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The Effect of Molybdenum Plus Chromium on the Corrosion of Iron-, Nickel, and Cobalt-Base Alloys in Basaltic Lava and Simulated Magmatic Gas at 1150°C

Stephen A. Ehrlich, D. L. Douglass
University of California
Materials Science and Engineering Dept
School of Engineering and Applied Science
Los Angeles, CA 90024

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THE EFFECT OF MOLYBDENUM AND MOLYBDENUM PLUS CHROMIUM ON THE
CORROSION OF IRON-, NICKEL-, AND COBALT-BASE ALLOYS IN
BASALTIC LAVA AND SIMULATED MAGMATIC GAS AT 1150°C

Stephen A. Ehrlich and D. L. Douglass
Materials Science and Engineering Department
School of Engineering and Applied Science
University of California
Los Angeles

Abstract

The compatibility of several binary and ternary alloys in a magma environment was studied. Binary alloys containing molybdenum and ternary alloys containing chromium and molybdenum were exposed to basaltic lava at 1150°C for periods of 24 and 96 hours. A cover gas was used to produce oxygen and sulfur fugacities corresponding to those of the gases dissolved in basaltic melts. Three base metals were used. These included iron, nickel, and cobalt. The primary reactions in binary alloys were found to be sulfidation. Oxide scales with a spinel layer formed on ternary alloys. The synergistic effect of molybdenum and chromium additions in ternary alloys exhibited superior corrosion resistance to binary alloys which formed base-metal sulfides down grain-boundaries. Extensive analyses of the reaction products by scanning electron microscopy, X-ray energy dispersive analysis, electron microprobe analysis, and metallography are presented for each alloy. The products formed are discussed with reference to thermodynamic stability diagrams, and the reaction path concept is used to explain some of the corrosion.

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MAGMA STUDY

1. INTRODUCTION

A program entitled the Magma Energy Research Project was instigated to investigate the feasibility of extracting energy from magma sources. The high temperatures, on the order of 1100°C, and the large mass of the magma bodies represent a vast quantity of high-quality energy. The thermal energy will be obtained by inserting a heat exchanger directly into the magma body and converting the thermal energy to a suitable form (electricity) by conventional methods.

Three major stages are involved in the program. These are:

1. Finding a magma body.
2. Developing the body (drilling into it and emplacing a heat-transfer device sufficiently strong and corrosion resistant to last an appreciable period).
3. Extracting the energy from the body.

Potential corrosion problems were considered and discussed at a Magma Workshop Session⁽¹⁾. Various materials were considered, such as those in a heat exchanger and those to be used for connecting pipe both in and above the magma chamber. These recommendations led to an initial materials compatibility study.

The purpose of this work was to determine the behavior of various alloys based upon previous experimental work. Major factors which will ultimately influence the selection of an alloy are cost and lifetime.

The main problem affecting alloy lifetime is the sulfurous environment. The magma environment has a very high sulfur fugacity, $\approx 10^{-3}$,

which causes extensive sulfidation of most metals. Since both oxygen and sulfur are present it is possible to have sulfidation and/or oxidation reactions. The simulated test gas conditions have been modeled⁽²⁾ to simulate at atmospheric pressure the actual conditions of a magma environment existing at pressures typical of a magma chamber.

Initial experiments used nickel, iron, 310 stainless steel, and Inconel 718 tested in molten lava only⁽³⁾. The alloy surfaces acquired an oxidized appearance, whereas, iron and nickel showed no visible reaction. Simulated magmatic gases were not used. It was later recognized that the more serious threat to long-term compatibility of many metals was posed by the sulfur-containing gases dissolved in magmas.

Preliminary results⁽³⁾ using gases from volcanic vents, which are derived in part from magmatic gases, indicated that pure iron, pure nickel, and ferritic 446 stainless steel are extremely susceptible to attack. Refractory metals such as molybdenum and tungsten, as well as the nickel-base superalloy Udimet 700 acquired a uniform dark corrosion product layer. Corrosion by pitting was observed in the stainless steels, whereas, tantalum and Inconel 718 (nickel-base superalloy) appeared inert. It should be noted that the temperature of the gases from the vents and the sulfur fugacity were much less than those to be encountered in a magma body.

The material compatibility studies were continued and three different environments were recognized. The conditions and environmental problems are shown below:

Magma/Metal Environments⁽⁴⁾

<u>Environment (Location)</u>	<u>Conditions</u>	<u>Problems</u>
1. Near Surface	Low temperature (150°C) oxidizing, H ₂ O rich gas	Oxidation corrosion
2. Hydrothermal Region	Moderate (150°-500°C) temperature, oxidizing, corrosive hydrothermal brines	Oxidation and brine corrosion
3. Magma	High (>1150°C) temperature reducing, high sulfur	Sulfidation, corro- sion, thermal strength degradation, metal dissolution

Note: Studies of material performance in environments 1 and 2 have been part of the development of hydro-geothermal energy sources.

The life of the heat exchanger is designed to be 30 years. During this time the normal temperature operating conditions are controlled not to exceed 500-600°C,* and in the event of an emergency shutdown, the heat exchanger can reach the ambient temperature of the magma of 1150 to 1250°C (during a projected time period of a few hundred hours). The above problems must be considered for a proper material selection for a heat exchanger that will survive a magma environment.

* During operation the extraction of heat will cause a large shell, ~3-4' diameter, to buildup on the heat exchanger which will reduce the wall temperature.

2. BACKGROUND

2.1 Base Metals - Iron, Nickel and Cobalt

The work performed⁽⁵⁾ to date with pure metals and other alloys has shown a wide range of corrosion resistance in the simulated magma environment. Both pure nickel and iron exhibited similar behavior in a magma environment, characterized by complete grain-boundary penetration of the metal by a liquid eutectic of metal and sulfide. In pure nickel, an external sulfide scale was formed, and the grain boundaries contained sulfide and small metallic particles of nickel. The heavy sulfidation seen in nickel was catastrophic. This is because nickel does not form an oxide layer in this environment. In the magma environment, pure iron has shown extensive sulfidation reactions. There was evidence of external sulfide scales and liquid sulfides in the grain boundaries. Eutectic structures of FeS and FeO were also observed in grain boundaries.

The best metal, used as an alloy base for superalloys, exposed to the simulated environment was cobalt. Pure cobalt in a magma environment formed a sulfide layer over the entire metal surface with preferential attack at grain boundaries. Grain boundary penetration was much less for cobalt than for the other metals. The external scale sometimes contained silicon and iron which resulted from reactions with the magma.

2.2 Alloys

Oxide scales would provide some degree of corrosion resistance. One goal of alloying element additions is to form oxides in the low oxygen pressure of the magma environment in order to provide a protective

oxide layer which reduces corrosion rates. Oxides are superior to sulfides as protective barriers to corrosion. This is because sulfidation rates are 10^3 to 10^6 times more rapid than oxidation rates at a given temperature. Another objective of alloying is to overcome a problem more important than rapid reaction rates, e.g., to prevent the formation of low-melting eutectics between the metals and their sulfides.

There are certain trends that have become apparent from additional work on stainless steels (Douglass, 1979)⁽¹⁰⁾:

1. The chromium content of both ferritic and austenitic stainless steels is the most important factor in providing corrosion resistance.
2. The nature and morphology of the corrosion products change with time.
3. There appears to be a difference in the behavior between commercial ferritic stainless steels and high-purity iron-chromium alloys.
4. A synergistic effect of chromium and nickel may exist in the austenitic alloys in providing corrosion resistance.
5. Molybdenum is a potentially good addition for imparting corrosion resistance.

2.3 Molybdenum Additions

Table 1 compares the melting points of some metals and their sulfide eutectic temperatures. Molybdenum additions enable the more stable and higher melting molybdenum sulfide to form, as opposed to the base-metal sulfides.

The addition of molybdenum is beneficial to corrosion resistance at low temperatures. However, in some high-temperature atmospheres molybdenum additions can result in catastrophic attack. This is due to the formation of the low melting, volatile, and non-protective oxide, MoO_3 . In the magma environment the oxygen partial pressure is not high enough to form this volatile oxide, and instead the protective oxide MoO_2 is formed.

2.4 Chromium Additions

Chromium additions to pure metal allow the formation of chromium sulfide in the magma environment which is more stable than the base-metal sulfides. Chromium sulfide has a higher melting point than the base-metal sulfides which penetrate grain boundaries and cause the alloy to disassociate. This is shown in the chromium-sulfur phase diagram in Appendix I.

Another benefit of chromium in alloys is the formation of Cr_2O_3 films when $P_{\text{O}_2} >$ the equilibrium dissociation pressure of Cr_2O_3 . It is the formation of a thin chromium oxide layer on the metal surface that develops resistance to further corrosion. The degree of protectiveness of these films increases with chromium content, but internal sulfidation occurs at long times. Internal sulfidation decreases with increasing chromium content. In addition to providing corrosion resistance, chromium additions are capable of improving certain high-temperature mechanical properties.

2.5 Chromium and Molybdenum Additions

The combination of molybdenum and chromium improves corrosion resistance, although chromium oxide films may become detached and highly

convoluted with increasing time. Internal sulfidation increases as the films become detached. The gas fugacities of the magma system fall within the thermodynamic oxide stability fields of Cr_2O_3 and MoO_2 (shown in the stability diagrams of Figs. 40-43).

3. EXPERIMENTAL PROCEDURES

Binary and ternary alloys were prepared by arc melting in a gettered argon atmosphere to form buttons of approximately 100 grams. Minimum purities of the metals are listed in Table 2. The buttons were remelted several times to insure homogeneity.

The buttons were sliced with a spark cutter into test samples approximately 15x10x1 mm. The samples were abraded through 600-grit silicon carbide paper, washed in acetone, and air dried. The corrosion tests performed employed the same experimental apparatus (Fig. 1) and method reported previously⁽⁵⁾. Briefly, this procedure was as follows.

Test specimens were inserted into a slotted alumina holder which held the sample vertical when placed into an alumina crucible. The alumina crucible had an I.D. of 28 mm and a height of 10 mm.

The samples were completely covered with finely pulverized tholeiitic basaltic lava from the 1971 Kilauea Iki eruption in Hawaii (composition listed in Table 3). Four crucibles per experiment were placed into a furnace at room temperature. After evacuation, the furnace was purged with argon for one hour, brought up to temperature, 1150°C, and the gases were turned on. A quartz tube was constructed for gas flow in the furnace which allowed for complete gas equilibration

to occur before the samples were exposed to the gas. The system schematic is shown in Fig. 1. This was accomplished by passing the gas through the tube to the hot temperature zone, back out to a colder region and then into the system. The gas flow rate was $80 \text{ cm}^3/\text{min}$, and the gas compositions, Table 4, were calculated to give a sulfur fugacity of 7×10^{-3} bar and an oxygen fugacity of 9.8×10^{-10} bar after reaching equilibrium at 1150°C and 1 atmosphere pressure. The fugacities were selected on the basis of extensive calculations by Gerlach⁽²⁾ to simulate gases dissolved in magma bodies at pressures believed to exist in situ. The water vapor was added to the gas mixture by bubbling through H_2O in a water bath. A list of all gaseous species and their fugacities after reaching equilibrium is given in Table 5.

After the desired experimental time, the system was shut down and cooled for 24 hours with argon gas. The crucibles were cut on a slow-speed diamond saw. These sections were mounted in epoxy and prepared for metallographic examination. The reaction products were characterized by optical microscopy, and an X-ray energy dispersive analysis system (EDX) in conjunction with a scanning electron microscope (SEM).

4. RESULTS

4.1 Binary Alloys Containing Molybdenum

4.1.1 Nickel-Molybdenum Alloys

4.1.1.1 Ni-5Mo

Nickel containing five percent molybdenum exhibited extreme sulfidation and disassociation as a result of sulfidation. Fig. 2 illustrates the extensive penetration of grain boundaries and severe intergranular attack after 96 hours.

4.1.1.2 Ni-10Mo

An increase in the molybdenum content to 10 w/o markedly increased the resistance to sulfidation. Fig. 3 shows the reaction product morphology on a sample exposed for 24 hours. Region A is a sulfide scale with slight finger-like, nickel-sulfide penetrations down the grain boundaries. The SEM micrograph and EDX pictures in Fig. 4 show the composition of the alloy and the sulfide scale.

The sulfidation was much more extensive at longer exposure times. A liquid sulfide-metal eutectic had penetrated extensively the grain boundaries (Fig. 5), and the increased reaction time led to appreciable internal sulfidation (Fig. 6).

4.1.1.3 Fe-15Mo

Extensive sulfidation still occurred in the alloy containing 20 w/o molybdenum. Microprobe analysis of a sample exposed for 24 hours (Fig. 7) showed that the alloy matrix, (region 1), contained only nickel and molybdenum, whereas, sulfidation of the alloy was seen in region 2 which also contained liquid nickel-sulfides in the grain boundaries. EDX analysis of needles, (region 3), within the alloy

revealed that they were nickel-sulfide. These needles did not form in grain boundaries. They appear to be a Widmānstätten precipitation of a sulfide within the sulfide scale (Fig. 7a).

This alloy showed a significant amount of nickel-sulfide penetration into the alloy when exposed for 96 hours (Fig. 8). The grain-boundary network in nickel exhibited a silicate phase as well as an oxide phase which contained some magnesium. 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 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. An oxide phase containing nickel also probably precipitated out. In other words, one liquid existed at temperature which was sulfur-rich, and the solidification of this liquid resulted in three solid phases⁽⁵⁾.

4.1.2 Iron-Molybdenum Alloys

4.1.2.1 Fe-5Mo

The addition of 5 w/o molybdenum to iron had little beneficial effect on corrosion resistance. An example of a sample tested for a short exposure time, e.g., 24 hours, is shown in Fig. 9. An external sulfide film formed (region A), grain boundary sulfides formed (region B), and internal sulfidation took place (region C). This figure also illustrates the large iron-sulfides in the grain boundaries.

This sample was tested further for 96 hours and disassociated sulfidation in the grain boundaries. The sulfide scale, iron-sulfides in the grain boundaries, and the alloy are shown in Fig. 10. Fig. 11 is an SEM micrograph with EDX analyses of selected areas.

4.1.2.2 Fe-10Mo

An increase in the molybdenum concentration to 10 w/o did not show a beneficial effect. Significant amounts of sulfidation and grain-boundary penetration occurred at short exposure. Fig. 12 shows a sample exposed for 24 hours containing metallic particles from the alloy in the magma (region A), and sulfidation in the alloy (region B). Another area of the same sample is shown in Fig. 13 illustrating cracking of the alloy and internal sulfides. This cracking probably occurred during alloy cutting and polishing after the experiment.

The longer exposure time of 96 hours caused extensive grain boundary penetration as shown in Fig. 14. Massive iron-sulfides were present in the alloy and are shown in Fig. 15. The amount of internal sulfide precipitation was not extensive, but in this alloy the

eutectic structures formed in the matrix of the alloy and along grain boundaries.

4.1.2.3 Fe-15Mo

The presence of 15 w/o Mo significantly improved corrosion resistance. The sample exposed for 24 hours did not exhibit extreme grain-boundary penetration as seen in previous iron alloys containing lower molybdenum concentrations. Sulfidation of this alloy and a cracked iron-sulfide scale are shown in Fig. 16. Cracking of the external scale was again observed which most likely occurred during metallographic preparation. This did not happen during the test run because the high temperature is so close to the sulfide melting point which yields a more plastic scale not conducive to cracking.

The cracked external scale was present in samples exposed for 96 hours, but with reduced amounts of internal sulfidation and less iron-sulfide formation in grain boundaries. The eutectic phases previously seen in iron base alloys with less molybdenum were not observed in Fe-15Mo.

4.1.3 Cobalt-Molybdenum Alloys

4.1.3.1 Co-5Mo

The addition of 5 w/o molybdenum to pure cobalt resulted in better corrosion resistance than iron or nickel containing much larger amounts of molybdenum. Microprobe analysis of samples exposed for 24 and 96 hours revealed an external sulfide scale containing cobalt-sulfide, iron-sulfide,^{*} and molybdenum-sulfide. A sample tested for 24 hours and analyzed with a microprobe is shown in Fig. 17. The alloy matrix in region 1 consisted of cobalt and molybdenum. There were several phases present in the external scale illustrated by light and dark shaded regions. The predominant lighter grey area (region 2) was cobalt-sulfide, and the darker grey area (region 3) was identified as cobalt-iron sulfide and some MoO_2 . The compositions of the alloy and scale are shown in the SEM micrograph with EDX in Fig. 18. The aluminum peak is due to trace amounts of polish remaining on the sample.

Microprobe analyses were performed on samples having longer exposure time (greater scale thickness). An example is shown in Fig. 19. The alloy substrate, (region 1), contained Co and Mo, and the thick external scale consisted of a light grey area, (region 2), which had a very high sulfur and cobalt content with no traces of molybdenum. The dark grey areas, (region 3), in the external scale contained Mo, Fe, and some sulfur.

4.1.3.2 Co-10Mo

The corrosion products formed on Co-10Mo were the same as those

^{*} FeO in the lava is reduced by Mo to metallic iron which subsequently sulphidizes on the alloy surface.

formed on Co-5Mo, but the nature of the scales was somewhat different for the two alloys. The scale on Co-10Mo was heterogeneous, ranging from very thin in some regions to very thick in other regions. Cracking of the scales occurred on Co-10Mo, but it is not certain if the cracks occurred during exposure or during sample preparation for metallography. The scale on Co-10Mo had a larger grain size than that on the Co-5Mo alloy. An example of the scale is shown in Fig. 20. Both cobalt sulfide and iron sulfide existed.

4.1.3.3 Co-15Mo

This alloy, containing the highest molybdenum content (15 w/o), formed the thinnest cobalt-sulfide external scale of all cobalt alloys tested. The outer sulfide layer contained the same phases observed in the other cobalt-molybdenum alloys. Microprobe analysis was performed on the external scale of a sample exposed for 24 hours (Fig. 21). The phases present in the scale included a light grey area, region 2, consisting of cobalt-sulfide with some iron, and dark grey sections, region 3, of a eutectic structure of cobalt-sulfide penetration in the alloy, and region 4 is the alloy matrix. SEM micrograph and EDX analysis in Fig. 22 show sulfide penetration in the alloy.

The sample exposed for longer times had a thin external scale containing second phase particles which were sulfides (Figs. 23-24), identified to be MoS, CoS, and Fe. The amount of internal sulfidation in these samples was low. This alloy exhibited the best corrosion resistance of all the binary molybdenum alloys tested.

4.2 Ternary Alloys Containing Molybdenum and Chromium

4.2.1 Nickel-Base Alloys

4.2.1.1 Ni-20Cr-10Mo

Nickel alloys containing both molybdenum and chromium had much better corrosion resistance than Ni-Mo binary alloys. A sample of Ni-20Cr-10Mo exposed for 24 hours (Fig. 25) formed a non-uniform scale structure. The external scale consisted of a thin, outer iron-chromium spinel (25a), and an inner oxide layer (25b). Neither scale was continuous, and there was no sulfide layer present. In the discontinuous regions of the scale, there were stray particles from the spinel present in the magma, (25c). Internal sulfidation, (25d), and grain-boundary penetration by the liquid base-metal sulfide (25e), also occurred.

When exposed for 96 hours, the alloy formed an external scale consisting of a thick oxide scale with a thin outer spinel layer. This is shown in Fig. 26. The oxide scale thickness (26b) is thicker for longer times as expected. The spinel structure is shown in region 26a and stray particles from this layer were observed in the magma as for the shorter times. The highly porous scale permitted for inward sulfur diffusion which resulted in some internal sulfidation, 26c. Eutectic structures and nickel-sulfides observed in this alloy were similar to those present in binary nickel alloys. Fig. 27 shows a SEM micrograph and EDX analyses of the scale. This micrograph showed that spinel formation occurred by the reaction of the Cr_2O_3 scale with FeO in the magma.

4.2.2 Iron Base Alloys

4.2.2.1 Fe-20Cr-10Mo

This alloy exhibited the same poor corrosion behavior as the binary iron alloys. The ternary iron alloys exhibited the poorest corrosion resistance of all three ternary alloys tested.

A discontinuous oxide layer formed at short exposure times. There was no evidence of a sulfide layer. The grain-boundary penetration by liquid base-metal sulfides and internal sulfidation are shown in Fig. 28.

The samples that were tested for 96 hours (Fig. 29) consisted of a similar external scale, but the oxide layer (29c) was thicker. The regions where the scale was detached gave rise to extensive grain-boundary penetration (29b) of sulfides into the grain boundaries. The spinel structure on the exterior of the Cr_2O_3 scale is shown in region 29a. The spinel layer forms later and is irrelevant to the mechanism.

SEM micrographs and EDX analysis of this alloy and scale are shown in Fig. 30. These illustrate the base-metal sulfides along grain boundaries as well as chromium and iron in the oxide layer which react together at longer times to form spinel structures.

4.2.3 Cobalt Base Alloys

4.2.3.1 Co-20Cr-10Mo

The external scale observed on this alloy when exposed for 24 hours consisted of a continuous but detached and convoluted oxide layer without a sulfide layer (Fig. 31). The thickness of the external scale for this exposure time was the same as for the iron and nickel base ternary alloys, but this alloy was the only one to form convoluted scales.

A longer exposure (96 hours) increased the oxide thickness as expected. The oxide (32a) formed on the ternary cobalt alloy was thicker than the oxides formed on either the ternary iron or ternary nickel alloys. The spinel layer (32b) was also thicker. The external scale was detached from the alloy, but these oxide scales did not exhibit the severe convolutions noted in the 24 hour test. Internal sulfide precipitates were also observed for this sample (32c).

The dark black regions in Fig. 32 are voids. Large areas of the Cr_2O_3 layer consisted of iron in solid solution or chromium-iron spinels of FeCr_2O_4 .

Iron precipitates were present in the magma adjacent to reaction products for only the longer exposure times. Iron forms in the melt by the reduction of FeO by chromium. An SEM micrograph and EDX analyses (Fig. 33) show the alloy and external scale compositions.

5. DISCUSSION

The results of alloy corrosion indicate the same compatibility problems exist in basaltic magma as were observed in previous work⁽⁵⁾ on pure metals. The reactions between alloys and magmatic gases were sulfidation and oxidation reactions. The type of reaction depends upon the relative stabilities of the sulfides and oxides in the alloy. The reactions being considered are only between the alloy and dissolved gases in the magma.

Using available free energies of formation, one can construct thermodynamic phase-stability diagrams to show areas in which a given compound is stable for a range of gas fugacities at a specified temperature. These diagrams are useful in predicting the reaction products, but in many cases the diagrams are inadequate. This may be due to two factors: (1) one concerning thermodynamics and (2) the other involving kinetics. The thermodynamic aspect takes into account whether the reaction is energetically favorable, and the kinetics factors consider how fast the reaction will occur. The kinetics factors often prevent the achievement of equilibrium, giving rise to different product phases than those predicted in stability diagrams. Thus, the stability diagrams may suggest oxidation when sulfidation actually occurs or vice versa.

5.1 Binary Molybdenum Alloys

Molybdenum was added to pure metals with the intent to form a protective sulfide layer. Sulfides are inherently non-protective, but the formation of a continuous molybdenum sulfide layer would represent a much more protective sulfide compared to the base-metal sulfides. The results have shown discontinuous sulfide scales containing both alloying addition and base metal.

The stability diagrams^{*} for the various binary alloys (Figs. 34-36) containing molybdenum indicated that the gas composition fell within stable fields for MoO_2 and the base-metal sulfides. However, the results reported for these alloys described the presence of base-metal sulfides, an oxide scale that was not continuous (even though thermodynamic stability diagrams suggested oxide stability), and the presence of subscales that consisted of porous mixtures of sulfides, oxides, and a molybdenum-depleted matrix.

The mechanism explaining these results is similar to the one proposed by Tiearney and Natesan⁽⁶⁾. Initially, the oxide and base-metal sulfide compete for surface sites, and the matrix is depleted of molybdenum as MoO_2 forms. The base-metal sulfides overgrow and then cover the oxide. This coverage occurs rapidly for two reasons. The first cause is due to the liquid base-metal sulfides, the phase equilibria being shown in the respective binary phase diagrams in Figs. 37-39. The second cause is because sulfides are more defective

^{*}The construction of superimposed stability diagrams using the activities of pure elements rather than using activities of components in the alloys does not change the diagrams significantly.

than oxides and have higher diffusivities. The base-metal sulfide scale grows by outward cation diffusion.

This mechanism is consistent with observed scale morphologies. These consisted of an outer, base-metal sulfide layer over an inner mixed sulfide layer containing molybdenum sulfide precipitates, and a porous sulfide-oxide subscale.

The main reactions occurring in the binary alloys are initial oxide and sulfide formation, rapid growth of base-metal sulfides, and subsequent reaction of molybdenum to form molybdenum-sulfides.

5.1.1 Ni-Mo Alloys

The catastrophic attack of nickel by sulfur at high temperatures is due to the existence of a Ni/Ni_{3-x}S₂ eutectic at 635°C. This is shown in the nickel-sulfur phase diagram (Fig. 37) which also reveals the wide range over which the solid sulfide phases exist. This gives rise to scales with high self diffusivities and poor protective characteristics.

Pure nickel with up to 20 w/o addition of molybdenum did not lead to a continuous layer of molybdenum sulfide, nor did it suppress internal sulfidation. Alloys consisting of Ni-5Mo were extensively sulfidized and fell apart. A significant improvement was observed in Ni-10Mo where the higher molybdenum content prevented alloy disassociation, but liquid nickel sulfides formed within the sulfide field.

5.1.2 Fe-Mo Alloys

Liquid sulfides formed on the alloy surface and in grain boundaries due to an iron-sulfur eutectic at 988°C. Increasing additions of molybdenum did not significantly reduce alloy sulfidation. This is a result of the rapid formation of the eutectic. Internal molybdenum-sulfide precipitates and FeS scale were predominant even though thermodynamics indicate stability for both FeS and MoO₂.

The crystals found in the sulfide-oxide grain-boundary network in iron are believed to be clinopyroxene which is a silicate of the type (Mg,Ca,Fe)₂ Si₂O₆. 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 FeS-FeO-Fe₃O₄-SiO₂, 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 2 w/o SiO₂ 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⁽⁵⁾.

5.1.3 Co-Mo Alloys

The thermodynamic stability diagrams indicate the stable phases should be CoS and MoO₂. Therefore, increasing amounts of molybdenum to cobalt progressively increased corrosion resistance. This is

possibly due to the preferential sulfidation of molybdenum to form a mixed scale of MoS_2 in a CoS mixture, which slows the diffusion rate of the reactive species in the scale. This type of scale morphology was observed by microprobe analysis in all of the Co-Mo binary alloys.

5.2 Ternary Alloys - Molybdenum and Chromium Additions

The corrosion-product morphologies of alloys containing only molybdenum differed significantly from alloys containing both molybdenum and chromium. Chromium was added to alloys in combination with molybdenum to investigate the potential synergistic effect. According to the thermodynamic stability diagrams one would expect formation of a continuous protective oxide scale and stable sulfide layer. The corrosion products consisted of discontinuous scales of Cr_2O_3 with outer spinel structures, and base-metal sulfides underneath. This is basically in agreement with the stability diagram.

Thermodynamic stability diagrams of these ternary alloys (Figs. 40-42) predicted formation of the base-metal sulfide, Cr_2O_3 , and MoO_2 . The stable oxide formed first as in the binary alloys. In this case, Cr_2O_3 was formed because it is more stable than MoO_2 . This initial oxide formation creates an activity gradient. The corrosion behavior of an alloy depends upon the reaction path which in turn depends upon the variation of activities at the oxide/sulfide interface. The activities of both sulfur and oxygen decrease from the gas phase to the oxide/sulfide interface. The activity levels at the interface will determine the reaction path that is followed.

Fig. 43 illustrates a schematic reaction path for the ternary alloys. After the initial oxide formation, the base-metal sulfide

forms underneath the oxide. This occurs after formation of Cr_2O_3 depletes the matrix of chromium and establishes an activity gradient. The base-metal sulfide forms, because the actual activity of sulfur at the scale alloy interface is above the equilibrium sulfur activity for sulfide formation. The rates of formation are influenced by kinetics and diffusivity of the base-metal in the scale. As previously stated the goal of alloying additions is to avoid formation of the liquid base-metal sulfides and form the more stable molybdenum or chromium-sulfides. The thermodynamic reasoning for this behavior is illustrated in the equations and diagrams in Fig. 44. These equations show how the alloying addition lowers the equilibrium sulfur pressure for the stable sulfide to form. This phenomena has been explained by Petit⁽⁸⁾ in the area of two simultaneous oxidants. He has shown that if the activity of the second oxidant (in this case sulfur) in the gas phase exceeds that required for the reaction with the alloy in the absence of oxygen and if it can penetrate the oxide scale, then the reaction between sulfur and the alloy scale will occur. The amount of second oxidant (sulfur) reactions increases as oxidation continues because of continued transport of sulfur through the oxide scale and displacement reactions.

Thermodynamic and kinetics reasoning can be used to explain more specific external scale structures observed. Scale morphologies studies by Wood and Stott⁽⁹⁾ concluded that more uniform and compact scale structures will form on alloys containing Ni-20Cr-10Mo and Fe-20Cr-10Mo than on alloys of Co-20Cr-10Mo. Wood's study also determined that the outward diffusion of chromium via a vacancy

mechanism determines the thickness and uniformity of the scale. The alloying additions of molybdenum and chromium provided for the formation of more stable sulfides which possessed lower diffusivities for the cations. This resulted in different morphologies depending upon the base-metal.

5.2.1 Ni-20Cr-10Mo

The spinel structure thicknesses for nickel-base ternary alloys exposed for 24 and 96 hours were almost equal, but as expected the oxide layer was significantly thicker after 96 hours. The oxide scale was not compact and sulfur was able to diffuse through the scale to form internal sulfides in the alloy. A sulfide layer was not present underneath the oxide. There was evidence of metallic particles in the oxide which were a result of displacement reactions.

5.2.2 Fe-20Cr-10Mo

The oxide layer was detached from the alloy which slowed outward cation diffusion into the scale. The porous and discontinuous oxide layer allowed for inward sulfur diffusion and there was evidence of sulfide grain-boundary penetration and base-metal sulfides.

5.2.3 Co-20Cr-10Mo

This alloy was the only one to form convoluted external scales of Cr_2O_3 . These scales were inconsistent in nature because they did not always form extensive convoluted structures. Convoluted scales may be a result of lateral growth within the scale. Lateral growth results from the formation of oxide within the existing oxide layer by a reaction between the oxygen diffusion inward down the oxide grain

boundaries and chromium diffusing outward through the bulk of the oxide. As the scale grows laterally, it detaches from the alloy and forms convolutions to accommodate scale growth. Another possibility for the formation of these scale structures may be explained by Wood's⁽⁹⁾ study which revealed the non-compact scale of cobalt base alloys as compared to iron and nickel. This effects cation diffusion for scale formation.

The oxide layer was significantly thicker after 96 hours as expected. The spinel structure attached to this oxide layer was the thickest of all three ternary alloys. Additionally, the voids and cracks within the oxide layer allowed for inward sulfur diffusion and internal sulfidation was observed.

6. CONCLUSIONS

The corrosive effect of molten basalt and/or magmatic volatiles of basaltic lavas was studied in alloy systems. The alloys which provided the highest degree of corrosion resistance were ternary alloys containing molybdenum and chromium. The result of these alloying additions was a transition from the deleterious effects of internal sulfidation to formation of a protective chromium-oxide external scale. The more stable molybdenum and chromium sulfides also formed.

The binary alloys containing molybdenum did not exhibit adequate corrosion resistance due to extensive sulfidation reactions and the formation of liquid base-metal sulfides. Alloys containing a high-enough molybdenum content (10-15 w/o for iron and nickel base alloys and 5-10 w/o for cobalt base alloys) formed a more stable MoS_2 and corroded less.

These conclusions suggest that further research with superalloys containing reactive metals such as chromium, aluminum, molybdenum titanium, yttrium, and other metals would provide valuable information on high temperature corrosion resistant materials.

TABLE 1
Some Metal and Metal-Sulfide Eutectic Melting Points

	Metal Melting Point		Metal-Sulfide Eutectic Temperature	
	F	C	F	C
Co	2723	1495	1610	877
Cr	3362	1850	2462	1350
Fe	2802	1539	1805	985
Mn	1079	1136	2264	1240
Ni	2651	1455	1194	645
Mo	4739	2615		

TABLE 2
Minimum Purity of Various Metals

Fe	99.9 %
Ni	99.99
Co	99.7
Mo	99.93
Cr	99.5

TABLE 3
Composition of Tholeiitic, Basaltic Lava, Kilauea 1971

SiO_2	50.4%
Al_2O_3	13.9
Fe_2O_3	1.4
FeO	9.9
MgO	7.4
CaO	11.2
Na_2O	2.3
K_2O	0.5
TiO_2	2.4
Others	0.6

TABLE 4
Gas Composition Used for Tests

Component	Amount
H_2O	1.8%
CO	7.4
CO_2	64.3
SO_2	26.5

TABLE 5
Fugacities of Various Species After Equilibration
of Simulant Gas at 1150°C

Component	Fugacity
CO	0.28
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. System Schematic

Fig. 2. Grain boundary penetration and sulfidation of Ni-5Mo after 96 hours.

Fig. 3. Sulfidation of Ni-10Mo after 24 hour exposure.

Fig. 4. SEM micrograph and EDX spectra Ni-10Mo alloy exposed for 24 hours.

1. Alloy
2. Sulfide scale

Fig. 5. Sulfidation of Ni-10Mo after 96 hours exposure.

Fig. 6. Extensive internal sulfidation of Ni-10Mo after 96 hours.

Fig. 7. Widmanstätten type precipitation of a sulfide within the sulfide scale in Ni-20Mo alloy tested for 24 hours.

Fig. 7a. EDX analysis of Widmanstätten type precipitate.

Fig. 8. Ni-20Mo exposed for 96 hours.

Fig. 9. Sulfidation of Fe-5Mo tested for 24 hours.

Fig. 10. Grain boundary penetration in Fe-5Mo tested for 96 hours.

Fig. 11. SEM micrograph and EDX spectra of Fe-5Mo after a 96 hour test.

1. Sulfide scale
2. Alloy matrix

Fig. 12. Corrosion of an Fe-10Mo exposed for 24 hours.

Fig. 13. Fe-10Mo cracking and penetration after 24 hours.

Fig. 14. Grain boundary penetration in Fe-10Mo after 96 hour exposure.

Fig. 15. Sulfides within Fe-10Mo tested for 96 hours.

Fig. 16. Fe-15Mo with scale cracking after 24 hour exposure.

Fig. 17. Structure of scale formed on Co-5Mo during 24 hour exposure.

- .1 Alloy matrix, Co-Mo
- .2 Sulfide scale, Co-S
- .3 Precipitate particle, Co-S, Fe-S, Mo-S

Fig. 18. SEM micrograph and EDX spectra of Co-5Mo after 24 hour exposure.

1. Alloy
2. Sulfide scale

Fig. 19. Structure of scale formed on Co-5Mo after 96 hour exposure.

- .1 Alloy Co-Mo
- .2 Co-S
- .3 Mo, Fe, S

Fig. 20. Sulfide scale of Co-10Mo after 24 hour test.

Fig. 21. Scale structure on Co-15Mo after 24 hour exposure.

- .1 Alloy substrate Co-Mo
- .2 Scale precipitate, Co-S, Mo-S
- .3 Sulfide scale, Co-S, Fe
- .4 Co, Fe

Fig. 22. SEM micrograph of sulfide penetration into Co-15Mo alloy.

.1 Alloy Matrix

Fig. 23. Scale structure of Co-15Mo after 96 hour exposure.

Fig. 24. Co-15Mo scale structure after 96 hour exposure.

Fig. 25. Ni-20Cr-10Mo after 24 hour exposure.

Fig. 26. Ni-20Cr-10Mo scale structure and internal precipitates after 96 hour exposure time.

Fig. 27. SEM micrograph and EDX analysis of scale and alloy of Ni-20Cr-10Mo after 96 hour exposure (continued on following page).

Fig. 27. (continued)

1. Oxide particle
2. Metallic fragment
3. Spinel
4. Alloy

Fig. 28. Fe-20Cr-10Mo after 24 hour exposure.

Fig. 29. Grain-boundary penetration in Fe-20Cr-10Mo after 96 hours.

Fig. 30. Internal sulfidation at Fe-20Cr-10Mo and external scale after 96 hour test.

Fig. 30. (continued)

1. Alloy
2. CrS/FeS in grain boundary
3. Cr_2O_3 layer
4. Oxide/spinel structure
5. Magma

Fig. 31. Convoluted scale of Co-20Cr-10Mo after 24 hour test.

Fig. 32. Scale structure of Co-20Cr-10Mo after 96 hours.

Fig. 33. SEM micrograph at Co-20Cr-10Mo after 96 hours (continues on following page).

Ca Fe Fe

Mo Cr Fe Fe
Cr

Cr Fe
Cr

S_{AU} Cr Fe

Mo Cr Co
Fe Co

Fig. 33. (continued)

1. Particle in the magma
2. Outer spinel structure
3. Cr_2O_3 layer
4. Sulfide
5. Alloy matrix

Ni-S-O
Mo-S-O

Fig. 34. Ni-Mo Stability Diagram

Fe-S-O
Mo-S-O

Fig. 35. Fe-Mo Stability Diagram

Co-S-O
Mo-S-O

Fig. 36. Co-Mo Stability Diagram

Fig. 37. Nickel-Sulfur Phase Diagram
(ref. Hansen)

Fig. 38. Iron-Sulfur Phase Diagram
(ref. Hansen)

Fig. 39. Cobalt-Sulfur Phase Diagram
(ref. Hansen)

Cr-S-O
 Ni-S-O
 Mo-S-O

Fig. 40. Ni-Cr-Mo Stability Diagram

Cr-S-O
 Fe-S-O
 Mo-S-O

Fig. 41. Fe-Cr-Mo Stability Diagram

Cr-S-O
 Co-S-O
 Mo-S-O

Fig. 42. Co-Cr-Mo Stability Diagram

Fig. 43. Schematic reaction path for ternary alloy corrosion.

Activities at the Alloy/Oxide Interface

$$a_O' = [\exp(\Delta G_{AO}^0/RT)]/a_A'$$

$$a_S' = [\exp(\Delta G_{AS}^0/RT)]/a_A'$$

$a_S' > (a_S)_{eq}$ because of A depletion by AO formation

$a_S < a_S'$ no formation of AS, but AS may form further inside it $a_S' > a_S^0$

where A = Mo or Cr
B = Fe, Ni, Co

Fig. 44. Schematic representation showing the decrease in oxygen activity over the surface of an alloy by the formation of a protective layer of AO on the alloy surface.

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APPENDIX I

Phase Diagrams^{*}

Chromium-Sulfur
Chromium-Nickel
Chromium-Iron
Cobalt-Chromium

^{*}Hansen, M., Constitution of Binary Alloys, second edition, McGraw-Hill (1958).

A-1. Chromium-Sulfur Phase Diagram

A-2. Chromium-Nickel Phase Diagram

A-3. Chromium-Iron Phase Diagram

A-4. Cobalt-Chromium Phase Diagram

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Los Alamos, NM 87546
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Reykjavik, Iceland

Texas A&M University (2)
Center for Tectonophysics
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G. Eaton

US Geological Survey
Box 25046
Denver Federal Center
Denver, CO 80225
Attn: F. Frischknecht, MS 964

University of Hawaii at Manoa
Hawaiian Inst of Geophysics
Honolulu, HI 96822
Attn: A. S. Furumoto

University of Hawaii
Hawaii Inst of Geophysics
Honolulu, HI 96822
Attn: C. Helsley, Head

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Providence, RI 02912
Attn: J. F. Hermance

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Oak Ridge, TN 37830
Attn: W. L. Marshall

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Earthquake Research Inst.
University of Tokyo
Hongo
Tokyo 113, Japan

Hans-Ulrich Schmincke
Rohr-Universitat Bochum
Institut fur Mineralogie
D-463 Bochum Postfach 102148
West Germany

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Earthquake Research Institute
University of Tokyo
Bunkyo-ku
Tokyo 113, Japan

University of Minnesota
Inst of Technology
107 Linda Hall
207 Church St, SE
Minneapolis, MN 55455
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Dartmouth College
Hanover, NJ 03755
Attn: R. E. Stoiber

Superintendent
Hawaii Volcanoes National Park
Hawaii 96718

Captain William J. Barattino, P.E.,
USAF

Department of Energy
Albuquerque Operations Office
P. O. Box 5400
Albuquerque, NM 87185

Thomas A. Ladd
Geothermal Program Manager
Department of Energy
200 Stovall Street
Alexandria, VA 22332

University of Hawaii
Hawaii Geothermal Project
240 Holmes Hall
2540 Dole St
Honolulu, HI 96822
Attn: P. C. Yuen

Dr. Richard Taschek
2035 47th St
Los Alamos, NM 87544

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Materials Science and
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School of Engineering and
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