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NICKEL - MAGNESIA CERMET COATINGS

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The Ohio State University
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June 1952

Power Plant Laboratory
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FOREWORD

This report No. 69 for Ohio State University Research Foundation, Project No. 488, was prepared under USAF Contract No. 33(616)-3. The contract was initiated under the research and development project identified by Expenditure Order No. R-506-67-C, entitled "Ceramic Components for Aircraft Power Plants;" it was administered under the direction of the Power Plant Laboratory, Aeronautics Division, Wright Air Development Center, with Mr. Bob L. Paris acting as the project engineer.

ABSTRACT

This report is supplementary to Reports Nos. 46 and 58 of this series. It reviews the possibilities of a metal-bonded refractory coating for the protection of the sheet metal parts of jet propelled mechanisms. Both the theory and practice involved in the preparation and application of a nickel-magnesia cermet coating are discussed. A means is suggested by which the No. 10Ni+MgO coating can be made impervious and at the same time more adherent, especially to low alloy and hence less strategic steels.

PUBLICATION REVIEW

The publication of this report does not constitute approval by the Air Force of the findings or the conclusions contained therein. It is published primarily for the exchange and stimulation of ideas.

FOR THE COMMANDING GENERAL:



NORMAN C. APPOLD
Colonel, USAF
Chief, Power Plant Laboratory
Aeronautics Division

INTRODUCTION

In current designs of jet-propelled mechanisms such as gas turbine engines, pulsejets, ramjets, guided missiles and ordnance rockets, the sheet metal parts are fabricated chiefly of stainless steels and high-nickel alloys such as Inconel. As demand and production increase, the supply situation with respect to strategic alloying elements tends to become critical. It is obvious, therefore, that considerations of cost, supply, and availability dictate that the highly strategic alloys be replaced as far as possible with the mild or intermediate steels

These steels are, of course, normally employed at temperatures below their critical temperatures, but in addition to being subject to oxidation corrosion they are at times subject to local hot spots due to flame impingement, resulting in local warping or buckling and burning. A protective refractory coating which should preferably be both impervious and thermally insulating is therefore indicated. In addition to this application there is interest in such a protective coating for parts fabricated of oxidation-resistant special alloys such as precision-cast stator blades or nozzle diaphragm partitions and machined shroud ring segments. In such applications a longer life is sought by providing protection against intergranular corrosion, including in some cases the maintenance of exact clearances, by means of thermal insulation to prevent excessive expansion. For some applications a suitable protective coating may be one of the high-temperature enamels without or with a dredged-on refractory-powder

cover coat. This latter combination may be considered a glass-bonded impervious refractory coating.

For applications where the temperature is too high for an enamel or where flame spraying is a more practical means of application, the metal-bonded refractory cermet coating which is the subject of this report is proving to be of increasing interest. This coating consists of nickel-bonded electrically-fused magnesium oxide. This No. 10 nickel-magnesia coating was originally developed for its refractory and thermal insulating properties combined with its high temperature stability arising from its inherent resistance to oxidation. It was intended primarily for application on oxidation-resistant sheet metals or cast alloys. In its original form it was not entirely impervious and hence not entirely suitable for use on mild and intermediate steels where oxygen penetration could destroy the interfacial bond between the flame sprayed coating and the substrate. The original development is covered in Reports Nos. 46 and 58 in this series to the Power Plant Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Dayton, Ohio.

The purpose of this study is to review the processing of this nickel-magnesia cermet preparatory to flame spraying and then explore means by which it can be made impervious to the passage of oxygen through the coating to the substrate at the operating temperature of the parts to which it is applied.

SECTION I

No. 10 Ni+ MgO CERMET POWDER FOR FLAME-SPRAYING

A. Basic Factors and Reactions.

The first question always asked is why was the nickel-magnesia cermet the one selected for flame spraying as a refractory coating for metals and alloys? Previous reports have explained that a mechanical mixture of a metal powder and a non-metallic refractory powder cannot be successfully flame-sprayed. The metal will adhere to the target sheet but the non-metallic particles bounce off. A presintered cermet solid body must first be made, then crushed and screened to properly size the powder for application by a powder flame-spray gun. This sintering operation must bond the metal particles to the refractory particles so thoroughly that after crushing the cermet compacts, each grain of refractory has metal attached. The first principle in selecting components for a refractory cermet is to know or determine that they will bond through a solid solution reaction without the production of a liquid phase. We will not here enter into a general discussion of the many different types of bonds between dissimilar materials but will confine ourselves to a consideration of the type which experience has shown to be important in the production of metal-oxide cermets. We believe that a strong bond between a metal and an oxide of another metal can be achieved if the oxide of the metal component is both adherent to the parent metal and isomorphous with the ceramic oxide component.

Let us consider first the chromium - aluminum oxide cermet. To develop a bond between these two components it is first necessary to produce a controlled film of Cr_2O_3 on the Cr grains; then under suitable sintering conditions, this oxide is taken into solid solution in the contiguous Al_2O_3 grains. On one side the chromic oxide is in equilibrium with the metal, and on the other side it is in equilibrium with the Al_2O_3 , thus producing a strong and stable bond to about 2750°F . This cermet, incidentally, cannot be flame sprayed because, in powder form, the chromium sparks and burns in the torch flame.

In the case of the nickel-magnesia cermet, the bond is developed in the same manner. A controlled film of NiO must first be produced on the Ni grains; then under suitable sintering conditions, this oxide is taken into solid solution in the contiguous MgO grains. On one side the nickel oxide is in equilibrium with the metal, and on the other side it is in equilibrium with the MgO , thus producing a strong and stable bond up to the melting point of nickel in a short-time test. This cermet may be flame sprayed with no appreciable oxidation of the metal during the process. After application it deteriorates in service only through the slow oxidation of the bonding nickel. Thus the rate of deterioration is a function of time, temperature, and the permeability of the coating. It therefore becomes obvious that if by one means or another the applied coating can be made impervious, the rate of deterioration of the coating itself is slowed down and at the same time oxygen

penetration direct to the substrate is stopped. This becomes of particular importance if the substrate is a mild or intermediate steel and hence not oxidation resistant.

This brings us to the consideration of a second type of bond which determines the adherence of the coating to the substrate. If this substrate is stainless steel, Inconel, or a similar oxidation resistant alloy, the flame spraying job can be worked hot and followed by torching with the oxyacetylene flame to alloy the nickel of the coating to the substrate. If, on the other hand, the substrate is readily oxidized, the job must be worked fairly cool to get good adherence, and at best it provides chiefly a mechanical bond to the rough sandblasted surface. If worked too hot or for too long a time it has been found that an iron oxide film, builds up at the interface between the coating and the sheet, which interferes with good adherence. As will be discussed in detail later in this report, we have found a means by which this difficulty can be overcome. This consists of adding to the No. 10 Ni+MgO cermet powder a small percentage of Wall-Colmonoy No. 6 hard-surfacing powder which consists of Ni+CrB. The mechanical mixture of the two components should be sprayed rather hot (a good red heat) and then torched until the coating shows a slate color rather than a tan color. This treatment produces a eutectic which is a low melting nickel boride. This eutectic phase promotes excellent adherence, apparently by dissolving the iron oxide as fast as it is formed and by diffusion into the substrate. An addition of Colmonoy No. 6 up to 25 weight percent has been found not

only to promote excellent adherence, but also produce an impervious coating without reducing the fusion point of the coating below 2680°F. Less than 25% may prove to be just as effective and the coating would be somewhat more refractory.

A cobalt - magnesia cermet may be made in the same way as the nickel - magnesia cermet, the bond being through the agency of the oxide CoO . However, cobalt is not as oxidation resistant as nickel and is more strategic.

Iron will wet probably all oxides and silicates and the bond is again through the oxides of iron, but a cermet in which iron is the binder metal is not oxidation resistant. In powder form iron burns in the oxyacetylene flame.

Flake aluminum metal and -325 mesh alumina can be combined mechanically by forming the powders into a compact and sintering in an oxidizing atmosphere at 2500°F. for 8 minutes. The aluminum in the interior of the compact, being heated 1300°F. above its melting point, flows and diffuses between the alumina grains. Upon cooling, the metal is firmly attached to the refractory alumina. This bond persists through grinding and sizing so the powder will flame-spray. However, this bond has been found to be purely mechanical. The oxide of aluminum is not adherent to the metal and hence no bond can be formed with corundum through the oxide.

Nickel and chromium boride make a cermet which can be flame sprayed and produces a hard surfacing coating, but it is not a refractory coating because of the formation, as explained above, of a nickel boride eutectic which melts at 1850°F.

Many other combinations have been tried in this laboratory and none but nickel and magnesia fulfill the requirements for a flame-sprayed refractory cermet coating. This will answer the question as to why we have concentrated on the development of the No. 10 Ni+MgO cermet for flame spraying.

B. Processing.

1. Raw Materials

The nickel was supplied by Charles Hardy, Inc., 420 Lexington Ave., New York 17, N. Y. It is specified as annealed nickel powder, 98/99% nickel, -325 mesh.

The magnesia was supplied by the Norton Co., Worcester, Mass. It is electrically fused magnesia specified as E214 220F "Magnorite" (Approx. 95% -325 mesh). Its chemical composition and physical properties are as follows.

MgO	93 -95	Melting Point	2800°C.
CoO	0.7-2.0	True Density	3.5
Al ₂ O ₃	1.0-2.5	Coef. of Exp- ansion	14x10 ⁻⁶ , 20 ⁰ -1400°C.
SiO ₂	1.0-2.5		
Fe ₂ O ₃	0.1		
TiO ₂	trace		

2. Composition

It has been found by experiment that to produce a cermet powder which will flame spray, the nickel content should be at least 66.6 percent by weight which is about 50.0 percent by volume. A higher content of metal will reduce the amount of fines produced when the compacts are pulverized after sintering and will produce a more ductile flame-sprayed coating.

3. Preparation of Compacts

To 66.6 weight percent of the nickel powder is added 33.3 weight percent of the magnesia powder and an additional 1.0 percent of gum tragacanth. This mixture is dry milled for one-half hour in a steel ball mill using steel balls. This treatment not only produces a thorough mixing but also smear-coats the magnesia grains with nickel. This mixed powder is then moistened with about 8.0 percent of water and pressed into compacts at about 10,000 p.s.i. We have found it desirable to use a compact about 5/16" thick x 1.5" diameter. The thinner the compact the easier it is to oxidize it uniformly and quickly in the preheating treatment.

4. Sintering

The sintering is accomplished in two steps using two separate furnaces, one heated to 1600°F. and the other to 2500°F. The former may be a wire resistance electric furnace and the latter a Globar resistance furnace. A charge of dry compacts well separated by potters pins or stilts is placed into the hot furnace at 1600°F. and held for about three hours for compacts of the above suggested thickness. This treatment will oxidize the surface of the nickel grains and harden the compact to the center, leaving no soft core. The color should remain a slate grey.

After this preheat to develop the thin oxide film on all of the nickel grains, the whole hot charge supported on a suitable alab or batt is transferred to the second hot furnace

held at 2450°F. to 2500°F. For a small charge, the furnace will come back to temperature in about 10 minutes and the charge should be held at temperature for about 20 minutes or a total of 30 minutes in the final sintering heat. The charge is immediately withdrawn and allowed to cool. The color of the compacts should be a greenish slate grey.

Since the oxidation of the nickel has already been accomplished in the preheat, the final sintering can be done in a neutral atmosphere to preclude the possibility of developing too much green NiO in the final sinter. We have used both methods and, with care, can get the same end product by doing the final sintering in a normal atmosphere.

Other variations in procedure will suggest themselves, such as preoxidizing the nickel powder in a separate operation before it is mixed with the magnesia powder and formed into compacts. This step would then replace the oxidizing preheat specified above and would permit the making of larger and thicker compacts. The sinter at 2500°F. would then bond the two components through solid solution of the NiO on the nickel grains into the contiguous MgO grains. This procedure has been successfully applied to chromium in the fabrication of chromium - alumina cermets.

5. Crushing and Sizing

The powder required for effective handling by the carburetor of the Powder-Weld gun is -100 +325 mesh. Therefore, the crushing operation should be such as to produce a

minimum of -325 mesh material which must be discarded or possibly reworked. These fines will consist of excess NiO and some fine MgO grains to which no metal is attached. Crushing rolls or a disc pulverizer may be used.

6. Flame-spraying

The flame-spraying itself requires experience and skill on the part of the operator. We use a Powder-Weld gun employing an oxyacetylene flame, nitrogen as the carrying gas through the carburetor, and an outside nitrogen sheath to protect the powder from oxidation by the air during the spraying operation. Considerations requiring the job to be worked cooler or hotter, or followed by torching with the flame alone, have been previously discussed. The thickness of coating which can be built up will depend upon the metal content. The composition here discussed is best applied at about 20 mils or less with 30 mils as the maximum.

7. Testing

The most significant laboratory tests for cermet coated sheets are (a) thermal cycling tests, (b) oxidation resistance tests, and (c) fusion tests of the applied coating using an oxyacetylene torch and optical pyrometer. Rate of heat transfer through a coating of given porosity is also important. Whether or not the coating is porous or impervious can be determined. A bend test for adherence is questioned. The nature of the No. 10 Ni+MgO coating is such that its ductility is low. If stressed in bending beyond its elastic limit, one of two things happens. If the coating is porous and weak but

well adhered to the substrate, the coating will follow the bend but the strain is relieved in the form of multiple hairline cracks. If, on the other hand, the coating is strong and impervious, the strain will be relieved by one break across the coating and a simultaneous separation of the stressed area from the substrate. The results of all of these tests have been discussed in some detail in Report No. 46, previously mentioned.

SECTION II

A METHOD BY WHICH THIS COATING CAN BE MADE IMPERVIOUS

The Wall Colmonoy Corporation of Detroit, Michigan makes a hard-surfacing material in powder form for flame spraying. One such product called Colmonoy No. 6 consists of chromium boride crystals in a nickel vehicle (Ni+CrB). When flame sprayed and torched, a eutectic is produced which is nickel boride melting at about 1850°F. This eutectic phase promotes excellent adherence by diffusion and alloying on steels and, so far as we know, on stainless and other alloys high in nickel. Knowing its properties, it was thought that additions of this composition to our No. 10 Ni+MgO powder should make it impervious and at the same time promote better adherence, especially on the mild and intermediate steels which are very susceptible to oxidation.

In the following table are shown the mixtures tested together with the fusion temperatures of the coatings. Mechanical mixtures of No. 6 Colmonoy and No. 10 Ni+MgO powders

were made and flame sprayed on TiNamel sheets. The mixtures flame-sprayed very satisfactorily and the adherence was good. Stain tests indicated that both mixtures produced impervious coatings. Fusion tests of the applied coatings were made using an oxyacetylene torch and an optical pyrometer.

TABLE I

Composition of Coating Weight Percent	Fusion Temp. °F.
100% No. 6 Colmonoy	1850°F.
A. 50% No. 6 + 50% No. 10	1650°-1700°F.
B. 25% No. 6 + 75% No. 10	2680°F.

A 25% addition of Colmonoy No. 6 apparently makes the Ni+MgO coating impervious without reducing the fusion temperature below 2680°F. Less than 25% might be just as satisfactory and the coating would be more refractory.

Compositions A and B on TiNamel were thermal cycled at 1500°F. for 10 cycles with no loosening of the coating. Composition B should be sprayed rather hot (a good red heat) or torched until the coating shows a slate color rather than a tan color. It can then be been hammered on an anvil until the TiNamel sheet is stretched, without loosening any of the coating.

Small sheet specimens of TiNamel have been flame sprayed on both sides and the edges with composition B and have been subjected to oxidation tests for 100 hours at both 1600°F. and 1800°F. At 1600°F. no visible deterioration resulted

from the test and the total gain in weight was only 1.56%. At 1800°F. there was a little evidence of deterioration on the edges only, after 100 hours at temperature. The total gain in weight was 2.28%.

Figure No. 1 is a photomicrograph at 250X and etched, of the interface between TiNamel as the substrate and flame-sprayed and torched composition B. This is a polished section photographed with reflected light.

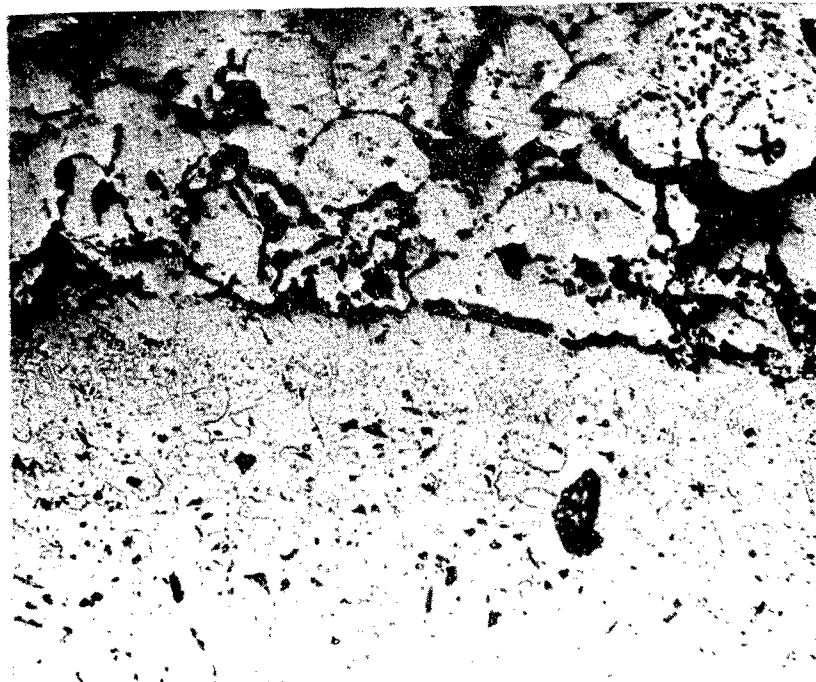


Figure No. 1

We feel that this coating should not be stressed beyond its elastic limit in a bend test. It is too strong and coherent to allow relief of the strain in the form of hairline cracks, and yet not ductile enough to bend with the base sheet.

One TiNamel J33 combustion-chamber liner has been coated both inside and outside with composition B. It will be submitted to the Power Plant Laboratory for engine test.

A second method was tried for sealing the pores of the No. 10 Ni+MgO coating. This consists simply of applying a suitable enamel over the part which has previously been coated with the No.10 Ni+MgO coating by flame spraying. Consider as an example the case of the combustion-chamber liners of a gas turbine engine. If made of mild steel or TiNamel, they need an all-over protection against oxidation. The inner surface is benefited by a thermal insulating coating such as the No. 10 Ni+MgO coating, but the outer surface should be protected by a coating which will least interfere with air cooling. After preliminary tests on small flat specimens, we tried a cover coat of O.S.U. enamel 252-4as applied all over a liner, the inner surface of which has been flame sprayed with the No. 10 Ni+MgO cermet coating. The enamel application was successful, but upon reheating to 1700°F. for thermal cycling tests it was found that after the first cycle small areas of the dual coating on the inner surface peeled off. Evidently the bond between the flame sprayed coating and the liner is not adequate to withstand the stress due to the differential in expansion and contraction of the dissimilar coatings.

It therefore appears that to make this coating impervious, we should rely upon additions of Colmonoy No. 6 or its essential constituents.