Properties of Evaporated Metal Films Related to Their Use for Surface Temperature Measurements

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Extension of the understanding of properties of films of metals produced on glass surfaces by vacuum evaporation has permitted the fabrication of film-resistance thermometers that with simple instrumentation accurately measure surface or average surface temperatures without altering the geography of that surface. Formerly unknown and unstable related properties of such films have been classified and may be anticipated or eliminated by recommended experimental procedures. Films of several of the most chemically inert and refractory metals 300 to 3,000 Å. thick have been shown to attain accuracies as high as 0.01°C. for practical periods of time. Their use, which is described, is developing satisfactorily, and the technique and equipment for their preparation are relatively simple.

Work on thin films as such, originating in 1889, has been extensive but has been directed principally toward the solution of problems related to solid state physics. Electrically and physically the behavior of thin films deviates considerably from that of bulk metal. Resistivities and temperature coefficients of resistivity frequently have no resemblance to those of the bulk metal. Film behavior is affected by the conditions under which it is formed. Tensile strength (*8*) and chemical inertness (*1*) generally increase as the film becomes thinner. This general subject is treated more extensively in reference *15*.

An interesting application of evaporated metal films has been their use as resistance thermometers for the measurement of surface temperatures. Not only may heat transfer studies and other specific situations require spot temperature measurements precisely at the surface, but also average values may be important in cases where temperature varies over a surface area. Many methods employed for such measurements have disadvantages that can be eliminated by the use of metal films. Optical methods of temperature measurements are incompatible with the thermal shielding that is frequently required. There is some disagreement regarding the effectiveness of the best designed thermocouples (*6*, *9*). Techniques in which the wall of the conduit itself is used as a resistance thermometer (*2*) suffer from the need to measure extremely low resistances and the fact that the temperature measured is not precisely that of the surface. Coatings of temperature-sensitive phosphors (*5*) have a restricted range and require optical measurements. Though closer to the thin-film concept, use of a wrapping of tin foil over a surface (*14*) was only a first approximation.

The initial investigation by Winding, Baus, and Topper (*15*) of the use of evaporated metal films on glass for the measurement of surface temperatures indicated that this method showed promise in the range of room temperature to 125°C. Chromium films and, for short periods, nickel films 200 to 1,500 Å. thick were found suitable and were successfully used for the measurement of an average surface temperature in the calculation of coefficients of heat transfer for condensing organic vapors. The antecedents and advantages of film thermometers have been discussed by these authors. Included are essentially zero heat capacity, no change in surface geography, equivalency of the electrical resistance to an average surface value, and convenient values of electrical properties.

Recently a thick evaporated nickel film was used on steel as a thermocouple for the measurement of an instantaneous surface temperature in a gun barrel (*4*) in a manner similar to some earlier work (*7*). Precision of results was not reported. The need for a greater understanding of film behavior again appeared necessary for more general application of the principle.

In this study an effort was made to perfect the utilization of evaporated metal films for average surface temperature measurements. In both the preceding studies the necessity for random choice of film parameters and inexplicable film phenomena indicated the need for a more careful, fundamental investigation. Extension of the range of temperatures that might be measured by film thermometers, improvement in film stability and accuracy, introduction of greater variety of suitable metals, and greater understanding of their behavior have been attained.

EXPERIMENTAL

The technique and equipment required to produce evaporated metal films are relatively simple, but considerable care must be exercised to produce films with desirable properties. In general, a system capable of producing vacuums of 10^{-4}mm. Hg or better in a closure big enough to house the evaporation apparatus is required. Metal is vaporized from a high-temperature source and, because the residual pressure is low enough so that the mean free path of a gaseous metal atom is greater than the dimensions of the enclosure, travels in a straight line until it hits an obstruction, where it condenses and forms a film. Shadows completely free of deposited metal can be produced by introducing obstructions or shields in front of the desired area. Metal is distributed in thicknesses varying as the inverse square of the distance from the source.

Problems of technique include the need for evaporation temperatures of 500° to 3,500°C. and evaporator materials resistant to the extreme reactivity and solvent power of metals at high temperatures. Furthermore, pretreatment of the target surface and excellent vacuum must preclude contamination since evolution of gases from the target and other surfaces is one of the principal factors causing unsatisfactory films.

In this study a vacuum system of the bell jar and metal base-plate type and an oil-diffusion pump were used. Vacuum of 1×10^{-4}mm. Hg deteriorated to as high as 3×10^{-4}mm. during deposition of films owing to the outgassing of the system caused by radiated heat from the hot evaporator. In addition to those electrically heated refractory metal sources described in reference *15*, V-shaped refractory metal strips 3 in. long were used. For the evaporation of nickel or cobalt, conical baskets of tungsten wire lined with thorium oxide prepared as recommended by Swanger (*12*) were used.

Metals requiring a higher temperature or more inert source for evaporation were heated by bombardment with electrons from a heated tungsten filament. Where necessary, a crucible, for example graphite, was used. Filament-to-target voltages up to 4,000 v. D.C., unfiltered, and current to ½ amp. could be obtained. Despite the highly efficiently transmitted power of up to 2,000 w., evaporation rates were limited when ionization and consequent glow discharge of the locally concentrated metal vapor occurred. This electron bombardment technique appears useful for the fusion, where these limitations would not apply, of large quantities of a wide range of substances.

Films were deposited on a 1/16- by 2- by 1-in. Vycor or Pyrex glass or fused-quartz substrate. One-half-inch electric contacts were made by firing Hanovia platinum paste 13A on each end. Initially the slides were cleaned with a good detergent, hot

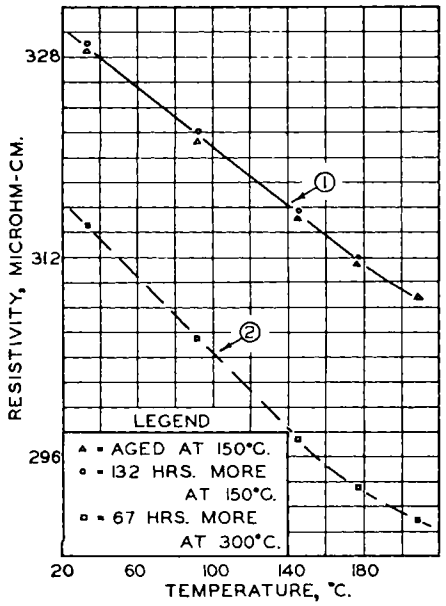

Fig. 1. Calibration of resistance of chromium films vs. temperature; (1) during 132 hr. aging at 150°C. and (2) after 67 hr. more at 300°C.

chromic acid, and boiling water. Following firing of the electrodes, the slides were cleaned with detergent and with boiling water. A shutter permitted the exclusion of all but the middle fraction of the evaporating metal vapors. The substrate could be heated in vacuum before or during the evaporation.

Films were removed from vacuum and electrical contact made through both a wire soldered to the surface of the platinum electrode and a tightly clamped brass plate. The effect of evaporation conditions and of various treatments on the electrical resistivity, temperature coefficient of resistivity, and appearance was then determined. A Wheatstone's bridge was used for the successive calibrations of the films while immersed in a Dowtherm-A bath.

EXPERIMENTAL RESULTS AND DISCUSSION

The types of metal films prepared, the method used for their evaporation, and the evaporation parameters resulting in films having the greatest stability and temperature coefficient of resistivity are listed in Table 1. Thickness was varied over the range 200 to 3,000 Å. in this study.

Thermal Properties

As a result of a large number of trial runs, a standardized procedure was adopted, and the data of Table 2 concerning the suitability of thoroughly aged films for average surface temperature measurements were obtained. Of these, nickel films are considered the most successful of the films developed. For short-term service, a few hours, they appear adequate for measurement of temperatures with accuracy approaching 0.01°C. No exceptions to good performance in the range to 200°C. were found for films 500 to 1,500 Å. thick, prepared as described on heated Vycor-glass slides. In the range up to 150°C. the performance of the tantalum film was considered the most satisfactory. The data show that further investigation is required to confirm the usefulness of platinum or molybdenum disilicide films for the measurement of higher temperatures than any of the other films measure. Since deterioration of the platinum-paste electrodes occurred at 450°C., use of chemically reduced platinum or elimination of special electrodes might improve performance. At this time use of films at temperatures in excess of 300°C. is not recommended.

Application of an evaporated magnesium fluoride film 600 Å. thick for the protection of some of these films proved moderately useful with some exceptions.

Table 2. Summary of Evaluation of Metals as Resistance Thermometers in Air

Metal	Performance up to 150°C.	220°C.	300°C.	400°C.
Au	m.s.	u.	u.	u.
Co	v.s.	s.	m.s.	u.
Cr	m.s.	m.s.	m.s.?	u.
Mo	?	u.	u.	u.
$MoSi_2$	?	?	?	?
Ni	v.s.	s.	m.s.	u.
Ni-Cr	s.	s.	u.	u.
Pt	m.s.	m.s.	m.s.	?
Ta	s.	?	u.	u.
Ti	m.s.	u.	u.	u.
Ti-Cr	u.	u.	u.	u.
V	s.	m.s.	u.	u.
W	u.	u.	u.	u.
Zir	u.	u.	u.	u.
Zir-Cr	u.	u.	u.	u.

v.s. indicates very satisfactory, < 1°C. calibration loss/32 hr. aging at indicated temperature.
s. indicates satisfactory, 1–3°C. calibration loss/32 hr. at indicated temperature.
m.s. indicates moderately satisfactory, 3–10°C. calibration loss/32 hr. aging at indicated temperature.
u. indicates unsatisfactory, >10°C. calibration loss/32 hr. aging at indicated temperature.

Mechanical and Chemical Properties of Films

Additional data were gathered in an effort to permit prediction of the behavior of these metal films under most conditions. The effect of abrasion of the films by the surface of a section of Kraft paper in a standardized procedure was determined by resistance measurement. Absolute changes in resistance and equivalent loss of temperature calibration were of interest. Suitable stability in the abrasion tests was considered indicative of probable satisfactory performance as a thermometer in gentle contact with solids. This test might also be considered to be a safe-side estimate of the calibration loss which would be caused by a rapid flow of water over the film. All the films were found to be at least satisfactory by this test. Tungsten, nickel, and cobalt suffered changes of resistance to 0.3%. Equivalent temperature-calibration loss for nickel or cobalt was, however, less than 1°C.

Films were immersed in Dowtherm-A at 190°C., 5% sodium sulfate at 90°C., and boiling water for periods of 2 hr. These liquids were chosen as typical examples of nonionic, strongly ionic, and weakly ionic systems respectively. There was no mechanical agitation of the test liquids.

Large initial changes, perhaps peculiar to the film state, were found and permitted to elapse prior to final evaluation. Performance was in specific cases disappointing. Cobalt was completely removed by boiling water; however it was not possible to distinguish between peeling of the film and chemical reaction. Vanadium suffered continual augmentation of its resistance in aqueous media. Tungsten proved highly sensitive to water and showed an unusual pattern of behavior. A platinum film which peeled in the water test was believed to have verged on nonadherence before immersion because of its thickness. The resistance of molybdenum also increased greatly in 5% sodium sulfate or water. However, zirconium, titanium, chromium, tan-

Table 1. Useful Films and Their Method of Preparation

Metal	Thickness, Å.	Evaporation method	Type of evaporator	Heated substrate	Resistivity ratio*	Temperature coefficient ratio*
Au over Bi_2O_3	450–2,500	Ohmic	Mo V	No	5.3	+0.45
Co	470–900	Ohmic	ThO_2 over W basket	Yes	2.2	+0.50
Cr	450–600	Ohmic	Ta V	No	21	−.051
			W basket	No		
Mo	≥770	Electron	None	Yes	14	+.043
$MoSi_2$	600	Electron	Mo crucible	Yes	19	−0.23
Ni	500–1,500	Ohmic	ThO_2 over W basket	Yes	2.0	+0.62
Ni	300–600	Ohmic	W wire	Yes	9	+0.15
Pt	400	Electron	ThO_2 over W basket	Yes	2.4	+0.30
Pt	1500	Electron	Graphite	Yes	2.4	+0.30
Ta	≥470	Electron	None	Yes	47	−.060
Ti	400–2,200	Ohmic	Ta V	Yes	4.3	−.032
Ti	700	Electron	Graphite	Yes	3.6	−.025
V	550	Electron	Graphite	Yes	9.3	−.001
V	500–3,500	Ohmic	Mo V	Yes	5.6	+.096
W	850	Electron	None	Yes	5.7	−.016
Zir	500–1,500	Ohmic	W wire	Yes	21	−.046

*Ratio of value of film to that of bulk

talum, and nickel were found generally satisfactory.

The films were then subjected to a more rigorous series of specific chemical tests. The tests were performed by simple immersion of the films in the desired reagent with lead wires removed. The reagents were not agitated. Depth of penetration by the reagent was estimated from the change in electrical resistance of the film. Various concentrations of hydrochloric, sulfuric, nitric, acetic, and phosphoric acids were used as test reagents.

The general statement may be made that the films retain a corrosion resistance at least equal to that of the bulk metal. Platinum appeared to be the sole exception since a platinum film disintegrated in concentrated hydrochloric acid at room temperature within 4 hr. Most of the metals may be said to be moderately superior to the bulk metals in their resistance to acids. Chromium and titanium films proved greatly superior.

Important Film Variables

The principal portion of the behavior observed which was unique to the film state could be explained by the variations in properties associated with the film. These properties were found to be chemical inertness of the metal, thermal aging to which the film had been exposed, thickness of the film, temperature of the substrate during deposition, type of evaporator used, and the atomic number of the metal.

Necessarily, the chemical resistance of the particular metal was the most important factor in determining long-range film stability. The original choice of metals consequently was dictated largely by this consideration.

The severity and duration of the thermally accelerated aging to which a film has been exposed cause unexpected changes. What was presumed to be a structural instability of fresh films was rapidly eliminated by aging, as evidenced by resistance and resistance-temperature-coefficient changes. However, this appeared to be a resistance-driving-force relationship, for exposure to a new maximum temperature or a temperature close to the previous maximum caused elimination of an additional increment of structural instability. Nickel was typical of metals whose films showed an initial rapid resistance decrease resulting from structural stabilization. Vanadium was typical of another type showing a diminishing rate of resistance increase.

Figure 1 illustrates these processes for a chromium film. It can be seen that the next higher temperature range has introduced a large rapid decrease in resistance.

However, this steady state rate was not wholly dependent upon chemical resistance to the surroundings. For some metals slow evolution, presumably also structural, may oppose the increase in resistance caused by corrosion. It is not considered impossible that this slower resistance decrease, not detected with all metals, contributed to the high steady state stability of nickel.

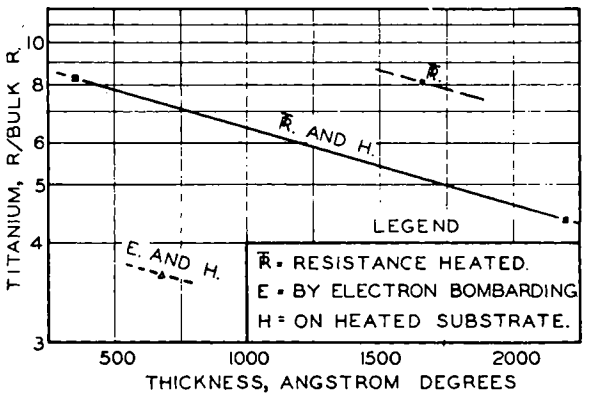

Fig. 2. Effect of varying deposition conditions on ratio of film resistivity to bulk-metal resistivity vs. thickness for titanium.

The magnitude of this slow type of evolution of properties was greatest for 400- to 700-Å. chromium films. With the extended knowledge of the behavior of these films (*10*), it is possible to obtain a stable film by using the foregoing decrease in resistance to offset oxidation-caused increases at temperatures varying with their age.

Protective magnesium fluoride films appear to reduce the rate of this slow type of evolution and may be used as a factor determining the range of greatest stability of the chromium films suggested above.

Variation of film thickness also permits unusual control over film behavior. Graphs presented in the prior publication (*15*) and the additional data obtained in this study have been combined to fit a curve by the method of least squares for ratio of resistance of film to that of the equivalent bulk metal vs. thickness with a correlation coefficient of 0.97. The relation becomes

$$\text{ratio} = 5{,}700(t)^{-0.86}; \quad 150 < t < 1{,}500 \text{ Å}.$$

and applies only to chromium films prepared on unheated substrates by evaporation from conical crucibles of tungsten wire. This exponential relation is typical of thin films. In a like manner most properties of thick films may be said to approach those of the bulk metal. The extent of the irreversible changes in the resistance of fresh thick films is less than that of thin films, for which the extreme case is evolution to an infinite resistance. The rapidity of the completion of this change in thick films is also favorable.

The behavior of a tantalum film particularly demonstrates the satisfactory fit of proposed concepts of structural evolution to this thickness-stability relation. This film had been found increasingly stable in successive aging periods at 220°C. The film was heated 2 hr. at 300°C. with minor resistance change. Heated again for 38 hr. at 300°C., it increased many hundredfold in resistance. According to current theory, structural evolution in the film proceeded at 300°C. to the point of agglomeration of the continuous film of metal into aggregates, forming a state found in electron microscope studies typical of films of thickness less than a maximum, dependent on the degree of annealing of the film. The maximum varied from 100 Å. for unannealed to 500 Å. for well-annealed films. This film was approximately 400 Å. thick. Utilization of a film several hundred Ångstroms thicker should permit aging to stability at 300°C. without agglomeration.

Table 3. Adherence Limits for Chromium Films

Type of evaporator	Substrate condition	Maximum thickness, Å
Tungsten cone	Unheated	1,100
Tantalum V	Unheated	>2,500
Tantalum V	Unheated	<3,100
Tungsten cone	Heated	1,650

When they were also found to have greater steady state stability, emphasis was shifted to the thicker films. Adherence then became a dominant problem, for although films of most metals are strongly adherent when thin, at greater thicknesses the film may peel spontaneously from the base.

Two-layer films from zirconium, titanium, or nickel over chromium were prepared, greater adherent thicknesses and better, more stable electrical properties being sought. Chromium is considered one of the most adherent of metals and hence was included in each pair. Though in general better electrical properties were not forthcoming, improvement in adherence was obtained, which was outstanding in the case of nickel.

Another variable, the substrate temperature during evaporation, is even more important in determining the maximum adherent thickness of a metal. Zirconium films of any thickness could be easily wiped off their substrates if they

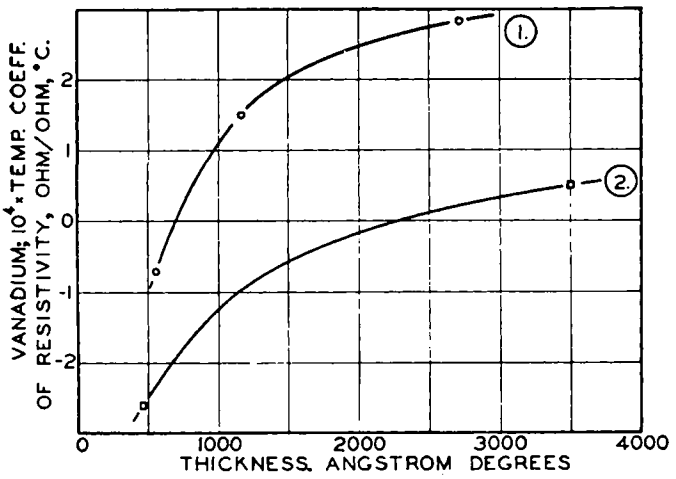

Fig. 3. Temperature coefficients of resistivity vs. thickness for vanadium films similar in all respects except that curve-1 films were deposited on heated substrates and curve-2 films on unheated substrates.

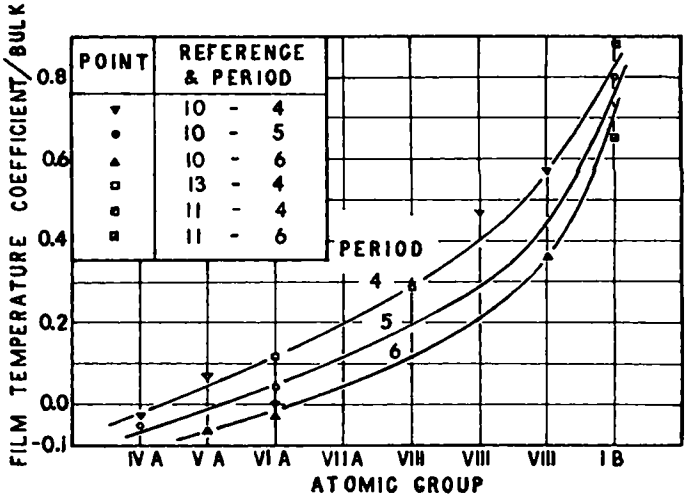

Fig. 4. Ratio of film temperature coefficient of resistivity to equivalent bulk-metal coefficient vs. atomic number.

had not been heated during deposition; on a heated substrate they became strongly adherent. Such improvement was true for many metals. The effect may be detected in Table 3.

This variable also strongly influences the film's electrical properties. Though the resistance of one reasonably thick film on an unheated substrate quickly became infinite and is not plotted, Figure 2 indicates that at equal thicknesses the film deposited on an unheated substrate has a greater resistance. The effect of this factor on the temperature coefficient of resistivity is best shown by the results for vanadium metal, presented in Figure 3. Coefficients may be seen to be significantly more positive for films prepared on heated substrates.

That these effects are not purely the result of the excellent outgassing achieved by heating the substrate is evidenced by the study of vanadium films. Substrates for some films were heated in vacuum and permitted to cool prior to deposition of the film. Only those deposited on hot substrates possessed the advantages enumerated above.

Film properties are strongly conditioned by the type of evaporator used in its preparation. This fact has led to the conclusion that contamination of the film occurs by evaporation of a minute portion of the refractory metal composing the evaporators. Outstanding is the dependence of the maximum adherent thickness on the type of evaporator. Chromium films, prepared by evaporation from tantalum V's, have a higher limiting thickness than those prepared from conical evaporators of tungsten wire. In all likelihood tantalum evaporators run hotter because of smaller contact area between them and the chromium and because of less likelihood of appreciable current flow through the chromium. Hence they are more suspect as sources of contamination. Table 3 clearly demonstrates this variation in limiting thickness.

Similarly the effect of type source on electrical properties appears to stem from contamination by the evaporator. In Figure 2 the curve of the ratio of the resistivity of the film to that of the bulk metal vs. thickness for titanium films prepared from tantalum evaporators lies above that for films prepared by electron bombardment of metal in a carbon crucible. In the latter case direct heating of the metal can be expected. Similar results were obtained for chromium, and, in addition, improvement in the temperature coefficient of resistivity for chromium occurred. Results for vanadium were uncertain.

An interesting correlation, presented in Figure 4, has been found between the temperature coefficients of resistivity of fresh films of this study and of other workers and the atomic number of the metal. Prediction of the temperature coefficient of unevaluated metals may be possible from this curve.

PRACTICAL USE OF FILMS

New techniques are available in assembling films as resistance thermometers and as elements in circuits. Evaporated films of chromium, molybdenum, cobalt, nickel, and molybdenum disilicide only 500 to 1,500 Å. thick on glass have been found satisfactory electrodes to which lead wires may be soft-soldered. It should be possible to increase the variety of metal films satisfactorily wetted by the use of solders of varying compositions. The chemical resistance of the films and ease of application as compared with fired platinum make them ideal for use as electrodes for the attachment of lead wires to a film of the same or different metal under severe or special conditions.

Protecting and insulating evaporated mineral films resulting in cumulative thicknesses exceeding the adherence limit of the metal have been successfully applied. Practical application of their properties should be possible in film circuits.

When the films are in use as thermometers, repeated complete calibration would not be necessary. During the aging of a film at temperatures below the maximum in its history, the successive calibration curves are simply displaced without affecting temperature coefficients. Since all the films considered for thermometers have linear or nearly linear calibration curves, a series of parallel lines results, each of which may be determined by a single new calibration point.

Where surface heaters of negligible bulk and known output or where resistances of low temperature coefficient are desired, evaporated metal films may be used. The near-zero temperature coefficients of resistivity of a wide range of thicknesses of chromium films prepared on heated substrates make them particularly suited for this purpose. Films of other metals fill this criterion when prepared in thicknesses at which their temperature coefficients change sign. Vanadium (*see* Figure 3) would be an unusually good metal of this type because its coefficient changes sign at a relatively great thickness and the stability associated with thick films would be retained.

SUMMARY

A number of types of evaporated metal films 400 to 3,000 Å. thick deposited on glass surfaces have been made that are useful as thermosensitive elements in air over ranges of temperature and periods of time far exceeding those previously offered. Nickel and cobalt films showed high sensitivity with usefulness at temperatures up to 300°C. as well as outstanding stability. Chromium, titanium, tantalum, gold, vanadium, and chromium over nickel films proved useful to intermediately high temperatures. Platinum and molybdenum disilicide films show promise of being suitable with further development at even higher temperatures.

These films as resistance thermometers may displace conventional devices lacking versatility and reliability.

The technique for evaporation by electron bombardment permitted the evaluation of the electrical properties of thick films of the refractories, molybdenum, tungsten, and tantalum.

The performance of films has been evaluated in three typical hot liquids, organic, weakly ionic, and strongly ionic in nature, to permit predictions of their behavior in other media. These and tests of their abrasion resistance indicate that suitable selected films should be rugged enough for service in most liquids, in gentle contact with solids, and in contact with gases and vapors.

Chemical behavior against mineral acids likewise has been compared with the behavior of the bulk metal. Generally films have been found to be moderately to markedly superior.

[illegible] been collected concerning the resistivities and temperature coefficients of resistivity of these films. The important variables causing behavior unique to the film state have been outlined. Deposition of metal on a substrate at 200°C. proved strikingly effective in producing films of superior adherence with greater stability and electrical properties closer to those of the bulk metal. The temperature coefficients of thick films show an interesting correlation with their atomic number.

Techniques and recommendations for the practical use of evaporated films have been outlined.

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Chemical Reactor Stability and Sensitivity

II. Effect of Parameters on Sensitivity of Empty Tubular Reactors

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In this paper extensive calculations on the quasi isothermal tubular reactor are presented. Temperature and concentration profiles were obtained on an analogue computer (R.E.A.C.). The calculations tend to show that there are regions of operation in which the reactor effluent is very sensitive to operating conditions. For example, it is shown that in some regions of operation a small change in the heat transfer coefficient at the reactor wall or a small dilution of the feed will produce large changes in the effluent. In such cases the reactor is said to exhibit *parametric sensitivity*. It is shown analytically that this sensitivity may be predicted by analyzing the frequency response or transient response of the reactor approximated by a local linearization. This linearization requires complete solutions of the steady state problem. Semiquantitative results are then obtained for the regulation required from a given specification of product limits. The frequency-response analysis should be useful in connection with the control problem.

If the reactor is fed partially with a recycle stream, then experience with electrical systems indicates that the possibility of instability exists. It is shown that at least theoretically these instabilities do exist, and a method based on the transfer function is developed for derivation of criteria of stability or instability.

In Part I of this paper the stability of the well-agitated reactor was examined in detail and criteria were developed based on the steady state values so that reactor behavior after perturbations, either small or large, might be predicted. This problem was not difficult because the transient behavior is described by ordinary differential equations. The treatment of stability problems for chemical systems exactly parallels the treatment of problems in nonlinear mechanics. This is fortunate as the theory therefore must only be restated in terms of the parameters of the chemical system. When one considers the tubular reactor, however, the problem is considerably more difficult, because transient reactor behavior is described by partial-differential equations which are nonlinear, and no adequate method of solution or estimate of the error in their linearization is available. Thus the treatment given in the following must be considered unsatisfactory from a rigorous point of view although it will be shown that machine solutions of the rigorous equations agree in a semiquantitative way with the solutions of the approximated equations. This may be

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