PROTECTION OF REFRACTORY METALS AGAINST ATMOSPHERIC ENVIRONMENTS

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Introduction

Materials with various special capabilities at very high temperatures is presently one of the main concerns of the materials engineer. The refractory metals, molybdenum, columbium, tantalum, and tungsten, are prime candidates for several applications in hypersonic flight and re-entry vehicles. In such structural uses these metals may be subjected to a variety of total environments such as different temperatures, heat fluxes, dynamic pressures, and mechanical loads. However, one factor of all potential structural environments can be generalized—a refractory metal will be exposed to air at elevated temperatures.

If the so-called "refractory" metals were truly refractory such a condition would not pose a serious problem. Unfortunately the refractory metals' behavior has been more nearly that attributed to chemically reactive metals, i.e., refractory only in a mechanical sense, by retaining relatively high strength at elevated temperatures. At high temperatures, especially temperatures above 2000°F, all four refractory metals suffer from the highly undesirable property of reaction with atmospheric gases. Although, serious variations in mechanical properties can result from reactions of these metals with nitrogen and hydrogen, the extremely rapid, frequently disastrous, reactions of the refractory metals with oxygen represent the most serious problem. Indeed the problem of preventing oxidations of the refractory metals at the very temperatures of their potential use probably represents the greatest remaining deterrent to their utilization as structural materials.

Oxidation

The severity of the problem of oxidation of the refractory metals cannot be overstated. Data accumulated by numerous investigators confirm the extreme rapidity with which each of the four metals reacts with oxygen. Tremendous amounts of information have been generated in efforts to characterize the oxidation of various alloys of the refractory metals, most of which have been experimental alloys formulated in attempts to develop oxidation-resistant compositions. Despite these widespread efforts very little understanding of the true nature of the oxidation reactions which occur has been achieved beyond phenomenological explanations, i.e., the kinetics and mechanisms of oxidation of the refractory metals have not been satisfactorily described. A more complete understanding and consistency in oxidation theories would be helpful in defining the problems so that adequate protection of the these metals from deterioration in oxygen atmospheres may be achieved.

Since the actual oxidation of the refractory metals cannot then be discussed in any detail, a brief review of the characteristics of reaction is pertinent to illustrating the depth of the problem.

The oxidation kinetics of any metal are usually expressed mathematically through one of several relationships according to the time dependent nature of the reaction. The relationships most commonly referred to are logarithmic (or inverse logarithmic), cubic,

parabolic, and linear equations wherein either film thickness or weight change is expressed as the corresponding function of time, e.g.:

$$w = k \log t - C \tag{1}$$

$$1/w = A - B \log t \tag{1a}$$

$$w^3 = k_c t \tag{2}$$

$$w^2 = k_p t \tag{3}$$

$$w = k_l t \tag{4}$$

where w represents either film thickness or specific weight
change (weight per unit area); k is a rate constant; A, B, and
C are constants; and t is time.

The logarithmic relationships describe thin film growth, cubic equation empirically describe growth of some thicker films, and the parabolic relation expresses growth of adherent protective thick films (scale) where reaction rate is probably controlled by ionic diffusion, as proposed by the classical Wagner-Hauffe principle. Linear (also accelerated or a symptotic) oxidation rates occur when reaction products are porous, nonadherent, molten, or volatile; these situations usually pertain to the refractory metals at these temperatures of greatest interest.

The progress of oxidation with time for each of the four metals under review has been frequently investigated, most commonly by measuring weight increases in oxygen or air at various temperatures. The agreement between investigators on the time laws in effect for each metal is as quite consistent, i.e., the shape of the curve of weight gain vs time plots is quite reproducible. Results are summarized cryptographically as follows:

	500°F	900°F	1200°F	1600°F	2000°F	2300°F
Mo	PAR	PAR-LIN		LIN		
W	PAR			PAR-LIN		LIN
Ta	LOG	PAR	PAR-LIN	LIN	ACCEL	
Cb	LOG	PAR	PAR-LIN	LIN	ACCEL	

where log is the logarithmic reaction rate; par, the parabolic reaction rate; par-lin, parabolic with transition to linear rate; lin, linear reaction rate; and accel, the accelerated or a symptotic reaction rate. Oxidation of the refractory metals can be generally described as being parabolic at low temperatures, progressing to an initially parabolic with transition to linear reaction rate at intermediate temperatures, and subsequently becoming linear at higher temperatures (ranging from 1000°F for Cb and Ta to 2200°F for W). Some quantitative idea of the magnitude of the oxidation reactions of the refractory metals is presented in representative curves for oxidation of the four refractory metals (figures 1 and 2).

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Figure 2 shows oxidation rates as a function of temperature over the temperature range from 1000°F to 2000°F. Higher temperature data is quite meager and difficult to correlate. Data has been obtained under such widely variant conditions of time, temperature, atmosphere (air or oxygen), and pressure (both total and oxygen pressures) as to make a plot such as this at best only approximate. These curves represent average data from three different investigators at the indicated temperatures in atmospheric pressure air, with times of 0 to 16 hours for Ta and Cb and 0 to 20 minutes for tungsten used to establish the reported rates. Oxidation of chromium at 2000°F under similar test conditions is shown as a point of reference. Molybdenum could not be shown here since the evaporation of MoO_3 at temperatures above about 1200°F renders such weight gain data useless; the oxidation becomes so rapid that virtually no data exists relative to oxidation rate of pure Mo above 1000°F. Tungsten is similarly difficult to characterize at still higher temperatures (above 2000°F).

Figure 2 compares the oxidation of the four refractory metals at 2000°F in terms of displacement of the metal-air interface at various reaction times. Such a plot serves to illustrate in a practical sense the effect of oxidation in removal of metal from an unprotected substrate. Material losses are potentially disastrous after relatively short times at even a comparatively low temperature, i.e., low compared to contemplated utilization temperatures for refractory metals. For example, we can visualize from this plot that a half-inch molybdenum rod would be completely consumed by oxidation after about six hours at.2000°F. The necessity for providing some means of averting such catastrophic behavior is evident.

Contamination

In the discussion of oxidation behavior of the refractory metals, an additional consideration asserts itself. From the oxidation rate curves shown it would seem reasonable to conclude that oxidation of molybdenum or tungsten, being so rapid as to be best described as catastrophic, poses a more serious problem than that of columbium and tantalum. Such is not the case, however, since this supposition overlooks a critical characteristic of the latter metals. Columbium especially, and to a lesser extent tantalum, exhibit great susceptibility to subsurface embrittlement due to high solubility and diffusion of oxygen. This phenomenon known as contamination occurs inevitably upon exposure of columbium to oxygen, even at fairly low temperature, and constitutes the first step of the gross oxidation reaction. The importance of this behavior lies in its deleterious effect on metal mechanical properties, combined with the fact that depth of contamination and accompanying embrittlement may easily exceed metal loss by surface secession. Upon any significant degree of oxygen contamination (and parts per million may be significant), the base metal is drastically changed in properties——increasing in hardness, losing ductility, and exhibiting higher temperature for ductile-to-brittle transition. Since the affected zone normally may include an amount of metal twice that converted to oxide, it is seen that contamination can render columbium totally useless structurally long before the effect of gross oxidation becomes important, or perhaps even observable. Thus susceptibility of columbium to contamination is a vital consideration in judging potential capability of any coating or alloy scheme for protection.

Protection from Oxidation

On the basis of the foregoing data it is not unreasonable to assert that the applicability of refractory metals to high temperature structural designs will be measured eventually by the ability of materials engineers to solve the problem of oxidation protection. In general there are two possible approaches to the protection of the refractory metals from

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oxidation: (1) the metal may be alloyed with one or more other metals to produce a protective oxide film; or (2) a coating may be applied which will provide protection by limiting access of oxygen to the substrate metal. Whichever approach is employed, the protection has to be accomplished without materially altering the desirable properties of the bare metal, i.e., especially high temperature strength and resistance to thermal shock and impact damage.

Alloying

The first general approach to protection of the refractory metals, that of alloying, has received considerable attention, particularly for columbium. There has been a modicum of success in discovery and development of ternary or quaternary compositions which represent considerable improvement in oxidizing behavior over the unalloyed metals, and there are actually columbium alloys extant which are comparable to the superalloys in oxidation resistance at 2000°F. However, the alloying solution cannot be described as having been successful in any case for two important reasons. First, the exhibition of good oxidation properties appears to be mutually exclusive with retention of desirable elevated temperature strength, ductility, and fabricability. Second, and actually most important, at any sufficiently high temperature that the refractory metals are attractive for structural applications on the basis of their physical or mechanical properties, there exist no alloys of adequate oxidation resistance for practical use. Moreover, on the basis of present experience and our limited understanding of the principles of oxidation of alloys, there appears very faint hope of any eventual development of such alloys.

Coating

The inability of alloying to provide a workable solution to the problem has channeled research efforts toward development of suitable coatings. This need actually has been clearly understood for several years now, and coating development by the laboratories of numerous organizations has recently been at an increasing rate. The remainder of the discussion will necessarily deal with the current state of the art of refractory metal protective coatings. The field of applications for such coatings is so broad, we will restrict the survey to those coatings currently under advanced development for use on leading edges or under surfaces of re-entry vehicles.

The overall problem of producing satisfactory protective coatings for the refractory metals and their alloys resolves itself into two principle areas. The first has to do primarily with development of protective coating compositions which will combine with the base metal to form compatible, useful materials systems. The second portion of the problem entails development of optimum techniques for application of coatings which exhibit maximum reliability. These two problem areas, although closely interrelated, will be discussed individually to simplify their treatment.

Coating Systems

The criterion for protective coating compositions is that the coating and base metal should not be considered separate entities but, rather, parts of an integral materials system. This interrelationship becomes much clearer when the requirements to be levied against the coating are studied. The basic primary function of the coating of course is that of a barrier to prevent access between oxygen and the refractory metal substrate. Thus, the coating must deter transport of oxygen or oxygen-containing species to the base metal and, conversely, must prevent movement of metal ions to the coating-air interface. The second major necessity is that the coating remain stably in place

throughout the duration of utility of the subtrate. Therefore, the coating must be tightly adherent, and diffusion of coating constituents into the substrate and volatilization of coating must be minimized. The coating and basic metal must be chemically and metallurgically compatible. Fluxing of the coating due to interactions such as eutectic formation between oxidation reaction products of coating and base metal would, as would diffusion of the coating constituents, either deplete the necessary constituents or cause deleterious effects on substrate mechanical properties.

The coating must form a mechanically compatible system with the substrate and should not be deleteriously affected by such conditions as stress imposed by either mechanical or thermal loads. Favorable to this condition is a coefficient of expansion of the coating closely approximating that of the base metal; otherwise, extremely high stresses are produced within the coating and at the coating-metal interface during temperature cycling. Also of great advantage in maintaining physical integrity of the system is the ability of the coating to withstand flexure such as that imposed by vibratory loading and possession to some degree of ductility to permit the coated piece to deform under creep producing loads. A situation to be avoided is the possible introduction of notched effects in the coating which may reduce its physical strength because of the characteristic brittleness accompanying this mechanical design.

In addition to the desired properties of the coating already enumerated, i.e., oxidation resistance, stability, and compatibility, it is highly desirable that the coating be capable of resisting damage from impact——both particle and mechanical——as well as erosion or abrasion. Although severity of these requirements depend somewhat on precise applications, we should be cognizant of the possibility of accidental damage during processing, fabrication, and handling of coated parts.

Still further criteria for measuring potential effectiveness of any prospective coating include general surface condition, coating emissive characteristics, and required thickness of the coating to achieve the desired level of protection. In the case of coated aerodynamic configurations, where air flow characteristics are important, a smooth finish is obviously desired. Coating emittance may be of little importance in most applications, but a re-entry vehicle skin temperature can vary several hundred degrees depending upon the surface emissive characteristics; thus, a high-emittance surface can lead to lower operating temperature and indirectly reduced severity of protective requirements. Since weight is one of the principal concerns of aerospace designs, a most desirable feature of any protective coating is its ability, with only a thin layer, to provide adequate oxidation protection for the metal substrate. In the case of fabricated sheet components, we could anticipate that a thick coating could contribute a major portion of total structure weight.

Selection of a composition to serve as a protective coating is far from simple. Probably no coating could meet all requirements imposed by the "ideal", and therefore any coating developed will probably represent a series of compromises between desired properties and those realizable. The actual degree of success in developing coatings for each of the refractory metals is in some measure dependent on the means by which a coating is applied or formed in place on the substrate.

Coating Techniques

Method, i.e., techniques, sequence of operations, and processing parameters of coating application, exerts considerable influence on the success of protection achieved by the resultant coating. Among the techniques available, at least in principle, for forming

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protective layers on refractory metals are cladding, electroplating, electrophoresis, liquid-phase chemical decomposition, flame-spraying, slipcasting (enameling), vacuum metallizing, slurry coating, and vapor deposition (including decomposition, chemical reduction, and pack cementation, and variations thereof). There are advantages and disadvantages associated with each technique, and each adapts itself especially to deposition of certain classes of material. Brief discussions of each technique follow, with more thorough treatment of those methods which have been found best suited to protecting the refractory metals.

Cladding

Historically, cladding has been successfully applied to protection of steel and aluminum. This approach demands the ready availability of an oxidation resistant alloy composition which is both compatible with the substrate and amenable to rolling and subsequent bonding operations. There are currently no such refractory metal alloys available, and the development of any such material would be a very considerable undertaking, if feasible at all. The development of a procedure to apply even a single alloy as a clad is in itself a major project. In addition to the fact that they must be applied only to sheet prior to joining or forming operations, claddings suffer a basic disadvantage in that they generally do not protect edges and cut or machined surfaces. Cladding is an unlikely candidate for protecting the refractory metals, with the somewhat remotely possible exception of platinum group metal claddings in certain highly specialized applications.

Electrodeposition

Electrodeposition from aqueous solution has been widely used to protectively coat steels and other metals from corrosion or low temperature oxidation. A great number of metals are depositable from aqueous solution and additional metals are depositable from fused salt electrolytes. Electroplated nickel and chromium were thoroughly evaluated as coatings for molybdenum several years ago, and proved protective at relatively low temperatures. Although electroplating is a relatively simple and convenient technique, deposits are characteristically porous, are not metallurgically bonded to the substrate, and tend to be brittle and nonadherent when plated on refractory metals which have not had complex pretreatments. Generally, extensive post-plating heat treatments would be required to obtain desirable coating properties. Many metals are depositable from aqueous solutions but unfortunately the very ones of greatest interest to refractory coatings (Si, B, Al, Be, T, and Zr) are not so depositable, and fused salt techniques are not sufficiently advanced in most cases to provide suitable means of deposition either. This fact, coupled with difficulty in coating intricate shapes, seems to rule out electroplating for application of most coatings; again the principal exception appears to be deposition of platinum group metals as intermediate layers or special coatings.

Electrophoretic Deposition

Electrophoretic deposition is primarily a technique for depositing oxide or metal powders, requiring subsequent densification (usually by isostatic pressing) and sintering. A valuable technique for forming certain composites not readily deposited by other means, electrophoresis is, in its present state, a quite cumbersome technique and has not been used in any large scale refractory coating development.

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Chemical Deposition

Deposition from liquids by chemical catalytic decomposition has been achieved for certain metals, primarily nickel, gold, and certain platinum group metals. It is an extremely simple process by practical measure, involving complex chemical reactions. None of the more interesting metals for refractory coatings have been reported deposited by this technique, and it is not likely that it can be used except as a substitute for electroplating.

Slip Casting

Slip casting is of greatest interest in its familiar role of deporting oxides from powders suspended in volatile media which are subsequently driven off before or during "firing" or bonding heat treatment. Resultant coatings are frequently porous and have not shown great promise in protecting refractory metals. Sound metallurgical bonds are frequently difficult to achieve, but in any event simple oxide coatings have satisfactorily permitted ready transport of oxygen to the base metal. Despite disadvantages, this method remains in consideration for those applications where it is desirable directly to deposit an oxide coating, since no other approach to that task is adequately advanced. An offshoot of this approach, termed slurry coating, will be discussed in greater detail.

The technique of hot dipping wherein the part to be coated is immersed in molten metal and the desired coating formed by reaction usually followed by diffusion heat-treatment is well known and widely practiced for depositing zinc, tin, aluminum, and other metals. Where the process is applicable, it is straight-forward and economical. It is possible to deposit metals of higher melting points by dissolution in low melting diluents such as lead or tin, or as alloys with aluminum. However, difficulty is encountered in coating large or complex shapes uniformly, due largely to temperature differences created by varying material thicknesses and clogging of inaccessible areas. The principal value of hot dipping presently is to serve as a simple small-scale technique for applying experimental compositions for laboratory evaluation.

Vacuum Deposition

Vacuum deposition, frequently referred to as vacuum metallizing and sometimes confused with vapor deposition, is a technique capable of depositing virtually any metal, as well as certain other materials. However, until now, vacuum deposition has been limited to formation of thin films; maximum thickness of coherent coatings obtainable by the technique has been considerably less than one thousandth of an inch. Thus, the technique currently has little potential for depositing oxidation protective coatings for refractory metals, since after brief exposure to temperature no coating remains unreacted with either substrate or environment. Another disadvantage is the limitation to line-of-sight deposition.

Of considerable interest because of its ability to deposit quite refractory compositions of an almost unlimited variety of materials is the arc-flame spraying technique, an offspring of flame metallizing. Both forms of the technique, oxyacetylene and arc-flame spraying, possess the advantage of requiring no heating of the substrate above a few hundred degrees, as well as that of having the capability of rapid deposit of many thick layers. Major problems encountered in flame spraying are porosity of deposits, frequently poor adherence, and difficulty in applying thin deposits; and, post heat-treatments are often required to densify and bond coatings. Conventional flame spraying is normally conducted under oxidizing conditions and therefore the coating is applied

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unsintered. Arc-spraying (most often and somewhat erroneously referred to as "plasma" flame spraying) however, can be accomplished in inert or reducing atmospheres; in addition, it possesses wider applicability due to higher operating flame temperatures. The versatility of this technique has given rise to a new concept of coatings, the so-called gradated metal-oxides; the composition of the coating overlay is varied continuously from 100-percent metal at the substrate-coating interface to 100-percent oxide at the surface by varying the material fed into the flame. It is, of course, possible similarly to gradate combinations of metals' oxides or intermetallics and combinations thereof. Despite the promise of this approach to solve certain problems, several barriers remain to its widespread utilization: density and porosity are difficult to control; coatings of uniform thickness or suitable thinness, especially to edges and complex configurations, are difficult to apply; and coating interior surfaces may indeed be frequently impossible.

Vapor Deposition

The area of vapor deposition, often confused with vacuum deposition through loose terminology, is receiving proportionately the largest share of attention in development of new coating systems for reasons which will become apparent. There are three major subdivisions of vapor technique, thermal decomposition, chemical reduction, and pack coating. Each of the first two is variously referred to as vapor plating, vapor deposition or gas plating, and the third is commonly known as either pack cementation or pack diffusion. By whatever title, the latter is by far the most widely adopted technique at present for application of coatings, especially silicide-base coatings, to the refractory metals. A recent survey performed by a subpanel of the MAB indicates that approximately 60 percent of all current coating development efforts utilize the pack cementation technique. Most familiar examples of this technique are siliconizing and chromizing of steels, and recently of molybdenum. The process consists generally of immersing the metal to be coated in a mixture of powders containing the metal element(s) to be deposited, carrier compounds (usually halides), atmosphere controlling compounds (such as ammonium compounds), and inert filler material (usually alumina); the whole pack is charged in a sealed retort and heated for several hours, in the absence of air, at temperatures between $1600°$ and $2200°F$. The essence of a pack process depends then on both thermal decomposition and displacement reactions of metal halides; the reaction temperatures lead to diffusion to form the required coating compounds and to produce metallurgical bonding. Since more than one halide can be present in the retort at any one time, quite complex coatings can be formed. The principal disadvantages of the pack method are: the requirement for long term heating of substrate at high temperature, which sometimes results in recrystallization; the requirement for uniformly heating very large packs and maintaining them at temperature for long periods, and occasional problems of removing sintered powders from coated surfaces, especially internal ones. The corresponding advantages of the process are considerable. It simultaneously forms and bonds the coating in place, a virtually unlimited number of elements can be deposited, operation is relatively simple and readily adjusted by proper selection of reactants, and the process is readily adapted to complex part geometry. Pack coating certainly deserves much of the enthusiasm which it is presently being accorded; however, pack cementation may not be a panacea to the coating problem since better solutions may present themselves for specific requirements.

Other variations of vapor deposition have not received such widespread attention. Both the chemical reduction and thermal decomposition approaches usually employ a flowing gas stream, which contains appropriate vapor reactants, and is passed over the substrate to be coated. Reactions are similar to pack reactions, except that reactants must be continuously added internally. Several metals can be deposited by thermal decomposition of

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halides on very hot surfaces; however, necessity for attaining and maintaining extremely high base metal temperatures (over 2200°F) imposes severe limitations especially for specimens of practical size. The alternate method of hydrogen reduction of volatile metal halides, at lower temperatures (1200-1600°F), has received deservedly more attention. This technique yields dense adherent coatings of most metals and can be adapted to deposition of refractory compounds, i.e., silicides, carbides, and perhaps oxides. Although it is not as versatile as pack coating, but rather, more cumbersome and somewhat limited by directional characteristics of deposition from streaming vapor, vapor deposition will continue to be of interest in applying protective refractory coatings.

As mentioned above, thermal decomposition of halides imposes temperature limitations too great to be considered practical. However, a similar process of current interest involves thermal decomposition at low temperatures (about 500°F) of organo-metallic compounds. Certain metal alkyls, carboryls and cyclic compounds have been successfully used in depositing nickel, chromium, and aluminum; and various similar materials could be considered for applying refractory coatings. This process is usually referred to as gas plating to differentiate it from other modes of vapor phase deposition.

Slurry

One other coating technique, which is based on long known practices, but has only recently been adopted to coating refractory alloys, is slurry coating. Here, powdered reactant materials (metals and activators) are suspended in an appropriate vehicle (usually organic) together with possible binders, thickeners, and suspension agents to form a slurry. The slurry is applied cold to the work piece by painting, dipping, or spraying; a bake treatment at low temperature is applied to volatilize the vehicle; and a diffusion heat treatment is performed at 1800° to 2100°F for a few hours in inert atmosphere or vacuum. The resultant diffusion coatings are quite similar to those formed by vapor processing and possess the advantage of simple application and less severe thermal treatments. Uniform thicknesses are attainable on different surfaces because of liquid flow into relatively inaccessible areas. This technique, widely used in depositing ceramic layers, is fairly new as applied to metal deposition and appears to offer very great promise in developing refractory metal coatings.

Overall Requirements

In all the foregoing discussions regarding coating application methods there has been a strong implication of necessity for convenience and simplicity of technique as well as necessity for uncomplicated specimen geometry. Despite the fact that the prime concern before the laboratory investigator is to discern a coating capable of protecting some refractory metal, the ultimate consideration is to protect adequately fabricated structures in a practical, user situation. Let us pause to consider what this includes: most importantly, how well and how long the protection is afforded, without failure. (This should not be an "average" figure.) This is the factor which governs the necessity for extensive evaluation and testing of myriad coated specimens and the establishment of failure criteria. Other aspects of practicality involve time and temperature requirements and the economics of coating processing. One further consideration is repair or reprocessing of imperfect or damaged coatings. A truly versatile coating process for which conditions were such that mishaps in processing did not predicate discard of valuable parts, and that local damage or premature failures could be repaired without adverse effects on properties of previously coated regions. These may be vital considerations as they apply to complex shapes such as re-entry vehicle designs utilizing refractory sheet. Additionally, assembly of structural sections could be accomplished by welding or riveting, which would further require that edges of all holes or joints be adequately coated.

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Current Development

Overall current status of coating development for the refractory metals can best be described as that of advanced laboratory development, ranging in intensity from very extensive effort for molybdenum and its alloys, through substantial effort for columbium, to almost negligible effort for tantalum and tungsten. Transition from laboratory development to experimental full-scale coatings is well underway for certain molybdenum coatings and planned for coatings for columbium. A survey of current efforts shows nearly fifty organizations (including industrial, governmental, and institutional) actively engaged in research, development, or evaluation of refractory metal coatings. Among these, over thirty are concerned with coatings for molybdenum, about twenty (many the same) are working with columbium, and only about ten are actively concerned with either tantalum or tungsten. Of these totals it is estimated that about thirty organizations are actively pursuing development efforts; the remainder are mostly concerned with property evaluations. A large number of these efforts are under direct government sponsorship or a result of other government programs. A total of about sixty "coatings"—the term coating here designating a particular application technique utilized to deposit a prescribed composition—have been reported in all, with the considerable majority (about forty) properly designated as primarily intended for molybdenum.

Further analysis of current effort shows over half of all efforts are devoted to development of pack cemehtation processes, and a similar proportion of total effort concentrated on coatings dependent on silicides for their protective features. Almost all coatings being developed, regardless of substrate, are (with the exception of ceramics) composed of some alloy or intermetallic combination of four principle elements: silicon, chromium, aluminum, or titanium, with certain other occasional additions such as boron and carbon. Virtually every known empirical approach was employed in pioneering efforts toward protecting molybdenum, and subsequent work on the other three metals has tended to follow the same trends established there. Thus, an almost disproportionate degree of effort has been and continues to dwell on optimization, scale-up, and establishment of reliability for those coatings found most successful to date for protecting molybdenum under such conditions as will be encountered in re-entry vehicle leading edge applications. This work is well-founded and designed to fill urgent immediate needs, but an unfortunate side effect has been dilution of remaining available resources for research and laboratory development of new coating concepts applicable to differing requirements of other base metals and applications. This remaining effort is nevertheless being applied profitably to development of new coatings and adaptation of application processes.

Status of current programs to protect each of the refractory metals is summarized briefly in the following remarks. Most of the coating developments outlined below have been with specific reference to unalloyed substrates of each metal under discussion. In the case of the Group VI metals, i.e., molybdenum and tungsten, it does not appear critical to distinguish between various alloys as possible substrates requiring coating. It is not likely that the low level additions to which structural alloys of Mo or W are limited would exercise sufficient variation in total chemical characteristics to significantly alter protective ability of a particular coating composition. On the other hand, when considering Group V basis metal substrates, tantalum and columbium, it is quite important to distinguish between abilities of various coatings to protect different alloys, since alloys based on Cb and Ta frequently contain large percentages of different classes of additives, and the chemical behavior of alloys in relation to the ability of a coating to provide protection is subject to considerable variation. For example, a coating which displays great potential for protecting high-titanium alloys of columbium may be less promising or even entirely unimpressive in its ability to protect tungsten-bearing alloys. Throughout the

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ensuing discussion, therefore, it is essential to remember the possible substrate variations when considering potential utility of different coatings for each refractory metal.

Molybdenum

As noted previously, primary effort for molybdenum is concentrated on pack-silicide coatings. This is the result of a tremendous amount of evaluation which has indicated the advantage of this type of coating over others promulgated over the past several years. To discuss in any detail the findings of the numerous evaluations which have been performed would be an undertaking both tedious and so large as to be completely beyond the scope of this discussion. A minimal background discussion, however, will show why this approach has evidenced itself as the prime candidate for reliably protecting molybdenum under specialized re-entry conditions.

Widespread past development efforts have employed almost every application technique to form a wide variety of protective compositions on molybdenum. Earliest efforts to coat protectively molybdenum were aimed at protecting heater elements. Historically, emphasis then shifted to protection of turbojet engine components; during this phase most of a wide variety of coatings were initially developed. As, more recently, interest centered on ramjet parts and now on aerodynamic structural applications, the requirements imposed, evaluation required, and testing performed have likewise undergone changes in emphasis so that now a vast array of data can be assayed to show a number of interesting coatings produced for molybdenum, depending on the intended use. Included among coating systems explored for molybdenum have been the following:

1. Electroplated coatings of nickel, chromium, various precious metals, and especially chrome-nickel composites;

2. Flame sprayed nickel-chrom-boron and nickel-silicon-boron, aluminum-chromium silicon, molybdenum disilicide, and refractory oxides;

3. Vapor or pack-deposited siliconized and/or chromized coatings; clads of platinum and nickel alloys;

4. Enameled coats utilizing chromium or zirconia frits; and

5. Hot-dipped (or solutionized) coatings of chromium and aluminum-silicon.

For purposes of comparison, generalized average data pertaining to exhibited properties of some of these various coatings is summarized in table 1, which is extracted from a DMIC report on molybdenum coatings. Such a compilation can only serve to provide general comparisons and more recent data may be available in many cases. The coatings represented in table 1 have been widely tested under varying conditions; all data must therefore be viewed with a highly critical attitude. However, such information does permit a broad view of relative capabilities of the various coatings of part or current interest for molybdenum.

Briefly extracting the data reflected in the table, the ensuing remarks serve to summarize molybdenum coatings. The pack diffusion silicide-base coatings- of which at least four commercial variations currently merit consideration-- provide the longest protected lifetimes at all temperatures above 2000°F. Although reliability has not been sufficiently demonstrated to satisfy exacting requirements imposed by aerospace designers, it appears higher than for most other coating types. Resistance to thermal

shock at high temperatures is good and hot ductility is reasonably satisfactory. Primary problems lie in low temperature brittleness of the coatings and attendant mechanical effects on the coated substrate. The most interesting coatings from among others previously developed for molybdenum were: (1) the nickel-chromium electroplated alloys, which possessed excellent oxidation resistance and fair reliability at intermediate temperatures; and (2) the flame-sprayed nickel-silicon-boron, nickel-chromium-boron and aluminum-chromium-silicon compositions which provided excellent oxidation protection and reliability, fair thermal shock characteristics, good hot ductility, with no detrimental substrate effects, but suffered from the typical foilings resulting from the inaccessibility of sprayed coatings to complex surfaces, and poor coverage of vulnerable corners and edges. Although it has since been surpassed in favor by the pack-coatings for aerospace vehicle application, the various nickel-chromium compositions still offer a degree of feasibility for certain special applications.

Columbium

Progressing to columbium coatings we find substantially less total effort and no clear-cut standout success among candidate coating systems. At least three approaches to protecting columbium appear quite promising and merit discussion. At first, development efforts toward columbium coatings followed the same general course as molybdenum coating research had undergone earlier. One expected consequence of that fact has been the establishment of pack-siliconizing as one method of adequately protecting columbium. However, performance of the silicide base coatings on columbium has not been nearly as spectacularly superior to other coating systems as it has been for coating molybdenum. Lifetimes achieved with this coating system are not so long at similar temperatures, and processing conditions apparently tend to more seriously affect properties of the base metal. In general, comments regarding these coatings on Mo can be similarly stated for Cb in greater or lesser degree.

In contemplating protection of columbium, an additional problem arises; not only must columbium be prevented from reacting directly with oxygen to avert structural loss of material, but the attendant oxygen contamination of the base metal with severe effects on substrate mechanical properties must be solved. Still another potential problem is the elimination of hydrogen from those processing steps where that gas might react readily with the Cb to produce unfavorable changes in substrate properties. For these reasons at least two additional coating systems, which have demonstrated potential protection from oxidation and contamination, bear further serious consideration for protecting columbium.

The first such promising coating to be discussed is the vacuum-pack deposited Cr-Ti-Si alloy. In this approach, columbium is packed in metal powders of 50 percent chromium and 50 percent titanium, and heated in vacuum to produce deposition of the Cr-Ti alloys and simultaneous diffusion; subsequently, a layer of silicon is similarly produced. The resulting ternary composition is capable of protecting columbium and alloy substrates for periods reproducibly exceeding ten to twenty hours at 2400°F. The principal advantage of the process is that the coating overlay and diffusion zone are essentially metallic in nature, and exhibit considerably more ductility, both hot and cold, than coatings based on intermetallics. Small quantity additions of halides to the vacuum-pack result in much more rapid deposition at lower temperatures, and also result in longer term, more reliable protection. The coating, which completely eliminates detrimental hydrogen and oxygen from the processing scheme, is not only protective against external oxidation reaction, but also eliminates contamination effects in the same temperature regime. One obvious problem arises in further utilizing this combined pack-vacuum vapor process; the necessity for maintaining high vacuum, although an important advantage in the

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processing environment, represents a major requirement possibly in conflict with practicality of coating application on a commercial scale. Further efforts on effects of additives to the pack might substantially alleviate this difficulty, however. From the standpoint of protection afforded, this vacuum-pack process has shown best results on columbium; the problem of adopting the process to potentially large-scale applicability remains to be completely solved.

The third coating scheme of major interest in relation to columbium, besides pack-silicides and vapor-pack chromium-titanium alloys, consists of slurry-depositing aluminum alloys, which form complex columbium aluminides on diffusion heat treatment. As an application technique, the slurry method possesses a major advantage in simplicity, including relatively low temperature and short processing periods. Also, the slurry aluminide coatings appear capable of providing adequate protection for columbium at temperatures up to 2500°F. Such a coating—an aluminum-silicon-chromium alloy applied by dipping or spraying— has successfully protected a large complex structure for a required time of 2 to 10 hours at 2500°F; thus, practical feasibility has been demonstrated. This coating system, perhaps, does not possess as great maximum protective capabilities as the other two but it exhibited practicality which may be more critical in the long run for the particular applications under consideration here.

Along with the approaches discussed in detail above, a considerable amount of coating development effort has been expended for columbium, resulting in a number of interesting systems. The current status of these programs is illustrated in table 2, which is extracted from a contract state of the art survey conducted for the Air Force by Thompson Ramo Wooldridge, Inc. Among systems which have received more than passing interest have been the zinc dip coating developed by Naval Research Laboratories, a series of hot dip aluminum alloys and sprayed alumina sealed with refractory glasses. The zinc dip coating has displayed an amazing capacity for correcting coating flaws and has demonstrated good protectiveness, but at temperatures far below our range of present discussion (1800° to 2000°F). The glass impregnated alumina coating, commonly designated "system 40," has demonstrated reliable protection of columbium for periods up to 500 hours at 2300°F. However, the coating is quite thick and heavy and suffers all the disadvantages in practicality ascribed to flame sprayed coatings. The various hot dip aluminizing treatments have lead to the development of the slurry coating process previously discussed, and appear to offer little advantage to compensate for difficulties of application to large or complex shapes. Data for other columbium coating systems is shown in the table and is self-explanatory.

The columbium coatings effort revolves about the requirement for optimization and selection from among at least three concepts currently considered most promising. Any of the three is probably capable of supplying the required protection, thus selection is wholly dependent upon the particular application considered. Further information on relative properties of the various coatings, as compared on identical samples of base metal and tested under exactly similar environments, will be available in Part II of ASD Technical Report 61-66, and should be of value in discerning advantages and limitations of each approach. Present indications are that each of the coatings discussed will have reached a status comparable or superior to that of present molybdenum pack cementation coatings within the year.

Tantalum

Until one year ago the status of protective coatings for tantalum could be described adequately in one word—nonexistent. Since then, however, interest in tantalum has been

heightened because of the properties exhibited by several experimental alloys. Aside from a few experiments where some tantalum specimens were added to the "batch" while processing molybdenum or columbium coatings, no information of real value had been produced on tantalum coatings until the new interest in tantalum alloys prompted the Air Force to sponsor two exploratory efforts. These new programs, based largely on previous work with columbium, have shown feasibility of protecting tantalum and its alloys for periods of varying length at temperatures to 3000°F and beyond. One effort has dealt primarily with the now familiar pack siliciding process and has indicated feasibility on a small laboratory scale of protecting tantalum alloys by that approach. Protection periods of 6 to 10 hours at temperatures up to 2800°F have been reproducibly recorded with either chromium or aluminum-modified silicide coatings. A second major effort has dealt with formation of aluminide coatings, first by hot dipping, and subsequently, after interesting compositions had been noted, by slurry coating. A number of compositions provided promise; however, an unusual coating has provoked greatest interest. As part of the hot dip studies, tin was utilized as a diluent to permit greater control of dipping time and temperature. The coatings produced by this means retained residual tin phases and such coatings performed extraordinarily well, providing complete protection reliably for 10 to 20 hours up to 2900°F. Subsequent study has shown that similar tin-bearing aluminides produced by slurry dipping, painting or spraying give still better protection, with lifetimes of 100 hours up to 2800°F and for a few hours above 3000°F. Apparently this unique coating depends upon a thin film of alumina for protection and the aluminum-bearing tin sublayer provides a reservoir of aluminum to heal flaws in the film. The coating is very simple to apply, appears quite reproducible, and withstands a surprising degree of physical abuse in addition to providing oxidation and contamination resistance. Also interesting is that the same coating provides good protection to molybdenum substrates (for somewhat shorter periods than for tantalum). One other approach to protection of tantalum has been cursorily studied: the formation of tantalum beryllides on the metal surfaces by vapor phase reaction with beryllium. Such coatings appear intrinsically quite oxidation resistant, but have not borne up well under thermal shock and react by diffusion quite rapidly with the base metal. (The latter effect is considerably reduced on tungsten containing alloys.) The beryllide approach still seems worthy of further investigation; however, silicides are presently more promising, and aluminides (especially the tin-aluminum system) appear best suited to long term high temperature protection of tantalum.

Tungsten

Tungsten, the one refractory metal not discussed thus far, remains an enigma so far as protective coatings are concerned. Results of only a very few preliminary feasibility efforts are available for comment. Electroplated rhodium, over complex alternate layers of silicon and chromium, has successfully protected resistance heated tungsten wire for about one hour at 3000°F. Vitreous bonded zirconia has protected tungsten wires at temperatures up to a reported 3600°F for about three hours. Siliconized tungsten wires have survived exposure to flowing 3300°F air for as long as ten hours. All these results have been quite tentative and have not been very reproducible; poor reliability is indicated by available data. There have been reports of similar protection by plated platinum or iridium, but all these approaches are limited by melting point considerations. We do not anticipate serious consideration of tungsten for structural applications until we encounter environmental temperatures exceeding 3000°F. Apparently other studies are being conducted on a proprietary basis. Some reports of flame spraying and pack coating have been circulated, but not substantiated. In comparison with the other refractory metals, little effort is being expended on developing protective coatings for tungsten. It is clear that tungsten will require protection at all temperatures above about 1300°F; it is equally

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clear little effort is currently being devoted to clarification and development of possible solutions to this problem.

From meager available information it appears probable that stable oxides will be the necessary protective species on which any coating for tungsten is to be based. On this assumption, one effort has been newly initiated to study the problem of forming thin metal-bonded oxides on the surface of tungsten by controlled reaction of deposited inter-metallic coatings at reduced oxygen pressures. Another program, Air Force sponsored, is seeking to definitely establish those parameters and material properties, a knowledge of which is necessary to logical formulation of a coating development program. At the extremely high temperatures contemplated for utilization of tungsten, thermo-dynamic and kinetic considerations will demand a thorough understanding if any hope of providing practical solutions to the protection problem is to be realized. We highly recommend that resources of industry, as well as those of government agencies, be enlisted in accomplishing the many tasks which form portions of the overall problem of providing some protective scheme to enable use of tungsten in atmospheric environments approaching 3500°F.

SUMMARY

The state of development of coatings for protection of the four refractory metals in atmospheric environments can be summarized briefly as follows: Pack cementation coatings are available which appear capable of providing required protection for molybdenum; new applications continue to impose further demands, however, which may not be readily met; therefore, continuing efforts to optimize present coatings are required, and room remains for new approaches. Altho no single coating for columbium is so fully advanced as the pack-silicide coatings for molybdenum, at least three, the vacuum vapor Cr-Ti-Si alloy, the slurry aluminide, and the pack silicide types, appear quite promising for providing necessary protection. Coatings for tantalum are comparatively new and unexplored; both silicide and aluminide coatings show great potential, and tin-bearing aluminide coating developed for tantalum looks especially promising, both for tantalum and the other refractory metals. No coatings for tungsten have progressed beyond laboratory feasibility studies or very early development. The total picture thus presented consists of a balance between severe problems and promising developments.

A number of special problem areas have been either mentioned briefly or implied. Obviously the first requirement of any protective coating is that it survive exposure at the environmental conditions, i.e., at any particular temperature. Probably the second major problem area is that of practicality of coating systems. A logical extension of this problem is the potential repairability of coatings; the ultimate in practicality would be a coating system amenable to spot repair (or patching) of either damaged or imperfectly coated specimens. Another prime requirement is the standardization of coating evaluation procedures. If any progress is to be made in the always difficult area of standardization of test techniques, it will be necessary to recognize that responsibility for testing against specific design requirements has to be delegated to design and applications engineers, while laboratory testing procedures should be standardized to give completely comparable data for various systems from which selections for advanced testing can be made. To guide the thinking and planning of coatings producers, more complete requirements in terms of total environment need to be spelled out by prospective users of coated refractory metal alloys. Accompanying this need for dovetailing of requirements information and coating development plans is a requirement for both realistic simulated service test development and nondestructive inspection procedures. Also, proper and/or possible sequences of operation and compatibility of various joining and coating procedures

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deserve separate study. Closely associated with this problem is the ever increasing pressure on the part of aerospace designers to utilize thinner and thinner gage sheet metal parts. Very little can be said regarding that problem, except that the popular and presently most reliable diffusion-formed coatings may be greatly reduced in applicability under such conditions.

There exists a continuous need for related efforts in support of coating development. Since direct effort developments are made on a basis of meeting immediate requirements, it is quite probable that resulting coatings suffer disadvantages necessitating design compromises. For example, diffusion may well represent mode of failure of many coatings; thus development of diffusion barrier layers may well be required. Also, the long term necessity for development of ceramic-base coatings for temperatures above 3000°F on tungsten and tantalum points the way to study of novel means of forming such compositions on metal. These related development efforts should include both investigations of feasibility of various application techniques to form classes of coating compositions and also development of alternate techniques to form specific proven compositions. The problems of developing added features of ductility and "self healing" should also be attended. Related efforts then revolve about the study of new application techniques and novel coating compositions. Despite gratifying progress recently in coating refractory metals, the need for original and unique approaches to solution of the problem continues.

A review of knowledge regarding oxidation protection of the refractory metals discloses, in addition to the above general problems, several areas of fundamental research where information is needed to support development efforts: mechanism of oxidation both of the refractory metals themselves and potential coating materials; nature and chemistry of oxidation products; and deterioration of coatings by physical processes, i.e., diffusion and volatilization. This is a fairly wide spectrum of fundamental investigation which is required to provide basic information for more intelligent coating development effort as opposed to strictly empirical "hit-or-miss" coat and test programs.

CONCLUSION

The oxidation of unprotected refractory metals is so rapid as to be properly termed disastrous. Of the two approaches open to adoption for solution of this vital problem, alloying to form oxidation resistant composition has been extensively tried and found wanting. The remaining alternative, development of protective coatings, has been recently explored quite extensively. As a result of these efforts, coatings to reliably protect molybdenum appear attainable for certain special applications. At least three interesting coatings are being developed for columbium. Several avenues appear promising for protecting tantalum. And, preliminary efforts indicate feasibility of protectively coating tungsten at lower than anticipated use temperatures. Many problems stand before the realization of development of practical reliable coatings for these metals, and recommendations in the areas of process optimization, supporting development, and fundamental research have been provided.
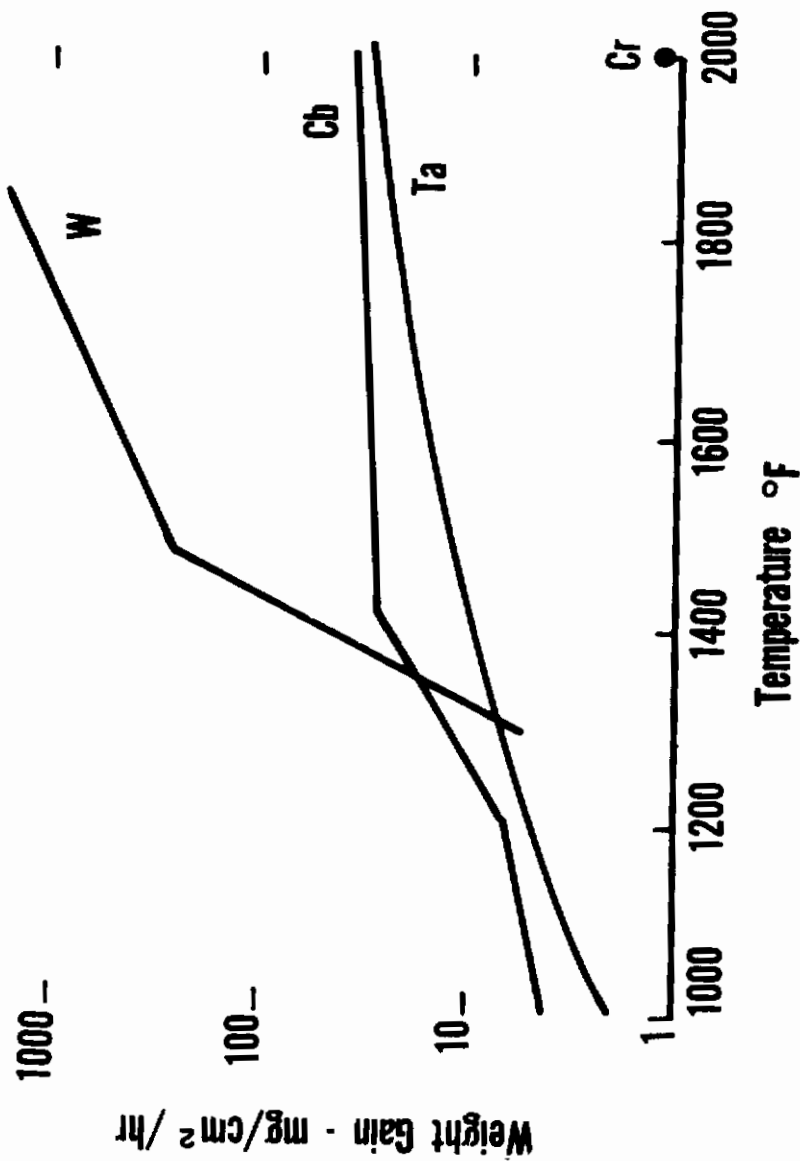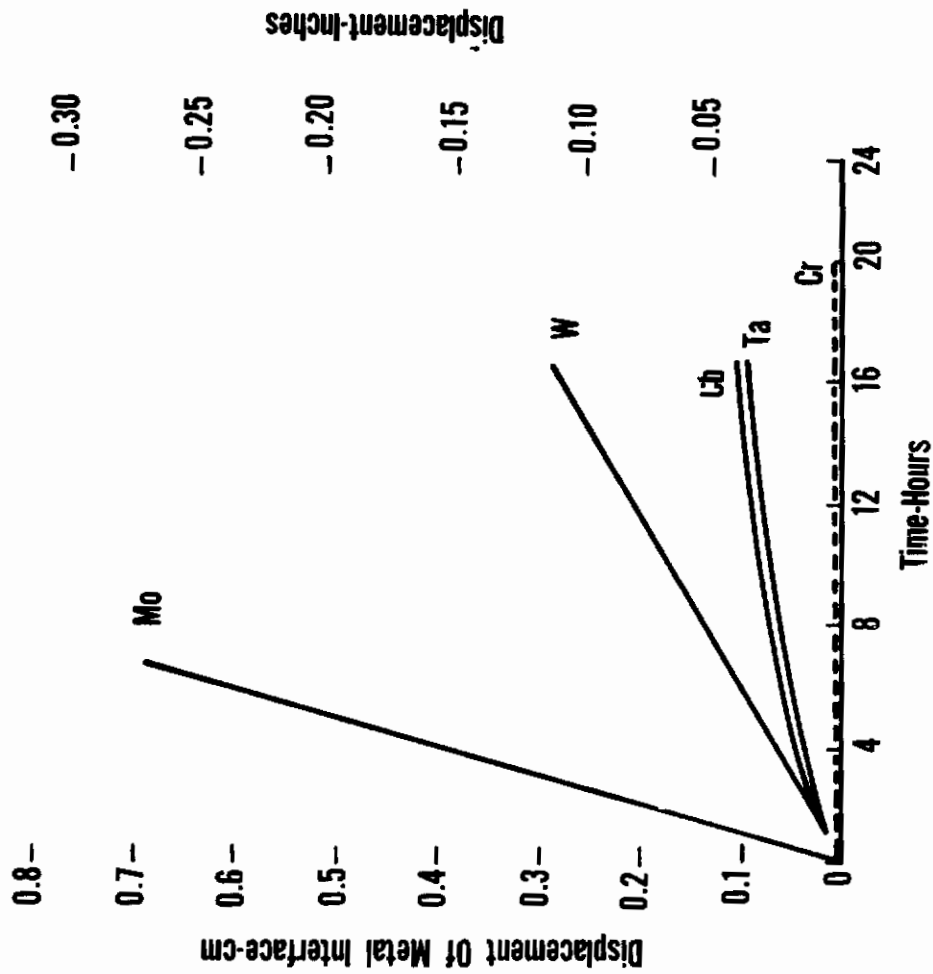
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COMPARATIVE OXIDATION RATES

Figure 1.

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Figure 2.