

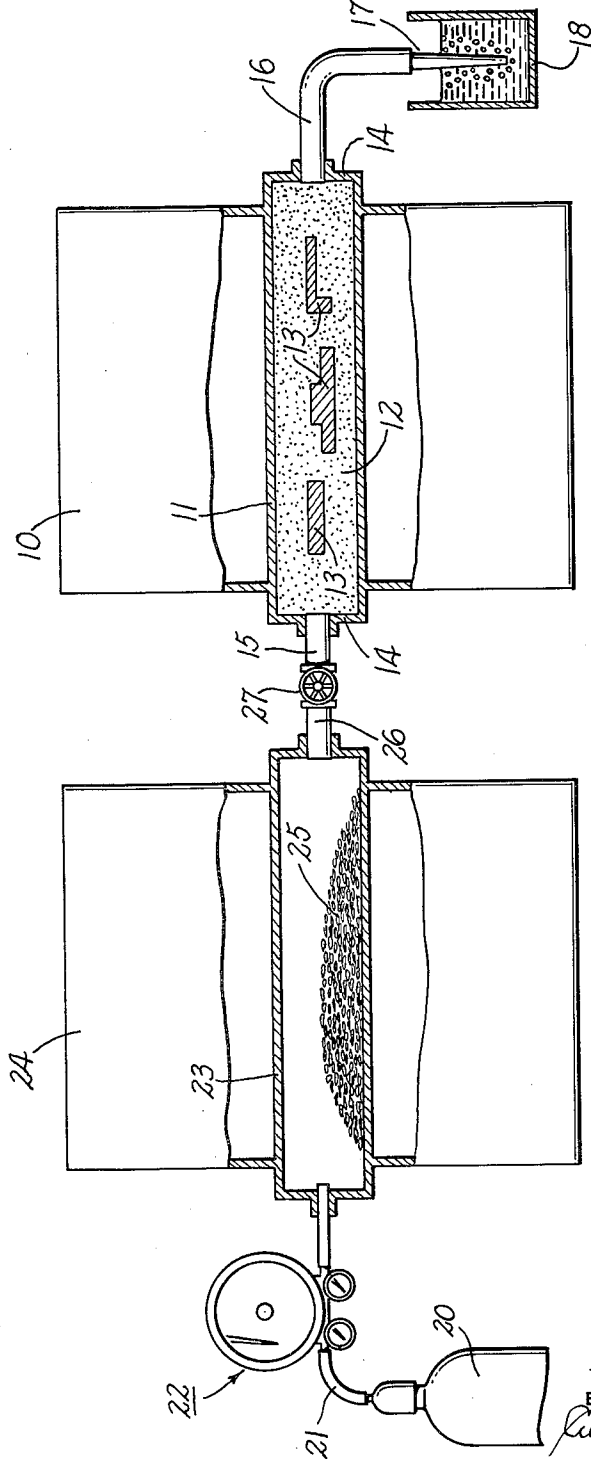
April 3, 1962

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3,028,261

CHROMIZING METALS

Filed April 24, 1958



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3,028,261

CHROMIZING METALS

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Filed Apr. 24, 1958, Ser. No. 730,724

11 Claims. (Cl. 117-107)

This invention relates to the chromizing or diffusion coating of chromium applied to various base metals and, more particularly, to producing a diffusion coating or casing of chromium having enhanced ductility and reduced embrittlement and decreasing the likelihood that the chromium coating or casing will chip or break or become discontinuous upon impact or bending or flexing of the base metal in use.

The art or technique of chromizing various metal parts to produce enhanced service characteristics (such as resistance to oxidation at high temperature, etc.) is by now well known. Such technique includes the diffusion of chromium at high temperatures into the surface of the base metal being chromized to produce a surface layer or coating or case of chromium or chromium alloyed with other metals including the base metal and, under readily controlled conditions, to various depths or thicknesses. Usually, one of the reasons for undertaking such a chromizing process is to provide, at the surface of the base metal, an outer skin having enhanced characteristics for the use to which the part is intended to be put. That is, since molybdenum forms a volatile oxide at very high temperatures, the usefulness of this metal and the other desirable properties thereof can be enhanced for machine parts subject to extremely high temperatures if the outside of the part is chromized to substitute an outer surface of chromium much more resistant to high temperature oxidation than the molybdenum base metal itself.

It has been found, particularly with non-ferrous base metals to which this invention relates such as titanium, zirconium, molybdenum, tungsten, and niobium, that the chromizing or diffusion thereof under techniques or conditions heretofore utilized may produce an outer chromium coating or casing which is quite hard even to an extent where, in some uses of the chromized part, impacts or bending or flexing to which the part is subjected may cause the diffusion coating or casing of chromium to break or chip and thus destroy the continuity of the case, with, of course, the formation of a point where undesired oxidation can occur directly of the base metal itself. Also, it has been found that, under conventional chromizing techniques, an actual embrittlement of the base metal itself may occur with, for example, titanium or zirconium.

According to this invention, however, a chromized or diffusion coating or case of chromium having substantially less microhardness and substantially increased ductility, as compared with chromizing coatings applied to non-ferrous metals but by prior processes, is provided and this invention includes controlling the atmosphere in the chromizing pack during the diffusion coating process to maintain such atmosphere essentially inert, as well as providing in the chromizing pack and during the chromizing process a substantial freedom of oxygen, hydrogen, and nitrogen and/or oxygen-, hydrogen-, and nitrogen-containing compounds or components.

One object of this invention is to provide methods and processes for the production on the surface of metals, particularly non-ferrous metals, of a diffused or surface alloyed casing or coating of chromium having increased ductility and decreased hardness for resistance to rupture and embrittlement.

A further object of this invention is to provide chromized or surface alloyed metal articles carrying on and

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into surface portions thereof a layer or casing of chromium of increased ductility and decreased hardness.

Still another object of this invention is to provide a process for the chromizing of non-ferrous metals in which the atmosphere within the chromizing pack and during the chromizing operation is maintained substantially entirely composed of inert gases.

Still another object of this invention is to provide a process for the chromizing of non-ferrous metals in which the chromizing pack and the atmosphere therein during the chromizing operation are maintained substantially free of oxygen, hydrogen, and nitrogen and oxygen, hydrogen, and nitrogen compounds.

Other objects and advantages will appear from the following description, the accompanying drawing, and the appended claims.

The drawing illustrates, somewhat diagrammatically, apparatus embodying and for practicing this invention.

Referring to the drawing, chromizing apparatus is illustrated as comprising a furnace 10 in which is disposed a chromizing retort 11, which may satisfactorily be made of a high temperature resistant, refractory, vitrified ceramic material. Retort 11 includes therein the chromizing pack material indicated at 12 immersed in which are the objects to be chromized and indicated generally by 13. Retort 11 as disposed in furnace 10, has end closure members 14 through which are provided a gas inlet conduit 15 and a gas exhaust conduit 16, the latter of which leads through a bubbler 17 in the form of a container 18 of low volatile liquid such as oil or mercury to act as a seal against back flow of gas and a gauge of gas throughput through retort 11.

In order to maintain the desired oxygen-, nitrogen-, and hydrogen-free atmosphere within retort 11 during the chromizing operation, a source of an inert gas is provided at 20 and is indicated as a conventional bottle or tank of compressed gas. The inert gas from tank 20 is led through a conduit 21 and through conventional flow meter and pressure reducing apparatus indicated generally at 22 into a drying and purifying tube 23 which is, in turn, disposed in a furnace 24. Tube 23 includes a quantity of a scavenger material for nitrogen, hydrogen, and oxygen, and may satisfactorily contain titanium chips or powder indicated at 25 to scavenge residual amounts of nitrogen, hydrogen, and oxygen, as well as any water vapor which may be entrained in gas 20. From scavenger tube 23, the purified inert gas passes through conduit 26 and valve 27 into gas inlet conduit 15 and thence through the chromizing pack in retort 11.

In operation, satisfactory results are achieved when purifying tube 23 is maintained at a temperature of above about 1700° F. Also, prior to the heating up of retort 11 in furnace 10, the hot and purified inert gas is run through retort 11 to purge it as completely as may be of air and other nitrogen-, hydrogen- or oxygen-containing substances including water vapor, and then the temperature of retort 11 is gradually raised to the desired chromizing temperature.

Satisfactory results are achieved with various inert or so-called noble gases such as helium, xenon, krypton, neon, etc. The chromium pack itself and the constituents thereof according to this invention comprise, as is understood in other chromizing techniques, a source of chromium (preferably powdered chromium), an inert filler of a refractory material (such as kaolin or alumina) and a source of volatile halide. According to this invention, however, the presence of oxygen, nitrogen, or hydrogen (either elementary or compounded in a manner subject to decomposition), is to be avoided in the pack. Thus, whereas conventional chromizing techniques may pre-

fer, as a source of volatile halide, ammonium salts, here elemental halogen and/or a halide such as chromium halide are used according to this invention. Similarly, if the inert refractory filler is chosen as one which has a substantial moisture content (such as kaolin), it is baked or dried to reduce the moisture content as much as possible. Preferably such a filler as alumina, which can be maintained substantially free of moisture, is preferred. Also urea compounds commonly used in other chromizing techniques, as well as other oxygen, nitrogen, and hydrogen compounds, are to be avoided in chromizing packs according to this invention.

As will be understood, the bubbler arrangement 17—18 not only provides a seal against the backward influx of air during, for example, cooling of retort 11, but also provides a visual flow indication for permitting the adequate regulation of a slight but continuous flow of gas through retort 11 to maintain a completely inert atmosphere therein, but a flow less than that which would sweep out of retort 11 gas elements of the chromizing pack which are to be depended upon for the desired diffusion coating of chromium onto the articles 13. As also will be understood, the provision of valve 27 is such that it may be closed for removal and/or replacement of retort 11 before or after the chromizing operation without contamination of the scavenging material 25 in scavenging tube 23, as well as to provide for convenient regulation of the throughput of dried and scavenged inert gas into and through retort 11.

As illustrative of one processing technique of which satisfactory results are achieved according to this invention, in the chromizing of molybdenum parts the following may be noted. Purifying tube 23 is approximately one-third filled with powdered titanium (approximately 80 mesh) as indicated at 25. The molybdenum parts to be chromized are placed in retort 11, embedded in a pack mixture 12 comprising about 50% alumina, 50% powdered chromium metal, and ½% elemental iodine.

A flow of approximately 1 liter per minute of argon is provided from the gas reservoir 20 by appropriate adjustment of the valve 27 and regulator 22 and after about two hours of purging, furnace 24 is brought to heat. When furnace 24 and purifying tube 23, etc., have reached a temperature of approximately 1900° F., the argon flow is reduced to perhaps .01 liter per minute, as indicated by very slow escape of bubbles at the bubbler 17, 18. Furnace 10, with retort 11 and its contents 12, 13 are heated to approximately 2000° F. and maintained at this temperature for about twenty-four hours to complete the chromizing cycle, during which the gas flow is maintained.

After completion of the heating cycle, furnace 10 and its contents are allowed to cool without interrupting the argon flow until room temperature is again reached, at which time the gas flow is cutoff, valve 27 closed, and the contents removed from retort 11. Preferably, a small positive gas pressure is maintained in tube 23 by means of regulator 22, to prevent entrance of air into the retort with consequent spoilage or deterioration of the chromium therein. The foregoing procedure has produced a chromized case on the molybdenum parts having a thickness of about .001" and a substantially lower micro-hardness than that found in conventionally chromized molybdenum.

While the methods and forms of apparatus herein described constitute a preferred embodiment of the invention, it is to be understood that the invention is not limited to these precise forms of apparatus, and that changes may be made therein without departing from the scope of the invention which is defined in the appended claims. What is claimed is:

1. In a method for the diffusion coating of chromium on the surface of a refractory base metallic body substantially in the absence of nitrogen-, hydrogen-, and oxygen-containing compounds, the steps which comprise

immersing said metallic body in a chromizing pack containing a source of chromium and a volatile source of halogen but being substantially free of nitrogen- and hydrogen-containing materials, subjecting said chromizing pack to an atmosphere of an inert gas which is substantially free of hydrogen and nitrogen, heating said chromizing pack and said metallic body therein for a prolonged period effecting said diffusion coating of chromium from said source of chromium in said chromizing pack into the surface of said metallic body, and maintaining said chromizing pack throughout said heating in said atmosphere of said inert gas and substantially free of hydrogen- and nitrogen-containing materials.

2. In a method for the diffusion coating of chromium on the surface of a refractory base metallic body substantially in the absence of nitrogen-, hydrogen-, and oxygen-containing compounds, the steps which comprise immersing said metallic body in a chromizing pack containing a source of chromium and a volatile source of halogen but being substantially free of nitrogen- and hydrogen-containing materials, subjecting said chromizing pack to an atmosphere of an inert gas which is substantially free of hydrogen and nitrogen, drying said inert gas prior to subjecting said pack thereto, heating said chromizing pack and said metallic body therein for a prolonged period effecting said diffusion coating of chromium from said source of chromium in said chromizing pack into the surface of said metallic body, and maintaining said pack throughout said heating in said atmosphere of said inert gas and substantially free of hydrogen- and nitrogen-containing materials.

3. In a method for the diffusion coating of chromium on the surface of a refractory base a metallic body substantially in the absence of nitrogen-, hydrogen-, and oxygen-containing compounds to produce a relatively ductile chromium coating of reduced hardness and brittleness, the steps which comprise immersing said metallic body in a chromizing pack in a substantially gas-tight retort, said chromizing pack containing a source of chromium and a volatile source of halogen but being substantially free of nitrogen- and hydrogen-containing materials, subjecting said retort and said chromizing pack therein to an atmosphere of an inert gas which is substantially free of hydrogen and nitrogen, heating said retort with said chromizing pack and said metallic body and said inert atmosphere therein for a prolonged period affecting said diffusion coating of chromium from said source of chromium in said chromizing pack into the surface of said metallic body and maintaining within said retort throughout said heating and diffusion coating step an atmosphere substantially free of hydrogen- and nitrogen-containing materials.

4. In a method for the diffusion coating of chromium on the surface of a refractory base metallic body substantially in the absence of nitrogen-, hydrogen-, and oxygen-containing compounds to produce a relatively ductile chromium coating of reduced hardness and brittleness, the steps which comprise immersing said metallic body in a chromizing pack in a substantially gas-tight retort, said chromizing pack containing a source of chromium and a volatile source of halogen but being substantially free of nitrogen- and hydrogen-containing materials, subjecting said retort and said chromizing pack therein to an atmosphere of an inert gas which is substantially free of hydrogen and nitrogen, drying said inert gas prior to interjection into said retort, heating said retort with said chromizing pack and said metallic body and said inert atmosphere therein for a prolonged period effecting said diffusion coating of chromium from said source of chromium in said chromizing pack into the surface of said metallic body, and maintaining in said retort throughout said heating a positive pressure of said inert gas effecting diffusion deposition of said chromium coating in an atmosphere substantially free of hydrogen- and nitrogen- and oxygen-containing constituents.

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5. In a method for the diffusion coating of chromium on the surface of a refractory base metallic body substantially in the absence of nitrogen-, hydrogen-, and oxygen-containing compounds, the steps which comprise immersing said metallic body in a chromizing pack in a substantially gas-tight retort, said chromizing pack containing a source of chromium and a volatile source of halogen but being substantially free of nitrogen- and hydrogen-containing materials, flowing into said retort through said chromizing pack therein an atmosphere of an inert gas which is substantially free of hydrogen and nitrogen, heating said retort with said chromizing pack and said metallic body and said inert atmosphere therein for a prolonged period effecting said diffusion coating of chromium from said source of chromium in said chromizing pack into the surface of said metallic body, maintaining said atmosphere in said retort during said heating and diffusion coating step substantially free of hydrogen- and nitrogen- and oxygen-containing materials, and maintaining said flow of said inert gas through said retort during said diffusion coating steps low enough to preclude flushing from said retort gaseous chromium and halide from said source of chromium and volatile halide.

6. In apparatus for the diffusion coating of chromium into the surface of a refractory base metallic body, the combination which comprises a retort for enclosing said metallic body embedded in powdered refractory filler material and a source of chromium to be diffusion coated thereinto, means for heating said retort to an elevated temperature during said diffusion coating of said chromium, a source of inert gas substantially free of nitrogen- and hydrogen-containing constituents, and means for introducing said inert gas into said retort during said diffusion coating operation.

7. In apparatus for the diffusion coating of chromium into the surface of a refractory base metallic body, the combination which comprises a closed retort for enclosing said metallic body embedded in powdered refractory filler material and a source of chromium to be diffusion coated thereinto, means for heating said retort to an elevated temperature during said diffusion coating of said chromium, a source of inert gas substantially free of nitrogen- and hydrogen-containing constituents, means for introducing said inert gas into said retort during said diffusion coating operation, and regulating means for controlling the volumetric flow of said inert gas through said retort during said diffusion coating of said metallic body.

8. In apparatus for the diffusion coating of chromium into the surface of a refractory base metallic body, the combination which comprises a closed retort for enclosing said metallic body embedded in powdered refractory filler material and a source of chromium to be diffusion coated thereinto, means for heating said retort to an elevated temperature during said diffusion coating of said chromium, a source of inert gas substantially free of nitrogen- and hydrogen-containing constituents, means for introducing said inert gas into said retort during said diffusion coating operation, regulating means for controlling the volumetric flow of said inert gas through said retort during said diffusion coating of said metallic body, and visual measuring means for indicating the throughput of said inert gas through said retort during said diffusion coating for controlling said throughput to a positive value assuring the absence of nitrogen- and hydrogen-containing constituents in said retort but less than a volume which flushes out of said retort diffusible chromium to be diffusion coated into said metallic body.

9. In apparatus for the diffusion coating of chromium into the surface of a refractory base metallic body to produce a surface coating of enhanced ductility and decreased brittleness and hardness, the combination which comprises a closed retort for enclosing said metallic body

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embedded in powdered refractory filler material and a source of chromium to be diffusion coated thereinto, means for heating said retort to an elevated temperature during said diffusing coating of said chromium, a source of inert gas substantially free of nitrogen- and hydrogen-containing constituents, means for introducing said inert gas into said retort during said diffusion coating operation, and means for removing moisture vapor and other nitrogen- and hydrogen-containing constituents from said inert gas prior to the introduction thereof into said retort and including means for passing said inert gas over a moisture-extracting composition and means for heating said inert gas during said passage thereof.

10. In apparatus for the diffusion coating of chromium into the surface of a refractory base metallic body to produce a surface coating of enhanced ductility and decreased brittleness and hardness, the combination which comprises a gas-tight retort for enclosing said metallic body embedded in powdered refractory filler material and a source of chromium to be diffusion coated thereinto, means for heating said retort to an elevated temperature during said diffusion coating of said chromium, a source of inert gas substantially free of nitrogen- and hydrogen-containing constituents, means for reducing the pressure of and regulating the flow of said inert gas from said source, means for introducing said inert gas into said retort at a controlled rate of flow during said diffusion coating operation, means for removing moisture vapor and other nitrogen- and hydrogen-containing constituents from said inert gas prior to the introduction thereof into said retort and including means for heating said inert gas and passing said inert gas over a moisture-extracting composition, and visual measuring means for indicating the throughput of said inert gas through said retort during said diffusion coating for controlling said throughput to a positive value assuring the absence of nitrogen- and hydrogen-containing constituents in said retort but less than a volume which flushes out of said retort diffusible chromium to be diffusion coated onto said metallic body.

11. In apparatus for the diffusion coating of chromium into the surface of a refractory base metallic body, the combination which comprises a closed retort for enclosing said metallic body embedded in powdered refractory filler material and a source of chromium to be diffusion coated thereinto, means for heating said retort to an elevated temperature during said diffusion coating of said chromium, a source of inert gas substantially free of nitrogen- and hydrogen-containing constituents, means for introducing said inert gas into said retort for maintaining therein an atmosphere of said inert gas during said diffusion coating operation, drying means for removing moisture vapor and other nitrogen- and hydrogen-containing constituents from said inert gas prior to the introduction thereof into said retort, regulating means for controlling the volumetric flow of said dried inert gas through said retort during said diffusion coating of said metallic body, and cut-off means separating said retort from said drying means for opening said retort after said diffusion coating in the absence of contaminating said dried condition of said inert gas.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,028,261

April 3, 1962

Richard L. Wachtell et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 42, for "coatnig" read -- coating --;
column 4, line 43, after "free" insert -- of --.

Signed and sealed this 24th day of July 1962.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents