GAS PLATING OF ALLOYS

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11 Claims. (Cl. 117—106)

This invention relates to the formation of alloys and particularly to phosphorous containing alloys such as those of nickel and iron.

Nickel-phosphorous alloys and to a lesser extent iron-phosphorous alloys find utility in a variety of applications. For example, nickel containing Ni₃P is relatively easily soldered, below 750° F. has good hardness characteristics and may be chrome plated for decorative applications. Such alloys are useful for example in electrical connectors, aircraft parts and the like. Further, bonding to other metals such as stainless steel, aluminum, nickel, copper and magnesium is advantageously achieved.

It is a primary object of this invention to describe a novel method for the attainment of alloys containing a base metal and a combination of the base metal with phosphorous.

Another object of the invention is to describe a process for the production of phosphorous containing alloys having a high degree of purity.

A particular object of the invention is the provision of an alloy of nickel phosphorous or iron phosphorous achieved by deposition of the components from the gaseous state.

In the practice of the invention a volatile phosphorous component such as the phosphine, phosphorous itself, or organic phosphorus compounds, such as the alkyl and aroyl, is volatilized. Nickel carbonyl or other volatile, heat decomposable metal bearing compound is present to a reaction chamber with the volatilized phosphorous component. The reaction chamber contains an object upon which a film of the alloy is to be deposited and this object is suitably heated to effect decomposition of the gases.

The decomposition of the metal bearing gas in the case of nickel carbonyl provides nickel as the base metal; iron pentacarbonyl provides iron as the base metal.

Simultaneous co-deposition of the phosphorous component and the metal bearing gas provide on the heated object the alloy. Specific characteristics in the alloy are attained by combining more or less of the phosphorous component with the metal bearing component in the gaseous state. In the case of nickel carbonyl and tri-methyl phosphine the alloy desired contains nickel metal and Ni₃P. The content of Ni₃P controls the ultimate properties of the product and the Ni₃P is dispersed throughout the nickel phase.

Tri-methyl phosphine is a preferred source of the phosphorous as it has a boiling point close to that of nickel carbonyl and volatilization is more readily controllable than with phosphine, for example, where high reaction temperatures are required due to the stability of the phosphine.

Tri-ethyl phosphine which has a higher boiling point is more suitable when iron pentacarbonyl is employed. However, methyl di-ethyl phosphine, methyl ethyl propyl phosphine and others though somewhat more expensive presently, will serve the purpose.

The alloy deposition rate is a function of the flow rate of the phosphorous and base metal components, the temperature of the article being plated and to some extent the area of the object and the size of the plating chamber. Deposition rate of 2 to 10 mils per hour are practicable while thickness may be from 0.1 mil to 10 mils or more. The flow sheet illustrates the essential steps of the process.

As will be noted from the flow sheet a liquid phosphorous containing component and a liquid metal bearing component are passed to a flash vaporizer and then to a reaction chamber wherein the heated object is contained. If desired a carrier gas, such as nitrogen, argon or carbon dioxide may be utilized to aid the flow of the vaporized materials to the reaction chamber. Within the reaction chamber the mixed gases contact the heated object and deposit thereon, forming a coating of the alloy.

As an example specific, liquid tri-methyl phosphine and nickel carbonyl are metered separately to a common flash vaporizer along with the flow of carrier gas and are then transported to the plating chamber. Specific conditions are:

<table>
<thead>
<tr>
<th>Sample area</th>
<th>square inches</th>
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<tbody>
<tr>
<td>10</td>
<td></td>
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</table>

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5–10</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Inert gas, CO₂</th>
<th>cc/min</th>
<th>400–1000</th>
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</thead>
</table>

<table>
<thead>
<tr>
<th>Vaporizer temperature</th>
<th>°F</th>
<th>112–170</th>
</tr>
</thead>
</table>

<table>
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<tr>
<th>Specimen temperature</th>
<th>°F</th>
<th>350–700</th>
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<table>
<thead>
<tr>
<th>Phosphorous content of deposit (Ni₃P)</th>
<th>percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1–10</td>
<td></td>
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</table>

<table>
<thead>
<tr>
<th>Nickel content of deposit</th>
<th>do</th>
</tr>
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<tbody>
<tr>
<td>99–90</td>
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</table>

As exemplary of the use of iron pentacarbonyl for the formation of an alloy containing iron and iron phosphorous the following data are applicable:

<table>
<thead>
<tr>
<th>Sample area</th>
<th>square inches</th>
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<tbody>
<tr>
<td>10</td>
<td></td>
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</table>

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5–10</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Iron pentacarbonyl, liquid</th>
<th>cc/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Optional) carbon dioxide</td>
<td>cc/min</td>
</tr>
<tr>
<td>400–850</td>
<td></td>
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</table>

<table>
<thead>
<tr>
<th>Vaporizer temperature</th>
<th>°F</th>
<th>260–285</th>
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</thead>
</table>

<table>
<thead>
<tr>
<th>Substrate temperature</th>
<th>°F</th>
<th>400–800</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Phosphorous content of deposit (Fe₃P and Fe₃P) in an iron matrix</th>
<th>percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>2–14</td>
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<table>
<thead>
<tr>
<th>Nickel</th>
<th>do</th>
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</thead>
<tbody>
<tr>
<td>98–86</td>
<td></td>
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</tbody>
</table>
nickel carbonyl, and contacting an object heated to the 
decomposition temperature of the combined vapors to 
effect deposition of a phosphorous-nickel alloy on the 
object.
3. The process of alloy formation which comprises 
combining in the vapor state a volume of a heat decom-
plosable phosphorous component and a volume of iron 
pentacarbonyl, and contacting an object heated to the 
decomposition temperature of the combined vapors to 
effect deposition of a phosphorous-iron alloy on the 
object.
4. The process of alloy formation which comprises 
the steps of combining in the vapor state a volume of 
tri-methyl phosphine and a volume of gaseous nickel car-
bonyl, and contacting an object heated to the decomposi-
tion temperature of the combined vapors to effect deposi-
tion of a phosphorous-nickel alloy on the object.
5. The process of alloy formation which comprises the 
steps of combining in the vapor state a volume of tri-
ethyl phosphine and a volume of gaseous iron pentacar-
bonyl, and contacting an object heated to the decomposi-
tion temperature of the combined vapors to effect deposi-
tion of a phosphorous-iron alloy on the object.
6. The process of alloy formation which comprises the 
steps of passing to a vaporizer a liquid phosphorous com-
ponent and a liquid heat decomposable metal bearing 
compound to effect vaporization of the component and 
compound, combining the vapors of the component and 
compound, and contacting an object heated to the decom-
position temperature of the combined vapors to effect 
deposition of a phosphorous containing alloy on the 
object.
7. The process of alloy formation which comprises 
the steps of metering liquid trimethyl phosphine and 
liquid nickel carbonyl to a vaporizer to effect vaporiza-
tion of the phosphine and carbonyl, combining the vapors 
of the carbonyl and phosphine in one atmosphere, and 
contacting an object heated to the decomposition tem-
perature of the carbonyl and phosphine to effect deposi-
tion of a phosphorous-nickel alloy on the object.
8. The process of alloy formation which comprises the 
steps of metering liquid triethyl phosphine and liquid iron 
pentacarbonyl to a vaporizer to effect vaporization of the 
phosphine and pentacarbonyl, combining the vapors of 
the carbonyl and phosphine in one atmosphere, and con-
tacting an object heated to the decomposition tempera-
ture of the carbonyl and phosphine to effect deposition 
of a phosphorous-iron alloy on the object.
9. The process of alloy formation which comprises the 
steps of vaporizing tri-methyl phosphine and nickel car-
bonyl at a temperatures of between 112° F. and 170° F., 
combining the vapors in a common atmosphere with an 
object heated to between 350° F. and 700° F. to thereby 
decompose the phosphine and carbonyl together to de-
posit an alloy of nickel-phosphorous on the object.
10. The process of alloy formation which comprises the 
steps of vaporizing tri-ethyl phosphine and iron 
pentacarbonyl at a temperature of between 260° F. and 
285° F., combining the vapors in a common atmosphere 
with an object heated to between 400° F. and 800° F. to 
thereby decompose the phosphine and pentacarbonyl to-
gether to deposit an alloy of iron-phosphorus on the 
object.
11. The process of alloy formation which comprises the 
steps of vaporizing tri-methyl phosphine and nickel 
carbonyl, combining the vaporized phosphine and carb-
ynol in one atmosphere, providing an object heated to 
the decomposition temperature of the carbonyl and phos-
phine, and directing the combined phosphine and car-
bonyl atmosphere with a carrier gas into contact with 
the heated object to thereby effect deposition of a nickel-
phosphorous alloy on the object.

References Cited in the file of this patent

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