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THE CORROSION OF SOME PURE METALS IN BASALTIC LAVA
AND SIMULATED MAGMATIC GAS AT 1150°C

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ABSTRACT

The extraction of thermal energy from subterranean magma can be achieved by the use of a suitable heat exchanger extending into the molten rock. Although the engineering feasibility of this scheme has not been proven, engineering data, including materials compatibility information, will be required ultimately. The work summarized in this report was designed to provide an understanding of the reaction mechanisms and modes of degradation of various metals so that the best generic types of alloys can be selected for structural components and instrumentation.

Fifteen pure metals were studied. These included base metals such as iron, nickel, and cobalt; some precious metals: platinum, rhodium and palladium (possible thermocouple or lead wire materials); refractory metals: tungsten, molybdenum, tantalum, niobium, vanadium, rhenium; plus other high melting metals such as titanium and zirconium. Samples were exposed to basaltic lava at 1150°C for periods of 24 and 96 hours. A cover gas was

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used to produce oxygen and sulfur fugacities corresponding to those of the gases dissolved in basaltic melts.

The corrosion behavior can be classified into five categories:

- A) "no" attack (Pt and Re)
- B) slight oxidation (Cr and Mo)
- C) heavy oxidation (W, Ta, Nb)
- D) sulfidation (Fe, Ni, Co, Pd, Rh)
- E) reaction with lava constituents (V, Ti, Zr)

Group (A) metals were inert for all practical purposes.

Group (B) metals formed thin adherent oxides initially, under which sulfides eventually formed in the substrate. Attack was minimal. Group (C) metals exhibited extensive oxide formation and virtually no sulfidation. Some reaction between the base-metal oxides and those in the lava took place. Group (D) metals all formed liquid sulfides which penetrated the substrate grain boundaries. All of these metals except cobalt were completely degraded. Cobalt was only partially penetrated by the liquid sulfide formed. Group (E) metals formed silicates, oxides, mixed oxides, and dissolved oxygen in the metal which completely embrittled the metal substrate. A small amount of sulfidation occurred, but sulfidation played virtually no role in the corrosion of these metals.

Extensive analyses of the reaction products by scanning electron microscopy, x-ray energy dispersive analysis, electron microprobe analysis, and metallography are presented for each metal. The products formed are discussed with reference to thermodynamic stability diagrams, and the reaction path concept is used to explain some of the corrosion product morphologies.

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INTRODUCTION

The amount of thermal energy contained in magma bodies located about six to ten miles beneath the earth's surface represents an incredibly large reservoir of energy which could supply the United States for hundreds of years. A program to investigate the feasibility of extracting this energy has been underway for several years at Sandia, the aims, objectives, problems, and status of which are summarized in various reports and papers [1-3]. One of the many engineering problems of considerable concern to the success of extracting thermal energy from magma bodies is the compatibility of metals which would be used as heat exchangers and other system components. The problem concerns reactions between metals and volatile components dissolved in the silicate melt. Some previous work has been reported in which lava-metal reactions were studied in the absence of a magmatic gas [4,5]. Extensive analyses of restored volcanic gases have been made by Gerlach [6,7] whose data are shown in the Appendix in Table A-1, from which it may be noted that sulfur exists as SO_2 , H_2S and S_2 . Calculation of sulfur and oxygen fugacities from these data indicate a range of values which depend upon temperature as well as the geochemical factors inherent to each volcano. The oxygen and sulfur fugacities are plotted as a function of temperature in the Appendix in Figs. A-1 and A-2. Values for the present study were obtained from the plots. The sulfur fugacity used was on the high side of the range and probably represents an "overtest" in terms of corrosiveness. However, the selection of the sulfur fugacity was based also on its increase with increasing pressure, which is characteristic of magma bodies. The study was made with basaltic lava which has the lowest oxygen fugacity and the highest sulfur fugacity of the commonly occurring magmas. Although small amounts of HCl exist in the volcanic gases and will further increase the corrosiveness of the gases, no attempts were made to study the effect of HCl presently. The tabulated gases and calculated fugacities clearly suggested that sulfidation in the silicate melt would be a major problem with respect to metal-magma compatibility.

The work reported herein involves reactions between a number of pure metals and molten silicate melts (basaltic lava) with a cover gas which simulates the low-pressure gas composition of basaltic melts. It should be noted that the gas composition used was a simulant designed to produce the same fugacities existing at a temperature of 1150°C.

The test temperature was 1150°C which is the temperature of a basaltic magma body. However, a heat exchanger immersed in a magma body would not be exposed to 1150°C due to the formation of a shell of solidified basalt on the metal surface. The actual temperature of the heat exchanger surface would probably be 700°C. The tests simulate conditions that would occur during a loss-of-coolant incident during which the shell of solidified rock would melt. The tests represent a "worst possible case."

Pure metals are hardly ever used as structural components for engineering application, but rather alloys of two or more metals are used for a variety of reasons which include strength and corrosion resistance. It was deemed of paramount importance to ascertain the behavior of pure metals so that the data base obtained could be used to understand the behavior of engineering alloys. The first part of the magma-metal compatibility program concerns pure metals, the results of which are reported in this paper. Work presently in progress concerns a number of binary alloys, stainless steels, and other alloys.

EXPERIMENTAL PROCEDURES

Samples of the metals were obtained in sheet form with the exception of chromium. Minimum purities of the metals are listed in Table I. The chromium samples were prepared from electrolytic chips which were vacuum arc-melted several times to form a button. The button was subsequently cut into thin slabs. Metallographic examination revealed isolated particles of Cr_2O_3 in the grain boundaries.

Test coupons were cut from the sheet about $1/2 \times 3/4$ ". The samples were abraded through 600 grit silicon carbide paper, washed, and dried. Samples were inserted into a slot cut in a small piece of alumina so that the samples were vertical when placed into an alumina crucible which had an internal diameter of $1-1/8$ " and a height of $3/4$ ".

Finely pulverized tholeiitic, basaltic lava from the 1971 Kilauea Iki eruption (composition listed in Table II) was placed in the crucible so that the samples were completely covered. The crucibles, four per run, were placed into a furnace tube at room temperature. After evacuation, the furnace was purged with argon for 24 hours. Following the purge, the system was brought up to temperature, 1150°C , and the gases were turned on. The gas composition, Table III, was calculated to give a sulfur fugacity of 7×10^{-3} bar and an oxygen fugacity of 9.8×10^{-10} bar at 1150°C and atmospheric pressure after the gas equilibrated. The completed list of gaseous species and their fugacities after equilibration at temperature is summarized in Table IV. These values were determined by T. Gerlach by means of a computer program [8]. The gas flow rate was 80 cc/min. The gas was passed through a closed alumina tube in the hot temperature zone, returned via a hairpin turn, and finally returned again into the system. This procedure allowed complete equilibration to occur before the samples were exposed to the gas.

The system was shut down after the desired time had elapsed, either 24 or 96 hours. The crucibles were sectioned on a cutoff wheel so that a portion perpendicular to the sheet axis was removed. These cross sections were mounted in epoxy and prepared for metallographic examination. Optical microscopy, scanning electron microscopy (SEM), and energy dispersive x-ray analyses (EDX) were used to characterize the corroded samples.

RESULTS

A very wide range of reactivity of the various metals was noted. This ranged from virtually no attack to complete disintegration of the samples. In general, the type of attack can be classified into several categories, although in some cases a given metal showed evidence of more than one type of attack, e.g., sulfidation and oxidation. The classifications are as follows:

- A) no attack (Pt, Re)
- B) slight oxidation* (Cr, Mo)
- C) heavy oxidation (W, Ta, Nb)
- D) sulfidation (Fe, Ni, Co, Pd, Rh)
- E) reaction with lava constituents (V, Ti, Zr).

A macroscopic view of the corroded samples is shown in Fig. 1 which portrays the gross effects. As will be noted subsequently the low-magnification views completely mask the extent of the attack in some specific cases. Nickel, for example appears to be slightly attacked in Fig. 1, but a liquid sulfide-metal eutectic had completely penetrated the grain boundaries and extended across the entire sample thickness. The nature of the attack and the details may be seen in higher magnification micrographs of the cross sections in Figs. 2-6, which correspond to the above classifications, A-E, respectively. Each of the classifications will be covered separately with a detailed discussion of each individual metal within a given category.

A) "No" Attack

Platinum

Platinum was truly the only metal of the fifteen tested that did not react to form a discernible reaction product. Examination of the sample by SEM at high magnification failed to reveal corrosion products. The only notable feature was

* These metals form thin oxides initially but subsequently form sulfides in the substrate beneath the oxide films. The extent of sulfidation is minor compared to those metals classified in the "sulfidation" category.

some slight rearrangement of the surface for certain grains which was manifested as a "bump" in Fig. 1 or as a depression in Fig. 2. EDX examination did not reveal the presence of platinum in the lava, and thus, if a dissolution rather than a reaction occurred, the amount of platinum dissolved was less than the detection limit of EDX.

Rhenium

Although rhenium has been classified as suffering no attack, there was a very slight, superficial surface roughening, shown in Fig. 7, which might correspond to the formation of rhenium oxide. The irregular protuberances were subjected to EDX analysis which revealed a slightly lower rhenium content than that of the base metal. However, ReO_2 contains over 85% Re by weight, and it is difficult to conclude unequivocally that the protuberances were an oxide. Regardless of whether some oxide did form, the extent of the reaction was extremely low, and the metal can be classified as "inert."

B) Slight Oxidation

Two metals, chromium and molybdenum, initially formed thin oxide scales. The gas fugacities fell within the oxide stability field of Cr_2O_3 and MoO_2 for Cr and Mo, respectively. However, after 96 hours, sulfides had formed beneath the oxide scales of each metal for reasons to be discussed subsequently. Fig. 8 shows oxide scales formed during 24 hours and the respective sulfides formed beneath the oxide scales during 96 hours.

Chromium

A more detailed examination of the chromium sample corroded for 96 hours is shown in Fig. 9. The outermost portion of the oxide layer, region A, is chromium-rich but contains an appreciable amount of iron with traces of aluminum and calcium. It is not known if the oxide depicted in A is Cr_2O_3 with the iron in solid solution or chromium-iron spinel of the type FeCr_2O_4 . It should be noted that oxygen cannot be detected by EDX but is indeed present as clearly shown by the electron microprobe analyzer (EMPA) which can detect oxygen.

The major portion of the oxide scale contains only chromium and oxygen (EMPA), regions B and C. The oxide has a duplex structure, the inner region being more porous than the middle region.

A region of chromium metal contaminated with a small amount of iron, region D, existed between the oxide and the sulfide. The iron contamination is from the molten lava. Iron forms in the melt from the reduction of FeO by chromium.

The sulfide is the internal layer (not completely continuous) as indicated by region E. The substrate beneath the sulfide contains no iron.

Chromium was one of six metals which caused the formation of iron precipitates in the lava adjacent to the reaction products. The other metals causing this phenomenon were Nb, Ta, V, Ti, and Zr. Some examples are shown in Fig. 10.

Molybdenum

EDX analysis cannot distinguish between molybdenum and sulfur because the x-ray peaks have nearly the same energy. However EMPA clearly revealed the presence of molybdenum sulfide beneath the oxide scale (seen in Fig. 8). In general, the reaction products were cracked. The cracking appeared to occur in the sulfide layer as may be noted in the SEM micrograph in Fig. 11. It also appears that two oxides existed in the scale.

C) Heavy Oxidation

Tungsten

Tungsten reacted extensively to form a thick oxide scale. No evidence of sulfidation was observed. The oxide scale was not identical on both sides of the sample. The oxide scale on the top of the micrograph in Fig. 4 is designated as side No. 1 and will be discussed first.

The scale on side 1 consisted of three zones of tungsten oxides which should be WO_2 , $W_{18}O_{49}$ and $W_{20}O_{58}$ based on thermodynamic stabilities of these phases. The inner zone, WO_2 , comprised about 25% of the total scale and had a columnar grain structure. The middle zone, $W_{18}O_{49}$, represented slightly more

than 50% of the total thickness and was also columnar, the grains extending across the entire region. The outermost oxide, $W_{20}O_{58}$, had a blocky grain structure and contained islands of a "foreign" oxide. The three regions were most apparent in the optical micrograph, Fig. 12-A. The SEM micrograph of this region (a mirror image) is shown in Fig. 12-B with an island of the "foreign" oxide denoted. The denoted area is shown in Fig. 12-C at a much higher magnification. The EDX spectra of the island and of the blocky matrix are given in Figs. 12-D and 12-E, respectively. The island contained tungsten, oxygen and iron and is most likely a mixed oxide of unknown structure and stoichiometric formula. The blocky matrix was tungsten oxide as were the two inner zones in the oxide scale.

Side No. 2, the bottom scale in Fig. 4, is thicker than the scale on side No. 1. Further, the outer, blocky oxide present on side No. 1 is missing. Pieces of this oxide were observed in the lava away from the sample. The outermost portion of the scale on side No. 2 is highly acicular and is the same oxide found in the center of the scale on side No. 1. None of the mixed tungsten-iron oxide was detected, but instead a different "foreign" oxide was observed as shown in Fig. 13. The EDX spectrum revealed an appreciable calcium content along with tungsten. Although it is not possible to positively identify this phase, there is a strong likelihood that it is calcium tungstate, $CaWO_4$, which formed by reaction of $W_{18}O_{49}$ and CaO from the lava. It is also not known why one side of the tungsten sample was more heavily reacted than the other side.

Tantalum

The corrosion of tantalum resulted in two characteristics which were particularly noteworthy but which are quite similar to those observed during the oxidation of tantalum in air or oxygen alone. First, a thick oxide scale formed which split along the corners to give the so-called "Maltese Cross" effect. The scale also contained numerous cracks parallel to the sample

surface. The nature of the cracked scale may be seen in Fig. 14-A. The second characteristic is the presence of a suboxide of unknown composition, the dark phase in Fig. 14-B. Tantalum has a high oxygen solubility at high temperature, and the suboxide probably forms during cooling by decomposition of a supersaturated solid solution of oxygen in tantalum.

The thick, cracked oxides scale is Ta_2O_5 which has a much higher molar volume than the metal from which it forms. The oxide offers virtually no protection because it always contains numerous fissures which allow direct access of the reactants.

Iron particles crystallized from the melt away from the sample. A small amount of copper sulfide was associated with the iron particles.

Niobium

Niobium formed a variety of reaction products, although the primary reaction was oxidation and was the basis of classifying niobium in the "oxidation" category. Some differences were noted between samples corroded for 24 and 96 hours, but the same general reaction product morphologies were observed. These consisted of an internal niobium suboxide of unknown composition, a continuous niobium oxide scale, and some small oxide particles on top of the oxide scale. These features are shown in Figs. 15 and 16 for exposures of 24 and 96 hours, respectively.

The niobium oxide scale contained small iron particles in all cases. The scale was continuous but was generally cracked parallel to the metal surface.

Small particles, assumed to be oxides based on their appearance in the SEM, existed on top of the continuous scale and slightly separated from the scale. However, a minor fraction of these oxide particles were attached to the niobium oxide scale. The particles were oblong, about 2 x 5 microns, and their composition depended upon the exposure time. Those particles formed in 24 hours had a high niobium content, a moderate titanium content, and a trace of iron, Fig. 15-B.

However, after 96 hours, the particles had picked up silicon and calcium plus a trace of aluminum as noted in Fig. 16-B. There is a complex silicate of the formula $\text{Ca}_4 (\text{Ti}, \text{Nb})_2 \text{Si}_2 \text{O}_{11}$ which might be the phase noted here. This phase could readily incorporate iron and aluminum in it and account for the observed spectrum.

The 96 hour sample also exhibited a thin continuous layer of copper sulfide containing some iron, Fig. 16-C. Although the copper content of the lava is low, on the order of 100 ppm, a calculation based on the observed thickness of the sulfide layer, the sample area, and the amount of lava in the crucible indicates that sufficient copper existed to form the layer. Furthermore, the system contained no parts made of copper, and thus contamination from external sources can be ruled out.

Two other features were observed which deserve mention. First, a large spheroid, approximately 200 microns in diameter, existed in the lava about 150 microns away from the sample surface. The spheroid, Fig. 17, consisted of iron as the major element with an appreciable amount of niobium present. The appearance of the particle in the SEM suggests that it was an oxide with small metallic regions present within. Second, a mound was found on one region of the surface. The approximate dimensions were 250 microns long and 100 microns high, as seen in Fig. 18. The mound consisted of an iron sulfide matrix, Fig. 18-B, with islands of iron oxide, Fig. 18-C. The oxides were not positively identified, but the appearance in the SEM once again suggests that they are oxides. The sulfide-oxide structure is consistent with the FeS-FeO phase diagram.

D) Sulfidation

Four of the metals exhibited heavy sulfidation which was completely catastrophic. These metals were iron, nickel, rhodium, and palladium. The fifth metal which underwent sulfidation as the major mode of attack was cobalt, but the extent of the attack was considerably less than that of the

other four metals. As will be discussed subsequently, sulfidation rates are orders of magnitude higher than oxidation rates, but in addition another problem exists which is even more severe than the rapid reaction rates. This concerns the formation of low-melting eutectics between the metals and their sulfides.

Cobalt

Cobalt formed a sulfide layer over the entire surface with preferential attack at grain boundaries. The extent of the grain boundary attack was minimal compared to both iron and nickel which exhibited complete penetration by their respective sulfides.

An outer reaction product also formed in some cases which was primarily cobalt with an appreciable amount of silicon and iron. This layer might be a cobalt-iron silicate. An SEM micrograph of the sulfide and of the silicate is shown in Fig. 19 with the corresponding EDX spectra from the indicated regions.

Iron

Iron reacted extensively to form an external sulfide scale plus a network of sulfide in the metal grain boundaries. The intergranular network consisted of two phases and had the appearance of a eutectic structure as seen in Fig. 20. The eutectic structure contained a light gray and a dark gray phase which were considerably different than the iron matrix in appearance. EDX revealed that the light gray phase contained both sulfur and iron (FeS) and that the dark gray phase contained only iron. However, the appearance of the dark gray phase is typical of FeO. A eutectic forms at 940°C between FeS and FeO which explains the grain boundary structure.

The intergranular network also contained another phase, the dark areas shown in Fig. 21. EDX analysis revealed a high content of silicon and calcium, a moderate amount of iron, and a trace of magnesium. The phase is probably a clinopyroxene which will be discussed subsequently.

Nickel

Nickel exhibited a similar behavior to iron, i.e., complete grain-boundary penetration of the metal by a liquid sulfide phase. The external sulfide scale and the grain-boundary sulfide

contained small metallic particles of nickel, as noted in Fig. 22. The nickel may have formed as proeutectic particles during solidification of a hypoeutectic Ni-S liquid.

Two separate runs were made for a period of 24 hours. One sample contained dark particles in the grain boundary network with an appearance quite similar to those formed in the iron sample. The second sample was free of these particles. EDX analysis of the particles revealed two distinct compositions, as seen in Fig. 23. The lighter particles were very rich in titanium with appreciable manganese, iron, and nickel plus a trace of magnesium. The darker particles contained copious amounts of nickel, silicon, and magnesium with traces of sulfur manganese and iron.

Rhodium

Rhodium formed a liquid sulfide, similarly to iron, nickel and palladium, which penetrated into the grain boundaries of the metal. The net result was nearly complete destruction of the sample with a significant amount of metal converted to the sulfide. An SEM micrograph of the grain boundary sulfide and a sulfur x-ray map of the micrograph are shown in Fig. 24.

Palladium

Palladium completely disintegrated by the formation of liquid sulfide. The extent of the reaction can be noted from Fig. 1, and the sulfide phase is apparent in Fig. 5.

E) Reaction with Lava Constituents

Vanadium

Vanadium formed a variety of reaction products. Reaction during 24 hours was minimal, whereas, reaction during 96 hours resulted in nearly complete consumption of the metal. Oxidation occurred, yielding a highly irregular, detached, non-continuous film, shown in Fig. 25-A for the 24 hour sample. The outermost portion of the detached oxide consisted of fine oxide needles, Figure 25-B, or oxide idiomorphs, Fig. 25-C. The idiomorphs were usually next to iron precipitates as shown by the iron x-ray map, Fig. 25-D. Some areas of the metal had remnants of a thin sulfide scale, Fig. 25-C, some of which was attached to

the oxide. The needle-like oxide was the remnant structure from a two-phase structure, the second phase having been either dissolved out during reaction or pulled out during metallographic preparation. The interface between the two-structure zone and the needle oxide is shown in Fig. 26 along with EDX spectra from each phase. The dark phase is vanadium oxide with a trace of titanium, whereas, the light phase is a vanadium oxide containing some silicon or, alternatively it may be a vanadium silicate. The two-phase structure has the appearance of a eutectic, and the isolated needles appear to have small dendritic globules of the light phase attached to the needles.

The 96-hour sample followed a similar behavior to the 24-hour sample except that the reaction was much more advanced, and more mixed products were observed. The extent of the reaction is illustrated in Fig. 27-A, in which the massive form of the reaction products can be noted on the bottom half of the sample. The substrate is cracked through its entirety, due to oxygen contamination and subsequent embrittlement. The oxide needles are clearly seen in Fig. 27-B which also shows a multiphase structure, Fig. 27-C, adjacent to the needles. EDX spectra indicate that point (1) is probably a vanadium silicate, point (2) is a vanadium sulfide, and point (3) is a vanadium oxide with traces of silicon, titanium, and iron. The rumpled phase partly attached to and mostly detached from the metal surface is a vanadium oxide with small areas of sulfide interspersed. The oxide phase contains a fair amount of iron and a trace of silicon.

Titanium

Titanium exhibited many of the same features as vanadium including cracking of the samples by oxygen contamination and embrittlement. In addition to the formation of oxides, silicates and mixed oxides, titanium absorbed aluminum into the metal.

The variety of reaction products is illustrated for the 24-hour sample in Fig. 28. The outermost phase, region B, appears to be a mixed oxide of titanium and aluminum Al_2TiO_5 .

Region C, from which the outer mixed oxide had blistered, is titanium oxide. The massive, irregular area representing the major portion of the scale, Fig. 29, is a mixture of titanium oxide and an iron-titanium silicate which some phosphorous present. The semi-continuous layer in the middle and the fingers extending away from the layer are predominantly titanium oxide.

Aluminum pickup by the substrate is shown in Fig. 30 along with an x-ray map of aluminum. A two-phase structure exists in the substrate, one phase having more aluminum than the other. Considerable aluminum also exists in solid solution in the substrate beneath the two-phase zone.

Exposure for 96 hours resulted in complete consumption of the metal as is readily apparent in Fig. 31-A. The center portion of the sample is a suboxide, tentatively identified as Ti_2O by electron microprobe analysis. The 96-hour sample was much more reacted than the 24 hour sample. SEM examination revealed titanium oxide, titanium-aluminum oxide and titanium-iron silicates as were found also in the 24 hour sample. The major difference was the presence of a small amount of titanium sulfide and a mixed titanium-iron sulfide in the unreacted metal plus more of the titanium-iron silicate in the 96-hour sample. The sulfides and their EDX spectra are also shown in Fig. 31.

Zirconium

Zirconium exhibited a behavior quite similar to that of titanium. The major difference was that zirconium reacted very readily with silica in the melt to form a zirconium silicate layer over the entire surface of the sample. An example of the many corrosion products is shown in Fig. 32. Starting in the melt, one notes the presence of iron precipitates, area 1, and iron silicate particles, area 2. A massive, discontinuous scale of zirconium-iron silicate, area 3, and ZrO_2 , area 4, exists on the sample but which is separated from the metal by a nearly continuous (although blistered in some areas) layer of zirconium silicate, area 5. Directly beneath the silicate layer an envelope of oxygen-stabilized alpha zirconium, area 6, exists

in the substrate. There are pockets of a two-phase structure in the metal which contain aluminum, similar to the structure observed in titanium. The zirconium silicate layer and two-phase metallic structures are shown better in Fig. 33. No sulfides were detected in any of the zirconium samples.

DISCUSSION

The results indicate the principal compatibility problems in basaltic magmas will be sulfidation-oxidation. The type of reaction expected between a metal and magmatic gases depends upon the relative stabilities of the sulfide and oxides in the particular system. If the free energies of formation are known, a thermodynamic phase-stability diagram can be drawn which maps out areas in which a given compound is stable for a range of gas fugacities at a specified temperature. Thus, to a first approximation, if the temperature and the fugacities of S_2 and O_2 in the particular gas considered are known, the stable phase favored on the metal surface can be predicted from the diagrams. This approach is quite useful in predicting the reaction products. However, in many cases the thermodynamic data are inaccurate, and the resultant stability diagrams suggest sulfidation when oxidation is the primary reaction and vice-versa. Furthermore, kinetics factors often prevent attainment of equilibrium at reasonable time scales and give rise to different product phases than would be predicted from the stability diagrams.

The complexity of the reaction products can be attributed also to another factor. The thermodynamic approach used here applies only to reactions between metals and gases. This technique will apply to lava-metal reactions as long as the lava does not attack the metal to any great extent. In other words, the reaction is one between the metal and dissolved gases in the lava. It was found that certain metals, i.e., Zr, Ti and V, reacted extensively with the lava to form silicates although their respective stability diagrams showed that the gas composition was deep within the oxide stability regions. The reaction

between lava and metal was more significant than the attack by the gas. Each of the categories listed previously will be considered individually.

"No" Attack

The stability diagram for platinum indicates that neither the sulfide nor the oxide is stable as noted in Fig. 34 which also shows the gas fugacities used in this study denoted by a cross surrounded by a circle. This metal was not expected to react, and no evidence of reaction was detected. The only modification to the metal was the slight surface roughening as mentioned previously. This process is one involving surface diffusion of platinum and represents an adjustment of the surface to achieve equilibrium based on the modification of surface energies by the gas. Thermal grooving, thermal etching of grain boundaries, and faceting are other examples in which the same mechanisms apply. The extent of the surface changes was minimal. Platinum appears to be truly inert under the test conditions used.

Although rhenium has been classified as undergoing "no" attack, the stability diagram indicates that ReO_2 might have formed. The gas fugacities were close to the oxide-metal stability line, and if the data from which the diagram was calculated are inaccurate, oxide formation might occur. EDX analyses suggest that a small amount of oxide could have been formed, but it is not known with certainty if this occurred. Regardless of whether oxide did or did not form, the extent of the reaction was virtually nil, and rhenium can be classified as essentially "inert."

Both platinum and rhenium would make excellent thermocouple cladding materials as far as compatibility is concerned, but their extremely high costs mitigate against their use for extensive applications.

Slight Oxidation

The gas fugacities fell within the Cr_2O_3 field for chromium and within the MoO_2 field for molybdenum, Fig. 35. Both metals formed adherent, protective oxides during the 24 hour test.

The oxides were thin, indicating that minimal reaction took place. This behavior is not surprising in view of the low defect concentrations existing in the oxides. Chromium is added to stainless steels and super alloys to enable a Cr_2O_3 film to form which provides a high degree of oxidation resistance to those materials. On the other hand, molybdenum cannot be used in oxidizing environments because MoO_3 forms under ambient oxygen pressure, and the oxide is volatile. Thus, no measure of protection is provided because MoO_2 is continuously converted to gaseous MoO_3 . The low oxygen fugacity in the volcanic gas suppresses the formation of MoO_3 , and the only stable oxide formed, MoO_2 , is protective.

Sulfides formed beneath the oxides on both metals during the 96 hour test. This behavior occurs frequently and depends upon the reaction "path," which in turn depends on the variation of activities across the oxide film and in the metal substrate. The activities of both sulfur and oxygen decrease from the gas phase across the oxide film and into the metal. Depending upon the relative rates of activity decrease with distance, a reaction path can be postulated as indicated in Fig. 36. "Path" A cuts across the sulfide stability field which means that a sulfide can form even though the initial gas composition is in the oxide field. "Path" B bypasses the sulfide region, and thus no sulfide would be observed if such a path were followed. Schmetaic activity gradients for both paths "A" and "B" are shown in Fig. 37. Both chromium and molybdenum followed reaction paths similar to "A" which traversed the sulfide regions.

It is also of interest to compare the scale morphologies for the two metals, Figs. 8, 9 and 11. The sulfide on molybdenum was sandwiched between the metal and the oxide, and the sulfide was contiguous with the oxide. Chromium formed a sulfide in the substrate which was not in contact with the oxide. This type of behavior occurs in the case of internal oxidation or internal sulfidation. However, formation of the

internal oxide (or sulfide) occurs as discrete particles rather than as a continuous film. The particles precipitate at a site removed from the oxide-metal interface. The site is that at which a value in excess of the equilibrium solubility product exists. The "supersaturation" of the solubility product value is required to overcome the nucleation barrier. An outward flux of the oxidizable metal and an inward flux of either oxygen or sulfur give rise to a specific concentration of each element at any given point. If the product of the two concentrations exceeds the equilibrium value, precipitation occurs.

The sulfide observed in chromium was nearly a continuous film. The region between the quasi-continuous sulfide and the oxide-metal interface had picked up a small amount of iron from the lava. The only logical explanation for the location of the sulfide film away from the oxide-metal interface is that the iron contamination reduced the chromium concentration by an amount sufficient to make the solubility product less than the critical value for sulfide formation. The necessary value did not exist until the iron level had dropped at some finite distance away from the interface.

Sulfidation rates are characteristically thousands or millions of times more rapid than oxidation rates for a given metal. Although both molybdenum and chromium formed sulfides, the rate-controlling step is the oxidation rate and the migration rate of sulfur through the oxide on the surface. These rates appear slow enough to conclude that both metals would make excellent materials for use in magma. However, it should be noted that unalloyed chromium or chromium-rich alloys are not used in practice due to the inherent brittleness of chromium. Chromium represents a very useful addition to other metals, such as iron, nickel, or cobalt, in amounts sufficient to form a continuous layer of Cr_2O_3 but insufficient to embrittle the alloys.

Heavy Oxidation

The gas composition fell within the oxide field, Fig. 38, for all three metals (tungsten, niobium, and tantalum) classified in the "heavy oxidation" category. The gas composition was located in the $W_{20}O_{58}$ field for the W-S-O system which means that only two oxides should exist on the metal. However, three oxides were clearly visible in the microstructure; therefore, either the gas composition was not exactly that which was predetermined or the free energy data for the $W_{20}O_{58}$ -- WO_3 line are incorrect.

Only oxides were observed on tungsten and tantalum. No evidence of sulfides was detected, and it may be concluded that the reaction paths bypassed the sulfide stability regions.

Tantalum formed a suboxide in the substrate immediately subjacent to the Ta_2O_5 scale. This phenomenon is usual when tantalum is oxidized in air or pure oxygen. Tantalum has a high oxygen solubility at high temperature, and the suboxide may form either during cooling, or alternatively, it may form at temperature when the oxygen solubility is exceeded. If the latter occurs, the edge of the suboxide zone represents the equilibrium oxygen solubility between the metal and suboxide. The rate of migration of this interface could be used to ascertain the rate of oxygen contamination of the substrate.

Tungsten oxidized in the lava-gas system to form three oxides as stated previously. The oxides formed rapidly and were not adherent to the metal. They offered little, if any, protection. Mixed oxides of tungsten and iron and of tungsten and calcium existed at the outer extremities of the tungsten oxide three-layer scale. The formation of the mixed oxides occurred by reaction of the tungsten oxide (most likely WO_3) and ingredients in the melt, namely, iron and calcium. Their presence had little to do with the overall reaction rate but merely indicate that tungsten oxides are not compatible with the lava.

Niobium also oxidized extensively, and as for tungsten and tantalum, the reaction path bypassed the sulfide region. However, foreign sulfides formed on the exterior of the oxide scale, namely copper sulfide and iron sulfide. The copper sulfide existed as a thin layer covering the oxide, whereas, the iron sulfide was present in a large mound at one particular region on the oxide surface. The mound also contained FeO. Both extraneous sulfides formed from constituents in the lava. It is postulated that a small amount of niobium dissolved in the melt and reduced both copper oxide and iron oxide. The resultant metals then reacted with the sulfur in the gases to form their sulfides which precipitated out on the sample surface. However, two aspects of this hypothesis are puzzling. First, no copper sulfide was observed in any other test. Many of the metals tested would be reducing agents for copper oxide, and at present no explanation exists for the specificity of niobium as the only metal which reduced copper oxide. Second, there is no explanation for the occurrence of the copper sulfide on the oxide surface. It would be reasonable to expect a general formation of the sulfide in the melt. For example, several cases were observed for which iron particles existed in the lava and the particles had been partially sulfidized.

Niobium oxide is unstable in the lava. The oxide reacts with constituents of the lava to form mixed oxides, primarily an oxide of niobium and titanium during the early stages and subsequently one containing other elements such as Al, Si, Ca and Fe.

The extraneous sulfides and reaction of niobium oxide with the lava actually have very little effect on the compatibility of niobium. The oxidation rate, the primary reaction mode, is much too high, and the cracked nature of the scale as well as the formation of suboxides in the metal all mitigate against the use of niobium as a structural metal in magma.

Sulfidation

The gas composition was in the sulfide fields, Fig. 39, of all five metals undergoing extensive sulfidation. From the thermodynamic viewpoint there was no possibility to form protective oxides. Sulfidation represents the worst possible case for two reasons. First, the reaction rates are orders of magnitude greater than oxidation rates. This behavior is directly attributed to the nature of the sulfides, i.e., they are among the most defective structures known. The point defect concentrations are orders of magnitude greater than those in the oxides, and because diffusion rates are directly related to defect concentrations, the sulfides offer virtually no protection as a physical barrier separating the reactants as in the case of oxide scales. Second, and even more deleterious, is the fact that the sulfides generally have low melting points or form low-melting eutectics with the metals. The eutectic temperatures for the three base metals, iron, nickel, and cobalt are listed below.

Eutectic Systems

<u>Binary System</u>	<u>Eutectic Temp., °C</u>
Fe-FeS	988
Ni-Ni ₃ S ₂	637
Co-Co ₄ S ₃	880

No phase diagrams are available for the Rh-S and Pd-S systems, but apparently liquids exist well below the test temperature of 1150°C as can be seen in the microstructures, Fig. 5.

The liquids readily penetrate the metal grain boundaries due to favorable interfacial energies between metal and sulfides. A solid material thus becomes "hot short" as a continuous film of liquid separates the solid grains. The infiltrated metal simply falls apart under its own weight.

The best of the metals undergoing sulfidation was cobalt. Grain boundary penetration was much less than for the other metals, the total penetration being just a fraction of the sample thickness. However, the reaction rate, regardless of

penetration depth, is still much too high to even consider cobalt as a structural material in magma.*

The crystals found in the sulfide-oxide grain-boundary network in iron are believed to be clinopyroxene which is a silicate of the type $(\text{Mg}, \text{Ca}, \text{Fe})_2\text{Si}_2\text{O}_6$. The phase relations in this very complex system are not known, but on the basis of liquid phase relations in a slightly less complex system $\text{FeS-FeO-Fe}_3\text{O}_4\text{-SiO}_2$ [9] it is possible to speculate on the formation of the silicate crystals. Generally, liquid sulfides and liquid silicates form immiscible liquids. Maclean [7] found that the composition of the two liquids in the above quaternary system at an invariant point at 1095°C contained 10 and 57 w/o FeS and 29 and 22 w/o SiO_2 for the silicate and sulfide rich liquids, respectively. Crystallization of the immiscible liquids was stated to result in a eutectic mixture of FeO and FeS plus crystallites which were silicates. It is postulated that the grain boundary liquid was in fact two liquids, which upon solidification gave rise to the structures observed.

The nickel sulfide grain-boundary network also contained a silicate phase as well as an oxide phase. The most likely form of the silicate is olivine, a magnesium silicate, in which iron or nickel can substitute for some of the magnesium. The EDX spectrum showed strong nickel and magnesium peaks, and a possible formula for this phase is $(\text{Mg}, \text{Ni})_2\text{SiO}_4$. The refractory nature of both Ni_2SiO_4 and Mg_2SiO_4 , melting points of 1630°C and 1890°C , respectively, and the fact that these silicates are binary isomorphous suggests that the mixed silicate (olivine) precipitated out from the liquid upon cooling rather than forming by the solidification of immiscible liquids as in the case of iron. The oxide phase containing titanium, iron, manganese and nickel also probably precipitated out. In other words, one liquid existed which was sulfur rich, and the solidification of this liquid resulted in three solid phases.

* Operation of metals at 1150°C in magma is only expected during "fault" or abnormal conditions. A skin of rock protects the metal in normal operation of heat exchange.

Reaction with Lava Constituents

Vanadium, titanium and zirconium all form relatively stable oxides, and according to their stability diagrams, Fig. 40, they should all readily oxidize. However, all three metals formed silicates in addition to oxides which means that the metals or oxides are very reactive towards the silicate melt in addition to the oxygen-bearing gas. In other words, although the gas phase has some bearing on the reaction, the overall reactions are determined to a large extent by the metals' affinities to form silicates.

Titanium and zirconium also have very strong affinities for both oxygen and aluminum. Both oxygen and aluminum are alpha stabilizers and have very high solubilities, particularly oxygen (approximately 30 atom percent). The contamination of the substrate by oxygen results in severe embrittlement which is readily apparent by cracks which extend completely across the samples. The amount of aluminum picked up by the metals is not known, but it is appreciable in order to obtain a two-phase structure in titanium (on the order of at least 8 w/o). Even if these metals were relatively non-reactive, the pickup of oxygen and aluminum would prevent their use in magmas due to the embrittling effect as well as the change in properties.

There are regions in the scales which are oxides and other regions which are silicates. This type of reaction product can be explained as follows. Titanium and zirconium are very strong reducing agents and will initially reduce iron oxides and silica in the lava, resulting in the formation of TiO_2 and ZrO_2 . Some of the reduced iron remains as elemental iron, but the silicon probably reacts with the new oxides formed to produce silicates.

The formation of iron particles in the lava has been attributed previously [5] to a disproportionation between Fe^{+3} and Fe^{+2} to form Fe^0 . It now appears that this explanation is not valid, but rather the iron formation occurs by the reduction of FeO in the melt by those metals which are strong reducing agents--V, Ti, Zr, Cr, Ta and Nb. Thermodynamic calculations

indicate that only these metals of those tested can reduce FeO. Experimental results clearly showed that iron particles formed when these metals corroded; the others did not reduce FeO.

CONCLUSIONS

Molten basalt and/or magmatic volatiles of basaltic lavas are very corrosive to the refractory metals. The metals which appear to be inert, platinum and rhenium are prohibitively expensive and could be used only for instrumentation or lead wires. The best metals which are more reasonable from an economic viewpoint are chromium and molybdenum. Chromium cannot be used as a pure metal because of its inherent brittleness but is perhaps the best element to be used as an alloying addition. The base metals, iron, nickel, and cobalt cannot be used without alloying due to extensive reaction to form liquid sulfides. The addition of chromium and molybdenum to these metals appears promising in order to achieve corrosion resistance. The refractory metals and Group IV elements in the periodic chart all corrode excessively and offer no promise for structural materials.

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TABLE I
MINIMUM PURITY OF VARIOUS METALS

Fe	99.9%
Ni	99.99
Co	99.7
Zr	99.8
Ti	99.6
Cr	99.5
V	99.95
Nb	99.9
Ta	99.9
Mo	99.93
W	99.95
Pt	99.95
Pd	99.9
Rh	99.9
Re	99.9

TABLE II
COMPOSITION OF THOLEIITIC, BASALTIC LAVA, KILAUEA 1971

SiO ₂	50.4%
Al ₂ O ₃	13.9
Fe ₂ O ₃	1.4
FeO	9.9
MgO	7.4
CaO	11.2
Na ₂ O	2.3
K ₂ O	0.5
TiO ₂	2.4
Others	0.6

TABLE III
GAS COMPOSITION USED FOR TESTS

<u>Component</u>	<u>Amount</u>
H ₂ O	1.8%
CO	7.4
CO ₂	64.3
SO ₂	26.5

TABLE IV
FUGACITIES OF VARIOUS SPECIES AFTER EQUILIBRATION
OF SIMULANT GAS AT 1150°C

<u>Component</u>	<u>Fugacity</u>
CO	2.8×10^2
CO ₂	0.567
C	2.01×10^{-24}
COS	4.23×10^{-4}
H ₂	3.80×10^{-4}
H ₂ O	1.73×10^{-2}
H ₂ S	1.71×10^{-4}
O ₂	9.76×10^{-10}
SO ₂	0.218
S ₂	6.96×10^{-3}
S	1.40×10^{-6}
S ₂ O	6.02×10^{-4}
SO	7.26×10^{-4}
HS	1.28×10^{-5}
SO ₃	3.78×10^{-7}
H ₂ SO ₄	5.52×10^{-13}
CS	7.35×10^{-9}
CS ₂	7.11×10^{-8}
CH ₄	9.78×10^{-16}

Fig. 1. Macrographs of Metals Exposed for 24 Hours at 1150°C.

Pt

Re

—
200 μ

Fig. 2. Micrographs of Metals Exhibiting "No" Attack in 96 Hours.

Cr

Mo

200 μ

Fig. 3. Micrographs of Metals Slightly Oxidized in 96 Hours.

W

Nb

Ta

200 μ

Fig. 4. Micrographs of Metals Heavily Oxidized in 24 Hours.

Fe

Co

Ni

Rh

Pd

200 μ

Fig. 5. Micrographs of Metals Heavily Sulfidized in 24 Hours.

Fig. 6. Micrographs of Metals Severely Reacted with Lava Constituents in 96 Hours.

Fig. 7. Surface of Rhenium after 24 hrs. Exposure.

Fig. 8. Effect of Time on Reaction Products Formed on Chromium and Molybdenum.

Fig. 9. Microstructure of Reaction Products on Chromium Exposed 96 hrs.

Cr

V

Zr

Nb

50 μ

Fig. 10. Formation of Iron Particles in Lava during Corrosion of "Strong" Reducing Agent Metals.

Fig. II. Microstructure of Reaction Products Formed on Molybdenum in 96 hrs.

Fig. 12. Reaction Products Formed on Tungsten, 24 hrs. Exposure.

A

B

C

Fig. 13. Details of Tungsten Reaction Products.

A

B

Fig. 14. Reaction Products Formed on Tantalum, 24 hrs. Exposure.

A

B

Fig. 15. Reaction Products Formed on Niobium.

A

B

C

A

B

Fig. 17. Globule Formed in Lava during Corrosion of Niobium.

A

B

C

Fig. 18. Mound Formed on Niobium during Corrosion.

A

B

C

Fig. 19. Reaction Products Formed on Cobalt, 24 hrs. Exposure.

A

20 μ

B

C

Fig. 20. Eutectic Grain Boundary Structure Formed in Iron.

A

B

Fig. 21. Clinopyroxene Precipitates in Sulfide Grain-Boundary Phase in Iron.

A

Sulfide Scale on Nickel

B

Nickel Islands in Sulfide

C

Sulfur X-Ray Map
of B

D

Nickel X-Ray Map
of B

Fig. 22. Reaction Products Formed on Nickel, 24 hrs. Exposure.

A

B

Fig. 23. Precipitates in NiS.

SEM Micrograph

Sulfur X-Ray Map

Fig. 24. Grain Boundary Sulfides Formed in Rhodium.

A

B

C

D

Fig. 25. Corrosion Products on Vanadium. 24 hrs. Exposure.

A

B

C

Fig. 26. Details of Vanadium Corrosion Products.

A

B

C

Fig. 27. Reaction Products Formed on Vanadium.

B

C

Fig. 28. Reaction Products Formed on Titanium.

A

B

C

Fig. 29. Details of Titanium Corrosion Products.

SEM Micrograph

Al X-Ray Map

Fig. 30. Aluminum Pickup in Titanium Substrate.

A

B

C

D

Fig. 31. Sulfides Formed in Titanium, 96 hrs. Exposure.

Fig. 32. Corrosion Products on Zirconium.

Fig. 33. Silicate Layer and Aluminum Pick up in Zirconium.

Pt-S-O

Re-S-O

Fig. 34. Stability Diagrams for Metals Showing "No" Attack.

Cr-S-O

Mo-S-O

Fig. 35. Stability Diagrams for Metals Showing Slight Oxidation.

Fig. 36. Possible Reaction Paths for an Initial "Oxide Former", Chromium Which Yield Different Reaction Products.

Path A

$$a'_s > (a_s)_{eq.}$$

Sulfide Forms Beneath Oxide

Path B

$$a'_s < (a_s)_{eq.}$$

No Sulfide Forms In Metal

Fig. 37. Activity Gradients Across Oxide Scales, Giving Rise to Various Reaction Paths.

W-S-O

Ta-S-O

Nb-S-O

Fig. 38. Stability Diagrams for Metals Showing Heavy Oxidation.

Fig. 39. Stability Diagrams for Metals Showing Sulfidation.

Zr-S-O

Ti-S-O

V-S-O

Fig. 40. Stability Diagrams for Metals Reacting with Lava Constituents.

TABLE A-I
COMPOSITION OF SOME RESTORED VOLCANIC GASES^(6, 7)

	MOLE %							
	H ₂ O	H ₂	CO ₂	CO	SO ₂	S ₂	H ₂ S	HCl
Surtsey (1964)	81.6	2.8	9.5	.7	3.6	.2	.8	.8
Surtsey (1965)	87.7	2.8	5.7	.4	2.5	.1	.5	.4
Surtsey (1967)	92.0	1.7	1.9	.1	3.3	.02	.1	.9
Erta Ale (1971)	69.7	1.6	17.8	.8	8.8	.5	1.0	ND
Erta Ale (1973)	70.8	2.2	18.9	1.4	5.8	.2	.6	ND
Erta Ale (1974)	77.1	1.6	11.7	.5	7.4	.3	.9	.4
Ardoukoba (1979)	77.5	1.7	3.7	.2	14.0	1.2	1.7	ND
Kilauea	37.1	.5	48.9	1.5	11.8	.02	.04	.1
(1918-19)	69.3	1.0	17.8	.6	10.9	.03	.1	.2
Mount Etna(1970)	47.1	.5	22.7	.5	28.7	.3	.2	ND
Nyiragongo (1959, 1972)	44.7	1.4	47.0	2.5	2.2	.6	1.6	ND

Fig. A-1. Oxygen Fugacities as a Function of Temperature for Various Volcanic Gases Reported in Table A-1.

Fig. A-2. Sulfur Fugacities as Function of Temperature for Various Volcanic Gases Reported in Table A-1.

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