ABSTRACT: Improved oxidation and sulfidation resistance can be imparted to a high-temperature metallic diffusion coating by bonding with metallic surface, such as nickel, cobalt or iron base alloy surface, by embedding in a coating outer portion between about 5 and 50 volume percent of oxide particles of up to about 20 microns in size and thermally stable to at least about 2000°F.
The useful life of metallic diffusion coatings applied to high temperature operating components such as gas turbine engines is dependent upon coating surface degradation resulting from contact with erosive, corrosive or oxidizing environments. However, inhibition of diffusion through the coating of oxidizing and sulfidizing agents toward the coating basis metal interface can significantly lengthen the useful life of the coating. The present invention recognizes that the introduction of the above defined oxide particles in an outer portion of the coating results in such a barrier to undesirable migration.

As an example, one form of the above described ternary alloy powder used in the evaluation of the present invention consisted nominally, by weight, of 61 percent Ti, 34 percent Al, and about 5 percent combined carbon. This ternary alloy in powder form will be hereinafter identified as "Alloy C." Prior to the preparation of specimens for the evaluation of the present invention, a blend of about 40 weight percent Alloy C powder and about 60 weight percent Al₂O₃ powder was mixed with about 0.2 weight percent NH₃. In this type of particulate mixture, the Al₂O₃ powder acts to inhibit sintering of the Alloy C powders but does not enter into the coating process.

The method of the present invention contemplates the application to the surface of an article to be diffusion coated of oxide particles, stable both to the processing temperature and mechanism, as an intermin or preliminary coating in a non-fused, loosely held vapor permeable condition. This can be and was in this example accomplished by first making a slurry of the oxide particles and a liquid binder which will decompose without residue upon heating. For example, an acrylic resin in toluene or acetone can be used. As will be discussed later, the thickness of the intermin coating is not critical. Therefore, the slurry can be adjusted in concentration to provide, for example, from about 1-25 mils of oxide on the surface. However, from a practical viewpoint no more than about 15 mils is necessary. Although the oxide particles are no more than about 20 microns in size, it is preferred that a variety in size of particles be present rather than particles all of the same size.

A variety of oxides of thermal and process stability, including oxides of titanium, aluminum and their mixtures, have been evaluated in connection with the present invention. It is preferred that TiO₂ or Al₂O₃ or their mixtures in particle sizes of about 1-20 microns be used in the present invention when coating surfaces based on one of the elements Fe, Ni or Co.

The slurry can be applied to the article surface by a variety of methods such as brushing, dipping, spraying, etc. In one example, a paint spray gun was used with a slurry to apply a coating of a powder mixture of about 50 weight percent each of Al₂O₃ and TiO₂.

After application of the oxide coating to the article surface to be coated, the article was placed in a container, such as a retort, along with the previously described particulate mixture, including powdered Alloy C. It should be recognized, however, that as indicated before, the Al₂O₃ in the particulate mix is included as a filler and does not enter into the coating reaction. Therefore, if a method such as is described in copending application Ser. No. 780,199, filed concurrently with this application, in which the article surface to be coated does not physically contact the coating material such as the particulate mixture, then the filler may be eliminated if particle sintering is not a problem. If the article is to be contacted by the particulate mixture as described in the above identified copending application Ser. No. 693,691, then inclusion of the Al₂O₃ filler is preferred.

The retort enclosing the particulate mixture and the article surface including the intermin oxide coating was provided with a nonoxidizing atmosphere, in this example hydrogen, and was heated in the range of 1400-2100°F. For 1-4 hours, for example, about 1950°F for 3-4 hours. This time and temperature was sufficient to allow deposition of such elements as alu-
Specimens of each of the nickel base alloys listed in Table I were coated in the manner described in the above specific example: A mixture of 50 percent by volume each of Al₂O₃ and TiO₂ of particle size in the range of 1–10 microns was applied as an intermetal coating by spraying from a slurry of the oxide particles and acrylic resin in acetone. The coating method was conducted at about 1950°F. for 3–4 hours in a hydrogen atmosphere. The resulting coating had a coating outer portion, including the entrapped oxides, of about 1 mil thick and a coating inner interdiffusion portion of about 1 mil thick for a total coating thickness of about 2 mils. The oxide particles in the coating outer portion comprised about 10–20 volume percent of the outer portion.

After coating, these specimens along with specimens coated without the intermetal oxide coating were tested under static oxidation conditions at 2100°F. for 100 hours. Typical of the results obtained are those shown in the following table II.

### Table II

<table>
<thead>
<tr>
<th>Specimen</th>
<th>100 Hr. Cyclic Hot Corrosion Test</th>
<th>Coating Life (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal alone</td>
<td>Metal + oxide</td>
<td>Metal + oxide</td>
</tr>
<tr>
<td>1</td>
<td>25</td>
<td>100+</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>100+</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>100+</td>
</tr>
<tr>
<td>4</td>
<td>45</td>
<td>100+</td>
</tr>
</tbody>
</table>

As shown from the data of table II, both coatings protected base metal adequately for 100 hours at 2100°F. However, the life of the coating including the entrapped oxide particles in the coating outer portion is significantly greater as evidenced by less than 1 percent of it being consumed compared with consumption of 50–75 percent for the non-oxide bearing metallic diffusion coating. Therefore, the improved coating of the present invention would continue to protect the article many times longer than the same coating without embedded oxides.

Another series of specimens coated in the same manner were placed in a hot corrosion testing apparatus cycled between about 1650 and 1725°F. Heat was generated from combustion of a natural gas/air mixture. At the same time, 100 parts per million of an aqueous sulfidizing contaminant containing about 9 percent NaCl and about 10 percent Na₂SO₄ was injected toward the specimen. Results of the hot corrosion testing is shown in the following Table III.

### Table III

<table>
<thead>
<tr>
<th>Specimen</th>
<th>100 Hr. Cyclic Hot Corrosion Test</th>
<th>Coating Life (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>100+</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>100+</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>100+</td>
</tr>
<tr>
<td>4</td>
<td>45</td>
<td>100+</td>
</tr>
</tbody>
</table>

*No failure at end of 100 hour test.

As can be seen by the data of table III, in the hot sulfidizing atmosphere described, the life of the coating of the present invention is significantly better than the same coating without entrapped oxides, even though both coatings were capable of withstanding more than 100 hours under oxidizing conditions alone as shown by the data from which table II was selected.

### Table I

Composition Wt. percent—Bal. Ni and incidental impurities

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Cr</th>
<th>Mo</th>
<th>Ti</th>
<th>Al</th>
<th>Zr</th>
<th>V</th>
<th>Cr/Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.6</td>
<td>2.5</td>
<td>4.1</td>
<td>1.5</td>
<td>0.3</td>
<td>0.1</td>
<td>0.6</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>3.5</td>
<td>2.4</td>
<td>4.0</td>
<td>1.4</td>
<td>0.3</td>
<td>0.1</td>
<td>0.6</td>
<td>1.0</td>
</tr>
<tr>
<td>3</td>
<td>3.4</td>
<td>2.3</td>
<td>3.9</td>
<td>1.3</td>
<td>0.3</td>
<td>0.1</td>
<td>0.6</td>
<td>1.0</td>
</tr>
<tr>
<td>4</td>
<td>3.3</td>
<td>2.2</td>
<td>3.8</td>
<td>1.2</td>
<td>0.3</td>
<td>0.1</td>
<td>0.6</td>
<td>1.0</td>
</tr>
</tbody>
</table>

*Maximum.
Thus, although the coating described by the above identified copending application Ser. No. 693,691 has significant benefits and uses particularly under oxidizing conditions, it has been recognized that the practice of the present invention provides an unexpected and significant improved combination of hot corrosion or sulfidation resistance along with oxidation resistance.

We claim:

1. In a diffusion method for applying a metallic coating to an article having a metallic surface including a basis metal element selected from the group consisting of Fe, Ni and Co, the steps of:
   applying to the surface an interim vapor permeable coating of about 1–25 mils in thickness of loosely adherent, non-fused, oxide particles of about 1–20 microns in size, thermally stable at least to about 2000°F. and which are stable during the diffusion method; and then
   applying a metallic diffusion coating of about 1–5 mils in thickness to the surface through the interim coating to entrap oxide particles in a coating outer portion.

2. In the method of claim 1 in which the oxide particles are oxides selected from the group consisting of oxides of Al, Ti and their mixtures; and the metallic diffusion coating is applied by:
   placing the article surface in a container including a mixture comprising:
   a. a ternary alloy consisting essentially of, by weight, about 50–70 percent Ti, 20–48 percent Al and 0.5–9 percent combined carbon, the alloy having a dispersion of Ti, AlC complex carbide in a matrix selected from the group consisting of Ti, Al and their alloys, and
   b. about 0.1–10 weight percent of the mixture of a halide salt activator which will react with a metallic element in the ternary alloy to form a halide of the metallic element;
   providing the container with a nonoxidizing atmosphere;
   and then
   heating the surface and the mixture in the nonoxidizing atmosphere at a temperature and for a time sufficient (1) to form a halide vapor of at least one metallic component of the ternary alloy, (2) to allow penetration of the vapor through the interim coating to the metallic article surface to deposit the metallic component on the surface and (3) to allow both
   i. diffusion of the deposited metallic component with the article surface and
   ii. entrapment of particles of the interim coating by the deposited metallic component to provide the metallic coating comprising a coating outer portion including the entrapped oxides and a coating inner interdiffusion portion intermediate of and diffusion bonded with both the article surface and the coating outer portion.

3. The method of claim 2 in which:
   the basis element is Ni;
   the interim coating is about 1–15 mils in thickness;
   the halide salt activator is selected from the group consisting of chlorides and fluorides of ammonium and of the alkali metals of Group IA of the Periodic Table of Elements; and
   the article surface and mixture are heated at a temperature of about 1400–2100°F. for about 1–4 hours.

4. The method of claim 3 in which:
   the article surface when enclosed in the container is contacted by the mixture in particulate form; and
   the mixture consists essentially of, by weight:
   a. about 20–90 percent of the powdered ternary alloy;
   b. about 10–80 percent of an inert filler material which will not react with other components of the mixture during use of the mixture; and
   c. about 0.1–10 percent of the halide salt activator.

* * * * *