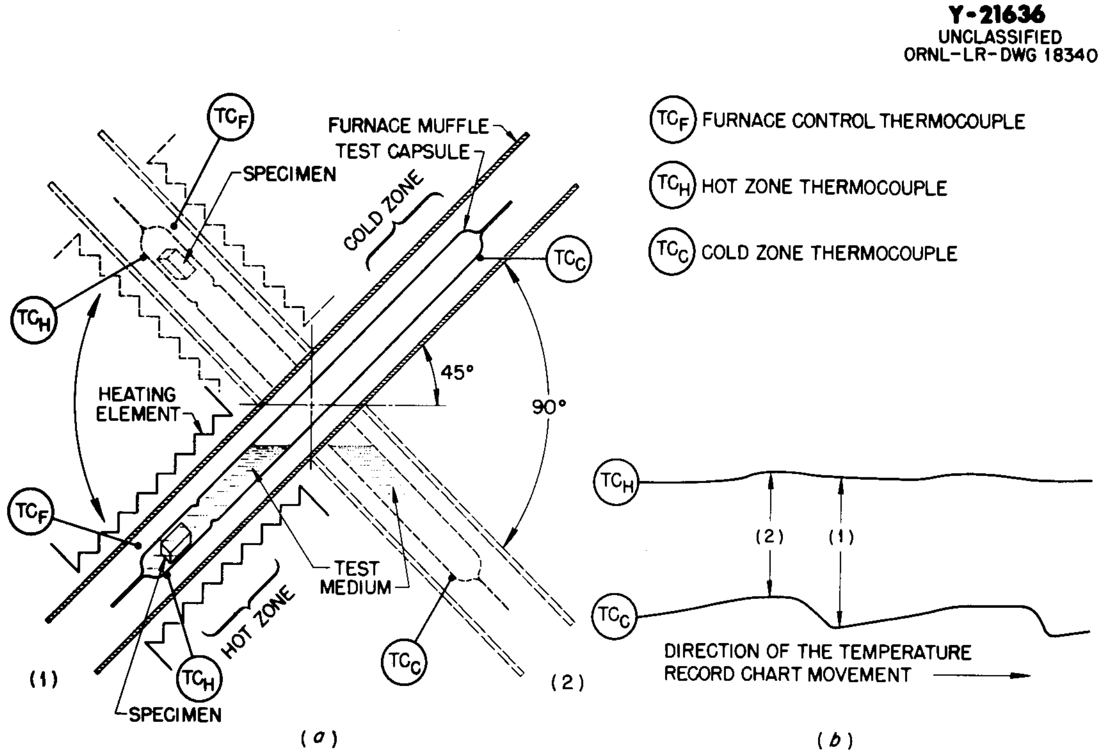


Fig. 2. A Simplified Schematic of a Seesaw Furnace Test; (a-1) the Start of a Cycle, (a-2) Half-Way Through a Cycle, and (b) a Simultaneous Thermocouple Temperature Record from the Hot and Cold Zones with Positions 1 and 2 of (a) Indicated.

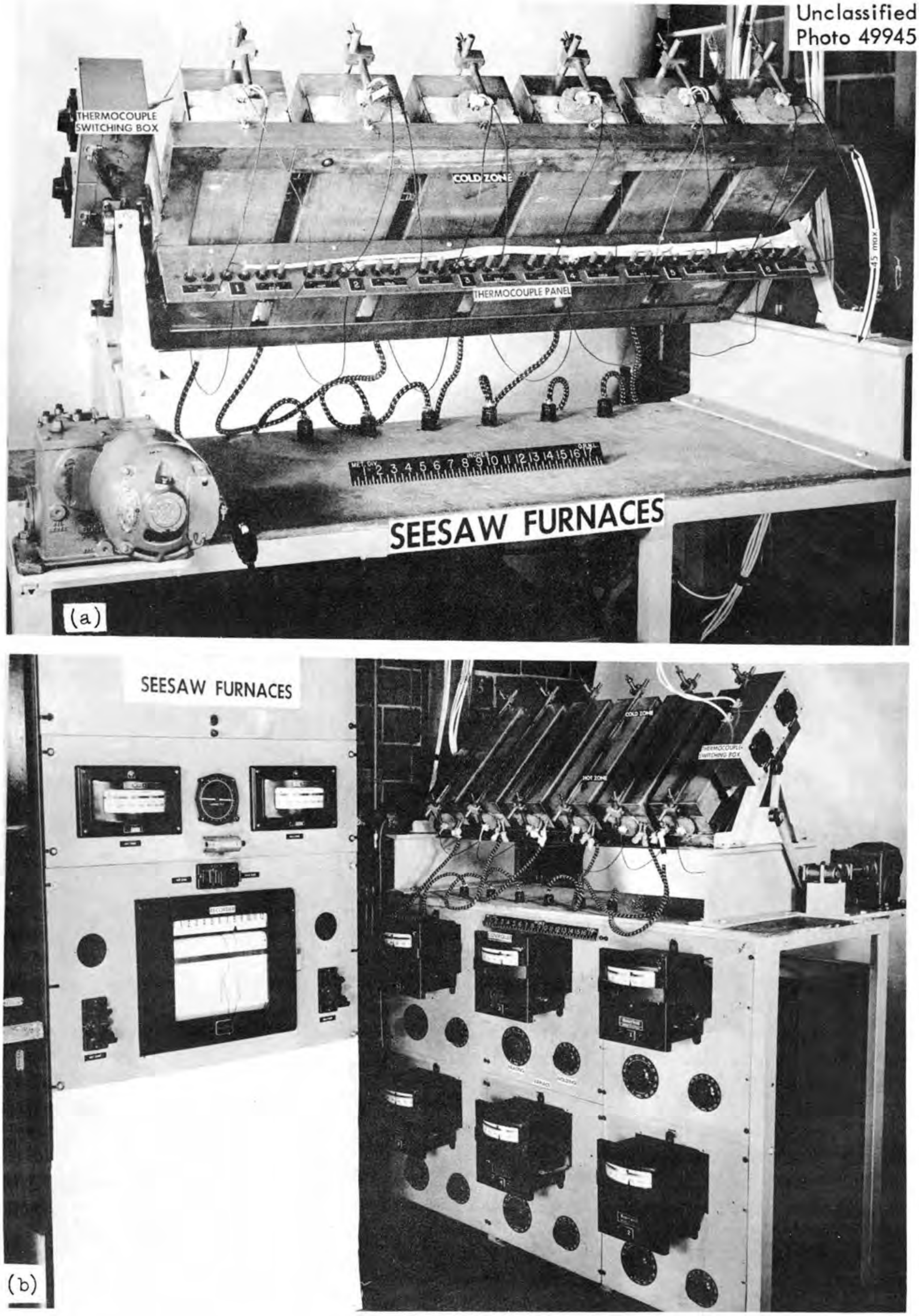


Fig. 3. Seesaw Furnaces, Test Equipment for Simple, Dynamic Liquid Metal Corrosion Tests.

Stripping a Test

At the conclusion of a test, static or dynamic, the test capsule at test temperature was withdrawn from the furnace and placed in a vertical position with its top end downward. This permitted all or almost all of the test medium to drain from the tested specimen which was retained in the bottom of the capsule by the retaining crimp. The sample of the test medium to be used for chemical analysis was taken in the dry box to avoid contaminating it.

Any residual medium on or in a tested specimen was completely removed if this was possible. In some instances, residual medium could not be completely removed because of its location in or reaction with the specimen. Lithium was removed by reacting it with distilled water. Sodium was removed by reacting it initially with ethyl alcohol and finally with distilled water. In a few instances, sodium was removed by vacuum distillation to prevent reaction of the specimens with sodium hydroxide or water. Lead did not usually wet or cling to the test specimens. If there were any residual lead on or in a specimen, the corrosion evaluation was made, exclusive of weight change data, without removing the lead.

Examinations

The extent and nature of the corrosion of the tested specimens were determined with two to five kinds of examinations. In the order of increasing importance, they were:

1. Weight changes
2. Dimensional changes
3. X ray analyses
4. Chemical analyses
5. Metallographic examinations.

The relative importance of each examination could be altered by the nature of the test specimens or experimental conditions. For example, weight change data for porous materials were frequently unsuitable for corrosion evaluations because they were modified by reaction products or traces of the test medium entrapped in the pores. However, weight change data on nonporous, single-crystal specimens were normally useful in the corrosion evaluations of these materials.

X ray analyses had a limited usefulness in identifying phases; first, the phases had to be present in sufficiently large quantities to be detected and second, the x ray diffraction data of the compounds of the corrosion products had to be in standard reference sources to be readily identified.

The test media were chemically analyzed if preferential corrosion were indicated. Occasionally, the test materials were chemically analyzed if there were doubts about their true compositions.

The metallographic examination was almost always the most important phase of the over-all evaluation. The standard procedure was to examine both untested and tested specimens of a material to determine the nature and extent of corrosion to within 0.001 in. This justified the somewhat difficult and time consuming operations of polishing ceramics and cermets. Most of the ceramics and cermets were nickel plated prior to the polishing. The nickel plate helped preserve the edges of the specimens during the polishing so that the metallographic evaluation of the nature and extent of the corrosion could be more accurate.

Electrically nonconducting ceramics were nickel plated by conventional techniques after placing a thin (less than 0.0005 in.) graphite film on their surfaces. The film was put on the specimens by (1) dipping the specimens in a suspension of fine particle size graphite in a thin, volatile organic cement and (2) drying the dipped specimens in an oven.

Photomicrographs of the specimens, aside from providing a permanent record, furnished a convenient and a very necessary reference by which one could determine if materials with the same chemical compositions were the same structurally.

RESULTS AND DISCUSSIONS

The microscopic structure was considered as important a property of the untested specimens as were the density, porosity, or chemical composition. Also, as previously indicated, the microscopic structure of the tested specimens was one of the major factors in determining the extent and nature of corrosion. For this reason, a few photomicrographs of some typical untested and tested specimens will be included with the discussions of the corrosion results.

Ceramics

Most of the structures of the ceramic specimens reported are given by Figs. 4–9.

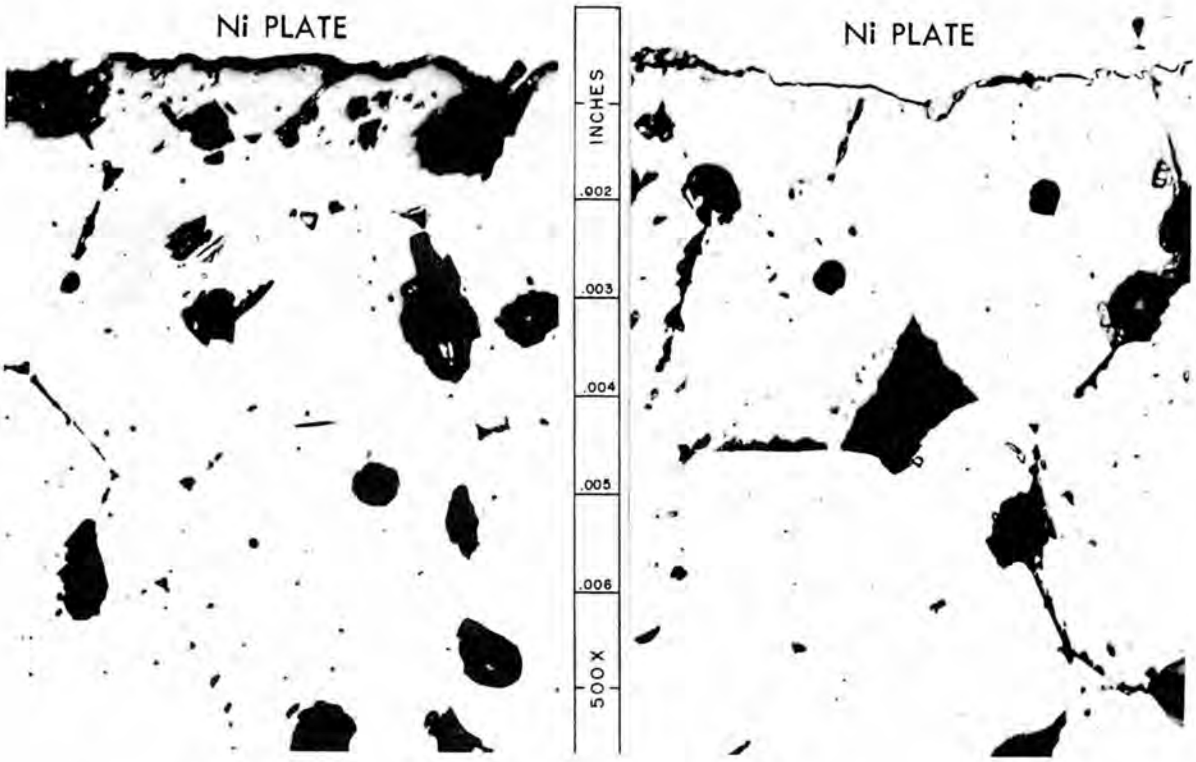


Fig. 4. (a) Y-14531 (b) Y-14532
Titanium Carbide, TiC. 4.81 gm/cc (97.4% theoretical density) (a) untested and (b) after a 100-hr exposure to static lithium at 1500°F in an ingot iron (99.50% Fe) container. Unetched. 500X.

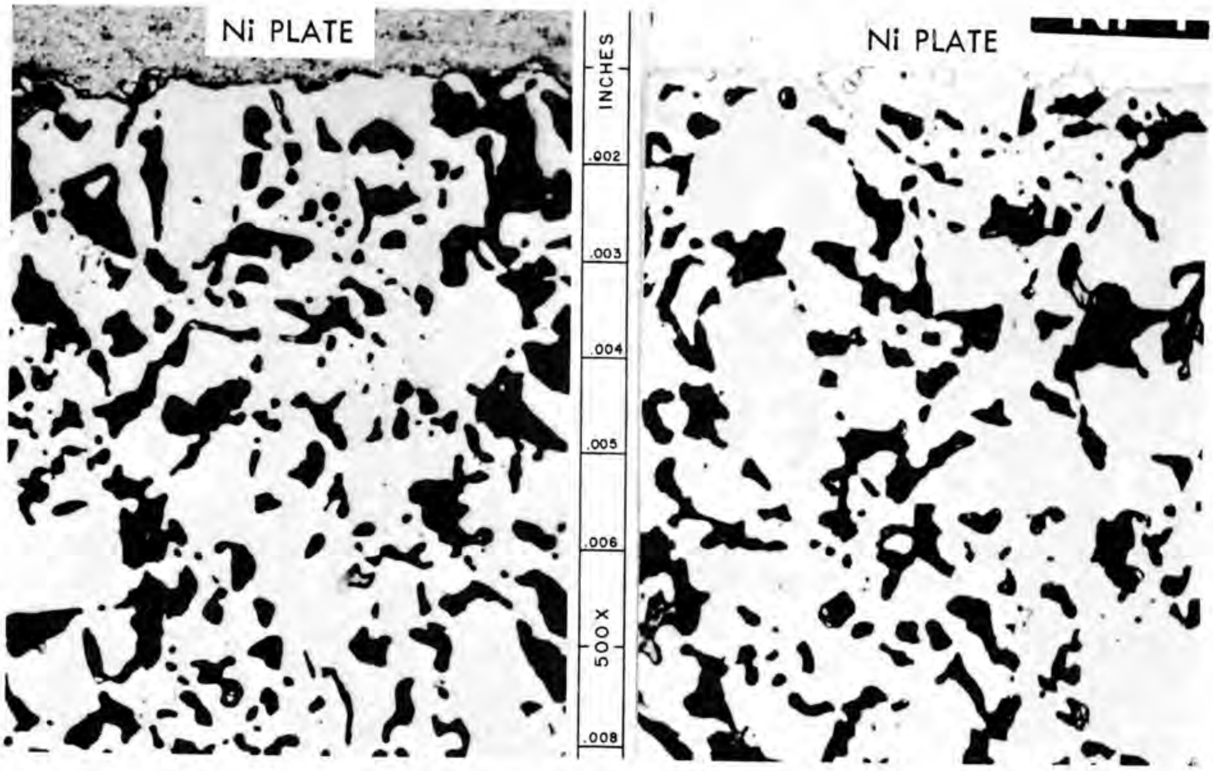


Fig. 5. (a) Y-16793 (b) Y-12962
Zirconium Carbide, ZrC. 6.91 gm/cc (103% of accepted theoretical density) (a) untested and (b) after a 100-hr exposure to static sodium at 1500°F in an Inconel container. Unetched. 500X.

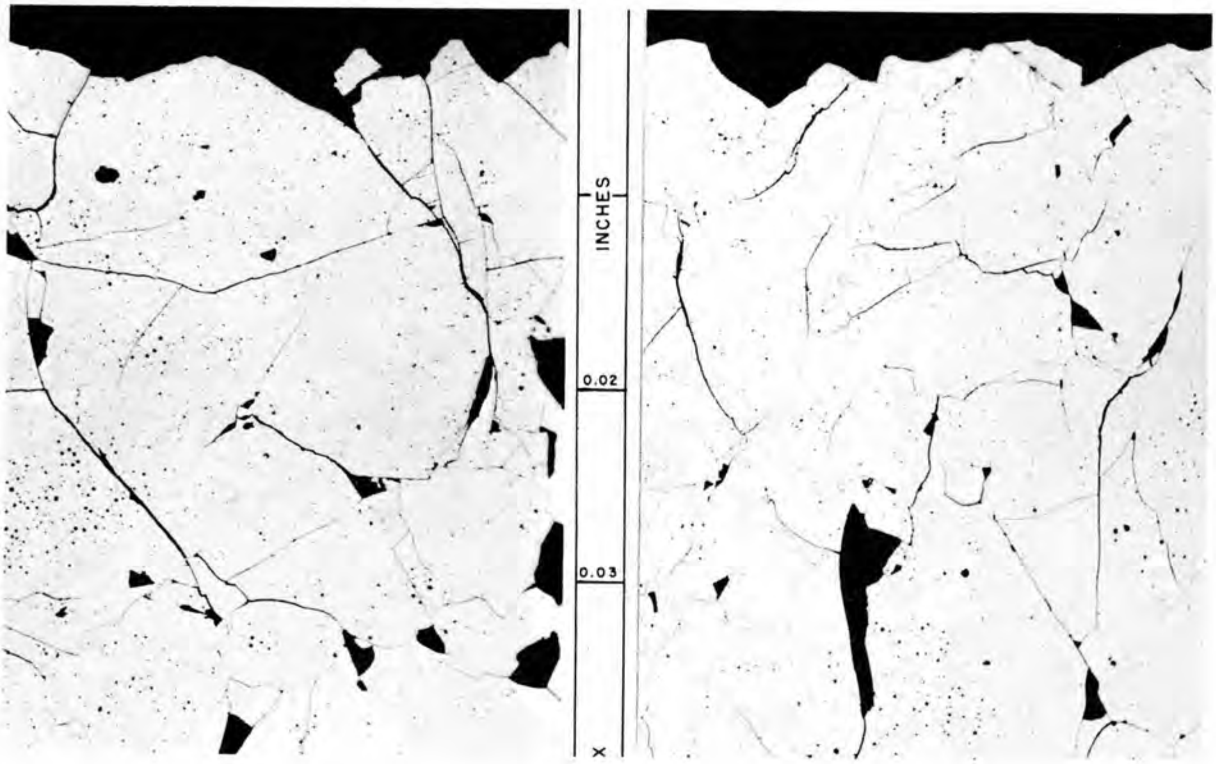


Fig. 6. (a) Y-13024 (b) Y-13025
Chromium Carbide, Cr_3C_2. 6.59 gm/cc (98.7% theoretical density) (a) untested and (b) after a 100-hr exposure to static sodium at 1500°F in an Inconel container. Unetched. 100X.

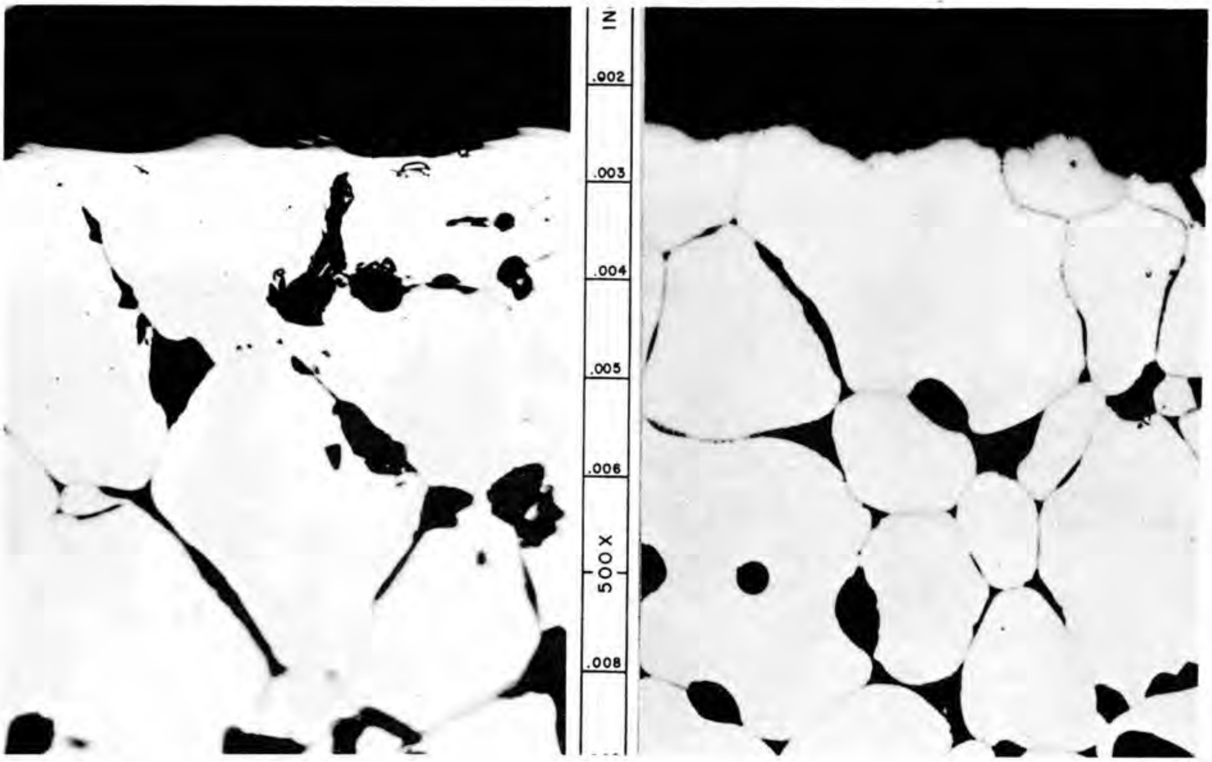


Fig. 7. (a) Y-15446 (b) Y-15592
Titanium Nitride, TiN. (a) Untested and (b) after a 100-hr exposure to static lead at 1500°F in an ingot iron (99.50% Fe) container. Unetched. 500X.

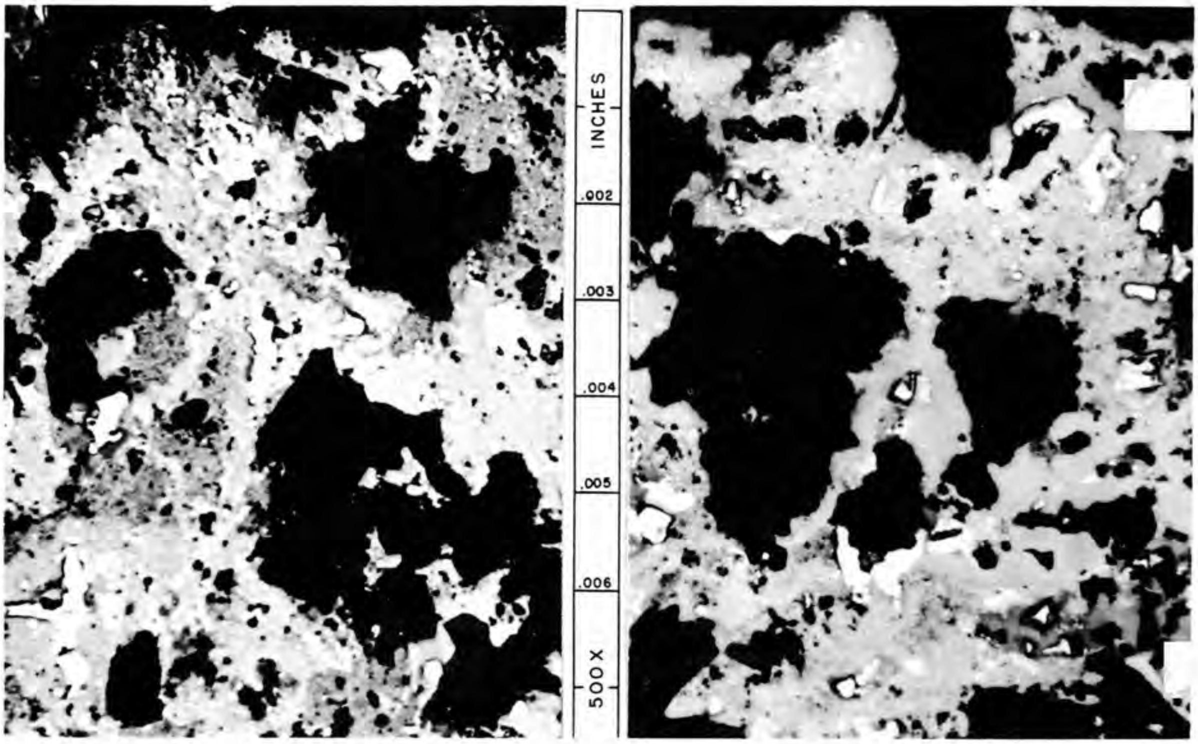
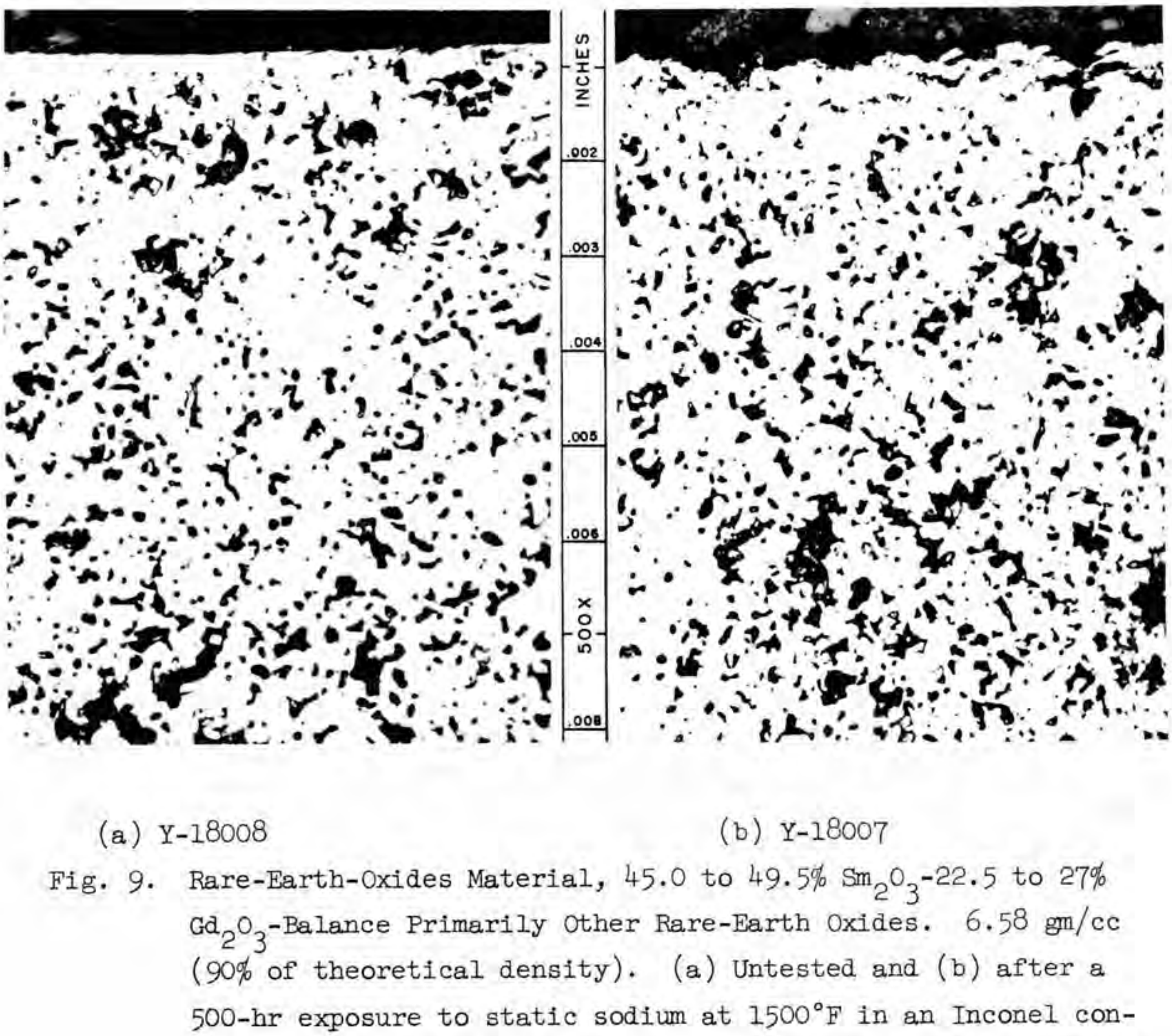


Fig. 8. (a) Y-15593 (b) Y-16803
Silicon Nitride, Si_3N_4. 2.33 gm/cc (68% of theoretical density) (a) untested and (b) after a 100-hr exposure to static lead at 1500°F in an ingot iron (99.50% Fe) container. Unetched. 500X.



(a) Y-18008 (b) Y-18007

Fig. 9. Rare-Earth-Oxides Material, 45.0 to 49.5% Sm_2O_3-22.5 to 27% Gd_2O_3-Balance Primarily Other Rare-Earth Oxides. 6.58 gm/cc (90% of theoretical density). (a) Untested and (b) after a 500-hr exposure to static sodium at 1500°F in an Inconel container. Attack was not uniform. Area shown in (b) is typical of most heavily attacked areas. Unetched. 500X.

The appearance of the TiC before and after exposure to lithium is shown in Fig. 4. No attack by lithium was evident. This was a well-bonded specimen with the grain boundaries still visible in the bonding zones. The trend was for the grains to be large and approximately the same size; there were few small grains. In this and other ceramics that were not single crystals, there was porosity even though the densities of the specimens approached theoretical values. It was noted that for these refractory ceramics the apparent porosities measured by liquid absorption indicated that there were virtually no sealed-pore spaces.

Figure 5 of the ZrC shows that its structure was strongly bonded and it was unaltered by its exposure to molten sodium. It was apparently fabricated from large and small grains of ZrC. In contrast with the TiC the bonding zones appear continuous.

The Cr_3C_2, large grained and brittle, had the typical appearance shown in Fig. 6. No attack by sodium was evident.

The TiN shown in Fig. 7 appears to be poorly bonded. The grain boundaries were clearly visible and the bonding between grains tended to be discontinuous. This was good enough to withstand attack during the exposure to lead but it is believed that the poor bonding zones probably aggravated the lithium or sodium attack on other specimens from this sample of TiN.

The Si_3N_4 in contrast with the TiN was a fine-grained, porous material as shown in Fig. 8. The lead did not penetrate or attack the Si_3N_4.

The photomicrographs of the rare-earth-oxides material are shown in Fig. 9. These are not necessarily typical structures for all sintered oxides but they were included to show that the structure was not altered even though the specimen had a relatively long exposure to molten sodium.

With this brief background of the structures of the ceramics tested, the summary of the corrosion results of all the ceramics tested in static liquid lithium, sodium, and lead are given in Fig. 10. Metallographic examinations, chemical analyses, weight change data, and dimensional changes were used as bases for these graphical representations of corrosion resistance. X ray data were not included because such data were not routinely sought on all materials. The arbitrary limits selected for each of the four examinations used in rating the various materials are given in the inset in Fig. 10. This does not mean that each bar graph was always based on all four examinations. Each was based on as many of these as were available. Most of the data were from single tests.

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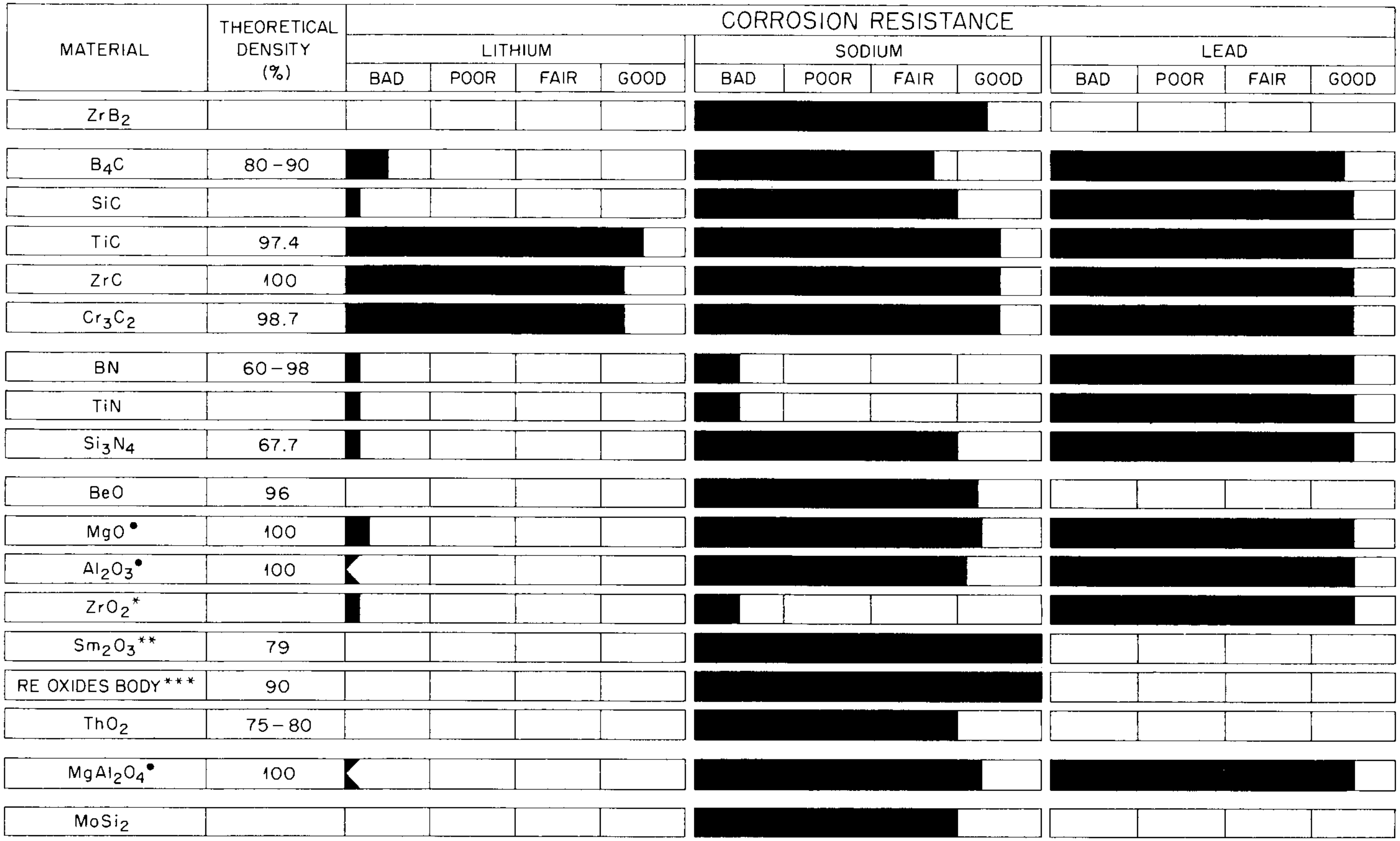

SIGNIFICANCE OF SHORTEST BARS: ▮ PIECES OF THE TESTED SPECIMEN REMAINED.

◣ THERE WAS NO VISIBLE TRACE OF THE TESTED SPECIMEN.

● A SPECIMEN FROM A SINGLE CRYSTAL.

* CaO-STABILIZED.

** A 1000-hr TEST.

*** A 500-hr TEST. (BODY COMPOSITION: 45.0 TO 49.5% Sm_2O_3 - 22.5 TO 27% Gd_2O_3 - BALANCE PRIMARILY OTHER RARE-EARTH OXIDES.)

TYPE OF DATA	ARBITRARY CORROSION RATINGS AND DATA RANGE BASES			
	BAD	POOR	FAIR	GOOD
DEPTH OF ATTACK, mils*	3	2	1	0
WEIGHT CHANGE (%)**	6	4	2	0
DIMENSIONAL CHANGE (%)	3	2	1	0

* MEASURED IN METALLOGRAPHIC EXAMINATIONS.

** DETERMINED BY DIRECT MEASUREMENT AND/OR BY CALCULATIONS BASED ON THE MATERIAL(S) FOUND IN THE TEST MEDIUM BY CHEMICAL ANALYSES.

Fig. 10. Corrosion Resistance of Various Ceramics in Static Li, Na, and Pb Media for 100 hr at 1500°F.

Of the materials tested in lithium, carbides of titanium, zirconium, and chromium were the only materials to have a high resistance to corrosion to this medium.

The severe attack by the lithium on the nitrides, BN, TiN, and Si_3N_4, produced pieces from each test with phases that did not correspond to any ASTM indexed powder x ray diffraction patterns.

Among the specimens from single crystals, MgO (periclase), Al_2O_3 (sapphire), and $MgAl_2O_4$ (spinel), tested in static lithium; MgO was the most resistant to attack. However, although the resistance to attack exhibited by the MgO was low, each of two specimens from separate tests lost 1.0 gm/in.^{2}. These specimens were cleaved from single crystals. One was exposed to lithium in an iron container and the other to lithium in a molybdenum container. In each test the surface area of the specimen to the volume of the lithium at 1500°F was 0.6 in.^{2}/in.^{3}.

A heavy attack of the MgO in the standard test in the iron container was concentrated where the MgO specimen touched the container wall. This lack of uniform attack plus a report that "molten lithium penetrates magnesia but does not attack it"[6] leads one to suspect that the iron container was not inert in this particular test. Therefore, the second test was made in a molybdenum container. At the test temperature of 1500°F, the molybdenum should have been inert to lithium and there should not have been any reactions between the MgO and the molybdenum. The duplication of the losses (1.0 gm/in.^{2}) of the MgO specimens indicated that the results from both tests were reliable and that MgO is attacked by lithium at 1500°F.

The low rating given to the corrosion resistance of the ZrO_2 in sodium was due to an 8.6% dimensional increase as determined by micrometer measurements rather than any material loss.

Samaria (Sm_2O_3) and the rare-earth-oxides material were given the highest corrosion resistance ratings to sodium in Fig. 10 because each had weight losses, based on the corrosion products found in the sodium, of less than 35 ppm. These ratings appeared justifiable since the samaria and the rare-earth-oxides material had been tested for 1000- and 500-hr periods, respectively. No structural changes were detected by x ray analyses and reflected-light microscopy.

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[6] R. C. Lyon (ed.), Liquid-Metals Handbook, 2d ed., p. 161, NAVEXOS P-733 (Rev.), Washington, D. C.: Department of the Navy (June, 1952).

As shown in Fig. 10, none of the ceramics were attacked in 100-hr exposures to static lead at 1500°F.

Cermets

The cermets, the ceramic-metal combinations, usually contain from a few to approximately 50 wt % of pure metals or alloys. The cermets that were tested in the liquid metals contained 6–30 wt % of metal and had carbides for the balance, the ceramic component.

The structure and results on two types of SiC–Si exposed to liquid sodium for 100 hr at 1500°F are shown in Fig. 11. The results of these exposures were the same, essentially all the silicon was removed and silicon was found on the walls of the test containers. This is consistent with previous results from similar tests on pure silicon and silicon-containing alloys. Even though dissimilar-metal transfer[7] was probably a factor, these data on the rapid and complete removal of silicon appear to disagree with other reports[8,9] which indicate that sodium does not react with silicon.

Among the most common of the commercial cermets are the titanium carbide- and tungsten carbide-base cermets. The typical structure and attack by sodium on a titanium carbide–nickel cermet is shown in Fig. 12. The slight attack appeared to be predominately on the nickel and to some slight extent on the TiC particles. The typical structure and absence of attack by lead on a tungsten carbide–cobalt cermet is shown in Fig. 13.

The corrosion resistance of cermets of SiC–Si, TiC–Ni, WC–Co, and Cr_3C_2–Ni to liquid sodium and lead are graphically summarized in Fig. 14. The arbitrary corrosion rating system used, as shown in the inset in Fig. 14, is the same as that used for the ceramic corrosion results presented in Fig. 10.

All four of the TiC–Ni cermets were attacked by sodium to a depth of approximately 0.0005 in. in a manner similar to that shown in Fig. 12. Other specimens of the same composition were not attacked by sodium in the same kind of tests. None of the WC–Co cermets were attacked by sodium.

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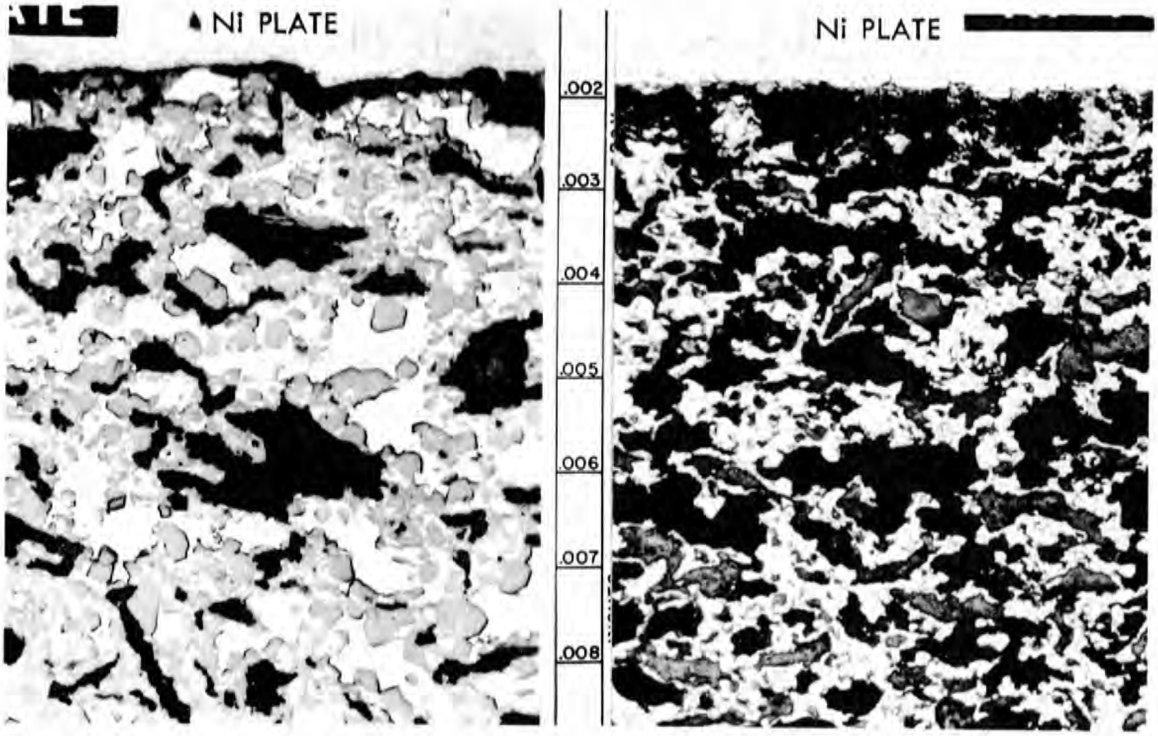
[7] W. D. Manly, "Fundamentals of Liquid Metal Corrosion," Corrosion 12 (July, 1956).

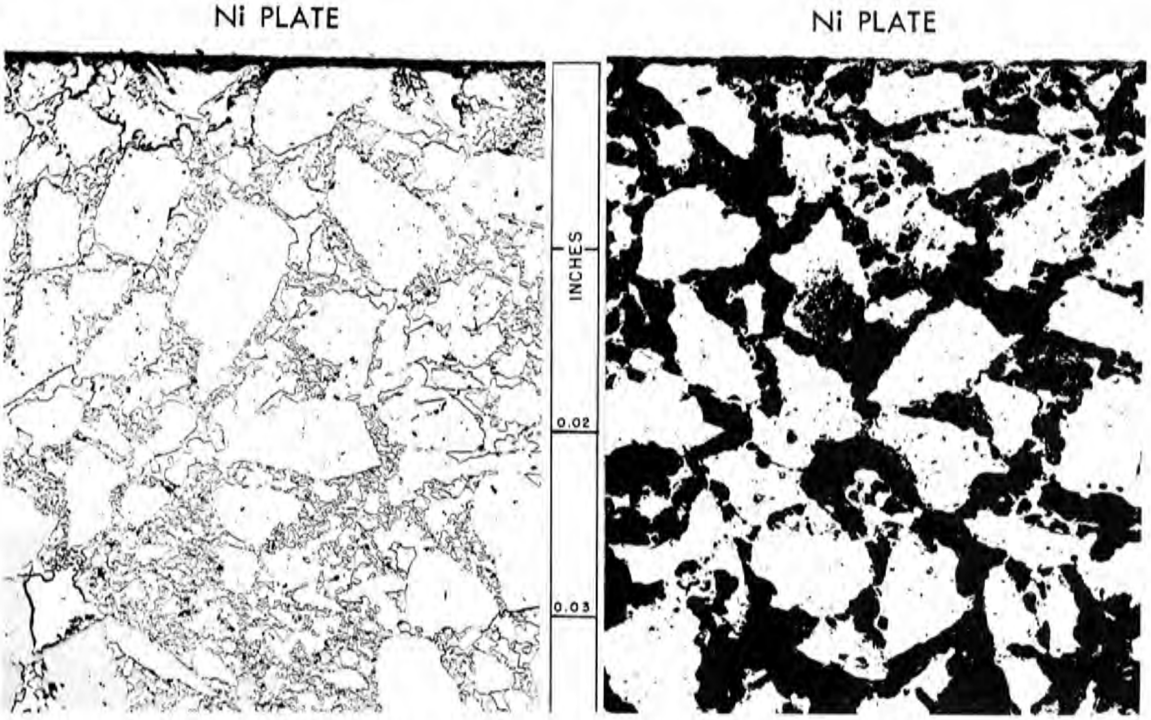
[8] M. Sittig, Sodium: Its Manufacture, Properties and Uses, pp. 53, 243, Reinhold Publishing Corporation, New York, 1956.

[9] H. Osborg, Lithium, p. 21, The Electrochemical Society, Inc., New York, 1935.



Untested (Y-12957) Tested in Static Sodium (Y-12958)

(a) Silicon carbide-silicon (Durhy). In the tested specimen the silica has been removed leaving only the light gray SiC and the dark graphite phases of the original specimen. In the tested specimen the holes are black. Unetched. 500X.



Untested (Y-21248) Tested in Dynamic Sodium (Y-21249)

(b) Silicon carbide-silicon, 85-90% (nominal) SiC. The white phase is silicon and the medium gray phase is SiC. Unetched. 100X.

Fig. 11. Two Silicon Carbide-Silicon Specimens before and after 100-Hr

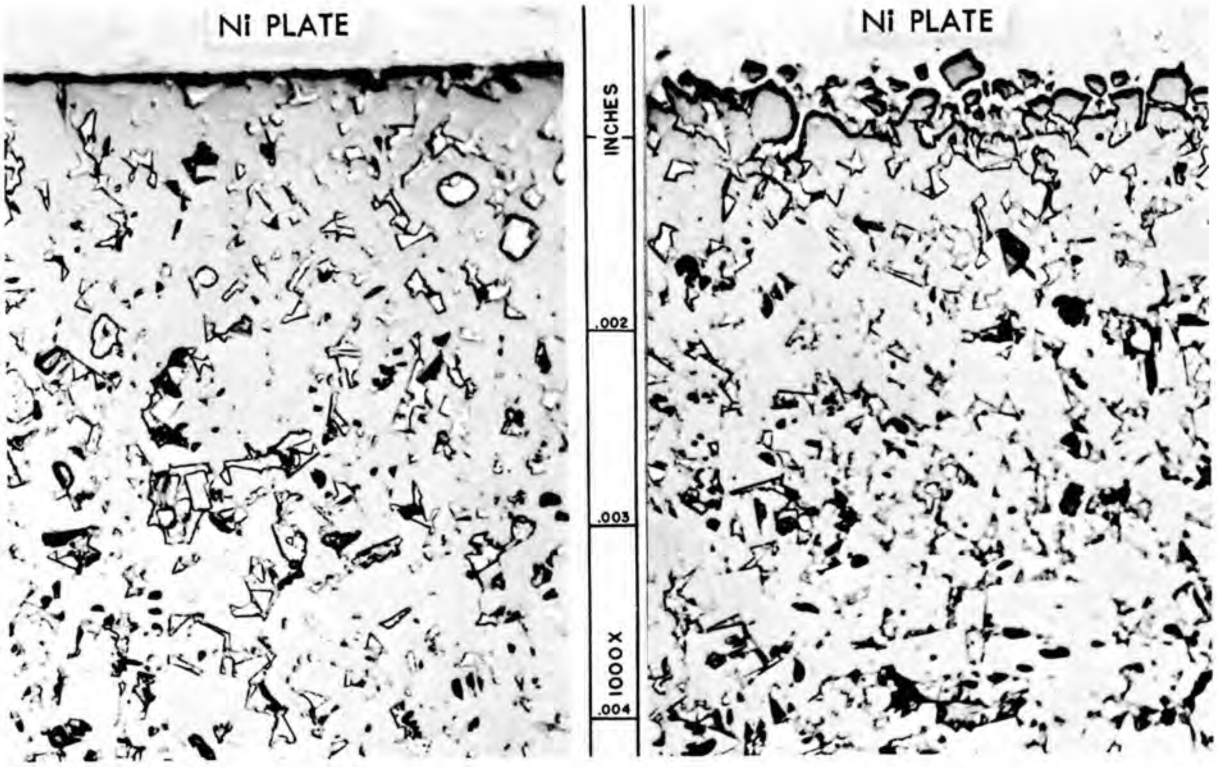
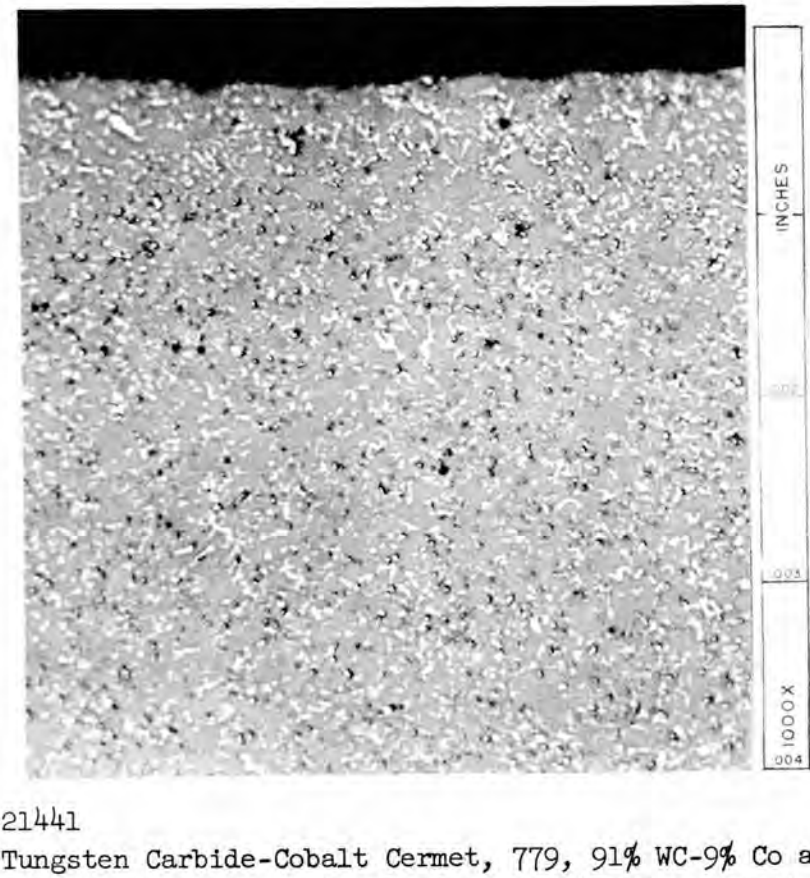


Fig. 12. (a) Y-21261 (b) Y-21262
A Titanium Carbide-Nickel Cermet, K151A, 70% TiC-10% NbTaTiC$_3$-20% Ni, (a) Untested and (b) after a 100-Hr Exposure to Dynamic Sodium in an Inconel Container in a Seesaw Test in which Hot and Cold Zones were 1500° and 1150°F, Respectively. Unetched. 1000X.



Y-21441

Fig. 13. A Tungsten Carbide-Cobalt Cermet, 779, 91% WC-9% Co after a 100-Hr Exposure to Static Lead at 1500°F in an Ingot Iron (99.50% Fe) Container. Unetched. 1000X.

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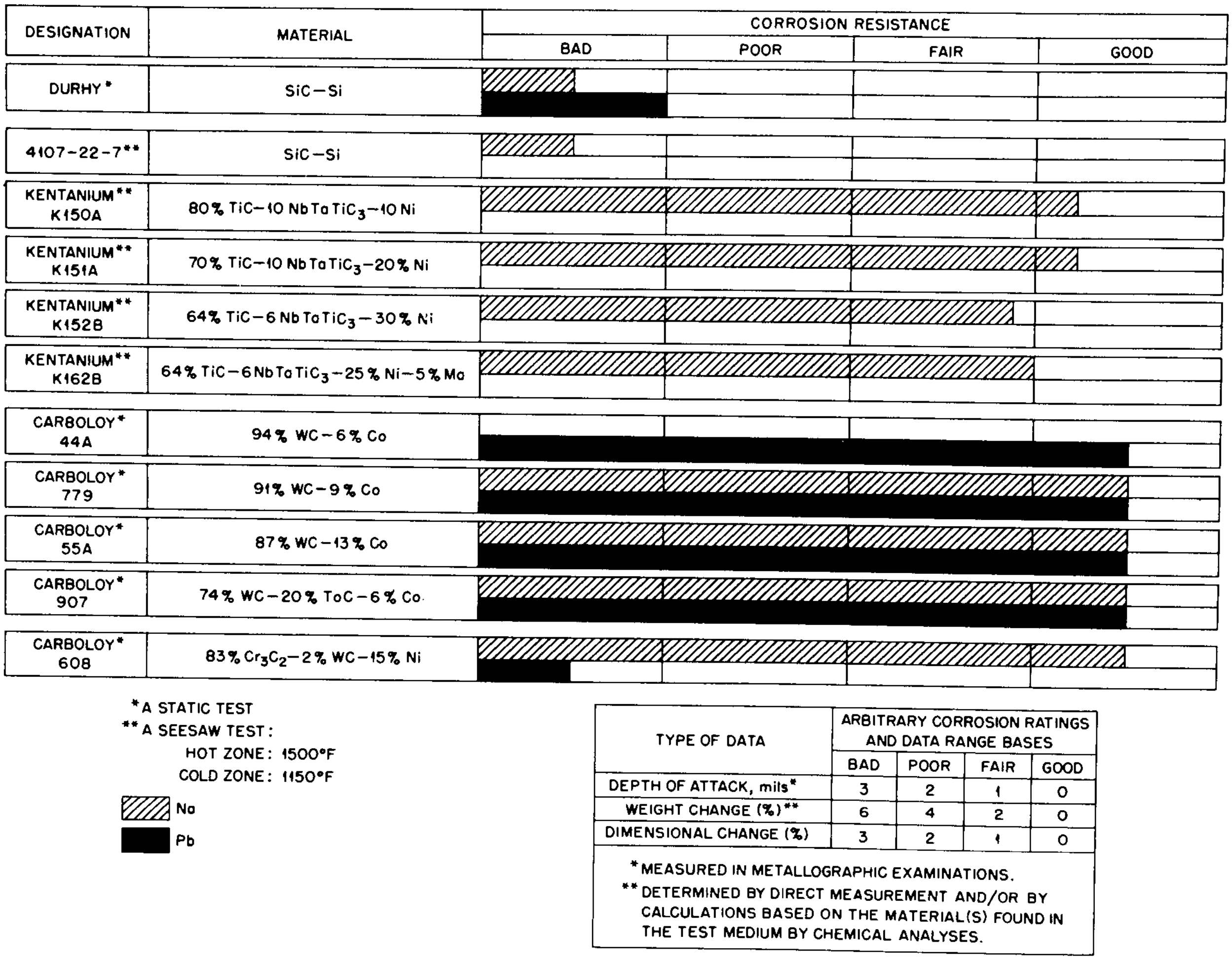

*A STATIC TEST
**A SEESAW TEST:
HOT ZONE: 1500°F
COLD ZONE: 1150°F

▨ Na
■ Pb

TYPE OF DATA	ARBITRARY CORROSION RATINGS AND DATA RANGE BASES			
	BAD	POOR	FAIR	GOOD
DEPTH OF ATTACK, mils*	3	2	1	0
WEIGHT CHANGE (%)**	6	4	2	0
DIMENSIONAL CHANGE (%)	3	2	1	0

*MEASURED IN METALLOGRAPHIC EXAMINATIONS.
**DETERMINED BY DIRECT MEASUREMENT AND/OR BY CALCULATIONS BASED ON THE MATERIAL(S) FOUND IN THE TEST MEDIUM BY CHEMICAL ANALYSES.

Fig. 14. Trends of Corrosion Resistance of Various Cermets in Sodium and Lead for 100 Hr at 1500°F.

Note: Kentamium is a trade name used by Kennametal, Inc., Latrobe, Pa. Carboloy is a trade name used by Carboloy Department of General Electric Company, Detroit 32, Mich.

Under equilibrium conditions and at room temperature, the metal and carbide phases of TiC—Ni or WC—Co cermets are essentially insoluble in each other.[10,11] Therefore, these cermets consist of approximately pure metal and pure carbide phases. It was shown in the corrosion results of ceramics that pure TiC was not attacked by sodium and it has been reported[12] that high-purity nickel has a high resistance to sodium at these temperatures. These data indicate that the TiC—Ni cermets should not be attacked by sodium. The attack that was found on one set of TiC—Ni cermets could have been caused by their being contaminated with oxygen during their fabrication.

The attack, to a depth of 27 mils, on the Cr_3C_2—Ni cermet by lead was limited to the nickel. This is clearly shown in Fig. 15, and was expected. As already pointed out (Fig. 10), Cr_3C_2 is not attacked by lead in these test conditions but it is well known that nickel is attacked by lead.[13,14]

CONCLUSIONS AND RECOMMENDATIONS

The summary of the corrosion results of ceramics in liquid lithium, sodium, and lead given in Fig. 10 indicate that lithium is by far the most severe corrodent. All of the ceramics tested had good resistance to attack by lead and sodium was slightly more corrosive than the lead. This is the same general trend that one would predict for these media and ceramic materials by their free energies of formation; however, thermodynamic data are not available for many of the materials.

The use of free energies of formation for predicting the corrosion resistance of ceramics and cermets to lithium, sodium, and lead are best illustrated by the

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[10] E. R. Stover and J. Wulff, Studies in the System Nickel-Titanium-Carbon, WADC Tech. Rep. 54-212.

[11] P. Schwartzkopf, Powder Metallurgy, p. 197, The MacMillan Co., New York, 1947.

[12] R. C. Lyon (ed.), Liquid-Metals Handbook, 2d ed., pp. 152—153, NAVEXOS P-733 (Rev.), Washington, D. C.: Department of the Navy (June, 1952).

[13] *Ibid.*, p. 173.

[14] J. V. Cathcart and W. D. Manly, "The Mass Transfer Properties of Various Metals and Alloys in Liquid Lead," Corrosion **12**, 44—45 (February, 1956).

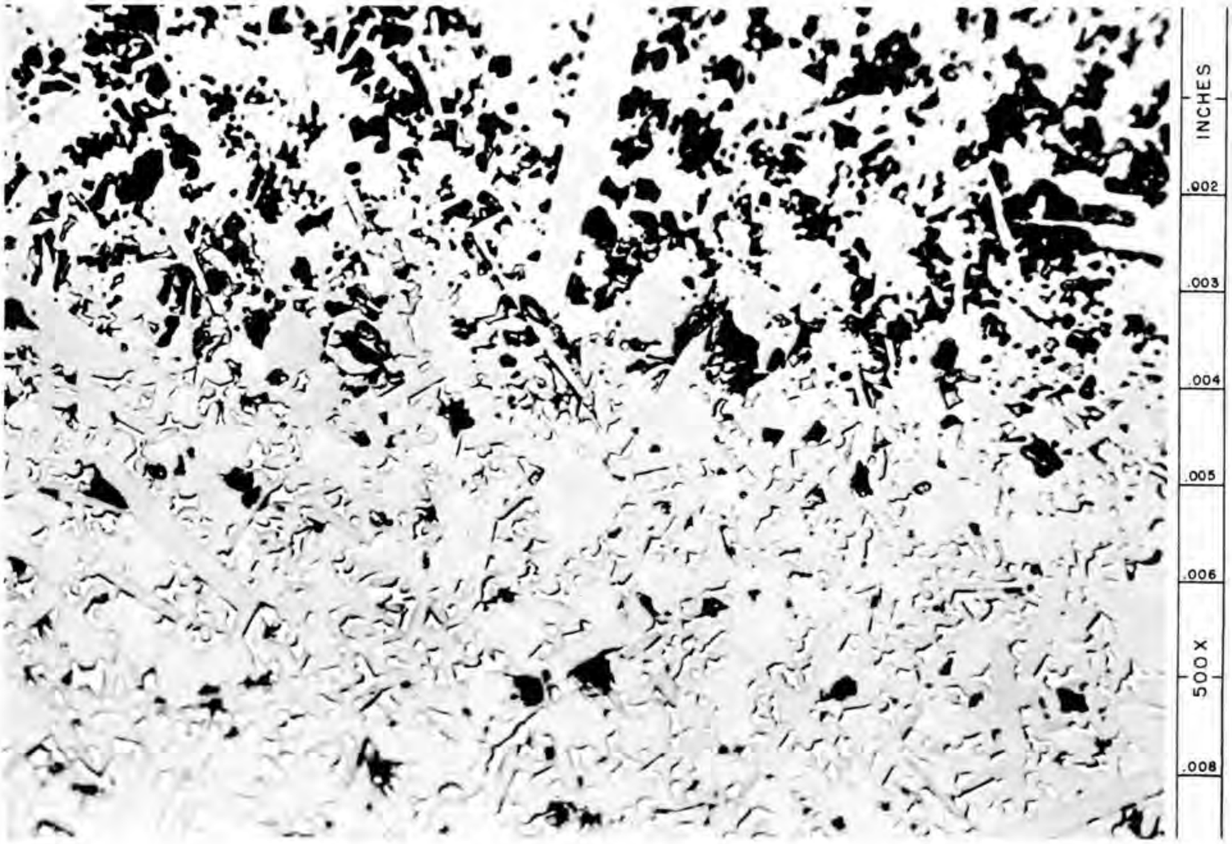

Fig. 15. A Chromium Carbide Nickel Cermet, 83% Cr_3C_2-2% WC-15% Ni, after a 100-Hr Exposure to Static Lead at 1500°F in an Ingot Iron (99.50% Fe) Container. The attack, a portion of it is shown in the upper half of the photomicrograph, was 0.027 in. deep and limited to the nickel phase. The holes are black in the photomicrograph. Unetched. 500X.

free energies of the oxides of these materials. The free energy data given in Table I shows that Li_2O is approximately as stable as most of the ceramic oxides studied. Therefore, lithium would be more likely to reduce the ceramic oxides than either sodium or lead which form oxides of relatively low stability.

The limited results obtained on single-crystal specimens tended to parallel predicted corrosive resistance trends while the results obtained on polycrystalline, sintered specimens did not.

These limited corrosion data suggest that thermodynamic data can be useful as qualitative guides for planning tests and for selecting materials to be tested but it is the corrosion test that secures quantitative information that will be ultimately needed for utilization of the materials.

As shown in Fig. 10, only TiC, ZrC, and Cr_3C_2 of the ceramic materials tested withstood attack by the lithium. The resistance to corrosion by lithium exhibited by these three carbides indicates that some qualifications may be in order for reports[15] that carbides are attacked by lithium.

The relatively good corrosion resistance of the porous Si_3N_4 and Sm_2O_3 in these corrosion screening tests in sodium (Fig. 10) qualified to some extent past generalizations[16] that porous ceramics usually had poor corrosion resistance.

Although no cermets were tested in lithium in this test series, there are data available that leads one to conclude that corrosion resistant cermets can be found for this medium. For example, TiC—Mo or TiC—W cermets might serve well since test results indicate that TiC is resistant to corrosion by lithium and it has been reported that molybdenum or tungsten have good resistance to lithium.[15]

These screening corrosion tests by no means covered the whole field of ceramics and cermets but they did show that industry has some commercial ceramics and cermets that appear promising for use in lithium, sodium, or lead at 1500°F. There are many more ceramic and cermet compositions and structures that should be investigated for use in liquid-metal systems. These and other similar screening corrosion tests provide useful data but fundamental investigations of the ceramic and cermet compositions and structures in relation to their stability with liquid

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[15] Lyon, _op_. _cit_., p. 161.

[16] Lyon, _op_. _cit_., p. 156.

TABLE I. Free Energies of Formation at 1500°F (1090°K) of the Oxides of the Liquid Metals and the Ceramic Oxides Involved in 100-hr Corrosion Tests at 1500°F[a]

Compound	Standard Free Energy of Formation [kcal/gram-atom of oxygen, 1500°F (1090°K)][b]
ThO_2	-122
Sm_2O_3	-121
BeO	-118
MgO	-115
ZrO_2	-106
Al_2O_3	-106
Li_2O	(-108)
Na_2O	-63
PbO	(-27)

[a] Alvin Glassner, A Survey of Free Energies of Formation of the Fluorides, Chlorides, and Oxides of the Elements to 2500°K, ANL-5750 (1957).

[b] The values in parentheses indicate where approximations were made while others were based on experimental heat capacities.

metals are necessary. These investigations must be conducted with starting materials of high purity and on materials in which the compositions, fabrication, and structural conditions are well known. Although such data could be helpful as a guide for corrosion tests, the greatest use would be for the development of ceramics and cermets designed for service in specific liquid metals. This would help ensure the maximum utilization of the potentialities of these materials.

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