

NASA TN D-302

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TECHNICAL NOTE

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USE OF LESS REACTIVE MATERIALS AND MORE STABLE GASES TO
REDUCE CORROSIVE WEAR WHEN LUBRICATING
WITH HALOGENATED GASES

By Donald H. Buckley and Robert L. Johnson

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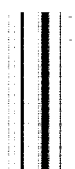
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON

August 1960

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SUMMARY

The gases $\text{CF}_2\text{Cl-CF}_2\text{Cl}$, CF_2Cl_2 , and $\text{CF}_2\text{Br-CF}_2\text{Br}$ were used to lubricate metals, cermets, and ceramics in this study. One of the criteria for determining the effectiveness of a reactive-gas-lubricated system is the stability of the halogen-containing gas molecule. The carbon-to-halogen bond in the ethane molecule has extremely good thermal stability superior to the methane analogs (CF_2Cl_2 and CF_2Br_2) used in earlier research. For this reason, the ethane compounds $\text{CF}_2\text{Cl-CF}_2\text{Cl}$ and $\text{CF}_2\text{Br-CF}_2\text{Br}$ were considered as high-temperature lubricants.

Friction and wear studies were made with a hemisphere (3/16-in. rad.) rider sliding in a circumferential path on the flat surface of a rotating disk (2 1/2-in. diam.). The specimens of metal alloys, cermets, and ceramics were run in an atmosphere of the various gases with a load of 1200 grams, sliding velocities from 75 to 8000 feet per minute, and temperatures from 75° to 1400° F.

The gas $\text{CF}_2\text{Cl-CF}_2\text{Cl}$ was found to be an effective lubricant for the cermet LT-1B (59.0 Cr, 19.0 Al_2O_3 , 20.0 Mo, 2.0 Ti) and the ceramic Al_2O_3 sliding on Stellite Star J (cobalt-base alloy) at temperatures to 1400° F. The bromine-containing gas $\text{CF}_2\text{Br-CF}_2\text{Br}$ was found to give friction and wear values that can be considered to be in a region of effective boundary lubrication for the cermet K175B (nickel-bonded metal carbide) sliding on the metal Hastelloy R-235 (nickel-base alloy) at temperatures to 1200° F.

INTRODUCTION

There is a need for the development of bearings and seals capable of operating at extreme temperatures. The extreme temperatures anticipated (above 1000° F) necessitate consideration of high-temperature

metals, cermets, and ceramics for bearing and seal construction. One part of the complete materials problem is that of the lubricants to be used at extreme temperatures. The temperature limitations of liquid and grease lubricants require consideration of some nonconventional lubrication methods. Solid-film lubricants and reactive-gas lubricants are two possible approaches to the high-temperature lubrication problem.

The use of halogen-containing gases as lubricants is discussed in reference 1 and in subsequent publications on high-temperature studies (refs. 2 to 4). The mechanism underlying reactive-gas lubrication is fundamentally the same as that applied in "extreme pressure" lubrication where reactive halogen-containing compounds are used as additives to gear oils. The gases (e.g., CF_2Cl_2) are stable in contact with surfaces of several metals at ambient temperatures of 1000°F (ref. 5). In lubrication systems where metals are in sliding contact, however, the frictional heat generated at contacting metal asperities is extremely high (1100°F above the environment temperature with effective boundary lubrication, ref. 6). These temperatures are sufficient to cause localized decomposition of gas molecules adsorbed on the metal surface. The active halogen atoms thus released react with the metal surface to form metallic halides at the sliding interface; these halides function as solid lubricants.

In reactive-gas-lubricated systems, corrosive wear can be the primary factor limiting the use of reactive gases at high temperatures. There are, however, a number of systems or devices that can be employed to reduce or eliminate this problem. One approach might be the use of less reactive materials as sliding components in the system. Based on the mechanism of gas lubrication, one of the components must be a metal in order that metallic ions be present for the formation of the metal-halide solid lubricants. High-temperature corrosion-resistant alloys with good hot hardness may be most effectively used. The other component, however, may be a relatively nonreactive material such as a cermet or ceramic. The use of a nonreactive material for surfaces in sustained solid contact should reduce the problem of corrosive wear at extreme temperatures.

Another method of approaching the corrosion problem is to use gas lubricants with extremely good thermal stability. It has been established in reference 2 that, in gas molecules such as CF_2Cl_2 , the carbon-to-fluorine bond is not ruptured upon molecular thermal degradation. The carbon-to-chlorine bond does cleave, however, and this separation liberates free chlorine, providing for the formation of the metal halides that function as the lubricant. Excessive liberation of free halogen can contribute to corrosion of the metallic components at extreme temperatures. Any molecular structure of the gas that would give greater stability to the carbon-to-chlorine bond will reduce corrosion at elevated temperatures. One such structure is the compound 1,2 dichloro-1,1,2,2 tetrafluoroethane ($\text{CF}_2\text{Cl}-\text{CF}_2\text{Cl}$). This type of compound could conceivably reduce the tendency for corrosion to occur at extreme temperatures.

One other method employed in the reduction of corrosion at extreme temperatures is the application of corrosion inhibitors. This concept has been employed with reactive-gas lubrication at temperatures to 1500° F (unpublished data; paper to be presented at ASLE-ASME Conference, Oct. 1960).

The object of this investigation was to study two methods of reducing corrosive wear. These methods are: (1) the use of a relatively nonreactive material as one of the two sliding components; and (2) the use of more stable gases. Metals, cermets, and ceramics were studied in various gas atmospheres at temperatures from 75° to 1400° F. Friction, wear, and corrosion characteristics were noted. In friction and wear experiments a 3/16-inch-radius hemisphere contacted the flat surface of a rotating 2 1/2-inch-diameter disk specimen. The rider was loaded against the disk with a 1200-gram load. The sliding velocities employed were from 75 to 8000 feet per minute.

LUBRICANTS

The gases used as lubricants in this study were the halogen-substituted ethane and methane compounds 1,2 dichloro-1,1,2,2 tetrafluoroethane ($\text{CF}_2\text{Cl}-\text{CF}_2\text{Cl}$), 1,2 dibromo-1,1,2,2 tetrafluoroethane ($\text{CF}_2\text{Br}-\text{CF}_2\text{Br}$), and dichlorodifluoromethane (CF_2Cl_2). The compounds $\text{CF}_2\text{Cl}-\text{CF}_2\text{Cl}$ and $\text{CF}_2\text{Br}-\text{CF}_2\text{Br}$ were selected because of the thermal stability of the carbon-to-chlorine and carbon-to-bromine bond. Although such ethane compounds are molecularly less stable than the methane analogs, the carbon-to-halogen bonds, which are of primary concern in lubrication, possess greater stability. When $\text{CF}_2\text{Cl}-\text{CF}_2\text{Cl}$ is heated, the first appearance of molecular degradation occurs in the form of a rupture of the carbon-to-carbon bond, leaving two symmetrical free radicals $\text{CF}_2\text{Cl}\cdot$. The nature of the radical is such that the two fluorine atoms exert an inductive effect on the single chlorine atom; this inductive effect results in a very stable bond existing between the carbon-to-chlorine atoms. In the compound CF_2Cl_2 , each of the carbon-to-chlorine bonds requires more energy to rupture than the carbon-to-carbon bond of $\text{CF}_2\text{Cl}-\text{CF}_2\text{Cl}$. However, the carbon-chlorine bond of the radical $\text{CF}_2\text{Cl}\cdot$ offers greater resistance to cleavage than do the bonds in the compound CF_2Cl_2 (ref. 7).

SLIDER MATERIALS

The rider and disk materials used in this investigation, together with the composition and hardness of each, are presented in the following table. Metals, cermets, and ceramics were used in these experiments.

Specimen	Nominal composition, percent											Hardness at 75° F
	Fe	Co	Ni	Cr	C	Mo	W	Si	Ti	Al ₂ O ₃	Others	
Metals: Stellite Star J	3.0	43.0	2.5	31.0	2.4		17.0	1.0				R _c 63
Hastelloy R-235	10.0	2.5	66.0	14-17	0.16	5.5		1.0			Mn, Al, Ti	R _c 28
Cobalt Chromium		99+		99+								R _b 68
Cermets: K-175B ^a			41.0		7.2	15.0			28.0		4.5 Cb	R _a 84
LT-1B				59.0		20.0				19.0	2.0 TiO ₂	R _c 50
LT-1				77.0						23.0		R _c 37
Ceramic: Al ₂ O ₃										99.6		Mohs 9.0

^aTi and Cb are present as mixed carbides.

The hardness of the three general classes of materials varies considerably from the hard ceramics to the soft metals. This difference becomes even greater at elevated temperatures where metals, in particular, become subject to thermal softening and hardness values decrease rather rapidly. The relative differences in hardness can have a profound influence on the wear of various material combinations. Hardness influences wear primarily through adhesion or abrasion (both forms of mechanical wear). In this study, the wear mechanism of most concern was corrosion (chemical wear). Since the object herein was to reduce corrosive wear at elevated temperatures, the good corrosion resistance of cermets and ceramics made them desirable for use in combination with metals.

APPARATUS AND PROCEDURE

The apparatus used in this investigation is shown schematically in figure 1. The basic elements of the apparatus consist of a rotating-disk specimen ($2\frac{1}{2}$ -in. diam.) and a stationary hemispherically tipped rider specimen ($3/16$ -in. rad.).

The disk specimen is rotated by means of a varidrive motor unit through a gearbox and spindle assembly. The drive shaft enters the housing of the apparatus through an interlocking labyrinth seal. The portion of the drive shaft inside the apparatus housing contains a heat shield and the disk specimen, which is held on the shaft by a lock nut. A magnetic speed pickup is used to monitor rotative speeds. The disk specimens were run at surface speeds of 75 to 8000 feet per minute.

The rider specimen is loaded against the disk surface by means of a retaining arm which is bellows and gimbal mounted to the apparatus. The load is applied to the arm by means of dead weights. At a right angle to the cable is a linkage connecting the arm with a strain-gage assembly for measuring frictional force.

The test specimens are heated by twelve 650-watt cartridge heaters located in an Inconel housing that fits around the circumferential surface of the disk specimen. The heaters are controlled by a Variac unit and a temperature controller. The controller is operated by a thermocouple located near the point of disk and rider contact. The apparatus was operated at temperatures from 75° to 1400° F.

The experimental gaseous lubricants were supplied, by means of an Inconel tube, at a rate of 1.0 liter per minute to an Inconel test chamber (0.7-liter volume) that housed the specimens and heater assembly. Prior to each run, a 10-minute purge period was employed to expel air from the system. A gas exhaust tube was used to remove effluent gases. A face plate containing a quartz window for experimental observation was bolted to the outer apparatus housing. The heater housing was isolated by asbestos gaskets to reduce heat transfer to the apparatus walls.

The disk and rider specimens used in the investigation were finish ground at 4 to 8 microinches. Before each experiment the disk and rider were given the same preparatory treatment. This treatment consisted of: (1) a thorough rinsing with acetone to remove oil and grease, (2) polishing with moist levigated alumina on a soft cloth, (3) a thorough rinsing in tap water followed by distilled water, and (4) a thorough rinsing of the specimens with absolute ethyl alcohol to remove the water. The specimens were then stored in a desiccator. For each experiment (data point) a new set of specimens was used. Some previous work with CF_2Cl_2 showed that, if a run was started with high loads and speeds, surface failure of the specimens was apt to occur; in accordance, in all experimental runs in this study (except where noted) a run-in procedure was used. High initial friction and wear can sometimes be attributed to lack of sufficient time for the formation of a reaction film. As a result it was found that, by incremental loading, a reaction film could form that markedly reduced the initial high friction and wear. The run-in procedure employed in the investigation started with an initial load of 650 grams for a period of 1 minute, then 850 and 1050 grams for intervals of 1 minute, and finally the full 1200-gram load.

RESULTS AND DISCUSSION

The results obtained in some of the experiments with the stable gas $\text{CF}_2\text{Cl}-\text{CF}_2\text{Cl}$ are presented in figure 2; these experiments were on

the friction and wear of Stellite Star J sliding on Stellite Star J at temperatures to 1000° F. Although the friction coefficient was between 0.1 and 0.2 over the temperature range, the wear was relatively high at 1000° F. The trend of the wear curve seems to indicate that Stellite Star J sliding on Stellite Star J is not a good material combination for use with CF₂Cl-CF₂Cl although cobalt alloys usually perform well in combination with chlorine-containing gases.

The increase in wear of the Stellite Star J rider at 1000° F can be attributed to the excessive reactivity of the rider surface with the halogen-containing gas. The increased reactivity of the rider specimen is due to the rider specimen being in continuous sliding contact while the disk specimen experiences only intermittent contact. This results in continuous high temperatures at the rider surface. The high surface temperature causes excessive reactivity of the rider with active halogen atoms. Friction and wear experiments were made with a less reactive material (the cermet LT-1B) used as the rider material sliding on Stellite Star J at temperatures to 1200° F with CF₂Cl-CF₂Cl as the lubricant. The data obtained are presented in figure 3. The wear decreased from 75° to 800° F. At 1200° F the wear increased rather rapidly. It is interesting to note that the temperature for onset of prohibitive corrosive wear with a reactive gas was significantly higher for the cermet-metal than for the metal-metal combination. The advantage gained by using a cermet can be seen in a comparison of rider wear in figures 2 and 3. The friction coefficient for LT-1B sliding on Stellite Star J was 0.2 or less over the entire temperature range.

Since the rider wear obtained with a cermet rider specimen was less than that with the metal Star J, friction and wear experiments were conducted with metals, cermets, and a ceramic sliding on Stellite Star J at 1200° F with CF₂Cl-CF₂Cl as the lubricant. A comparison of the friction and wear values obtained is presented in figure 4. The wear measurements made in this study were on the rider, and the values reported do not reflect the wear to the disk specimen. The relative hardness of cermet and ceramic rider specimens can plastically deform a softer metal disk material when these materials are used in combination. In addition to plastic deformation, the relative nonreactive nature of cermets and ceramics can result in only the disk material reacting with the halogen-containing lubricating gas. Still another factor to be considered in cermet-metal and ceramic-metal combinations is the low thermal conductivity of cermets and ceramics, which contributes to higher sliding interface temperatures and greater chemical activity. All of these factors can have an effect on disk wear. Qualitative data, however, have indicated that disk wear of Stellite Star J disks was low at 1200° F when run against cermets and ceramics.

The exceptionally good friction and wear properties of Al₂O₃ sliding on Star J at 1200° F in a CF₂Cl-CF₂Cl environment indicated that this

combination should be considered over a broad temperature range. Experiments were, therefore, conducted at temperatures from 75° to 1400° F with $\text{CF}_2\text{Cl-CF}_2\text{Cl}$ as the lubricant. The friction and wear results obtained in the experiment are presented in figure 5. The friction and wear properties improved at temperatures above 600° F but were satisfactory over the entire temperature range. The rider wear remained low even at 1400° F. The wear of the Stellite Star J disk was low to 1200° F. At 1400° F the disk specimen began to deform plastically under the Al_2O_3 rider specimen, and an increase in disk wear was noted.

Because ceramics such as Al_2O_3 have poor thermal conductivity, the temperature attained at the sliding interface as a result of frictional heat may be considerably greater when such a material is used as the rider. Surface films on the metal should then develop much more rapidly in metal-ceramic than in metal-metal systems. A special experiment was run at 800° F with Al_2O_3 sliding on Stellite Star J with $\text{CF}_2\text{Cl-CF}_2\text{Cl}$ as the lubricant to determine whether surface films form more rapidly in metal-ceramic than in metal-metal systems. With metal-metal systems a run-in procedure is normally used to allow for surface-film formation in order to avert incipient specimen failure. In this particular experiment the run-in procedure was not used. The friction tracing obtained with time is presented in figure 6. The initial period of the run shows a decreasing friction trend during progressive surface-film formation. After a period of 8 minutes the friction achieved a low value that was maintained for the remainder of the run. The surface film was formed without the benefit of a run-in procedure. The surface film was identified by X-ray analysis as a metal halide.

A comparison of friction coefficient with various temperatures and sliding velocities was made with Al_2O_3 sliding on Stellite Star J in a $\text{CF}_2\text{Cl-CF}_2\text{Cl}$ atmosphere. The results presented in figure 7 indicate that the friction coefficient was 0.2 or less at all temperatures with velocities above 1600 feet per minute.

The friction coefficient obtained in figure 5 with Al_2O_3 sliding on Stellite Star J in $\text{CF}_2\text{Cl-CF}_2\text{Cl}$ was above 0.2 at temperatures to 600° F. In order to reduce the friction at temperatures below 600° F, a more reactive gas, CF_2Cl_2 , was used with Al_2O_3 sliding on Stellite Star J. Friction and wear experiments were made with CF_2Cl_2 over the temperature range of 75° to 1400° F. The results obtained are presented in figure 8. Some reduction in friction was achieved with CF_2Cl_2 gas as the lubricant. However, the more reactive nature of CF_2Cl_2 had the adverse effect of increasing rider wear above 1000° F. This effect was not experienced with $\text{CF}_2\text{Cl-CF}_2\text{Cl}$ as the lubricant.

The thermal stability and lubricating properties of the ethane gas $\text{CF}_2\text{Cl}-\text{CF}_2\text{Cl}$ indicated that the bromine-substituted compound $\text{CF}_2\text{Br}-\text{CF}_2\text{Br}$ should be considered as a lubricant. Data obtained in reference 3 indicated that the bromine-containing gases CF_2Br_2 and CF_3Br are good lubricants for nickel-base alloys. Experiments were, therefore, conducted with the nickel-bonded cermet K175B rider sliding on Hastelloy R-235 rider at temperatures to 1400°F with $\text{CF}_2\text{Br}-\text{CF}_2\text{Br}$ as the lubricant. The results obtained are presented in figure 9. The coefficient of friction was less than 0.2 over the entire temperature range. The wear data indicate a decreasing trend to 1200°F . At 1400°F , the wear increased rather markedly. This increase was due to a degradation of K175B in the halogen atmosphere resulting from a reaction of the halogen gas with the titanium carbide to form volatile titanium halides and carbon (ref. 4).

SUMMARY OF RESULTS

The experimental results obtained in studies of the reduction of corrosive wear with halogen-containing gas lubricants are summarized as follows:

1. Low rider wear can be maintained to higher operating temperatures (above 1000°F) with reactive-gas lubrication by using less reactive materials such as cermet-metal and ceramic-metal systems as the lubricated components. For example, Al_2O_3 sliding on Stellite Star J was effectively lubricated to 1400°F by the gas $\text{CF}_2\text{Cl}-\text{CF}_2\text{Cl}$. The rider wear was low to 1400°F . The disk wear was low to 1200°F but began to increase at 1400°F because of plastic deformation of the Stellite Star J by the Al_2O_3 .

2. The symmetrically substituted ethane compound $\text{CF}_2\text{Cl}-\text{CF}_2\text{Cl}$ offers improved chemical and thermal stability over the methane analog CF_2Cl_2 , thereby contributing less to corrosive wear at extreme temperatures.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, May 12, 1960

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CV-2

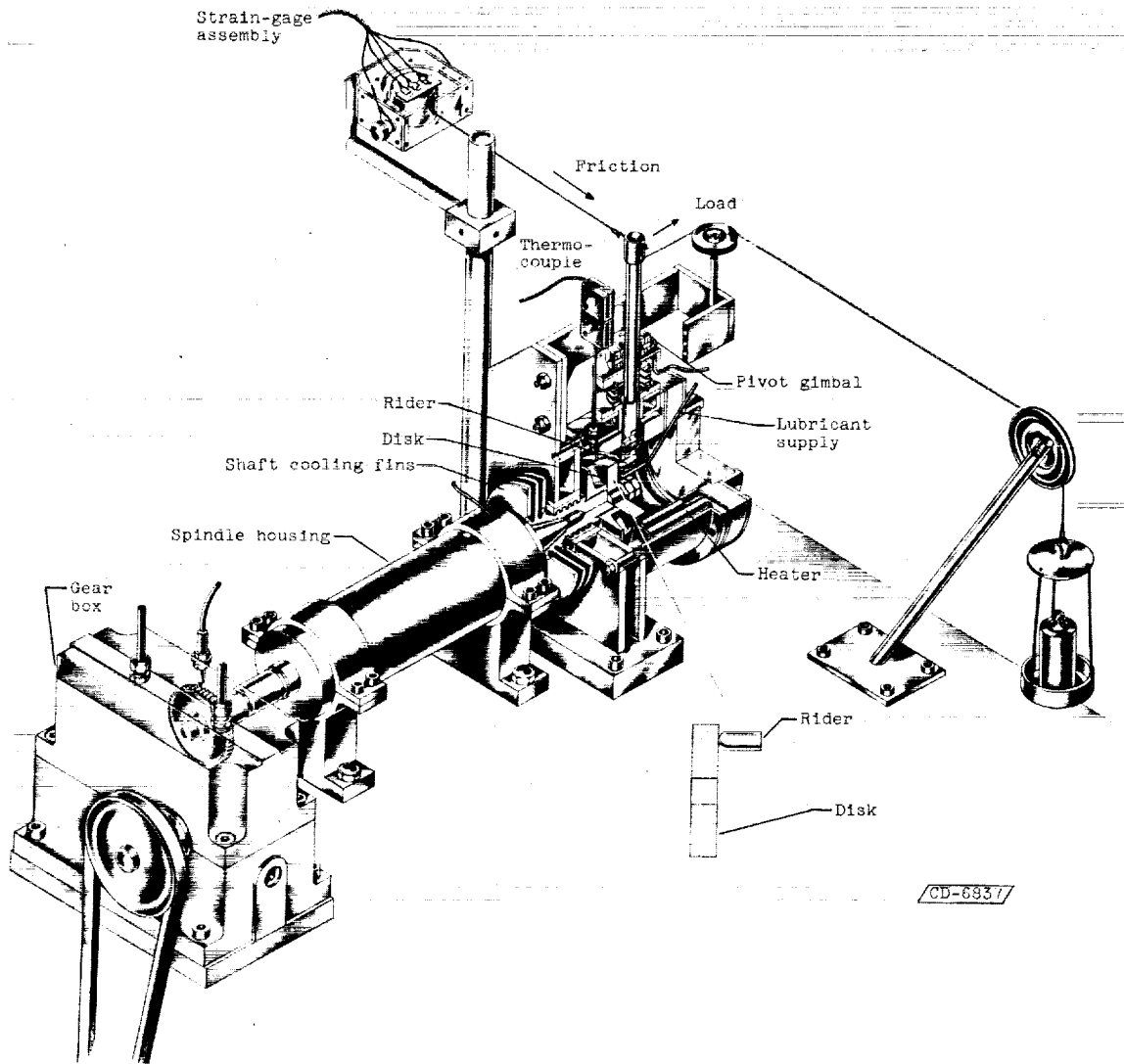


Figure 1. - High-temperature friction apparatus.

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CV-2 back

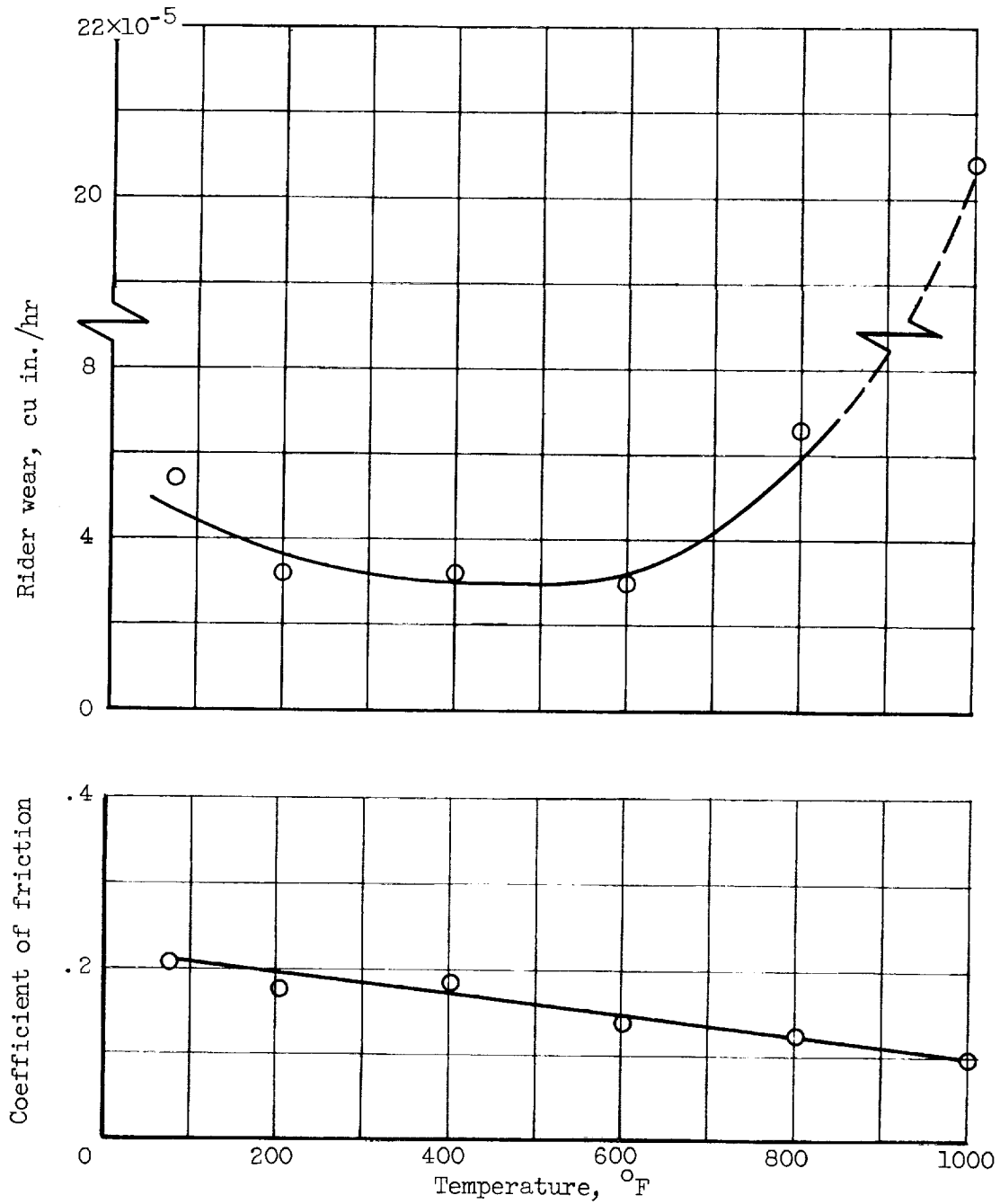


Figure 2. - Friction and wear of Stellite Star J rider sliding on Stellite Star J disk at various temperatures with $\text{CF}_2\text{Cl}-\text{CF}_2\text{Cl}$ as lubricant. Sliding velocity, 3200 feet per minute; load, 1200 grams; duration, 1 hour.

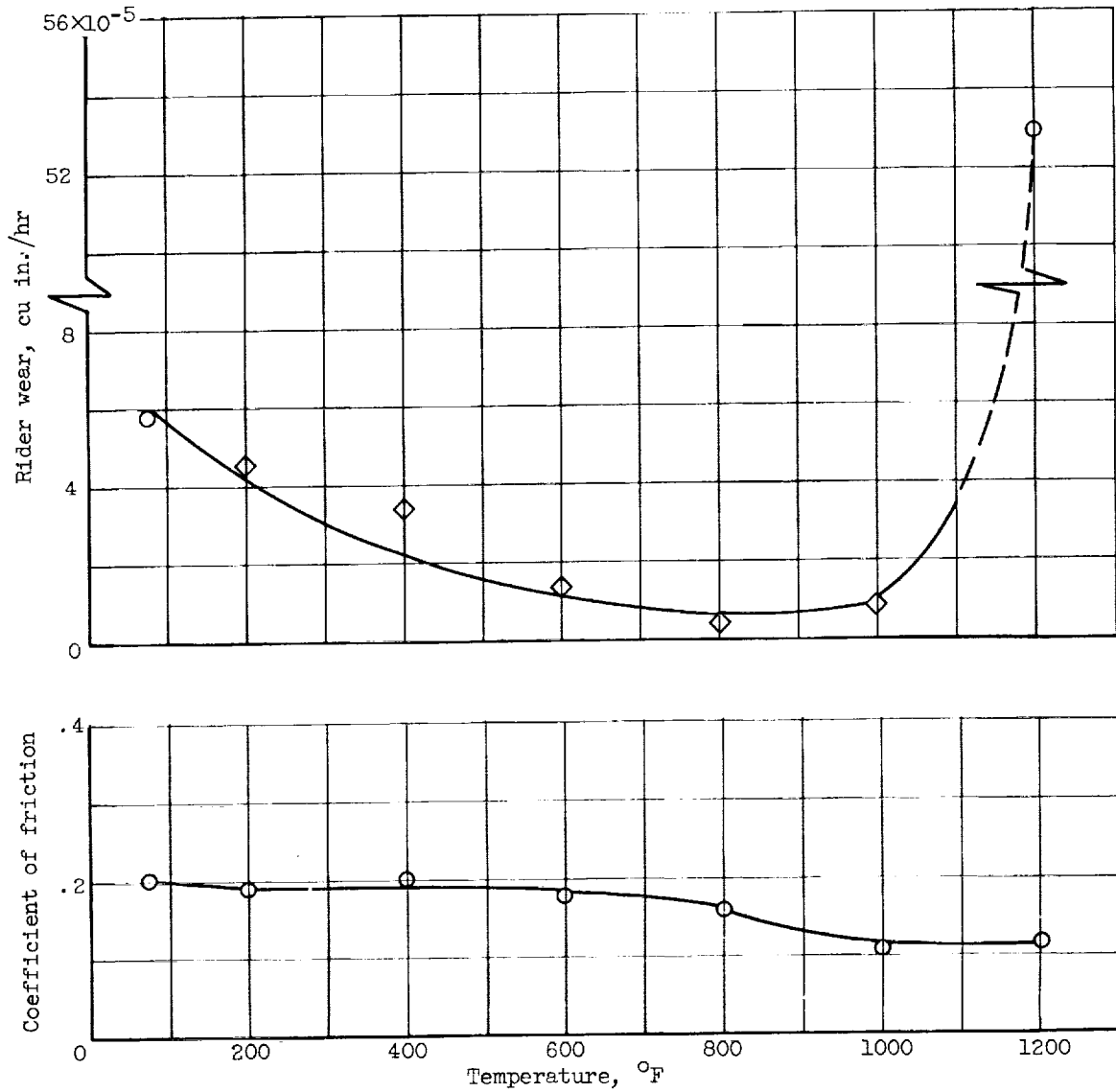


Figure 3. - Friction and wear of LT-1B cermet rider sliding on Stellite Star J disk with $\text{CF}_2\text{Cl}-\text{CF}_2\text{Cl}$ as lubricant. Sliding velocity, 3200 feet per minute; load, 1200 grams; duration, 1 hour.

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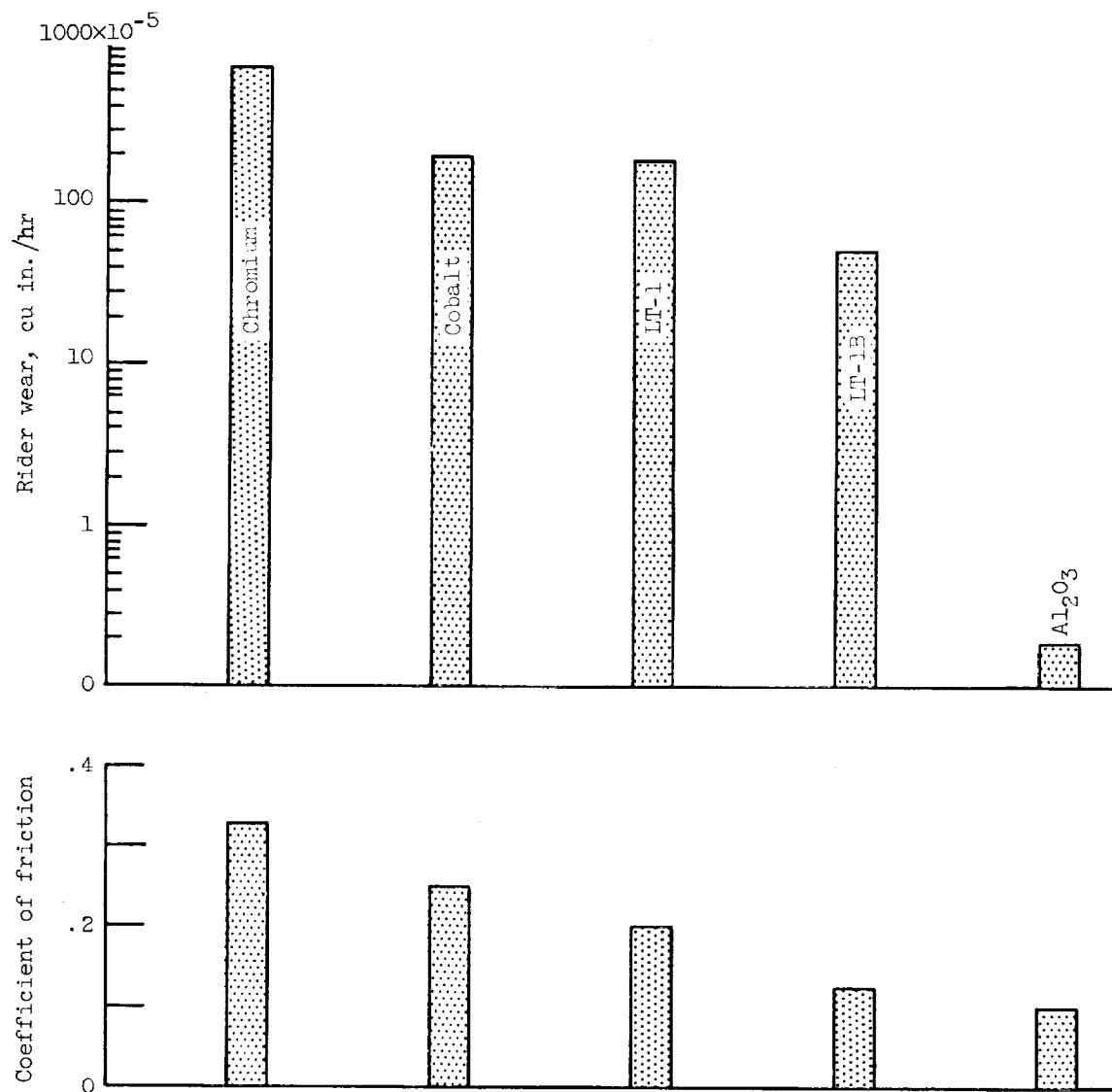


Figure 4. - Comparison of friction and wear of rider materials of various reactivity sliding on Stellite Star J disks at 1200° F with CF₂Cl-CF₂Cl as lubricant. Sliding velocity, 3200 feet per minute; load, 1200 grams; duration, 1 hour.

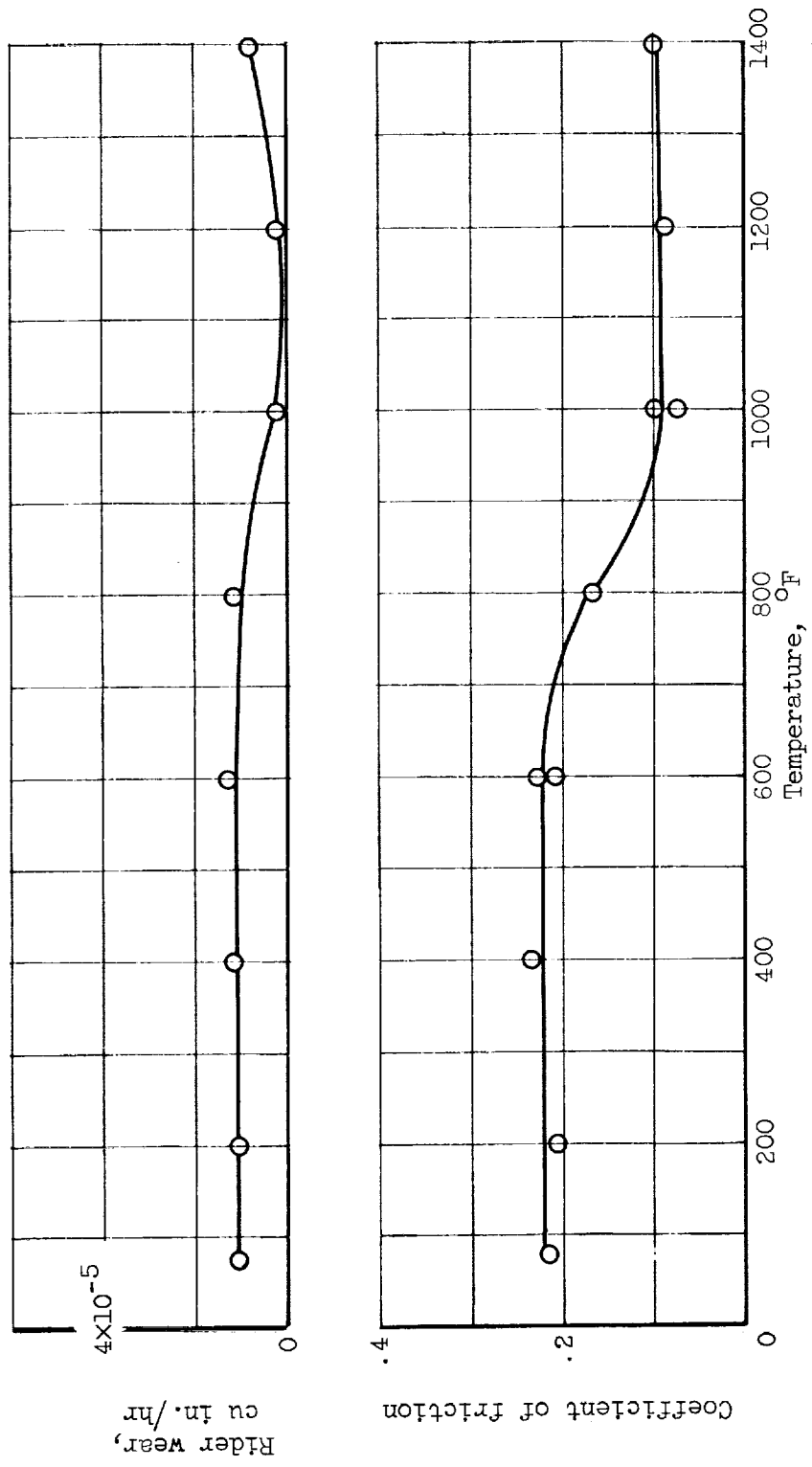


Figure 5. - Friction and wear of a nonreactive Al_2O_3 rider sliding on Stellite Star J disk at various temperatures with $\text{CF}_2\text{Cl-CF}_2\text{Cl}$ as lubricant. Sliding velocity, 3200 feet per minute; load, 1200 grams; duration, 1 hour.

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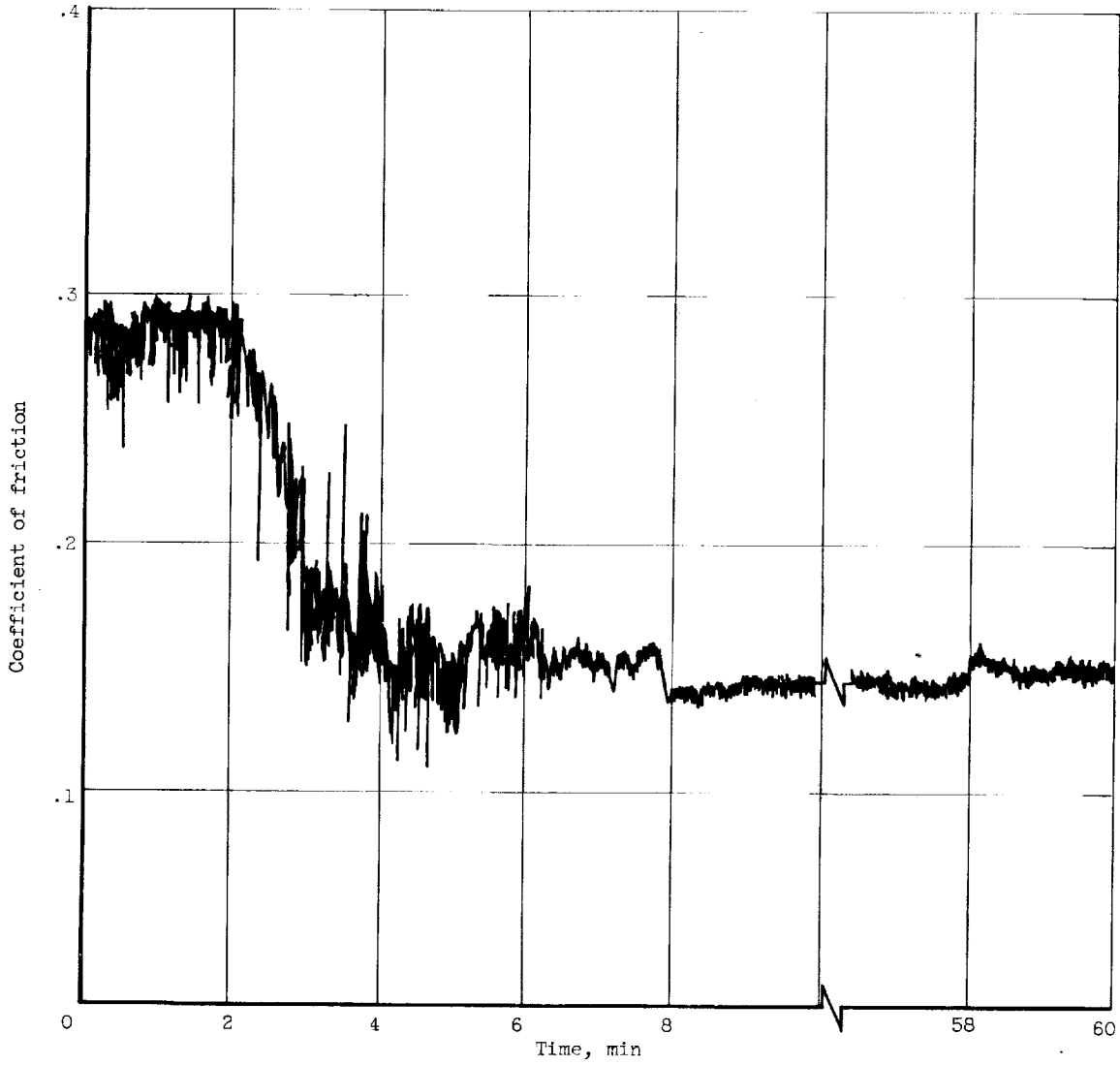


Figure 6. - Coefficient of friction of Al_2O_3 sliding on Stellite Star J with CF_2Cl-CF_2Cl as lubricant. Temperature, $800^{\circ}F$; sliding velocity, 3200 feet per minute; load, 1200 grams.

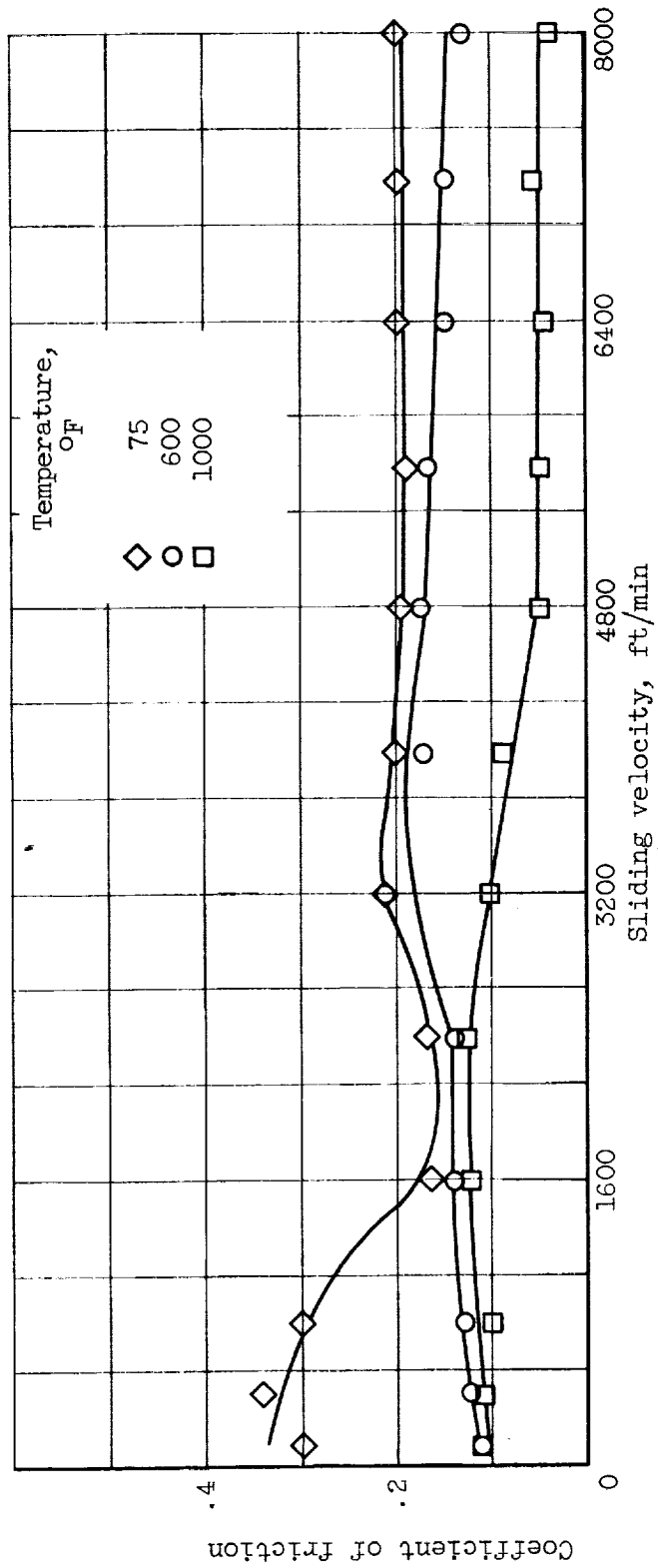


Figure 7. - Effect of temperature and sliding velocity on coefficient of friction of Al₂O₃ rider sliding on Stellite Star J disk with CF₂Cl-CF₂Cl as lubricant. Load, 1200 grams; duration, 1 hour.

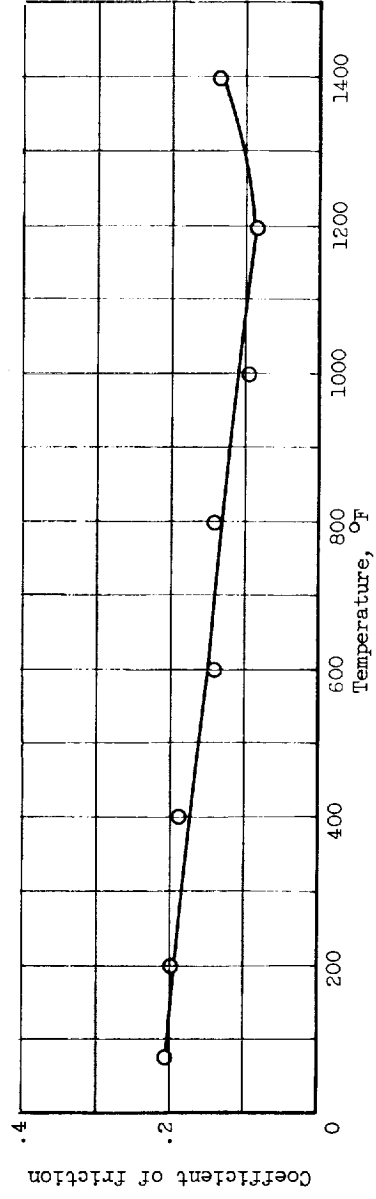
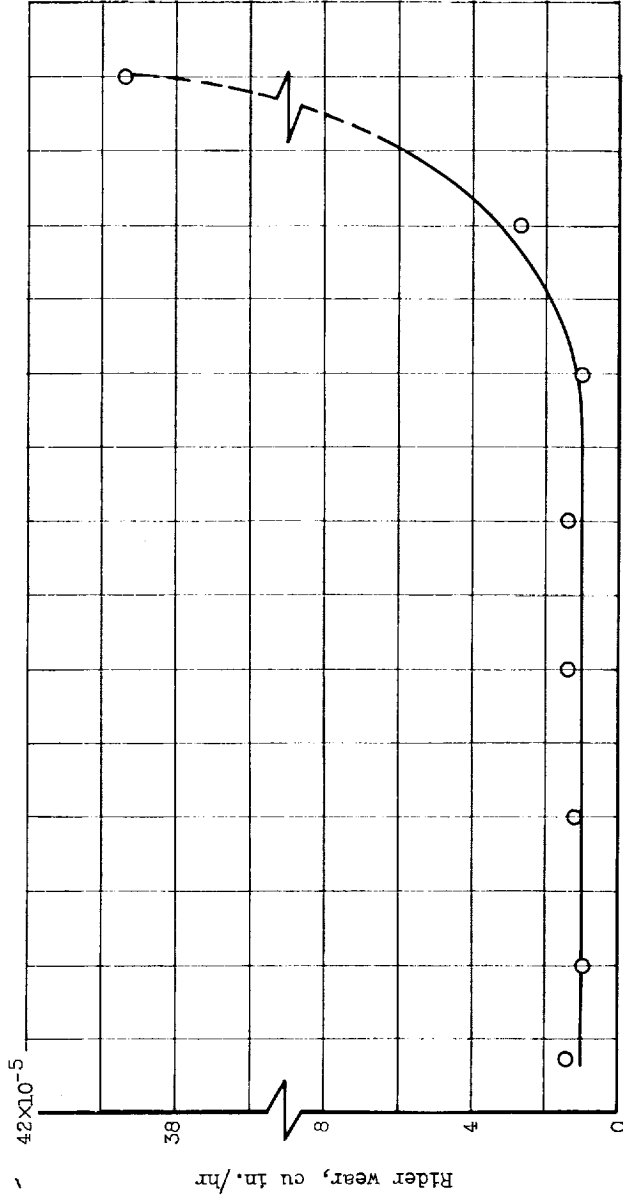


Figure 8. - Friction and wear of nonreactive Al_2O_3 rider sliding on Stellite Star J metal disk at various temperatures with CF_2Cl_2 as lubricant. Sliding velocity, 3200 feet per minute; load, 1200 grams; duration, 1 hour.

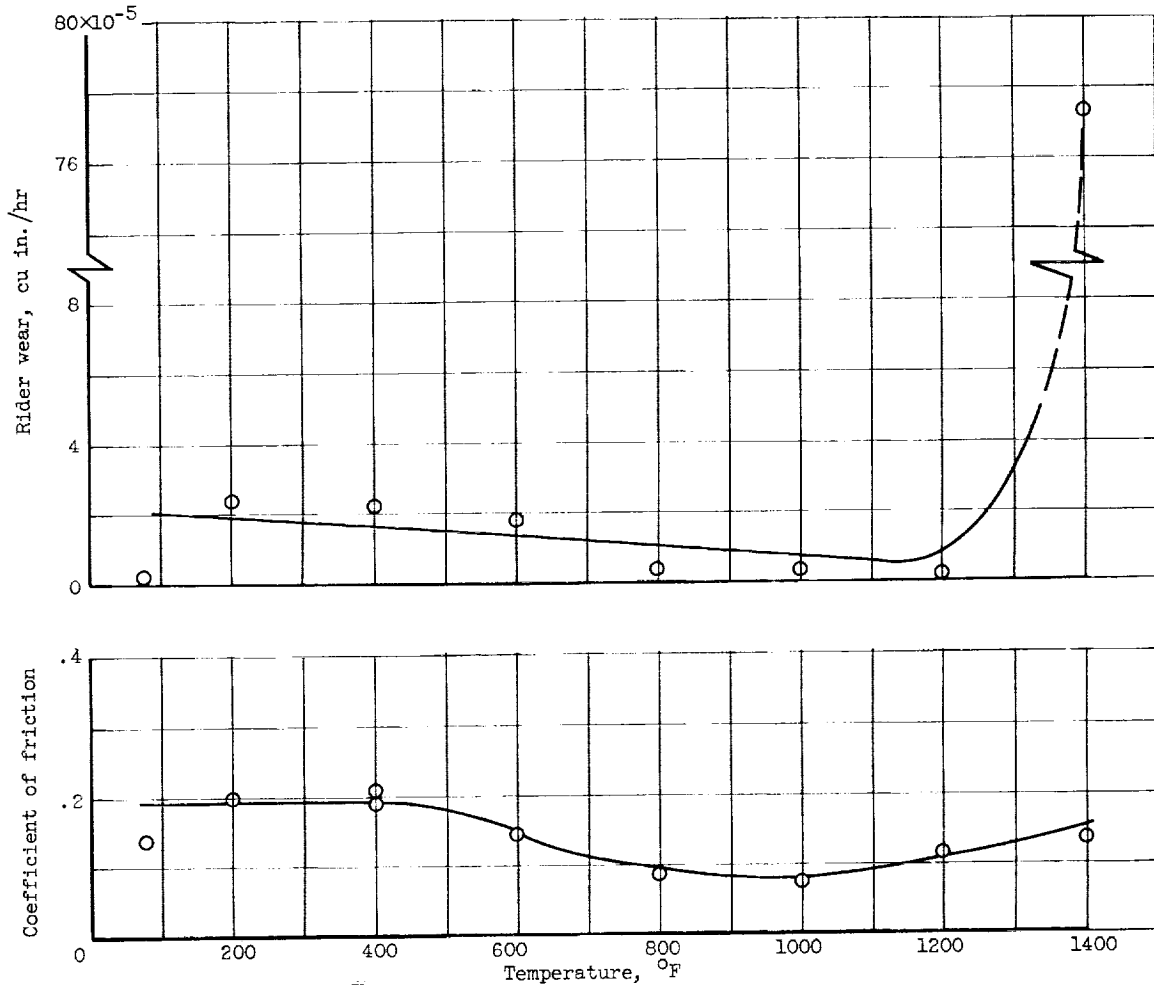


Figure 9. - Friction and wear of a cermet Kentanium K175B rider sliding on a metal Hastelloy R-235 at various temperatures with CF_2Br-CF_2Br as lubricant. Sliding velocity, 3200 feet per minute; load, 1200 grams; duration, 1 hour.