Sept. 7, 1965 S. D. CAPLOW 3,205,090

COATING METHOD

Filed July 2, 1963

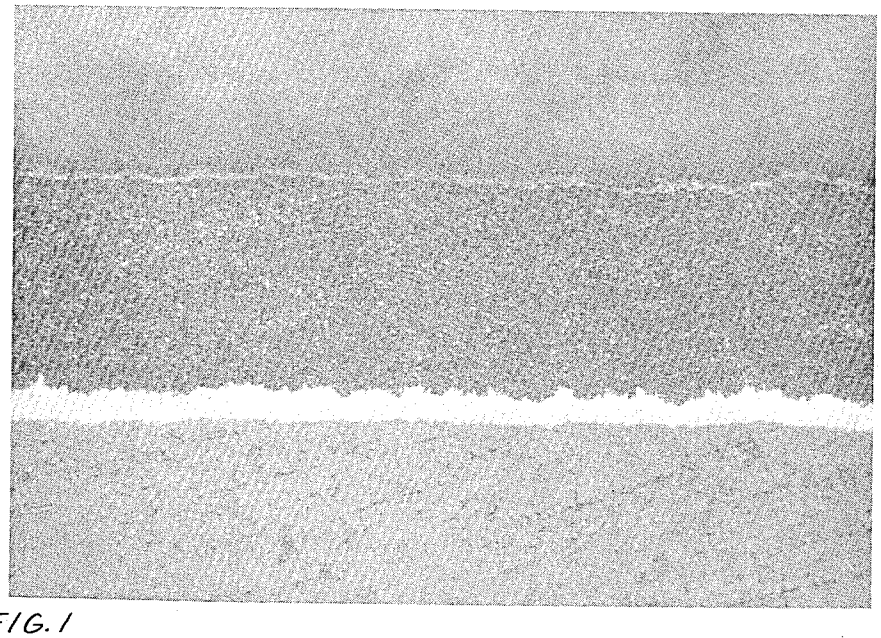


FIG. 1

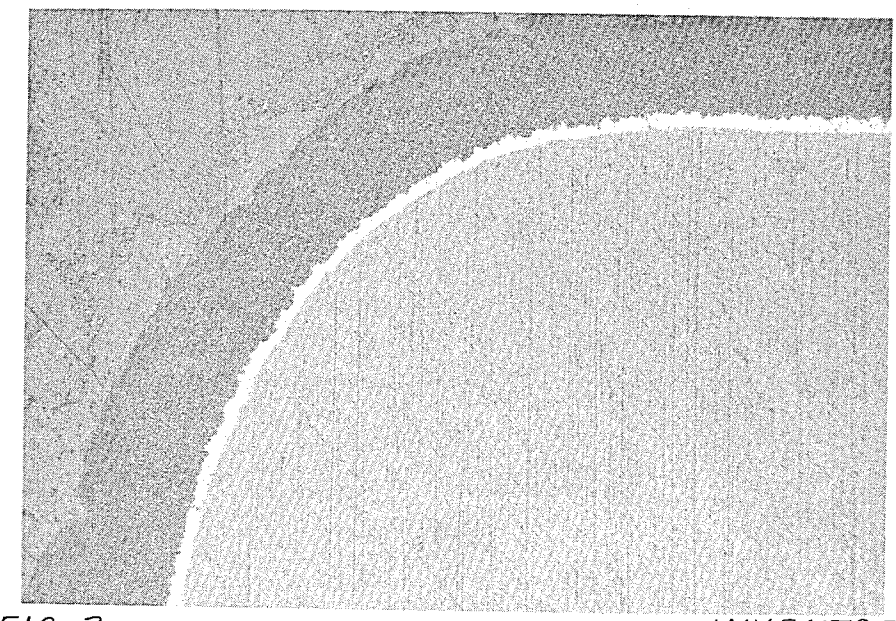


FIG. 2

INVENTOR
STUART D. CAPLOW

BY M. B. Tasker
ATTORNEY

United States Patent Office 3,205,090 Patented Sept. 7, 1965

3,205,090

COATING METHOD

Stuart D. Caplow, Wallingford, Conn., assignor to United Aircraft Corporation East Hartford, Conn., a corporation of Delaware

Filed July 2, 1963, Ser. No. 293,231
6 Claims. (Cl. 117—113)

This invention relates to a new and superior method of applying aluminum enriched surfaces to metal parts.

In the manufacture of gas turbine engine blades, heat exchangers utilizing high temperature liquid metals and nuclear reactors there is a need for metals which have high tensile strength at very high temperatures, in the range of 1800° F.–2200° F. Yet these metals must be sufficiently workable to permit them to be fabricated into tubes, thin sheet and forgings of irregular shape.

Certain of the refractory metals such as tantalum, columbium and titanium and alloys of those metals have such properties but are subject to catastrophic oxidation, especially at higher temperatures.

It is an object of this invention to provide an improved method for applying aluminum enriched surfaces to parts fabricated from these high temperature resistant metals which can protect them against oxidation even at the higher temperatures to which they may be subjected in use.

These surfaces are applied in a fused salt media in an argon or other protective atmosphere. To a mixture of salts consisting of aluminum fluoride and sodium fluoride, aluminum metal is added in any convenient form. From one to twenty weight percent aluminum metal is suggested, although the quantity is not critical. The aluminum metal will dissolve in the salt according to its equilibrium solubility. Any excess metal will lie molten at the bottom of the bath. There it will serve as a source of replenishment to the active aluminum metal which is dissolved in the salts.

The relative proportion of aluminum fluoride and sodium fluoride is not critical either. One concentration which has been found effective consisted of 55 weight percent aluminum fluoride, 45 weight percent sodium fluoride. In place of the sodium fluoride other alkali-metal fluorides or an alkaline-earth metal fluoride such as calcium fluoride may be substituted.

The advantages of the invention will be apparent from the following detailed description of one example of an actual application of the improved coating and from consideration of the accompanying drawing which shows photomicrographs of parts having oxidation resistant coatings applied in accordance with this invention.

The following description of an actual use of the coating method of this invention is given by way of example. A salt bath was prepared consisting of 55 weight percent aluminum fluoride and 45 weight percent sodium fluoride. To this was added 10 weight percent aluminum metal. The bath was heated to an operating temperature of 1940° F. While maintaining a protective atmosphere of argon gas over the bath, parts of 99 weight percent columbium-1 weight percent zirconium alloy were suspended in the bath for various periods of time and the coating thickness measured. The results are given in the following tabulation.

Immersion time, (minutes):	Coating thickness, (inches)
10	0.0008
45	0.0020
120	0.0080

The coatings were of exceptional uniformity with no evidence of liquid metal dragout. Also parts of irregular shape and sharp corners were noted to be uniformly coated. Oxidation tests in air in excess of 200 hours at

1800° F. showed no effect on the coated parts. The oxidation test was not continued due to failure of the furnace.

FIGS. 1 and 2 show cross sections of surface coatings on 99 Cb–1Zr parts applied in a mixture of salts consisting of aluminum fluoride and sodium fluoride in the proportions described above to which aluminum metal was added to at least the equilibrium solubility of the aluminum metal. The bath was maintained at a temperature of 1940° F. and a protective atmosphere of argon gas was maintained over the bath. The parts were immersed for 45 minutes.

In FIG. 1 the magnification is 1000 times and the photomicrograph clearly shows a total coating of 2 mils with a columbium-aluminum intermetallic layer of about 0.3 mils on a flat surface. FIGS. 2, which has a magnification of 500 times, shows the coating continuously and uniformly distributed over the curved surface of a 99 Cb–1Zr part and conforming exactly to part geometry without cracks and fissures in the coating so prone to occur in coatings on curved surfaces. The complete absence of liquid-metal dragout will be noted in both FIG. 1 and FIG. 2.

Effects of the coating process on the Cb substrate were measured. The 99 Cb–1Zr remained ductile and easily passed bend tests. The samples which were immersed for 45 minutes developed a 2 mil coating and remained soft and ductile. In a hardness test the base metal had a hardness of 104 D.P.H., the coating a hardness of 472 D.P.H. The samples immersed for 120 minutes showed a hardness of 104 D.P.H. for the base metal and 493 D.P.H. for the coating.

By the method of this invention coatings of remarkable uniformity are obtained. Unlike the usual liquid metal baths that are used, the parts, as withdrawn from the bath, are completely free of liquid metal dragout. The throwing power of this process is very high and the coating will conform to parts of any geometry.

A further advantage of the process of this invention is its versatility and adaptability to mechanization. Different parts may be immersed simultaneously for different periods of time. Unlike other bath or pack processes, there are no problems with loading and unloading operations.

A uniform temperature can be maintained during the process, thereby reducing distortion of the parts being coated. Also, the process can be scaled up to any desired size.

While the invention has been described in connection with columbium and specifically with one of the well-known columbium alloys, it will be understood that it is equally applicable to other metals of the refractory metals group, such as tantalum and titanium.

What I claim is:

1. The method of applying an aluminum enriched surface to metal parts from the group of refractory metals consisting of tantalum, columbium, titanium and their alloys which consists in preparing a coating bath by adding aluminum metal to a mixture of aluminum fluoride and a second metal fluoride from the group consisting of the alkaline earth metals and the alkali metals, heating the bath, and suspending the metal parts to be coated in the heated fused salt bath in a protective atmosphere until the desired coating thickness has been formed on the parts.

2. The method of forming an aluminum based coating on a metal part from the group of refractory metals consisting of tantalum, columbium, titanium and their alloys in a fused salt media which includes preparing a coating bath by adding aluminum metal to a mixture of aluminum fluoride and sodium fluoride, heating the bath, and suspending the metal part to be coated in the heated

fused salt bath in a protected atmosphere for a time period of from 10–120 minutes.

3. The method of forming an aluminum based coating on a metal part from the group of refractory metals consisting of tantalum, columbium, titanium and their alloys in a fused salt media which includes preparing a coating bath by adding aluminum metal to a mixture of aluminum fluoride and calcium fluoride, heating the bath, and suspending the part to be coated in the heated fused salt bath in a protective gas atmosphere for a time period of from 10–120 minutes.

4. The method of forming an aluminum based coating on a metal part from the group of refractory metals consisting of tantalum, columbium, titanium and their alloys in a fused salt media which includes preparing a coating bath by adding aluminum metal to a mixture of aluminum fluoride and an alkaline-earth metal fluoride, heating the bath, and suspending the metal part to be coated in the heated bath in a protective atmosphere for a time period of from 10–120 minutes.

5. The method of forming an aluminum based coating on metal parts from the group of refractory metals consisting of columbium, tantalum, titanium and their alloys which consists in preparing a coating bath by adding aluminum metal to a mixture of aluminum fluoride and sodium fluoride, in about the weight proportion of 55 percent aluminum fluoride to 45 percent sodium fluoride, to

at least the maximum equilibrium solubility of the aluminum metal, heating the bath to approximately 1940° F., and suspending the metal parts to be coated in the heated bath in a protective atmosphere of argon gas until the desired coating thickness has been formed on the surface of the parts.

6. The method of applying an aluminum enriched surface to a 99 columbium-1 zirconium part which consists in preparing a coating bath by adding 10 weight percent of aluminum metal to a mixture of 55 weight percent aluminum fluoride and 45 weight percent sodium fluoride, holding the bath at 1940° F., in a protective atmosphere of argon gas, and suspending the metal part in said bath for a time sufficient to form an aluminum enriched surface of the desired thickness.

References Cited by the Examiner

UNITED STATES PATENTS

2,953,473	9/60	Mitchell	117—144
3,013,899	12/61	Price et al.	117—114
3,027,268	3/62	Linden	117—114

FOREIGN PATENTS

547,188	4/42	Great Britain.

RICHARD D. NEVIUS, *Primary Examiner.*

REUBIN EPSTEIN, *Examiner.*