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SURFACE TREATMENTS FOR TITANIUM ALLOYS

By Manley W. Mallett

Prepared Under the Supervision of the
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ABSTRACT

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This report describes procedures that have been developed for the surface treatment of titanium alloys. It was not possible to obtain conclusive information on the relative utility of the various coatings. Therefore, information has been included on all coating systems for which reports of significant development work were available, without attempting to assess the usefulness of the particular coating or to compare it with similar coatings applied by other techniques. Coating processes which are described include mechanical treatments, electrochemical treatments, treatments for applying metallic coatings other than electroplating, and treatments for applying hard, nonmetallic coatings. Special treatments to control thermal radiation are also described.

Author

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Prepared for

Manufacturing Engineering Laboratory

In Cooperation with

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PREFACE

This report is one of a series of reports being prepared by Battelle Memorial Institute, Columbus, Ohio, under Contract DA-01-021-AMC-11651(Z) in the general field of materials fabrication.

This report deals with surface treatments for titanium alloys, and is directed toward the interests of processing and manufacturing engineers. The treatments covered in the report include mechanical working of the surfaces, electrochemical plating, polishing and anodizing, applying metal coatings other than electrodeposits, forming nonmetallic coatings and diffusion layers, and the coating of titanium alloy surfaces to control thermal-radiative properties. In general, workable procedures are given in detail. Problem areas are identified and recommendations for future work are made.

The intensive literature search carried out in connection with the preparation of this report concentrated on information made available since 1960. Pre-1960 references are included where appropriate. In addition to the literature search, personal contacts were made at Battelle with a number of individuals specializing in the various surface-treatment fields.

In accumulating the information necessary to prepare this report, the following information sources within Battelle were searched: for the period from 1960 to the present:

Main Library
Slavic Library
Chemistry Library
Defense Metals Information Center
Atomic Energy Commission Library.

The NASA Research and Technology Program Digest Flash Index FY 64 and the NASA Program Summary FY 65 were also searched for leads on current programs and research reports.

In addition, the following information centers were searched:

Redstone Scientific Information Center
Defense Documentation Center
The American Society for Metals Information Searching Service.

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SURFACE TREATMENTS FOR TITANIUM ALLOYS

SUMMARY

Although titanium alloys have been generally available for only about 15 years, a large number of surface-hardening treatments have been developed for use on these alloys. Most of these treatments have been developed either to improve resistance to wear and galling, or to improve resistance to oxidation at elevated temperatures. However, a number of treatments have been designed for other purposes, such as to improve corrosion resistance, radiation characteristics, or appearance. Unfortunately, many more data are available relative to coating procedures than to the serviceability of coated parts.

This report presents a summary of the various coating processes that have been developed for titanium alloys. Whenever they are available, data are also presented regarding the properties of the coated material. However, no attempt has been made to evaluate the relative merits of the various coating processes for a particular end use, since those data which are available do not permit a valid judgment to be made.

A limited examination has been made of the use of shot peening to improve the properties of titanium alloys. Fatigue properties are improved in some cases. Polishing procedures for developing high-quality finishes are also available.

Titanium alloys are inherently difficult to electroplate due to the tenacious oxide film that forms on the surface and the difficulty of developing a suitable surface for plating. However, techniques have been developed for plating a number of metals on titanium. Methods have also been developed for anodizing titanium alloys and for polishing titanium alloys by electrochemical or chemical means.

Metallic coatings have been produced on titanium alloys by flame spraying, by hot dipping, and by baking metallic paints, as well as by electroplating processes. Hot-dip coatings of aluminum are of some interest, especially for improving oxidation resistance. Baked-on gold coatings also have been used to some extent in service to improve the heat-reflection characteristics.

The production of hard surface coatings to improve wear resistance has been studied quite intensively. Titanium alloys dissolve significant quantities of oxygen, nitrogen, and carbon. These interstitial elements result in appreciable surface hardening. A variety of procedures have been developed to control the degree of surface hardening and to prevent roughening of the surface and distortion of the part during treatment. Primary emphasis has been directed toward studies of surface coatings containing oxygen or nitrogen. Oxygen coatings can be produced at lower temperatures, and thus, there are fewer problems with distortion of the part. Oxygen coatings are more difficult to control, however, and do not result in as high a level of surface hardness as is observed with nitride coatings. Sprayed carbide coatings have been used to reduce erosion of titanium turbine blades, but gas carburizing has not proved to be particularly useful.

Several ceramic coatings have been developed for titanium alloys. These are designed primarily to reduce oxidation during processing of titanium parts. Much of the work on coatings of this type is proprietary.

Despite the large amount of study devoted to surface treatments for titanium alloys, this area warrants further work. In particular, a critical comparison of the effectiveness of the various treatments in improving the usefulness of titanium-alloy parts needs to be examined. Specific treatments that appear to warrant additional study are so indicated in this report.

INTRODUCTION

Surface treatments may be applied for a variety of decorative or functional reasons, depending upon the end use of the coated article. In the case of titanium alloys, the chief interest in surface treatments has resulted from the desire either to improve wear and galling resistance or to improve oxidation resistance at high temperatures. However, special coatings have been developed for several other purposes, such as, to improve corrosion resistance, radiation characteristics, or appearance.

Surface treatments applied to titanium alloys have been summarized in recent reports by Wood (Ref. 1) and by Finch and Bower (Ref. 2). The present survey examines in greater depth the surface treatments applied to titanium alloys, with special emphasis on work reported since 1960. Whenever possible, details of the coatings procedures are given. Unfortunately, very little information was found regarding the behavior of the various coatings on production titanium parts. For this reason, it was not possible to compare their usefulness or to present recommendations concerning the best coating system for obtaining a desired improvement in the behavior of titanium alloys.

Because so little data are available regarding the properties of coated titanium alloys, it was decided to summarize the available information in terms of the type of coating rather than the intended application. Thus, this report describes mechanical surface treatments, electrochemical surface treatments, methods of applying metallic coatings other than electroplating, and methods of forming hard, nonmetallic coatings. In one case, that of coatings designed to improve radiative properties, it was possible to describe coatings designed for a specific end use. Areas where further study is needed are also indicated.

PRETREATMENT CLEANING OF SURFACES

A good introduction to the cleaning of titanium alloys preparatory to various surface treatments appears in the ASM Metals Handbook (Ref. 3). Cleaning procedures designed to remove scale, tarnish, films, and other contaminants which form on the surface of titanium and titanium alloys during hot working, heat treating, and other processing operations are described. Since this reference is usually readily available, details of the various cleaning procedures are not reported here. Additional information of interest on grit blasting may be found in Reference 4. Surface cleanliness is generally of considerable importance in obtaining a useful coating. Special cleaning techniques required for specific coating treatments are described in the appropriate sections of this report.

MECHANICAL SURFACE TREATMENTS

Mechanical surface treatments of titanium may be used for hardening, cleaning, or polishing. Although mechanical surface treatments have not been used extensively in practice, some investigations have been conducted to determine the effects of mechanical treatments on titanium alloys.

SHOT PEENING

Working of the alloy surface by shot peening can improve fatigue life of titanium and titanium alloys. The Titanium Metallurgical Laboratory Memorandum, dated November 9, 1956 (Ref. 5), points out that the degree of cold working to be achieved by this process is critical. Underpeening is of no value and overpeening may produce cracks and shorten fatigue endurance.

The Western Gear Corporation phosphorus-nickel-coated gears showed (Ref. 6) residual tensile stresses up to 40,000 psi. These tensile stresses were replaced by compressive stresses induced by cold-working methods, either by shot peening or glass peening. Both peening treatments increased fatigue life somewhat for the coated gears. Shot peening was the more effective.

MECHANICAL POLISHING

Success in producing a high-luster finish has been reported. This has led at least one company into the sale of titanium jewelry. However, very finely polished titanium has functional applications in orthopedic implants and probably in instrumentation. A description of one polishing procedure which has been used successfully on titanium is given below (Ref. 7).

(1) After major metal-removal operations, i.e., filing and grinding, the surface should be finished with No. 320 silicon-carbide, wet or dry paper. When using the carbide paper, it is desirable to use water to which a commercial dishwashing detergent has been added in the proportions of approximately 1 teaspoon per 1/2 gallon of water. This solution will prevent paper clog-up and promote faster cutting action.

(2) Follow the use of No. 320 paper with a No. 400 (or 600) grade, again using the detergent and water solution.

(3) Wash metal parts thoroughly in a detergent and water solution to remove traces of abrasive grains.

(4) Parts can now be semipolished on a polishing machine using a jeweler's grade of tripoli on a soft bristle brush. The tripoli which proved best is a brown grade of tripoli used in polishing precious metals. Robert's

"Bright Boy", an abrasive rubber available in blocks or wheels, may also be used.

(5) After semipolishing, buff the parts using tripoli on a soft-muslin buffing wheel. For orthopedic work, the polishing with tripoli on soft buffs may be sufficient. However, if a higher degree of finish is desired, parts should be washed again with a detergent solution.

(6) Final high finish can easily be obtained using jeweler's water-soluble rouge on a soft flannel buff. "Ruby powder" may also be used. A paste should be made and applied to the work rather than to the wheel.

Caution should be used when buffing titanium. If excessive force is used, the compound has a tendency to smear and produce a clouded finish. The compounds mentioned above do not require excessively high pressures of work on the buff or brushing wheel.

Polishing may also be done by the electrochemical procedure described in the section, Electrochemical and Chemical Polishing.

ELECTROCHEMICAL SURFACE TREATMENTS

PLATING PROCEDURES

Conventional methods of plating on common metals are not completely satisfactory on titanium (Ref. 8). Titanium is covered with a thin, natural oxide film that re-forms almost instantly when a cleaned surface is exposed to air or water. As with other metals that form similar films, e.g., aluminum and magnesium, adherent electrodeposits can be obtained only if this film is either removed for a sufficient time to permit an initial electrodeposit, or if it is replaced by another film that does not interfere with adhesion, of if it is incorporated into the deposit in a compatible manner. Another technique, which is less satisfactory, is to etch the metal surface severely and depend on mechanical keying to supply the bond. In this latter technique the bond obtained is strictly mechanical, and the process should be applicable to all alloys and all electrodeposits. Of course, severe etching cannot be used where the attendant surface roughening and the loss of metal are not permissible. However, some degree of etch roughening is associated with all chemical and electrochemical preparation for plating.

The essential details as assembled by Wood (Ref. 1) on various procedures for plating on titanium are given in Tables I through V (Refs. 9-28). The subjects covered include anodic etching and zinc strike plating in ethylene glycol solutions, activation of titanium in chromic and acetic acid-fluoride baths and in hot hydrochloric acid solutions, and plating of nickel-phosphorus alloy on vapor-blasted titanium. Several of the same processes were described in a 1960 survey by Harding (Ref. 8). Several newer techniques developed for plating titanium alloys are discussed below.

W. G. Lee (Ref. 29) patented a process for plating on the Group IV B metals: titanium, zirconium, and hafnium. The parts were first pickled in the following solution for 10 to 15 seconds.

HCl (18° Baume or 30%)	900 cc
HF (70%)	100 cc
$FeCl_3 \cdot 6H_2O$	50 g

After rinsing, the parts were pickled a second time in the same solution, rinsed, and electroless nickel plated in conventional solutions. The parts were then baked at 800 F.

Foisel and Ellmers (Ref. 30) patented a process in which the titanium part is etched in a solution containing trivalent chromium ions and fluoride ions. A typical solution is

CrF_3	40 g/l
HCl (36%)	40 ml/l
Temperature	160 F
Time	3 minutes

After rinsing, the part was nickel plated in a Watts bath and baked at 750 F for 30 minutes. The hydrochloric acid etch tends to introduce hydrogen into titanium. The Ti-13V-11Cr-3Al alloy in particular will absorb large quantities of hydrogen. This may be evolved during subsequent nickel plating and cause blistering or embrittlement of the base metal depending on its susceptibility.

Good adhesion of electrodeposits to a Ti-5Al alloy was obtained after pickling the metal in concentrated hydrochloric acid at room temperature for 1.5 to 2 hours (Ref. 31). The surface of the titanium specimens became slightly rough, with a thin layer of smut which was easily dissolved in a solution of 185 to 200-ml/l hydrofluoric acid (40 per cent) and 8 to 10-ml/l nitric acid (70 per cent). After

TABLE I. VARIOUS TECHNIQUES FOR ELECTROPLATING ON TITANIUM

Purpose	Titanium Alloy Considered	Preparation for Plating and Postplating Treatment	Plating	Comments	Reference Number
Method development patent	Not specified	Degrease, activate in solution of stannous chloride, copper, coat by chemical reduction	Copper plate: Copper sulfate-Rochelle salts- triethanolamine bath for chemical reduction; cyanide copper bath at pH 10	No data on evaluation.	9
Cadmium coating for antisiezing coating on titanium bolts	Not specified	Vacuum evaporate films of copper, nickel, and cadmium on titanium	Cadmium plate	Nonadherent.	10
Nickel-phosphide and cobalt-phosphide coating on molybdenum, titanium and zirconium	Not specified	Preparation not specified. Heat treatment at 1112 to 2012 F (600 to 1100 C) in nonoxidizing atmosphere to melt the phosphide coating	Plating bath: 30 to 45-g/l nickel chloride and phosphite or cobalt chloride and phosphite	No data.	11
Nickel and iron coating on metals of Groups IV, V, and VI	Not specified	Cathodic treatment in acid or alkaline solutions to produce metal "hydrides" on the surface before plating. Vacuum fire at 842 to 1382 F to improve the as-plated adhesion	Nickel plate in pH 4, Watts type of nickel bath - 0.3 mil; iron plate in pH 4, iron sulfate-chloride bath - 0.3 mil	Adherent to a bend test, knife test, and chisel test.	12
Brazing of titanium	Not specified	Metal deposition from chloride salts onto titanium surfaces as a basis for silver brazing	Silver, copper, manganese, tin coatings	Metal-halide fluxing principle established as a basis for silver and silver-solder brazing.	13
Roll cladding titanium-clad steel	Unalloyed	(1) Solvent clean (2) Alkaline clean (3) Rinse (4) Activation etch HNO_3 - 10% HF - 1 to 2% Room temperature, 1 to 2 min (5) Cold rinse and plate	Nickel: Watts type of bath pH 2.5 Iron: Hot $FeCl_2$ - $CaCl_2$, pH 1.0 Chromium: Chromic-sulfuric acid bath Copper: Acid copper sulfate Silver: Cyanide strike and plate Cobalt: Watts-type bath, pH 5.0	Roll clad titanium-steel-titanium sandwich: effectiveness of various bonding metals: Ag + Ni = best bond Silver poor bond to steel. Plate — Best Temp — Bond to Titanium Iron — 1400 — Brittle Nickel — 1300 — Better than iron Cobalt — 1450 — Good Chromium — 2000 — Hard, brittle Copper — 1500 — Fair	14
Brazing	Not specified	Pickle in HF-HBF_4 solution	Silver plate: $AgBF_4$-HBF_4 bath	Silver braze.	15
Wire drawing NAB scale	Unalloyed	(1) Remove heavy scale from wire Descaling bath NaOH - 48% KOH - 4% Bal $NaNO_3$ 900 F, 1 to 6 min (2) Water quench (3) Remove residual scale (a) Hot aqua regia, 5 min (b) Rinse (c) HNO_3 - 20% HF - 2% (4) Activate H_2SO_4 - 25%, hot 5 to 10 min (5) Outgas (vacuum anneal)	Copper plate 0.3 to 0.6 mil	Copper recommended for drawing wire. Copper stripped for intermediate annealing operations and replated.	16

TABLE II. ELECTROPLATING ON TITANIUM BASED ON ANODIC ETCHING AND ZINC STRIKE PLATING IN ETHYLENE GLYCOL SOLUTIONS

Purpose	Titanium Alloy Considered	Preparation for Plating and Postplating Treatment	Plating	Comments	Reference Number
Development of ARL procedure	Unalloyed 4Al-4Mn	Zinc Strike Ethylene glycol - 87.5% $ZnCl_2$ - 0.5% HF - 4 to 6% H_2O - 6% Room temperature 5 amp/sq ft, 5 min	Copper Plating: Strike CuCN - 23 g/l NaCN - 34 g/l Na_2CO_3 - 15 g/l Room temperature 50 amp/sq ft reduced to 15 amp/sq ft, 3 to 5 min	Adherent copper deposits; best anodic Etch A. Fairly adherent with anodic Etch B and zinc strike plate.	17
		Anodic Etch A Ethylene glycol - 79% HF - 15% H_2O - 6% 130 to 140 F 50 amp/sq ft anodic, 15 to 30 min Anodic Etch B H_3PO_4 - 53.9% HF - 12.5% NH_4FHF - 15.5% H_2O - 18.1% 95-115 F 30 to 50 amp/sq ft, 15 to 30 min	Plate $Cu(BF_4)_2$-448 g/l H_3BF_4 to pH 0.6 Room temperature 50 amp/sq ft for 10 min/ 0.0005 inch 100 amp/sq ft for 40 min/ 0.004 inch	Cadmium, silver, and nickel plates on titanium using ARL anodic etch and copper plating method passed bend test, heating test in 400 F oil, and heating test in gas-burner flame.	18
Lubrication of titanium balls	Unalloyed 4Al-4Mn 2.8Cr-1.5Fe 3Al-5Cr 4Al-4V 6Al-4V	(1) Preclean HNO_3-HF (2) Rinse (3) Ethylene glycol rinse (4) Etch anodically Ethylene glycol - 800 ml/l HF - 200 ml/l ZnF_2 - 100 ml/l 48 amp/sq ft 20 min (5) Rinse quickly (6) Iron plate and carburize	Iron plating $FeSO_4 \cdot 7H_2O$ - 300 g/l $FeCl_2 \cdot 4H_2O$ - 42 g/l $(NH_4)_2SO_4$ - 15 g/l NaCOOH 15 g/l H_3BO_3 - 30 g/l 140 F, 20 amp/sq ft 2 mils, 2 hr, pH 4.1	Carburized iron plate 1600 F, 2 hr; no evidence of blistering, cracking, or peeling.	19
Electroplated braze metals	Not specified	Cathodic electrolysis Ethylene glycol - 800 ml/l 40% HF - 200 ml/l ZnF_2 - 100 g/l 70 to 80 F 6 volts about 10 amp/sq ft 5 to 10 min	Conventional plating for copper, chromium, nickel, tin, silver, and cadmium. Successive layers of silver-copper and zinc or silver and brass were plated to provide 60Ag-32Cu-8Zn braze layer	Lap joint of 60Ag-32Cu-8Zn brazing layer. Braze at 800 C for 30 min. Braze joint strength 2 kg/mm^2 of contact area.	20

TABLE III. ELECTROPLATING ON TITANIUM ACTIVATED IN CHROMIC ACID-FLUORIDE AND ACETIC ACID-FLUORIDE BATHS

Purpose	Titanium Alloy Considered	Preparation for Plating and Postplating Treatment	Plating	Comments	Reference Number
Plating hard chromium and copper Menasco's method	3Al-5Cr 6Al-4V 4Al-4Mn	Prior to etching immerse in 60% HF - 250 ml/l, 69% HNO_3 - 750 ml/l until red fumes appear; rinse in distilled water. Immerse in hot etchant of $Na_2Cr_2O_7$-HF-H_2O at 210 F for 20 min; rinse in distilled water; plate. Bath for 3Al-5Cr alloy $Na_2Cr_2O_7 \cdot 2H_2O$ - 400 g/l 60% HF - 25 ml/l Bath for 6Al-4V and 4Al-4Mn alloys $Na_2Cr_2O_7 \cdot 2H_2O$ - 250 g/l 60% HF - 50 g/l Distilled water to make up baths	Copper plate in acid copper sulfate bath. Chromium plate in 250 g/l CrO_3-H_2SO_4 bath, 3 amp/sq in., 130 F.	Copper adherent to soldered-wire peel test. Chromium adherent to steel-ball indentation test. Chromium plated 3Al-5Cr alloy tested in bearing-journal test against aluminum-bronze shoe, 11,000-psi load. Chromium was not applied satisfactorily to Ti-8Mn alloy.	21
Plating low-contraction chromium and copper. NBS's method	Unalloyed	Immersion etch: Immerse in chromic acid-hydrofluoric acid etchant at ambient temperature for 2 to 4 min prior to chromium plating. Bath CrO_3 - 136 g/l 48% HF - 220 ml/l Distilled water-balance Electrolytic etch: Immerse in acetic acid-hydrofluoric acid solution for 10 to 15 min followed by electrolytic treatment at about 20 amp/sq ft using 60 cycle ac for 10 min prior to chromium plating. Bath Glacial acetic acid - 875 ml/l 48% HF - 125 ml/l Avoid dilution, use at 120 F Heat treat at 1472 F in helium for 2 min.	Chromium plating CrO - 400 g/l H_2SO_4 - 4 g/l 185 F - 8 amp/sq in. Chromium plate without rinising after immersion etch. Chromium plate after electrolytic etch. Copper plate in acid sulfate bath after cathodic treatment in electrolytic etch bath. Copper plate in cyanide bath after anodic treatment in electrolytic etch bath.	Electrolytic-etch treatment produced best as-plated adherence. Heat treatment required for best bonding of copper and chromium plates to titanium. Chromium adherence, up to 18,000 psi; fractures in chromium plate. Copper adherence about 8,000 psi.	22
Protective coatings for titanium to prevent stress corrosion in dry salt at 700 F	6Al-4V	Electrolytic etch similar to above (decreased water content) Glacial acetic acid - 875 g/l Acetic anhydride - 100 g/l 60% HF - 125 g/l Immersion 10 to 15 min Electrolytic 15 to 30 min 60 cycle ac - 40 volts 0.05 to 0.1 amp/sq in. Anodizing H_3PO_4 - 85% 20 to 110 volts 1 to 2 amp/sq in. maximum decreasing to 0.05 amp/sq in.	Chromium plating CrO_3 - 250 g/l H_2SO_4 - 2.5 g/l 130 to 150 F, 1 to 2 amp/sq in. Silver plating AgCN - 30 g/l KCN - 56 g/l K_2CO_3 -.45 g/l 72 to 78 F, 10 amp/sq ft Nickel plating $NiSO_4 \cdot 7H_2O$ - 240 g/l $NiCl_2 \cdot 6H_2O$ - 45 g/l H_3BO_3 - 30 g/l 150 to 160 F, 38 amp/sq ft Gold plating $KAu(CN)_2$ - 8 dwt/l Free CN - 30 g/l K_2CO_3 - 15 g/l K_3PO_4 - 30 g/l 150 F, 5 amp/sq ft	Chromium and nickel adherent. Gold and silver moderately adherent. One mil of nickel, anodized coating, and conversion coatings plus silicone resins passed 500-hr lab test in dry salt at 700 F. Other coatings cracked.	23

TABLE IV. NICKEL-PHOSPHORUS ALLOY ON VAPOR-BLASTED TITANIUM

Purpose	Titanium Alloy Considered	Preparation for Plating and Postplating Treatment	Plating	Comments	Reference Number
Wear-resistant coating for titanium gears	3Al-5Cr 2Cr-2Fe-2Mo 4Al-4Mn 6Al-4V Unalloyed	Degrease; vapor blast (keep wet); rinse and brush clean of vapor blast slurry; activate - 150 F acidified solution of nickel chloride, immersion for 2 min.; electroless-nickel plate; heat to 1500 to 1600 F by high-frequency induction; water quench; age harden in air furnace at 900 F for 4 hr; air cool; and shot peen	Alkaline-citrate, electroless nickel bath (National Bureau of Standards): $NiCl_2 \cdot 6H_2O$ - 30 g/l NH_4Cl - 50 g/l NaCl - 5 g/l $Na_3C_6H_5O_7 \cdot 2H_2O$ - 100 g/l $NaH_2PO_2 \cdot H_2O$ - 10 g/l pH: 8 to 9 Temp: 190 F Plating rate: 0.3 mil/hr	Uniform coating over gear surface; diffusion alloy with titanium beneficial; no instances of scoring due to lubrication failure. Failed ultimately by pitting, or bending fatigue at such load levels as to compare with precision case-hardened steel gears	24
Process specification for electroless nickel coating on titanium	Not specified	Vapor blast; electroless-nickel plate immediately; heat treat in vacuum to 1500 F, 30 min at 1500 for 1-mil coating, 1 hr for 1 to 2-mil coating; cool at a rate of 100 F/hr to 900 F	Nickel-phosphorus alloy; up to 2 mils in thickness	After diffusion, the nickel and titanium have diffused to provide a nickel-titanium alloy on the surface. The alloy is somewhat harder than the titanium and has less tendency to gall. It has sufficient ductility to allow yielding without cracking	24

TABLE V. ELECTROPLATING ON TITANIUM ACTIVATED IN HOT HYDROCHLORIC ACID SOLUTIONS

Purpose	Titanium Alloy Considered	Preparation for Plating and Postplating Treatment	Plating	Comments	Reference Number
Activating titanium for plating	Titanium-base alloys	Immerse in concentrated hydrochloric acid at 194 to 212 F for 5 to 15 min	Silver plate	No data	25
Cadmium-coated titanium screws to fasten aluminum structure	RS-120 6Al-4V 4Al-4Mn Unalloyed	Immerse in 1:1 hydrochloric acid at 160 F for 5 min, rinse in distilled water	Nickel strike plate $NiCl_2 \cdot 6H_2O$ - 300 g/l H_3BO_3 - 30 g/l pH - 2.0 Temperature - 120 to 160 F Current density - 25 to 100 amp/sq ft Cadmium plate CdO - 26 g/l NaCN - 128 g/l Temperature - 70 to 100 F Current density - 10 to 50 amp/sq ft Voltage - 1 to 4 volts	Cadmium OK on Ti-6Al-4V and Ti-4Al-4Mn. Blisters and pits in cadmium on unalloyed titanium.	26
Evaluate plating process and brazing of titanium	Unalloyed	Activate in boiling hydrochloric acid, rinse, plate, and heat treat. Recommended heat treating conditions: Chromium-1000 F - 1 hr Nickel-900 F - 1 hr Iron-850 F - 1 hr Silver-Brazing temperature (time not indicated)	Cr-Unichrome CR 110 Fe-Iron chloride (no rinse) Ni-Nickel sulfamate Ag-Silver strike and plate	Change in hardness due to plating and heat-treating temperatures Chromium-1000 F - no change Iron-1000 F - no change Chromium-1200 F - increase of 80 KHN Iron-1700 F - increase of 160 KHN Semi-adherent plate as plated	27
Evaluate methods for coating aluminum and titanium propeller blades	8Mn	Activate in boiling hydrochloric acid, iron strike plate, and nickel plate over iron-plated titanium. Nickel plate over Wood's-nickel strike plate. Chemical activation in NBS bath: CrO_3-250 g/l, 48% HF - 220 ml/l and chromium plating plus heat treatment at 1472 F for 2 min in helium	Iron-chloride strike bath at 195 to 210 F. Sulfamate nickel plate 5 or 10 mils in thickness. Low contraction chromium: CrO_3 - 250 g/l, H_2SO_4 3.83 g/l 185 F, 8 amp/sq in., 30 min	Heating to 1800 F did not blister plates.	28

pickling, the metal was activated in concentrated hydrochloric acid and was nickel plated in a bright nickel bath with the addition of 2 to 4-g/l naphthalenedisulfonic acid at room temperature and a current density of 0.5 to 2 amp/sq ft. This method is not suitable for plating polished titanium because the surface becomes somewhat rough as a result of pickling.

Halpert (Ref. 32), in his patent, claims a process for plating on titanium in which the part is immersed in a 15-ml/l solution of 48 per cent hydrofluoric acid until a purple film forms. After rinsing, the part is plated with nickel, cobalt, or a nickel-cobalt alloy from a sulfate solution. Harding (Ref. 8) made a few attempts to apply this process without success.

A process consisting of anodic activation in an acetic acid-hydrofluoric acid solution followed by conventional electroplating was used by Schlosser and Lowery (Ref. 33) to produce adherent coatings on Ti-6Al-4V alloy. The coatings appeared to afford some protection to the alloy substrate from reactions with LOX under impact. The 40-minute activation treatment used may leave the titanium surface roughened but this may be alleviated by shortening the treatment. An activation treatment of as little as 2 minutes still results in excellent plating adherence.

SPECIFIC METAL PLATES

Nickel. Two types of electroless-nickel-plating solutions that may be used to plate titanium alloys are given in Table VI (Ref. 8).

TABLE VI. ELECTROLESS-NICKEL BATHS

Constituents	Concentration[(a)], in g/l Acid Process	 Alkaline Process
Nickel chloride	--	30
Nickel sulfate	80	--
Sodium hypophosphite	24	10
Sodium acetate	12	--
Boric acid	8	--
Ammonium chloride	6	50
pH	4.8 to 5.3	8 to 10
Temperature	200 F	195 F

(a) Concentrations are in terms of the usual hydrated forms of the salts.

Since titanium will not catalyze the deposition of nickel, plating may be started by making the part cathodic for about 5 seconds. Preplates as thin as 0.02 mil produced by this process permit excellent adhesion of other plates, e.g., gold. Relatively thick preplates of about 0.3 mil also may be produced.

As-deposited electroless nickel has adequate adhesion for normal handling but will not hold up under a bend test. Excellent adhesion is achieved by heat treating to cause partial diffusion of nickel into the titanium. Vacuum heat treatment at 1250 to 1550 F for 4 hours is recommended. Diffusion layers from 3 to 6 mils thick result at 1550 F. Treatment is an argon atmosphere at about 1000 F for 1 hour also gives good adhesion. Minimum conditions for satisfactory adhesion with the argon atmosphere appear to be 15 minutes at 750 F.

Neither electrodeposited nor electroless nickel (Ni-8P alloy) possesses good adhesion without subsequent heat treatment to alloy the nickel with the titanium. The method of preparing titanium surfaces for nickel plating is extremely important in influencing the as-plated adhesion which, in turn, will influence the bond after heat treatment (Ref. 31).

Electroless-nickel plates also were reported (Ref. 34) as well bonded after induction heating at 1050 ± 50 F. However, the experience of Dumnikov (Ref. 31) has indicated that adherent electroless-nickel coatings, regardless of the thickness (0.2 to 2.0 mils), were very brittle and crumbled in bend testing (possibly due to oxygen embrittlement resulting from induction heating under normal atmospheric conditions).

Another method of bonding electroless nickel to titanium involves a specific heating cycle to 1020 F, then to 1470 F and 1830 F, followed by quenching. Of course, the heat treatment must be compatible with the heat treatment which is optimum for a given alloy.

A method for the production of an adherent nickel electrodeposit on titanium has been presented by Babkes (Ref. 35). The system was used to build up overmachined parts and to obtain improved finish on cases of gas floating gyros. The program included a preplate of electroless nickel followed by a bright-nickel electroplate or a conventional rhodium plate. The plated titanium cases were polished lightly, then color buffed to the desired surface finish.

Conventional plating cycles make it difficult to obtain an adherent plate on titanium because of the speed with which a surface film forms. Therefore, it must be stressed that parts should be transferred from tank to tank as rapidly as possible. The following process cycle was found to be satisfactory by Babkes (Ref. 35).

(1) Rack parts on carbon steel or stainless steel racks and vapor degrease

(2) Clean in a nonetching alkaline cleaner

(3) Rinse in cold water

(4) Rinse in hot water

(5) Immerse in mixture of 1 part 60 per cent hydrofluoric acid and 3 parts 69 per cent nitric acid until red fumes are evolved

(6) Rinse in distilled or deionized water

(7) Immerse in a solution of 1 part sodium dichromate and 1 part hydrofluoric acid in distilled water for 20 minutes at 180 to 212 F

(8) Rinse in cold distilled water

(9) Place immediately in electroless-nickel bath of the following composition:

Nickel chloride	80 oz/gal
Sodium hypophosphite	1.33 oz/gal
Sodium citrate	1.33 oz/gal
Temperature	180 to 195 F
pH	4.0 to 4.5

A deposit of approximately 0.3-mil thickness will be obtained in 30 minutes. (Container should be glass or porcelain.) To obtain bright deposit, 1/2 oz/gal of sodium hypophosphite is added after 4 hours of operation. Sodium hydroxide is added to maintain pH at 4.0 to 4.5. The bath should be discarded after 8 hours of operation.

(10) Rinse in cold water

(11) Place in bright-nickel-electroplating bath for length of time needed to form coating of specified thickness

(12) Rinse in cold water

(13) Plate in conventional bath for the desired metal.

McGargar, Pohl, Hyink, and Hanrahan (Ref. 36) developed a procedure for plating titanium gears with electroless nickel. The titanium parts were first vapor degreased, then vapor blasted, quickly rinsed and brushed free of abrasive, and immersed in an alkaling electroless-nickel-plating bath. If necessary, deposition was initiated by momentarily making the part cathodic. After the desired thickness of nickel was deposited, the parts were vacuum baked at 1550 F for 4 hours. This operation improved the adhesion by causing a degree of interdiffusion of the nickel and the titanium. In order to improve the fatigue strength of the parts, they were then shot peened, an operation that also served as a check of the plating adhesion. The alloys studied were commercially pure titanium, Ti-5Al-2Cr-2Fe-2Mo, Ti-2Cr-2Fe-2Mo, Ti-4Al-4Mn, and Ti-2.5Al-16V.

Levy and Romulo (Ref. 37) used this process to produce nongalling and nonseizing surfaces on titanium parts of Army weapons. They added a 2-minute activation dip in acidified nickel chloride before electroless-nickel plating, and aged the plated parts for 24 hours at room temperature before heat treating. The alloys they worked with were Ti-5Al-2.8Cr-1.5Fe, Ti-2Cr-2Fe-2Mo, and Ti-6Al-4V.

By the proper choice of grit, the vapor-blast process will produce a wide range of surface finishes. If roughening of the surface must be avoided, the grit mesh size should be finer than 1000 as illustrated by Harding's data (Ref. 8) given in Table VII. Results will vary, of course, with alloy and nature of the abrasive. After abrasion, some workers have started electroless-nickel plating within 15 seconds. However, others have allowed parts to remain in a water slurry of abrasive for 10 minutes followed by an acidified nickel-chloride dip, or else, have rinsed parts to remove abrasive and stored the parts in deionized water for up to 40 minutes before plating.

TABLE VII. EFFECT OF VAPOR BLAST ON SURFACE FINISH

Pressure: 80 psi; nozzle size: 3/16 inch; blast distance: 2 inches; blast angle: 70 deg (approximate); and blast time: 2 minutes.

Grit(a) Size	Initial Finish RMS, microinches	Final Finish RMS, microinches	Finish Change RMS, microinches
200	6.5	17.5	+11.0
325	7.0	9.0	+2.0
625	6.0	7.0	+1.0
1250	8.0	7.5	-0.5
5000	7.0	6.5	-0.5

(a) Grit was ground quartz and decomposed quartz.

Chromium. Different titanium alloys present different cleaning problems and require individual approaches. A method for activating Ti-4Al-4Mn and Ti-6Al-4V alloys was reported as successful for chromium plating (Ref. 38). Parts are immersed in the following solution at room temperature to evolution of red fumes: 1 part by volume hydrofluoric acid (60 per cent) and 3 parts by volume nitric acid (69 per cent). Parts are then thoroughly rinsed (preferably by spray) with distilled or deionized water, and are treated in the following solution: 33-oz/gal sodium dichromate, 6.2-fl oz/gal hydrofluoric acid (60 per cent), balance distilled or deionized water. The temperature is 180 F to boiling, and the immersion time is 20 minutes. This treatment is followed by a cold-water rinse. Chromium deposits plated from a standard bath after this activating procedure were of a good quality and possessed good adhesion.

Another method (Ref. 22) of activating titanium prior to chromium plating produces a temporary titanium-fluoride coating which protects commercially pure titanium (99.0 per cent) during transfer from the activating solution to the chromium-plating tank. Parts are first degreased, scrubbed with pumice, and etched in a solution containing 9-ml/l concentrated HNO_3 and 185-ml/l hydrofluoric acid (48 per cent). Following this cleaning, parts are dried and treated at room temperature in a solution of 125-ml hydrofluoric acid (48 per cent) per liter of acetic acid for 10 to 15 minutes without current, followed by an electrolytic treatment (40 volts, 60 cycles alternating current, 1.5 to 3.0 amp/sq ft) for 10 minutes in the same solution (the temperature may rise to 120 F). Parts are then rapidly rinsed and plated in a standard chromium-plating bath containing 400-g/l chromic acid and 4-g/l concentrated sulfuric acid (185 F, current density 120 amp/dm^2). Chromium deposits produced by this method possessed good adhesion, which was strengthened by heat treating in a helium atmosphere at 1470 F for 2 minutes. The bond strength (measured by peel-testing samples that were plated with about 1-mil-thick chromium on the titanium, and then plated with about 6 mils of nickel over the chromium deposit) ranged from 4000 to 18,000 psi. Fracture occurred in the chromium plate.

Chromium (0.6 mil) plated on anodized or zinc-strike-plated titanium was reported as adherent (Ref. 39). Chromium plated over nickel plate on a third metal coating on titanium has also been reported as successful (Ref. 40).

Copper and Brass. Copper was successfully plated (Ref. 17) on titanium that had been electrochemically etched to provide mechanical bonding of the electroplated metal. The electrolytic etch was accomplished in an ethylene glycol-zinc chloride-hydrofluoric acid solution.

Copper deposits of 1-mil thickness, applied from standard baths on Ti-4Al-4Mn, Ti-6Al-4V, and Ti-3Al-5Cr alloys using the same preplate treatments as for chromium plating (Ref. 38), possessed good adhesion of an order greater than that of 60Sn-40Pb solder to copper, and were capable of withstanding the heat of a soldering iron.

Copper plated on titanium according to the method used for chromium plating (Ref. 22) was not adherent in the as-plated condition but acquired fair adhesion after treating for 10 minutes at 930 F, or 1 minute at 1470 F, in helium. The bond strength, as measured by a soft-solder peel test, was on the order of 8000 to 9000 psi. Rupture occurred in a weak titanium-copper compound layer.

Soviet scientists have developed a method (Ref. 41) of brass plating the surfaces of titanium components. The method uses a combination of electroplating and a subsequent diffusion treatment, and produces a deposit with good adhesion and the antifriction properties of brass.

The first step in the treatment is the preparation of the titanium surface before electroplating. Before pickling, the surface of the specimen is degreased with chalk and washed in water. Trials with several methods of pickling have shown that a satisfactory surface preparation is obtained by pickling in concentrated hydrochloric acid at a temperature of 60 F for 1 hour. Following earlier investigations by Japanese scientists, it was concluded that a protective film consisting of titanium hydride is formed, which prevents oxidation and possesses good conductivity.

Copper plating was carried out in a standard acid electrolyte containing copper sulfate and sulfuric acid. Plating was carried out at a temperature of 64 to 68 F and a current density of 1 to 2 amp/sq. dm.

After a series of tests, it was found that a special technique was required to obtain copper deposits of arbitrary thickness with good adhesion. A deposit of 0.6 to 0.8 mil was plated. The specimen was then subjected to vacuum annealing (at less than 1 micron mercury) at a temperature of 1470 F for 1 hour which accomplishes hydrogen removal as well as diffusion of copper into titanium. Additional copper can be deposited to any desired thickness after the treatment and passivation of the specimen in a solution of nitric and hydrochloric acids. The total copper deposit can reach 40 mils.

The copper deposit was converted into brass from a mixture consisting of zinc powder, fireclay powder, ferrosilicon, and ammonium chloride by diffusion at a temperature of 1350 to 1380 F. Tests in an Amsler friction machine for the anti-friction properties of the deposit thus obtained have shown that the brass deposit behaves like ordinary brass. With lubrication, a coefficient of 0.08 was measured.

Gold. Gold is sometimes applied to titanium alloys prior to a brazing operation. Harding (Ref. 8) tried the following procedure based on the hydrochloric acid process for plating gold on titanium.

Panels of both commercially pure titanium and the Ti-3Al-11Cr-13V alloy were prepared. After cleaning, they were immersed in hot (200 F minimum) concentrated hydrochloric acid for 5 minutes, rinsed, and immersed in the gold bath with the current on. Both a conventional cyanide gold bath and a citric acid gold bath were used. The deposits were uniform and smooth but they had little adhesion to the base metal and could be peeled away.

Adherent gold plates may be produced by preplating with electroless nickel. Following heat treatment, the nickel is lightly scrubbed with pumice and water to remove any slight film that may have formed. It is rinsed and then activated cathodically at 6 volts in a room temperature, 45-g/l potassium cyanide solution, rinsed, dipped for 1 to 2 minutes in a 30 per cent by volume solution of hydrochloric acid, and rinsed. At this point, if the part is to be plated in the citric acid gold bath, it is placed directly in the gold bath. If the conventional cyanide gold bath is used, the part is first dipped briefly in a 45-g/l solution of potassium cyanide and then gold plated. In both gold baths, an initially higher current density is used for a few seconds and then the current is lowered to the operating value. The adhesion of the gold plating may be evaluated by heating test pieces to 350 F for 1/2 hour and examining for blisters.

Platinum. Certain of the platinum-clad titanium anodes that have been available commercially for the past few years are produced by platinum plating following the hydrochloric acid etch. In one study, completely adherent platinum deposits were obtained on commercially pure titanium but no adhesion was obtained on Ti-3Al-11Cr-13V alloy (Ref. 8).

A coating of platinum will permit titanium to be used as an auxiliary anode in a variety of plating processes.

Zinc. One method (Refs. 31,39) that has been recommended as a good preplate treatment prior to deposition of a variety of metals consists of a zinc strike in an essentially nonaqueous solution of 200-ml hydrofluoric acid (40 per cent), 100-g zinc fluoride, and 800-ml ethylene glycol. Prior to the zinc strike, the titanium must be cleaned thoroughly and the oxides destroyed. The plating time is 5 to 10 minutes at 68 to 77 F, with a current density of 10 amp/sq ft and 6 volts; the anodes are of graphite. Copper, brass, tin, cadmium, nickel, and chromium can be plated from standard solutions on titanium with this zinc underplate.

Another zinc-strike bath containing zinc chloride instead of zinc fluoride was reported as successful (Ref. 20). However, copper deposits in excess of 5 mils in thickness applied over the zinc strike were reported as unsatisfactory.

Some Soviet workers have examined a complex system of underplates (Ref. 31) such as consecutive deposits of zinc, nickel, and copper. Following copper deposits, any metal may be plated.

For activating and plating polished titanium, they recommend the following procedure:

(1) Degrease with solvent, wipe with Vienna lime, and rinse in running cold water.

(2) Activate for 40 to 60 seconds in a solution containing 185 to 200-g hydrofluoric acid (40 per cent), 8 to 10-g nitric acid (sp gr 1.41), and 1 liter of water; temperature 64 to 77 F.

(3) Rinse in running cold water.

(4) Rinse in ethylene glycol for 2 to 3 minutes without subsequent water rinse. This operation is necessary to prevent dilution of the zinc electrolyte with water (drying can be used instead).

(5) Zinc plate in the following bath: 200-g hydrofluoric acid (40 per cent), 100-g metallic zinc, and 800-ml ethylene glycol. Zinc powder or filings can be dissolved easily in hydrofluoric acid. The temperature of the zinc bath is 64 to 77 F. Zinc plating can be conducted chemically or electrochemically. Chemical deposition, without the use of current, requires 1.5 to 2 minutes. Electrodeposition of zinc is conducted at a cathode current density of 0.5 to 1 amp/sq dm for 1.5 to 3 minutes. Zinc anodes are used.

(6) Rinse in cold water.

(7) Nickel plate in a standard sulfate bath at 64 to 77 F and initial current density of 1 to 2 amp/sq dm subsequently reducing the current after 1 to 2 minutes to 0.5 to 1 amp/sq dm. The plating time is 1 to 1.5 hours. Solution agitation is desirable.

(8) Rinse in cold running water, dry in hot air, heat treat in a drying oven for a muffle furnace at 480 to 570 F for 40 to 60 minutes.

After heat treating, nickel-plated titanium is activated in concentrated hydrochloric acid and is plated with copper or other metals, or is polished. After polishing, the deposit (nickel or copper) may be plated with nickel, chromium, rhodium, gold, silver, etc., depending on the service applications.

ANODIC COATINGS

Titanium is very resistant to many corrosive media because of the presence of an extremely adherent and inert surface oxide film. This chemically stable oxide film forms almost immediately when titanium is exposed to air; in solution, even a trace of oxygen is usually enough to maintain the protective layer. It is resistant to neutral salt solutions and oxidizing acids, and is moderately resistant to alkalis. However, the oxide is not resistant to hot, strong alkalis nor to hydrochloric, sulfuric, or phosphoric acids of moderate strength at ambient temperatures.

Titanium can be anodized in nearly any electrolyte. The characteristics of the film formed in each solution are quite different. Some give hard, thin crystalline coats; others are soft and thick. As titanium is anodized it first forms a series of thin, highly colored films. As the thickness of the coating is increased, it tends to become a uniform grey or brown. Numerous anodizing solutions have been used by several investigators to achieve the desired characteristics of anodized coatings on titanium. Several of these procedures are described in the following paragraphs.

Much use is being made of titanium as a construction material in the metal-finishing business. Under anodic conditions, the protective film can be maintained in environments that would otherwise lead to corrosion. For example, a positive potential of 500 mv will limit the corrosion rate in 40 per cent sulfuric acid at 140 F to less than 5 mils per year. The anodically reinforced oxide film insulates electrically and severely limits the current passing to the electrolyte. However, the film does pass current to metal pressed against it, thus enabling titanium to be used for anodizing jigs or for the construction of anode baskets used in nickel plating.

Anodic films may be produced on titanium for other than corrosion protection. For example, anodizing is one means of controlling, within limits, the thermal-radiation properties of metals used in spacecraft. Another use is for decorative finishing or finishes for "cosmetic" purposes; that is, to prevent fingerprinting and soiling of titanium surfaces. Conventional titanium mill-surface finishes, as with other metals, are quite easily soiled with fingerprints and dirt, and soon present a dirty, grimy appearance which is not easily cleaned. From an aesthetic viewpoint this is not a desirable feature for many titanium parts. Anodized films offer a fair degree of protection against staining and discoloration of the surface in addition to a wide range of pleasing colors. The colored films are very thin and are characterized by the voltage at which they are formed.

Covington and Early (Ref. 42) recently reported on anodizing methods for protecting titanium against hot-salt stress corrosion. Their procedure is as follows:

(1) Equipment

  (a) A variable d-c power supply 0 to 100 volts of sufficient capacity to provide a current density to 50 amp/sq ft.

  (b) A container to hold the electrolyte of sufficient volume to accommodate piece to be anodized.

(2) Pretreatment

  (a) In order to assure a standard surface for all coatings, the following pretreatment is recommended:

    (1) Pickle 30 seconds in 35 per cent HNO_3-3 per cent HF solution.
    (2) Wash thoroughly in distilled water.
    (3) Agitate in methyl alcohol.
    (4) Remove alcohol immediately with warm-air blast.
    (5) Anodize immediately.

(3) Electrolyte

The following electrolyte and anodizing conditions have been found to produce a coating showing a promising degree of corrosion protection.

Electrolyte	$NaNH_4HPO_4$
Concentration	Saturated
Temperature	32 to 80 F
Current Density	30 amp/sq ft
Time	30 min

The film developed on titanium has a high electrical resistance and the resistance increases with film thickness so that it is necessary to gradually increase the voltage to maintain a constant current. At the start of anodization, about 2 volts will give the required current density. Anodization was considered complete when the film appeared thick. In order to assure reproducible film thicknesses, the anodization is halted after a definite time interval.

The final voltage obtained varies from 60 to 90 volts depending on the electrolyte temperature and the alloy being anodized.

It is important that the anodizing bath temperature be held to less than 80 F. At higher temperatures the coating produced is porous and not protective. An impervious coating is only formed at low temperatures.

Janssen, Luck, and Torborg (Ref. 43) reported another procedure for anodizing on two specific alloys, Ti-5Al-2.5Sn and Ti-13V-11Cr-3Al.

Prior to anodizing, sheet specimens were mechanically polished to establish uniform and reproducible surfaces. Finish polishing was accomplished with a canvas lap and oil-mixed lapping compounds. The specimens were polished to have the same appearance as aluminum and magnesium with surface smoothness of 2 microns in root mean square.

Before electrolytic treatment, all samples were degreased in trichloroethylene, cleaned in an alkaline cleaner (Oakite 61A, 45 g/l, at 200 F, for 5 min) and rinsed in cold water. Those titanium samples that were not to be electropolished were pickled in a solution of 40 per cent by volume nitric acid after alkaline cleaning. Samples were electropolished in a solution of 160-ml/l 50 per cent hydrofluoric acid and 500-g/l chromic acid at 64 F and 325 amp/sq ft for 10 minutes. The samples were rinsed in cold water and anodized by one of the following processes.

Sulfuric acid anodizing was performed in a 20 per cent by weight solution at 68 F and 18-volt direct current for 20 minutes with lead cathodes. Sodium hydroxide anodizing was performed in a 5 per cent by weight solution at 205 F and 50 amp/sq ft for 20 minutes with mild-steel cathodes. The coating thickness was varied by varying the anodizing time. After anodizing, the specimens were rinsed in cold water and sealed in boiling water for 15 minutes. The Ti-5Al-2.5Sn specimens were anodized satisfactorily by this method, while the Ti-13V-11Cr-3Al alloy coatings were unsatisfactory.

Thickness of the anodized coating was measured by sectioning the coupons and examining the cross sections on a metallograph.

The coating thicknesses thus determined are presented in Table VIII.

TABLE VIII. ANODIZING VARIABLES AND COATING THICKNESSES

Solution	Electropolished	Sealed	Thickness, mil Ti-5Al-2.5Sn	 Ti-3Al-11Cr-13V
Phosphoric acid	Yes	Yes	--	0.075
Phosphoric acid	No	Yes	--	0.043
Sodium hydroxide	Yes	Yes	0.016	--
Sulfuric acid	Yes	Yes	0.016	--
None	Yes	No	--	--

A zinc-strike solution (Ref. 39) also has been used for anodizing titanium. The anodized surface thus produced was a good base for adherent electrodeposits. The anodizing is conducted for 10 to 20 minutes at a current density of 50 amp/sq ft and 18 volts, at 68 to 77 F. After anodizing, the parts are plated. Adherent brass, cadmium, copper, chromium, nickel, silver, and tin deposits were reported.

In another procedure, parts are anodized in a 20 per cent solution of sulfuric acid (sp gr 1.84) at 68 F and 18 volts. The color of the oxide film changes from yellow to purple depending on the length of treatment. The purple color appears after 10 minutes of treatment.

At Watervliet Arsenal (Ref. 44), an anodic coating has been developed that will provide the protection required, simply, inexpensively, and with no reduction in physical properties. This coating, called titanium hard coat, is a tenacious conversion coating of complex nature that cannot yet be identified. A patent has been applied for to cover the process for producing the hard coat.

The coating itself exhibits excellent wear and corrosion resistance. Hardness readings, though difficult to obtain, reach as high as 500 Brinell. In addition to maintaining the mechanical properties of untreated titanium, the fatigue life of coated titanium is increased from 108,500 revolutions to 3,765,000 as tested on a Rotating-Beam Fatigue Tester (Ref. 45). These results are shown in Table IX. Wear tests on unlubricated specimens, using a Modified MacMillan Wear Tester (Table X), show an increase of wear life (at a 40,000-pound load) from 216 revolutions for an uncoated specimen to 43,200 for a coated specimen. Additional tests on hard-coated specimens covered with a dry-film lubricant exhibit a wear life of more than 500,000 revolutions.

TABLE IX. RESULTS OF ROTATING-BEAM FATIGUE TEST

Condition of Specimen	Calculated Stress, psi	Cycles to Failure
Uncoated	99,000	38,000
Uncoated	61,500	1,075,000 (no failure)
Uncoated	84,000	108,500
Uncoated	84,000	66,000
Hard coated (2 min)	84,000	127,000
Hard coated (3 min)	84,000	3,765,000 (no failure)
Hard coated (4 min)	84,000	1,266,000
Hard coated (5 min)	84,000	89,000

TABLE X. TITANIUM HARD-COAT WEAR TEST

In Modified MacMillan Wear Tester
Load: 40,000 psi

Surface Finish		Revolutions to Failure
Timken Race	Bearing Block	
Lubricated hard coat[a]	Lubricated hard coat[a]	500,000[b]
Lubricated hard coat	Lubricated hard coat	174,684[b]
Lubricated hard coat	Lubricated hard coat	104,039[b]
Lubricated hard coat	Bare steel	51,471
Unlubricated hard coat	Unlubricated hard coat	43,200
Lubricated hard coat	Bare titanium	37,726
Diffused electroless nickel[c]	Diffused electroless nickel[c]	31,104[d]
Diffused electroless nickel	Bare steel	25,560[d]
Bare steel	Bare steel	9,792[d]
Diffused electroless nickel (oxide removed)	Diffused electroless nickel (oxide removed)	9,360[d]
Unlubricated hard coat	Bare steel	1,588
Unlubricated hard coat	Bare titanium	593
Electroless nickel (no diffusion)	Electroless nickel (no diffusion)	360
Untreated titanium	Untreated titanium	216
Untreated titanium	Untreated steel	216

(a) Lubricant: inorganic solids in a thermosetting resin.
(b) No failure occurred.
(c) Diffused in vacuum at 1550 F.
(d) Watertown Arsenal data.

The data in Table XI show that the coating process does not cause drastic hydrogen embrittlement and produces no change in tensile properties.

TABLE XI. RESULTS OF TENSILE TESTS

	Uncoated Samples (Average of Three Tests)	Hard-Coated Samples (Average of Six Tests)
Ultimate Strength, psi	140,300	140,100
Yield Strength, psi	127,700	127,700
Elongation, per cent	17	17
Reduction in Area, per cent	50	50

It is claimed that the equipment for hard coating is simple, inexpensive, and rapid. The solution used is controlled at near room temperature; inexpensive chemicals are used for the makeup and the power requirements are comparatively low. Solution control and operation of the equipment are comparatively easy and can be done by semiskilled personnel.

ELECTROCHEMICAL AND CHEMICAL POLISHING

An electrochemical method for producing a jewelry finish on titanium is as follows (Ref. 7). Prepare a solution of 90 per cent ethyl or No. 30 denatured alcohol and 10 per cent n-butyl alcohol, for each 100 cc of alcohol, sequentially dissolve 6-g anhydrous $AlCl_3$ (exothermic solution – add slowly) and 28-g anhydrous $ZnCl_2$. This solution is stable for about 1 week. Electropolishing conditions are: 30 to 60-volt direct current, 1 to 5 amp/sq in. of anode (the specimen) with a stainless steel (or other suitable) cathode, 1 to 6 minutes, 73 to 86 F, and solution agitated.

Any convenient means for specimen holding and electrical contact can be employed. Small specimens may be mounted in Bakelite to facilitate handling, sample coding, and storing. In this case, a 1/16-inch-diameter hole is drilled through the Bakelite to the specimen and a copper wire is force fit into the hole and into close contact with the specimen. This serves to make electrical contact and to hold the specimen in the solution. Because of its nonexplosive character relative to perchloric acid solutions, organic materials like Bakelite can be safely placed in the bath. More elaborate equipment can, of course, also be used.

A considerable number of electrolytic polishing baths have been evaluated (Ref. 7) for titanium. The alcoholic chloride solution is the best found to date for a wide variety of titanium-base materials. Chemical polishing of titanium can also be performed in an aqueous solution of the following composition:

Ammonium bifluoride	NH_4FHF	100 g/l
Nitric acid	70% HNO_3	400 ml/l
Hydrofluosilisic acid	31% H_2SiF_6	200 ml/l
Titanium (to stabilize reaction rate)		0.5 g/l
Water		Balance

The rate of chemical dissolution and the degree of polishing are related to the solution temperature, the titanium alloy, and the condition of the initial surface. Dissolution rates of about 0.1 mil/min occur in solutions of 80 to 90 F for Ti-6Al-4V alloy that has been surface ground.

METALLIC COATINGS OTHER THAN ELECTRODEPOSITS

Metallic coatings may be applied to titanium by several methods other than electrodeposition. The most versatile of these is the metal-spraying method also called flame spraying or metallizing. Hot-dipping methods such as the patented Aldip and Mollerizing processes are used for coating with aluminum. Both aluminum and gold are applied to titanium as metal pigments suspended in a vehicle that is subsequently removed by drying and baking.

Two methods which cannot be recommended for applying metal coatings to titanium are vacuum deposition of metal vapor and metal deposition by decomposition of volatile compounds. Very limited experiments with vacuum deposition have produced layers 0.04 mil thick. The vapor decomposition method has been used to coat titanium with molybdenum. However, the high temperature (above the transition temperatures of titanium alloys) necessary to produce good bonding will cause detrimental changes in the titanium structure. Another disadvantage is the high cost of the coating equipment and the highly skilled labor required.

FLAME-SPRAY METHOD

Hard-facing materials may be applied to titanium by flame-spraying methods. For details on equipment, methods, ventilation, safety measures, etc., related to metal spraying or thermospray processes, see the Metco Metallizing Handbook (Ref. 4). The metal-spraying process is also described in considerable detail in the ASM Metals Handbook (Ref. 3). Many of the points presented in these handbooks are summarized in the following discussion. Four types of flame spraying are the rod, detonation-gun, powder, and plasma methods. The methods are summarized in Table XII which was presented by Westerholm (Ref. 46). Although the rod method he described in detail was used to apply ceramic coatings, it also has been used to apply metallic coatings to titanium.

Development of the patented Rokide process (rod method) of flame spraying was based on the theory that when the coating material is in rod form, the particles have to become fully molten before they are released. The process uses compressed air to atomize the molten oxides and to project them to the work surface. The high velocity imparted to the oxides imbeds, flattens, and assures mechanical adherence of the particles on the prepared surface. The compressed air also helps cool the work parts, keeping them below 350 F.

According to McGeary (Ref. 46), flame plating (detonation or D-gun method) is a patented process used to upgrade standard materials including titanium and titanium alloys with coatings of tough, wear-resistant compounds — both metallic and nonmetallic. In the process, measured quantities of fuel and particles of coating material are detonated in a specially constructed gun, somewhat resembling a machine gun, see Table XII. The molten particles are blasted from the gun and imbedded into the surface of the workpiece where a microscopic welding action produces a tenacious bond at the interface. Successive detonations build up the coating material to the required thickness. Because of the noise of the process, the gun is isolated by double concrete walls insulated with sound-absorbing materials. Aiming and firing is remotely controlled from a panel outside the firing chamber.

Coatings can be applied as needed on selected areas of the base material. Warpage, distortion, or other physical change in precision parts is minimized because of the low temperature maintained in the base material during plating. Although temperatures above

6000 F are reached within the gun, the part temperature is maintained below 400 F.

Huff (Ref. 46) reports that the Aircospray (powder spray) process was developed expressly for hard-facing and brazing operations in which molten or heated powder metals are sprayed on a base metal through an oxyacetylene flame. This method uses a standard oxyacetylene welding outfit with a modified tip which permits the powder metal to be sprayed through the flame, see Table XII. A carrier gas – argon, helium, nitrogen, or carbon dioxide – conveys the powdered metals to the torch tip. The fuel gas can be acetylene or hydrogen.

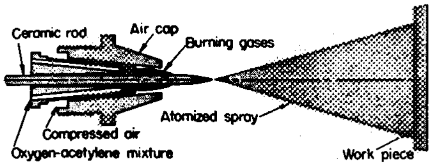
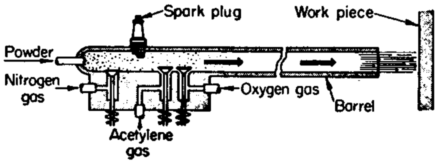
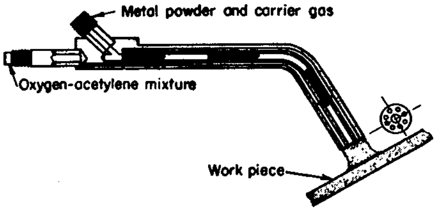
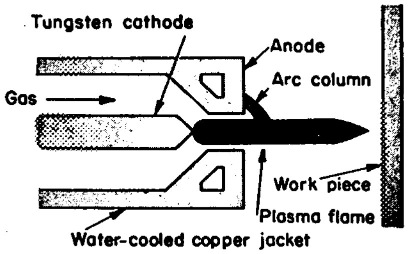
The primary use of the process is to deposit and simultaneously fuse powder metals on a base metal. In other cases, an incompletely bonded coating can be fused to an underlying metal surface in a subsequent heating operation. The powder-spray method can be used also for brazing. This discussion concentrates on the first two functions only.

Plasma plating is described by Wolff (Ref. 46) as a patented companion process to flame plating. It is used to upgrade standard materials with coatings of exotic metals, refractory compounds, and other substances. In this process, no combustion takes place; the flame consists of a jet of highly ionized, heated gas (plasma), produced by an electric arc, Table XII.

Two basic types of the plasma-jet device are currently used. In one, the arc leaves the nozzle of the torch and is transferred along with the gas stream to the workpiece. This is the basis for metal cutting. In the second type, the arc is forced into and through the nozzle by the gas flow, but it ends on the nozzle while the gas continues to flow to the work. This is the nontransferred arc device – the basis for the plasma-plating process.

Flame-Sprayed Molybdenum. Flame-sprayed molybdenum deposits are used extensively to provide wear- and seizure-resistant surfaces on a wide range of metals. A particularly attractive feature of the process is that thick, adherent deposits can be built up without any distortion of the base metal. Basically, the process (Ref. 47) consists of continuously feeding a pure molybdenum wire through the oxyacetylene flame of a wire-spraying gun. The molten droplets of molybdenum that are formed are sprayed onto the work surface until the required thickness has been built up. By masking-off techniques

TABLE XII. SUMMARY OF FOUR FLAME-SPRAY METHODS (REF. 46)

Equipment	Process	Coating Material
 **Rod Method** **(Rokide), Norton Co.**	A solid, 1/8 to 1/4 in. diam ceramic rod (the coating material) is supported and centered in the special nozzle by three spring-loaded balls. The rod is mechanically fed into the oxy-acetylene flame at a controlled rate. Molten oxide particles from the rod are accelerated and propelled toward the workpiece at about 550 fps by compressed air (80 psi supply pressure).	Any ceramic or refractory material that melts (rather than sublimes) and forms droplets (rather than threads). Most work, however, has been done with aluminum oxide, zirconium oxide, zirconium silicate, chrome oxide, and magnesium aluminate.
 **Detonation-Gun Method** **(Flame-Plating), Linde Co.**	Controlled quantities of oxygen, acetylene, and suspended particles of coating material are admitted into the gun chamber. Detonation of the mixture by a spark heats the particles to a plastic condition and propels them at a supersonic velocity toward the workpiece.	Formulations of tungsten carbide with cobalt, nickel, or chromium-carbide additives, chromium carbide with a nickel-chromium additive, and aluminum oxide.
 **Powder Method** **(Aircospray), Air Reduction Sales Co.**	Powdered coating material, propelled by gravity and a carrier gas, is sprayed through the flame of a modified welding-type nozzle onto the workpiece. Fusion is accomplished by the torch flame which contacts the work. This process is also used for capillary brazing of joints.	Chromium-nickel and tungsten-carbide compositions with boron added.
 **Plasma Method** **(Plasma-Plating), Linde Co.**	A high-current electric arc is concentrated and stabilized in the controlled atmosphere of a special nozzle. Some of the gas (usually argon) flows through the arc where it is heated as high as 30,000 F and accelerated to supersonic speed. The gas forms a highly ionized plasma jet. Particles of coating material, in powder or wire form, are introduced into the plasma where they are melted, then accelerated to a high velocity toward the workpiece. The work is cooled by jets of CO_2 or air.	Tungsten, tantalum, molybdenum, aluminum oxide, and zirconium oxide.

the coating can be confined to selected areas. In the "as-sprayed" condition, the deposit has a rough surface and variable thickness. It is, therefore, normal procedure to deposit an oversize coating thickness that can be ground to final dimensions and surface finish.

Work reported by Mitchell and Brotherton (Ref. 47) has shown that satisfactory molybdenum deposits can be obtained on all titanium alloys by applying the spraying conditions recommended for other metals (Ref. 4). Coatings up to 20 mils thick can be produced with excellent adhesion; thicker deposits, however, tend to chip at corners and edges because of inherent brittleness.

During the spraying operation the titanium base metal does not normally exceed a temperature of 480 F; consequently, there is no distortion and static mechanical properties are not affected. Fatigue strength, however, is reduced and recent tests have shown that a 10-mil molybdenum deposit on Ti-5Al-2.5Sn alloy decreases the endurance limit by 30 per cent.

The coating consists of a mixture of molybdenum and molybdenum oxide with a hardness of 500 to 600 VHN. The hardness can be increased to 800 VHN by using an oxidizing oxyacetylene flame, owing to the presence of an increased proportion of oxide. Unfortunately, this procedure also increases the brittleness of the deposit and reduces adhesion; an oxidizing flame should therefore be avoided.

Sprayed molybdenum is most easily applied to the external surfaces of components of relatively simple shape which can be easily ground after spraying; small internal diameters cannot be sprayed owing to problems of accessibility. The coating provides excellent wear resistant and friction properties under conditions of sliding contact and also where lubrication is limited, since the high porosity of the layer assists retention of lubricant. Sprayed molybdenum, however, is unsuitable for resisting severe abrasion and high-shock loads.

This process has recently been adopted for use on titanium alternator shafts and proved, in fact, to be the only technique suitable for this application. Each shaft is sprayed with a thickness of 20 mils in two bearing locations. The layer is then ground to 10 mils to obtain a uniform coating thickness and the required surface finish. Overspraying is prevented by masking with adhesive tape or metal foil.

HOT-DIPPED ALUMINUM

Aluminum coatings may be applied to titanium by two hot-dipping processes. Hot-dipped coatings do not appear to be detrimental to the bend or tensile ductility of unalloyed titanium at temperatures up through 600 F. Limited tests indicate that after exposures of about 3 hours at 1100 F, sufficient diffusion of the aluminum into the titanium occurs to cause a significant decrease in the tensile and bend ductility of thin aluminum-coated sections.

Aluminum coatings improve the short-time oxidation resistance of titanium and titanium alloys at temperatures up to 1800 F and are being used extensively by one airframe manufacturer for this purpose. After exposure in air at high temperatures, a thin alloy layer is retained on the surface of aluminum-coated materials. While reports on the effects of the residual layer on the base-metal properties are not consistent, the available information indicates that the residue is detrimental to the ductility of thin-sheet materials, if it is not removed.

The patented Aldip process for coating titanium is similar to the process bearing the same name (Aldip) developed by the General Motors Corporation for the hot-dip aluminum coating of steel. In the process (Ref. 48), titanium articles of the proper cleanliness are first heated in a fused-salt bath at approximately 1325 F to provide a suitable surface for aluminum coating. Suitable compositions for the salt bath are given as 37 to 57 per cent KCl, 25 to 45 per cent NaCl, 8 to 20 per cent cryolite, and 0.5 to 12 per cent aluminum fluoride. The article is then transferred to an aluminum bath, which is covered by a layer of the same type of salts, and held until it reaches a temperature at least equal to the melting point of aluminum (1220 F). The article is then withdrawn and shaken to free it from excessive aluminum.

Alternatively, the process can be carried out in a single step by using a dual bath in which a thick layer of salt is floated on the aluminum. Limited tests indicate no hydrogen pickup occurs during Aldipping.

This process produces a coating which is metallurgically bonded to the base material. The results of work at Allison (Ref. 49) indicate that an alloy layer not exceeding 0.5 to 0.9 mil is produced between the base metal and the aluminum coating. While no information on the actual overall coating thickness is available, it is estimated that Aldip coatings could be prepared in thicknesses of about 1 to 20 mils. The process has been used successfully to aluminum coat unalloyed titanium, Ti-5Al-2.5Sn, Ti-2Fe-2Cr-2Mo, Ti-4Al-4Mn, and Ti-6Al-4V.

The Mollerizing process was developed and is licensed by the American Mollerizing Company of Beverly Hills, California. In the process (Ref. 50), 99 per cent pure aluminum or a 98Al-2Si alloy is floated on a salt bath consisting of about 80 per cent $BaCl_2$, 20 per cent NaCl, and less than 2 per cent Na_3AlF_6. The workpiece and the molten aluminum are electrically anodic, while the salt bath is cathodic.

Prior to coating, the article is cleaned by washing in CCl_4, pickled in HCl, and then scrubbed and rinsed in boiling water. The piece is then dipped into the salt bath, held for the desired time, withdrawn, air cooled, and scrubbed in water to remove traces of the salt. The bath temperature is maintained at 1400 to 1500 F. Under these conditions, commercially pure unalloyed titanium sheets of 0.016 and 0.063-inch thickness were covered with a 0.1-mil-thick coating after holding times of 2 and 4 minutes, respectively (Ref. 51).

As with the Aldip process, Mollerizing produces a coating which is metallurgically bonded with the base metal. Available data (Ref. 52) indicate that an alloy layer from 0.06 to 0.2 mil thick is formed at the interface between the titanium and the aluminum coating on Mollerized material. Limited data indicate that some difficulty has been experienced in obtaining uniformly thick aluminum coatings on heavier gage sheet materials. Thus, one Mollerized unalloyed titanium sheet of 0.016-inch thickness had a uniform aluminum coating of 1 mil (Ref. 52). However, the coating thickness on two separate samples of 0.050-inch-thick titanium ranged from 0.5 to 2 mil in one instance (Ref. 52), and from 1 to 20 mils in another (Ref. 50).

Both unalloyed titanium and the Ti-8Mn alloy have been successfully aluminum coated by the Mollerizing process.

BAKED METALLIC PAINTS

A number of paints with metallic pigments which are applicable to titanium are treated briefly in a later section of this report concerning control of thermal radiative properties. Of particular interest are the aluminum- and the gold-pigment paints.

Aluminum. Both the Boeing Airplane Company (Ref. 53) and the Solar Aircraft Company (Ref. 54) have developed similar processes for applying aluminum paints to titanium. In the general process, aluminum pigment is mixed with a flux and sprayed on the titanium part. The flux is subsequently baked off. The coating can be built up into layers of several mils thickness, but for better adherence, it is usually applied as a thin layer.

Generally, the spray-painted aluminum coatings are more porous and less adherent than hot-dipped coatings. Boeing has reported (Refs. 53,54), for example, that some spalling of the painted aluminum coatings on Ti-6Al-4V sheets occurs during heating of these materials. Also, some peeling occurs at points of contact with the furnace rolls. However, as heat-treatment temperatures are lowered from 1700 F, the bond between the coating and base metal is improved and better protection is afforded.

Both the Boeing and the Solaramic processes have been used to coat a variety of sheet materials including unalloyed titanium, Ti-5Al-2.5Sn, Ti-6Al-4V, Ti-8Mn, and Ti-2Fe-2Cr-2Mo.

Gold. An interesting application of gold-coated titanium appears in the fabrication of the RA5C (earlier known as A3J) reconnaissance airplane. This is the gold-coated titanium sheet used around the J-79 engines which power the Vigilante.

The gold-plating process (Ref. 55) was developed by North American Aviation's Columbus division and involves spraying a gold-coating liquid (described below), long used in the ceramic industry, on chemically clean titanium sheet, followed by a suitable baking treatment. The coating thickness is about 0.1 mil. The purpose of the coating is to reduce the temperature of the titanium part during service. Without the gold coating to reflect the heat, temperatures would rise and either a heavier titanium or steel structure would be required.

Typical gold solutions are described in Du Pont Electrochemical Department Bulletin CP 4-361. A liquid bright-gold solution applied by spraying is fired at 950 to 1100 F. Fast firing can be tolerated if the coating is predried at 250 F to remove volatiles. Gold-paste metallic suspensions, which may be brushed on, are also available. These are fired at 1000 to 1400 F for 20 minutes to 3 hours depending on the time needed to equalize temperature of the furnace charge. The firing should always be done at the highest temperature compatible with the base alloy.

NONMETALLIC COATINGS

HARD COATINGS

Various methods of surface hardening of titanium to improve wear resistance have been reported. These hard coatings may consist either of oxides, nitrides, carbides, or borides, or of a titanium layer containing soluble amounts of one of the interstitial elements.

Oxide. Oxygen dissolves readily in titanium and raises the transformation temperature thereby tending to stabilize the alpha phase. Both the solubility and the diffusion coefficient of oxygen in titanium are relatively high. In this respect, oxygen is considered to be quite suitable as a diffusion element for the surface hardening of titanium. However, when titanium is heated in air or in an oxygen atmosphere, a considerable amount of oxide scale is formed. This scale can roughen the surface, and can lead to serious embrittlement problems. The controlled addition of oxygen to titanium under a reduced pressure of 10^{-2} to 10^{-3} mm mercury, which reduces this undesirable scaling, does not appear commercially feasible.

Takamura (Ref. 56) has described two methods of surface hardening of titanium by the diffusion of oxygen without causing undesirable scaling and embrittlement of the base metal: (1) the diffusion treatment in argon after preliminary oxidation in dry oxygen, and (2) the direct diffusion of oxygen in a molten-glass bath.

Diffusion in an Argon Atmosphere After Preliminary Oxidation in Dry Oxygen. Oxidation of titanium was carried out in a fused-silica tube which was designed so that purified oxygen and argon could be introduced. Titanium parts were completely degreased before oxidation. After oxidation in dry oxygen, the thin oxide scale that formed on the surface of the specimen was dissolved into the metal surface by heating at 1560 F in an atmosphere of purified argon. The degree of the solution of the scale depended upon the nature and the condition of the formation of the scale. The thin, uniform scale, which was usually gray and very adherent, was readily soluble. However, it was difficult to dissolve a heavy scale, and often spalling of the scale was observed.

When the weight gain in oxidation was less than 2 mg/cm^2, irregardless of the time and temperature of oxidation, the scale was easy to dissolve. The relationship between the weight gain in oxidation and the time required for complete dissolution of the oxide scale is shown in Figure 1. The amount of oxygen diffused was calculated from the literature values of the diffusion coefficient and the solubility of oxygen in α-titanium. Although the calculated time was sufficient for complete dissolution, it was necessary to increase the time for diffusion in order to obtain appreciable depth of the hardened layer.

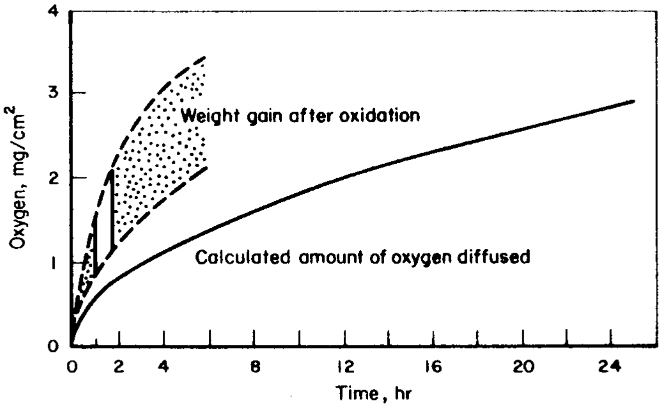


FIGURE 1. MEASURED OXIDATION RATE OF TITANIUM AND CALCULATED DIFFUSION RATE OF OXYGEN IN TITANIUM AT 1560 F (REF. 56)

Figure 2 shows the hardness gradient of the specimens, which had absorbed various amounts of oxygen, after diffusion treatment at 1560 F for 24 hours in argon. All specimens had a bright metallic luster and solution of the scale was complete. The specimens, oxidized in an oxygen atmosphere at 1560 F for 1 and 1.5 hours, showed weight gains of 1.38 and 1.90 mg/cm^2, respectively. Both had surface hardnesses above 1000 VHN and it seems probable that in these specimens the surface had been almost saturated with oxygen at the diffusion temperature, see Figure 2. However, in specimens having absorbed oxygen to 0.70 and 0.58 mg/cm^2, the surface oxygen concentration after diffusion for 24 hours was considerably lower than the solubility at 1560 F. The minimum amount of oxygen required for effective hardening after diffusion treatment of 24 hours or longer was estimated to be 1 mg/cm^2.

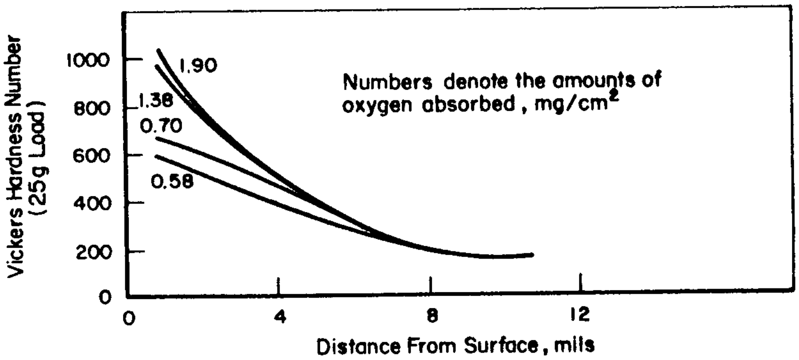


FIGURE 2. EFFECT OF THE AMOUNT OF OXYGEN ABSORBED ON THE HARDNESS GRADIENTS (REF. 56)

Diffusion: 1560 F for 24 hours in argon.

As shown in Figure 3, the depth of the hardened layer increased with the diffusion time. For instance, the depth of the specimen treated for 24 hours was about 8 mils and increased to about 12 mils after 48 hours. The microstructure of a specimen subjected to argon diffusion for 48 hours after having absorbed 1.38 mg/cm^2 of oxygen showed a hardened layer consisting of large α-grains in which oxygen had dissolved. The hardness gradient of specimens subjected to argon diffusion treatment for 24 hours and then to nitrogen for 24 hours was the same as that of a specimen subjected to argon diffusion treatment for 48 hours. Nitrogen hardens titanium in much the same manner as oxygen. However, when the specimen was directly treated

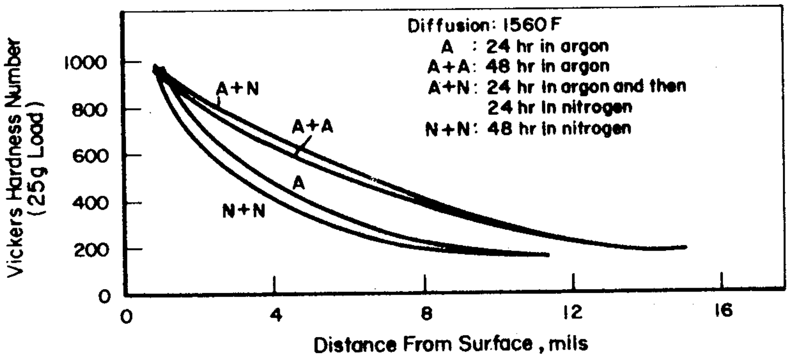


FIGURE 3. EFFECT OF THE DIFFUSION METHOD ON THE HARDNESS GRADIENTS (REF. 56)

Amount of oxygen absorbed: 1.4 to 1.9 mg/cm^2.

in nitrogen immediately after preliminary oxidation, it was observed that the black scale was retained on the surface even after diffusion for 48 hours and the hardness level was very low compared with that of the specimen treated in argon. Since the atomic radius of nitrogen is larger than that of oxygen, it is probable that nitrogen retards the diffusion of oxygen in the titanium lattice.

Direct Diffusion of Oxygen in a Molten-Glass Bath. When titanium is heated in a fused-salt bath, it is more or less corroded or oxidized as the result of the chemical reaction. In some kinds of glass, even at high temperatures the rate of the surface reaction is so low that the corrosion or the formation of oxide film on the surface is negligible and the diffusion of oxygen into titanium can take place to an appreciable extent. Table XIII lists the chemical compositions of several glasses that have been used as heating mediums.

TABLE XIII. CHEMICAL COMPOSITIONS OF GLASSES USED TO FORM OXYGEN-HARDENED SURFACES ON TITANIUM

Ingredient	Composition, wt per cent			
	No. 1	No. 2	No. 3	No. 4
SiO_2	43	53	42	36.8
Na_2O	19	24	25	31.5
B_2O_3	33	16	26	18.9
K_2O	--	6	6	6.3
CaO	4.2	--	--	--
BaO	--	--	--	6.3

By controlling their chemical compositions, glasses were obtained with various viscosities at high temperatures. As shown in Figure 4, the relative viscosities* of these glasses decreased from No. 1 to No. 4. At 1560 F, No. 1 and No. 2 had almost the same viscosities.

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*The relative viscosity means the reciprocal of the length, L, (cm) of the glass flow when a glass pellet (400 mils in diameter by 520 mils in length) made from pulverized glass that had been passed through a 500-mesh sieve was placed on a porcelain plate inclined at 30 degrees and heated at the indicated temperatures.

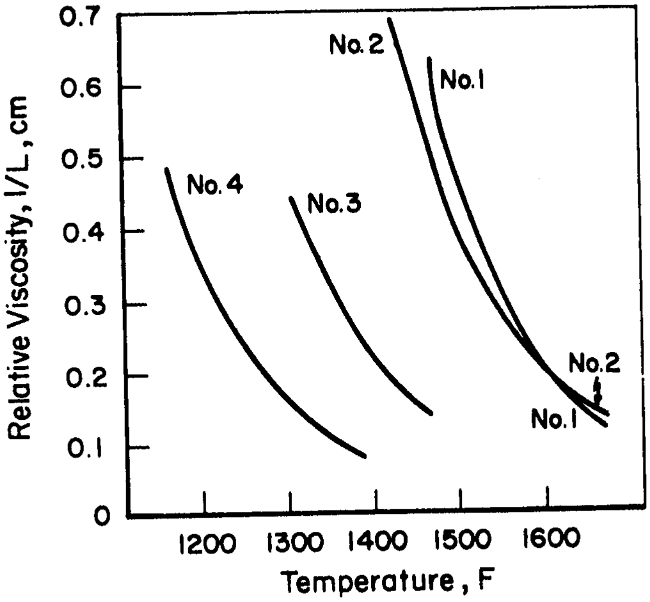

FIGURE 4. RELATIVE VISCOSITIES OF GLASSES USED AT HIGH TEMPERATURES (REF. 56)

About 1 kg of glass was placed in an agalmatolite crucible and melted in an electric furnace. The titanium specimens to be oxidized were dipped in the glass bath and heated. Then the specimens were taken out of the crucible and quenched in water. In order to remove all of the traces of the glass adhering to the specimens, the specimens were dipped in a molten alkali bath (NaOH 80, NaCl 10, Na_2CO_3 10 wt %) at 660 F and a nitric-hydrofluoric acid bath (HNO_3 10, HF 2 vol %) at room temperature, 5 minutes for each bath, and then rinsed with water.

The hardness gradients of the specimens heated in the glass baths at 1560 F are shown in Figures 5, 6, and 7. Figures 5 and 6 show that similar results were obtained in baths No. 1 and No. 2. The hardness near the surface was about 1000 VHN in both cases, and the depth of the hardened layer increased progressively with the time, 8, 12, and 14 mils for 24, 48, and 72 hours, respectively. These values agreed well with the values obtained with specimens diffused in argon after preliminary oxidation in oxygen (Figure 3). In addition, the microstructures were the same as those of specimens with the argon diffusion treatment.

In baths No. 3 and No. 4, although the depth of the hardened layer was the same as that in baths No. 1 and No. 2 for the same heating time, the hardness near the surface increased to about

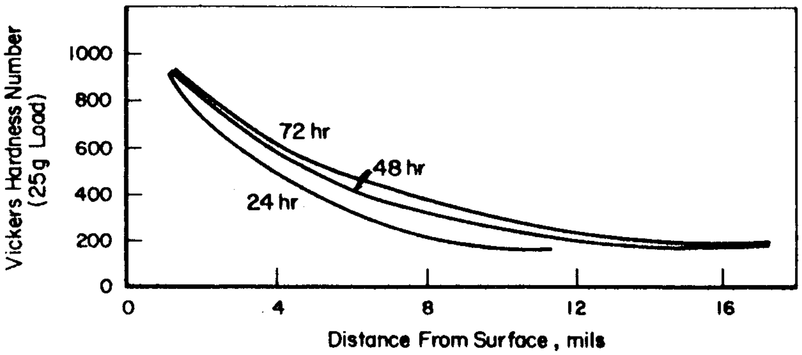

FIGURE 5. HARDNESS GRADIENTS OF SPECIMENS HEATED IN GLASS BATH NO. 1 AT 1560 F FOR 24, 48 AND 72 HOURS, RESPECTIVELY (REF. 56)

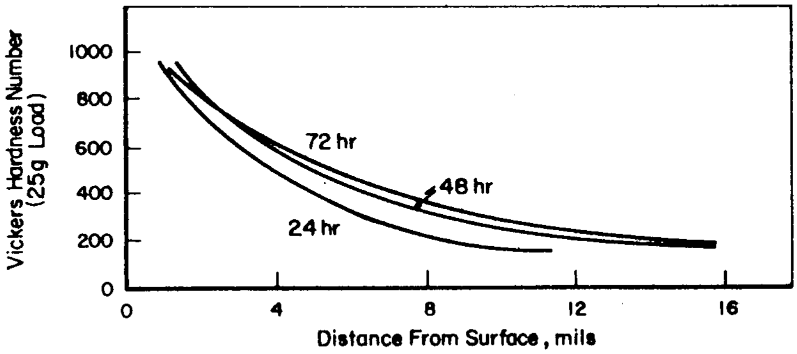

FIGURE 6. HARDNESS GRADIENTS OF SPECIMENS HEATED IN GLASS BATH NO. 2 AT 1560 F FOR 24, 48 AND 72 HOURS, RESPECTIVELY (REF. 56)

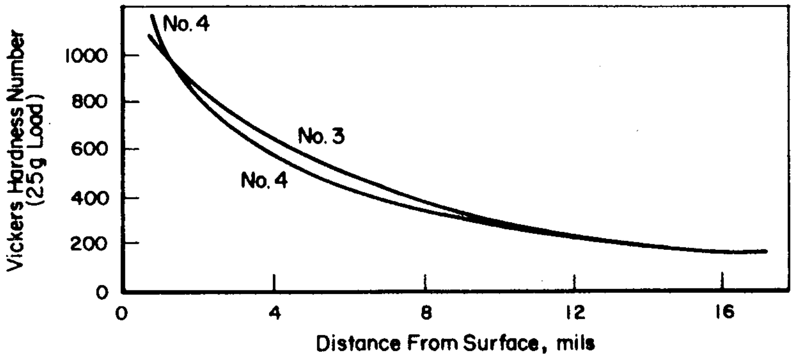

FIGURE 7. HARDNESS GRADIENTS OF SPECIMENS HEATED IN GLASS BATH NO. 3 AND NO. 4 AT 1560 F FOR 48 HOURS (REF. 56)

1100 and 1200 VHN for baths No. 3 and No. 4, respectively. In these cases black scale was found adhering to the molten-glass bath. Moreover, serious embrittlement resulting in surface cracks was observed when the specimen was polished.

After the specimens were removed from the molten baths No. 1 and No. 2, their surface appearance remained almost unchanged. Therefore, it was considered that in the comparatively viscous baths (No. 1 and No. 2), the supply rate of oxygen was lower or the same as the rate of diffusion of oxygen into the metal core at the operating temperature. This is a necessary condition for surface hardening of titanium by oxygen without serious embrittlement and surface roughening. It was fortunate that, in such cases, the rate of growth of the hardened layer was almost the same as when an excess amount of oxygen was supplied. It is also interesting that similar results were obtained by both baths No. 1 and No. 2 in spite of the fact that their chemical compositions differed considerably.

When the agalmatolite crucible was replaced by a heat-resistant austenitic stainless steel crucible, the formation of a black oxide scale and serious embrittlement were observed on the specimen even in the No. 1 and No. 2 baths. The glass could be used repeatedly without loss of activity. From these facts, it is considered that oxygen is supplied to the specimen by a chemical reaction between titanium and glass and the resulting deficiency of oxygen near the specimen is recovered by diffusion or convection from the atmosphere. When a stainless steel crucible was used, the oxide scale formed by oxidation of the steel was mixed into the glass and the bath became yellow. It is probable that in this case the ferric or chromic ion acts as the oxygen carrier in the molten-glass bath. In conclusion, Takamura (Ref. 56) states that the viscosity of the glass plays an important role in carrying oxygen to the specimen.

It may be inferred that both the direct oxidation of titanium followed by diffusion treatment in an inert-gas atmosphere and the combination oxidation-diffusion treatment in a glass bath might show commercial promise. However, Mitchell and Brotherton (Ref. 47) consider that the control is too critical and that this renders these methods generally unsuitable for industrial use. The latter method would probably be the more simple and practical. An oxygen case has the advantage over a nitrogen case in that it becomes three times as deep for the same treatment time.

In an effort to develop a more practical process, Mitchell and Brotherton (Ref. 47) investigated the possibility of surface-hardening titanium by utilizing the inherent oxidation potentials of molten salts. It was considered that the most suitable salts would be alkali metal carbonates and chlorides, since these have suitable melting ranges and are not decomposed at temperatures of interest.

Titanium specimens were heated in various combinations of these salts at temperatures between 1110 and 1650 F. Mixtures of sodium and potassium chlorides and carbonates produced hard layers but they also corroded the specimens. In contrast, salt baths consisting predominantly of lithium carbonate gave excellent results, and hard layers were formed without corrosion or changes in dimensions.

A typical microstructure obtained when commercially pure titanium was heated for 2 hours at 1380 F in a lithium-carbonate salt mixture showed a white-etching layer with a maximum hardness of 650 VHN and a depth of ~1 mil.

Although controlled oxidation in lithium-carbonate salts gives satisfactory layers at all temperatures between 1110 and 1650 F, it is considered that the most useful temperature is 1470 F, since above this level titanium is extremely susceptible to distortion. The best treatment time is between 2 and 4 hours; longer times cause a thin oxide skin to develop, which tends to flake away from the hard underlayer.

A recent application of this technique to titanium pistons completely eliminated a severe galling and seizure problem, and production batches of these components are now regularly treated. Its use is also being considered for titanium shafts and rotors.

In the opinion of Mitchell and Brotherton (Ref. 47), the controlled oxidation of titanium alloys in lithium-carbonate-base salt mixtures is the most attractive interstitial-hardening process available, since hard, wear-resistant layers can be formed at low temperatures by short treatments using relatively simple equipment.

Minkevich and Shul'ga (Ref. 57) surface hardened titanium in fused borax. Spectrographic analysis showed the boron content in the surface zones of the variously treated samples to contain less than 0.1 per cent boron and hardening was attributed to oxygen absorption. The microstructure and hardness did not differ from titanium oxidized in air. This work was carried out on a forged alloy of Ti-0.5 W composition in an electrochemical setup.

They concluded that treatment in fused borax and using an electrochemical method of protection appears to be an effective way of hardening the surface of titanium. With this treatment, the surface hardness (Vickers, 5-kg load) is increased from 250/300 to 700/950. The wear resistance of titanium oxidized in this way is comparable with that of case-hardened and nitrided steel (tests carried out on dry samples using the Amsler machine). The treatment of titanium in fused borax lowers its mechanical properties (strength and, particularly, plasticity and ductility); and this is coupled with a pronounced grain growth of the titanium on prolonged heating and hardening of the surface.

The treatment of titanium in fused borax may be carried out at 1650-1700 F over a period of 3 hours and using a current density of about 0.1 amp/cm^2 with titanium as the anode. Treatment at higher temperatures and over longer periods causes a marked increase in the brittleness of the layer and a deterioration in the mechanical properties of the titanium.

The bright surface needles formed in this treatment are said by the authors (Ref. 57) to represent a solid solution of oxygen in titanium. Quenching from the saturation temperature does not change the acicular character of the microstructure of the diffusion layer.

On treatment of titanium in fused borax at high temperatures (1830 to 1920 F) and with a high current density (1.5 to 2.5 amp/cm^2), a very hard, unetchable layer (2500 microhardness units) is formed on the surface of the titanium. Such treatment, however, causes marked breakdown of the surface of the sample.

The hardening of unalloyed titanium or Ti-2Al-2.5Cr alloy may be carried out at 1470 F over a period of 6 to 9 hours, in a bath made up of 60 per cent borax and 40 per cent boron carbide. This method of hardening, however, is suitable only for small parts; also the surface hardness is only increased by 200 to 250 VHN (5-kg load) and 300 to 500 microhardness units.

All the samples treated in the bath containing boron carbide (irrespective of temperature and duration of treatment) exhibited a clean, even, slightly gleaming surface which required no additional grinding and polishing.

Nitride. Titanium has a strong affinity for nitrogen and a hard nitride layer is formed when it is heated in nitrogen or ammonia. The diffusion rate of nitrogen in titanium is lower than that of oxygen. Nitrogen increases the transformation temperature. It is claimed that nitriding proceeds at a faster rate in an ammonia atmosphere than in nitrogen, but unfortunately the presence of hydrogen, formed by the dissociation of ammonia, introduces the danger of embrittling the titanium. For this reason, nitrogen is the preferred nitriding atmosphere.

Experiments by Mitchell and Brotherton (Ref. 47) showed that trace amounts of oxygen in the nitriding gas led to undesirable scaling effects and also affected the depth and hardness of the case. To insure an atmosphere of high purity, super-pure nitrogen containing a maximum impurity level of 6 ppm was used. In addition, all experiments were carried out in a vacuum furnace, applying a vacuum-purge technique to remove air from the furnace before the introduction of the nitrogen.

Nitriding temperatures of 1560 to 1830 F were investigated for treatment times of between 4 and 48 hours, and a range of nitrogen flow rates and pressures. Microhardness gradients for the Ti-5Al-2.5Sn alloy are shown in Figures 8 and 9. From these experiments it was concluded that the depth and hardness of nitrided layers are not significantly affected by nitrogen flow rate or pressure, or by extending the period of nitriding beyond 16 hours. An increase in temperature, however, produced a substantial increase in case depth and hardness.

Nitrided titanium is of a uniform golden color if the nitriding atmosphere is completely oxygen free. A slight roughening of the surface also occurs and increases with temperature and duration of nitriding. Metallographic examination (Ref. 47) of nitrided titanium alloys shows that two well-defined layers are formed. The thin surface layer is probably the compound TiN with a reported hardness of ~1500 VHN; this is extremely brittle and difficult to retain during preparation. The thicker, secondary layer is nitrogen-stabilized alpha solid solution, with a maximum hardness of ~700 VHN. The thicknesses of the compound and secondary layers formed on the two alloys by nitriding for 16 hours at temperatures between 1560 and 1830 F are given in Table XIV. The core structures produced were in accordance with the thermal history and transformation temperature of the alloy.

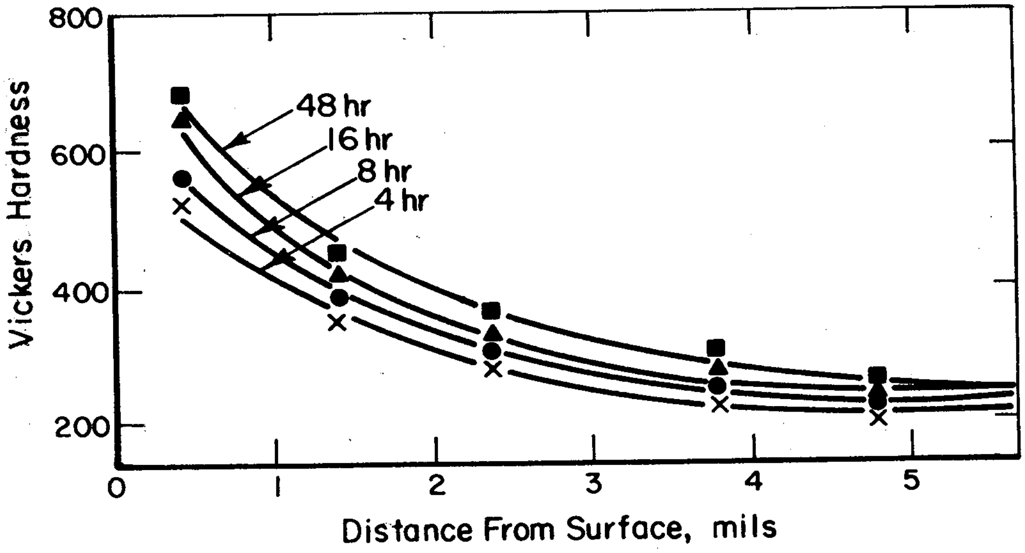

FIGURE 8. HARDNESS GRADIENTS PRODUCED BY NITRIDING A Ti-5Al-2.5Sn ALLOY FOR VARIOUS TIMES AT 1650 F (REF. 47)

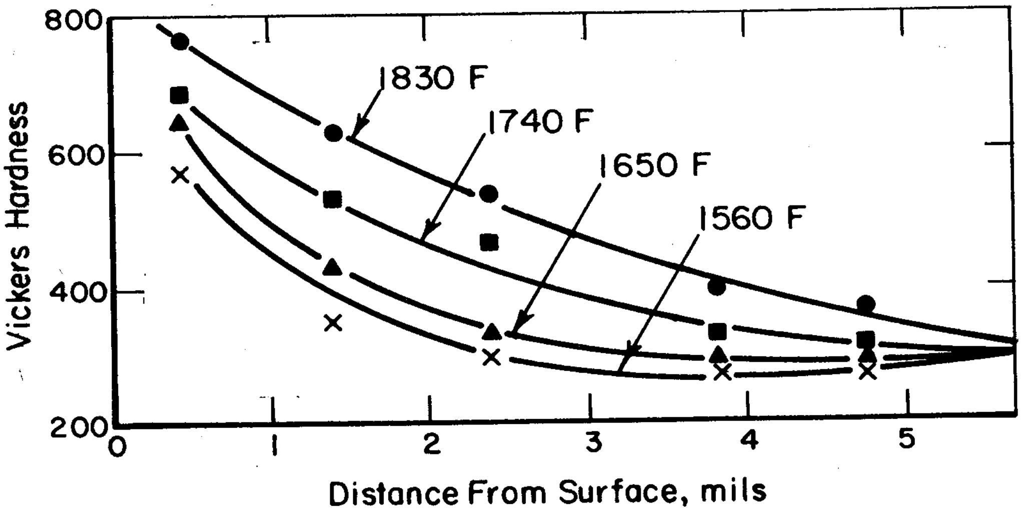

FIGURE 9. HARDNESS GRADIENTS PRODUCED BY NITRIDING A Ti-5Al-2.5Sn ALLOY AT VARIOUS TEMPERATURES FOR 16 HOURS (REF. 47)

TABLE XIV. THICKNESSES OF NITRIDED TITANIUM LAYERS

Alloy	Nitriding Temp, F	Titanium Nitride Compound Layer, mil	Alpha Stabilized Secondary, Layer, mils
Ti-5Al-2.5Sn	1560	0.1	0.8
	1650	0.2	1.2
	1740	0.25	1.5
	1830	0.3	2.0
Ti-4Al-4Mn	1560	0.2	0.5
	1650	0.2	0.9
	1740	0.3	1.2
	1830	0.3	1.7

Nitriding between 1560 and 1830 F has no appreciable effect on the ultimate strength, yield strength, or impact properties of the alloys tested. After nitriding above 1650 F, however, the Ti-4Al-4Mn alloy showed a drastic reduction in elongation (see Figure 10).

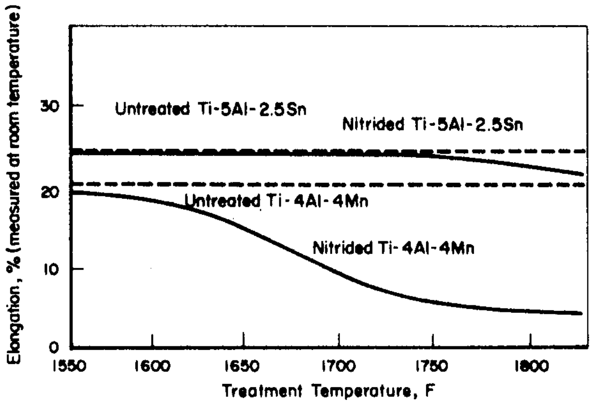

FIGURE 10. ELONGATION PROPERTIES OF TITANIUM ALLOYS AFTER NITRIDING FOR 16 HOURS AT TEMPERATURES BETWEEN 1560 AND 1830 F (REF. 47)

This was attributed to the development of a condition known as "β embrittlement", caused by heating in the all-β range. To avoid embrittlement, α/β alloys must be nitrided (or oxidized) below the $\alpha \rightarrow \beta$ transition temperature, since this condition cannot be rectified by later heat treatment.

Attempts to establish the effect of nitriding (Ref. 47) on fatigue properties were hampered by the severe distortion that occurred on heating specimens above 1560 F and only the Ti-5Al-2.5Sn alloy test pieces nitrided at 1560 F were considered suitable for testing. The results, presented in Table XV, show that nitriding decreases the endurance limit by ~20 per cent in the unnotched condition and by 35 per cent in the notched condition. A possible explanation is the presence of the brittle surface nitride and the surface roughening produced by nitriding.

TABLE XV. THE EFFECT OF SURFACE TREATMENTS ON THE FATIGUE PROPERTIES OF TITANIUM ALLOYS (REF. 47).

Alloy	Test-Piece	Treatment	Endurance Limit (2×10^7 Cycles), tons/sq in.
Ti-5Al-2.5Sn	Unnotched	Untreated	26.0
	Unnotched	Nitrided for 16 hr at 1560 F	21.0
	Unnotched	Cyanided for 2 hr at 1470 F	15.0
	Unnotched	Molybdenum sprayed (10-mil coating thickness)	18.0
	Notched	Untreated	15.0
	Notched	Nitrided for 16 hr at 1560 F	9.6
Ti-4Al-4Mn	Unnotched	Untreated	34.2
	Unnotched	Cyanided for 2 hr at 1470 F	21.0

The wear resistance (Ref. 47) of nitrided titanium alloys sliding against hardened steel without lubrication is shown in Figure 11.

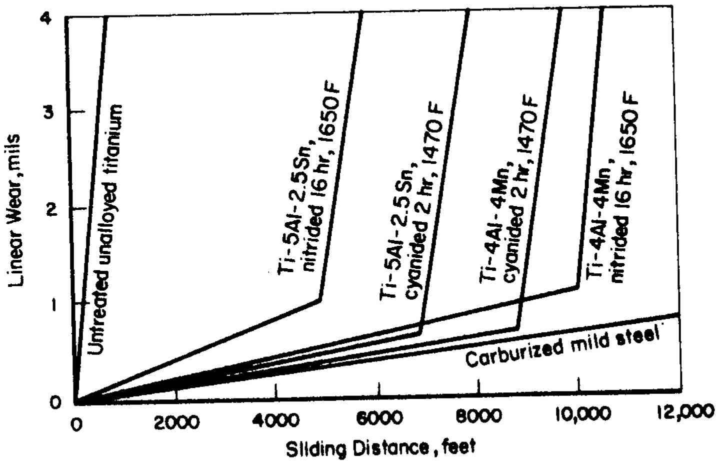

FIGURE 11. WEAR RESISTANCE OF TITANIUM ALLOYS AFTER VARIOUS SURFACE TREATMENTS (REF. 47)

Sliding rate, 10 ft/min; stress, 30 lb/in.^{2}; unlubricated.

Wear rates for untreated titanium and carburized mild steel, applying the same test conditions, are included for comparison. The results show that nitrided titanium has a high wear resistance almost equal to that of carburized mild steel. Since the layers are extremely shallow, however, they would probably collapse under heavy loads. Nitriding is therefore recommended only for components operating under medium or lightly loaded conditions.

Although many investigators suggest that nitriding is the most promising technique available for the surface hardening of titanium, it has limitations. The temperatures necessary to produce even shallow layers can distort components, processing conditions are critical, and a precision-built furnace is essential. Nitriding of titanium parts should be approached with these considerations in mind.

Cyanide. During the case hardening of ferrous materials in salts containing molten sodium cyanide, both nitrogen and carbon are liberated at the surface of the metal. Provided that similar reactions occur between cyanide and titanium, this process would seem to offer a convenient method of interstitial hardening with nitrogen and carbon. Additional hardening might also occur as a result of the presence of atmospheric oxygen dissolved in the salt.

The application of this process to titanium alloys does not seem to have received much consideration and the only detailed reference is by Griest, et al. (Ref. 58), who report that the antigalling properties of cyanided titanium compare favorably with those resulting from other surface treatments.

Work by Mitchell and Brotherton (Ref. 47), using molten mixtures of sodium and potassium cyanides and carbonates, has established that, although titanium alloys can be hardened by this process, there is a serious limitation in that all titanium alloys are dissolved by salts containing molten cyanide. The active constituent causing dissolution is sodium cyanate which is progressively formed in cyanide baths by the oxidation of cyanide, as shown in Figure 12. The rate of dissolution increases with temperature and cyanate concentration (Figure 13). Attempts to retard the rate of cyanate formation by maintaining inert and reducing atmospheres over the bath were unsuccessful. From this work, it was concluded that a treatment temperature of 1470 F represents the most useful compromise between the rapid dissolution rates at higher temperatures and the relatively shallow case depths formed at lower temperatures. It is

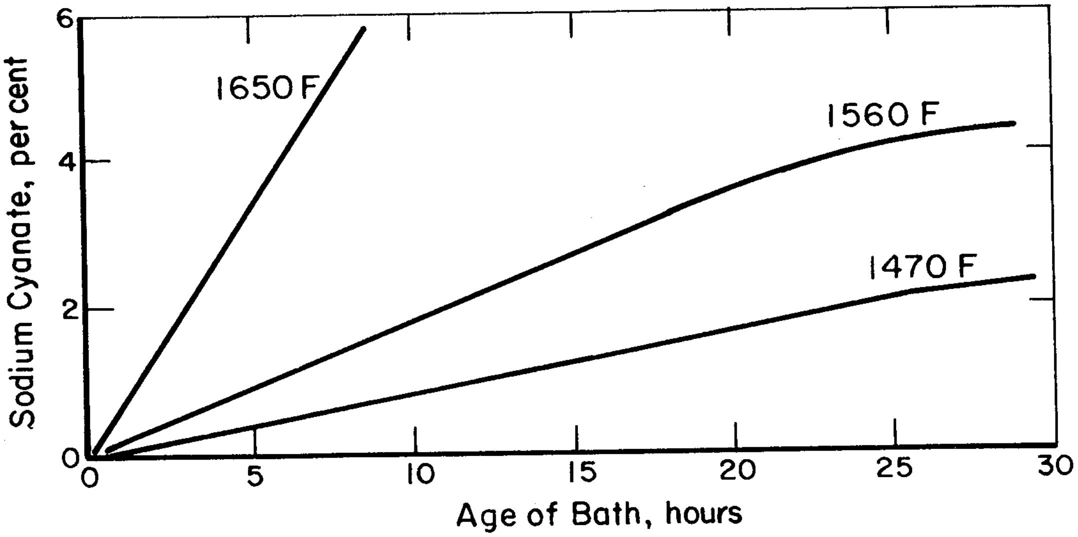

FIGURE 12. EFFECT OF TEMPERATURE ON CYANATE FORMATION IN A 35 TO 40 PER CENT SODIUM CYANIDE BATH (REF. 47)

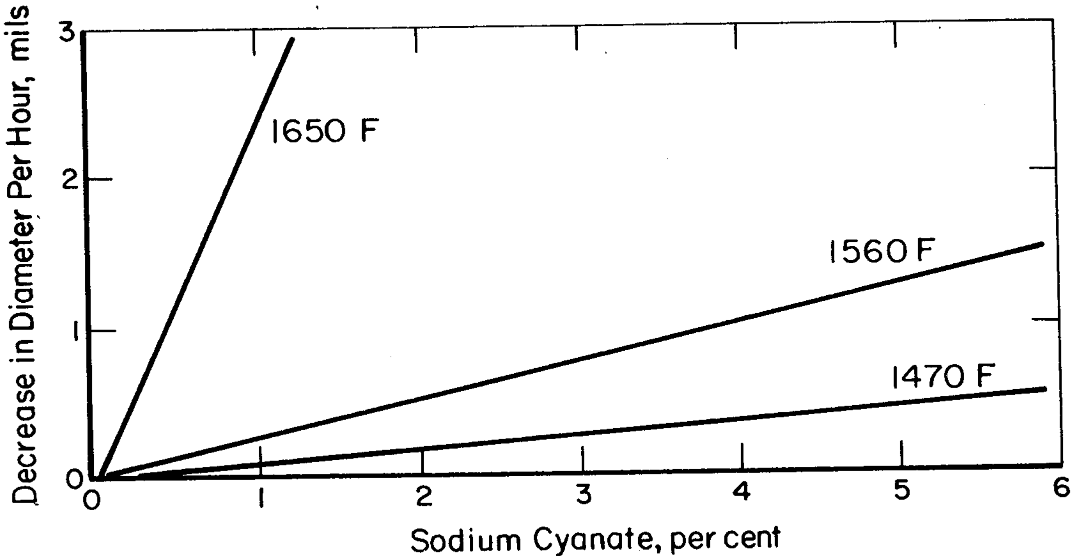

FIGURE 13. EFFECT OF CYANATE CONTENT ON THE SOLUTION RATE OF TITANIUM IN A 35 TO 40 PER CENT SODIUM CYANIDE BATH AT VARIOUS TEMPERATURES (REF. 47)

emphasized, however, that even at 1470 F substantial dimensional losses will occur, especially in cyanide baths that have aged for longer than a few hours.

The effects of cyanide concentration and treatment time at 1470 F on the depth and hardness of cyanided layers on the Ti-4Al-4Mn alloy are given in Figure 14(a) and (b). The best layers were formed by a 2-hour treatment in a mixture containing 35 to 40 per cent cyanide. The layers produced on all alloys are light-etching alpha solid solutions, reported to consist predominantly of a solid solution of nitrogen in titanium (Ref. 58). The case depths obtained in this work would, however, indicate that oxygen and not nitrogen is the major interstitial element present.

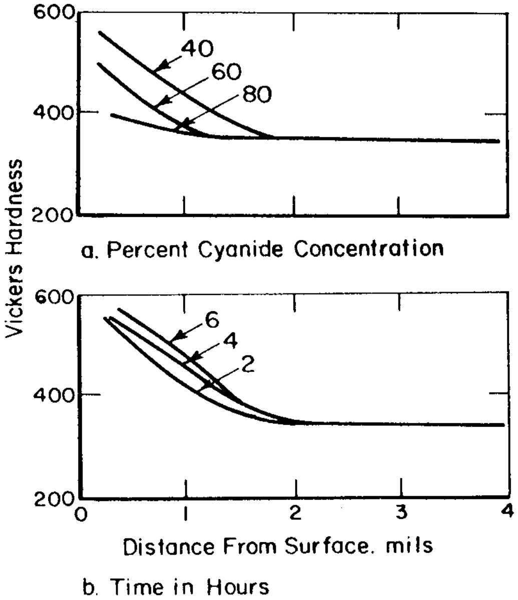

FIGURE 14. EFFECT OF CYANIDE CONCENTRATION AND CYANIDING TIME AT 1470 F ON THE DEPTH AND HARDNESS OF LAYERS FORMED ON Ti-4Al-4Mn (REF. 47)

In comparison with gas nitriding, the distortion problems associated with cyaniding are not serious, since lower temperatures can be used. This treatment, however, reduces fatigue properties more drastically than nitriding, and decreases the endurance limit by approximately 40 per cent in the unnotched condition (Table XV). The wear resistance of cyanided titanium (Figure 11) is slightly higher than that produced by nitriding, but it is probable that heavy loads would cause the layer to collapse. Data showing the improved performance of lubricated cyanided surfaces are available. (See the section on lubricant finishes in the present report.)

In view of the difficulties associated with the dissolution of titanium in molten cyanide salts, this process is considered inferior to nitriding, and cannot be recommended for use at the present stage of development.

Carbide. No recent work with carbide coatings produced by carburizing was found. However, in older studies it was shown that 0.2 to 0.8-mil coatings of TiC are produced by carburizing by the pack method or treatment with carbon monoxide or hydrocarbon gases at 1750 to 1840 F (Ref. 1). The case depth cannot be increased by heat treatment (Ref. 58) because of the low solubility of carbon in titanium. Cases of TiC greater than 0.2 mil tend to be brittle and spall off. Carburizing shows little promise for producing nongalling surfaces on titanium alloys.

Tungsten carbide with 13 per cent cobalt has been applied to titanium-alloy turbine-engine parts by the detonation-gun process (Ref. 59). During the coating process, the workpiece is kept cool so that the titanium-alloy structure is not damaged. The tungsten-carbide coating is used in sections of engine compressors where it offers superior wear resistance. However, its use is limited to service temperatures below 1000 F; above this, the coating oxidizes severely.

An outstanding example of the use of the detonation-gun-deposited tungsten carbide is in the coating of the contact surfaces of a midspan shroud of a fan blade of Ti-6Al-4V alloy where the coating provides wear resistance to protect the blade from high unit loads, both sliding and impact. Such coated shrouds have operated successfully in commercial-aircraft turbine engines for thousands of hours with negligible wear (Ref. 59).

Boride. The Soviet workers Minkevich and Shul'ga (Ref. 57) treated a sample of a Ti-5Cr alloy in vacuum in powdered boron at 1830 to 2100 F. This resulted in the formation of a diffusion layer having a thick, unetchable surface zone of great hardness (Vickers 1000 to 1150, microhardness >2200). The change of hardness with depth is given in Table XVI. The type of lattice and the parameters of the surface zone of this layer correspond to TiB. Spectrographic analysis of the surface of the sample showed the presence of 12 to 16 per cent boron in the surface zones of the layer. This amount represents the average boron content in the layer into which the spark penetrates (to a depth of up to 0.8 mil). It may, therefore, be assumed that in the unetchable surface zone the boron content is higher. The second phase in the surface might obviously be an α-phase or TiB (for which more than 18 per cent boron is necessary), but, because of the insignificant amount of the second phase, it was not possible to reveal it by X-ray.

TABLE XVI. CHANGE IN DEPTH AND HARDNESS OF THE BORONIZED LAYER (REF. 57)[(a)]

Treatment Temperature, F	Depth of Unetchable Zone of the Layer, mil	Vickers Hardness (5-Kg Load)	Microhardness (100-Gm Load) at Various Distances From the Surface, mil				
			0.4	1.	2.	4.	6.
1830	0.39	904[(b)]	1244	887	504	398	366
1920	0.43	1030	1583	964	504	400	343
2100	0.51	1160	2010	1607	512	404	366

(a) Treatment time = 6 hr.
(b) Vickers hardness at center = 350.

In view of the general lack of information on boride surface treatments for titanium, this treatment cannot be recommended for use at the present stage of development.

CONVERSION COATINGS

Chemical conversion coatings are used on titanium to improve lubricity. They act as a base for lubricants, promoting their retention and alleviating the tendency for severe galling in moving contact.

No recent developments in conversion coatings were found. However, examples of procedures are given in ASM Metals Handbook (Ref. 3). In brief, it states that conversion coatings are commonly applied by immersing the parts in a coating solution, by spraying or by brushing. Three conversion-coating baths with immersion times and bath temperatures are given in Table XVII. The resultant coatings are comprised of primarily titanium and potassium fluorides and phosphates. Cleanliness of the part is critical; finger marks or grease cannot be tolerated. The pH of the bath must be carefully controlled, according to the composition of the bath. The coating thickness depends on immersion time, which typically may be 2 to 10 minutes.

TABLE XVII. CONVERSION-COATING BATHS FOR TITANIUM ALLOYS (REF. 60)

Bath	Bath Composition, grams per liter	Temperature, F	pH	Immersion Time, min
1	50 $Na_3PO_4 \cdot 12\ H_2O$ 20 $KF \cdot 2\ H_2O$ 11.5 HF solution(a)	185	5.1 to 5.2	10
2	50 $Na_3PO_4 \cdot 12\ H_2O$ 20 $KF \cdot 2\ H_2O$ 26 HF solution(a)	80	<1.0	1 to 2
3	40 $Na_2B_4O_7 \cdot 10\ H_2O$ 18 $KF \cdot 2\ H_2O$ 16 HF solution(a)	185	6.3 to 6.6	20

(a) 50.3 wt % HF.

Coatings are easily removed without excessive loss of metal by pickling in an aqueous solution containing 20 per cent HNO_3 and 2 per cent HF by weight.

LUBRICANT FINISHES

For a review of lubricants for titanium see the DMIC review (Ref. 1) which deals with both solid and liquid lubricants including hydrocarbons, inorganic liquids, synthetic long chain compounds, sugar solutions, and halogenated hydrocarbons. Only a few of these decrease the coefficient of friction from that for unlubricated titanium.

Some improvement in wear resistance was obtained from lubricated cyanided surfaces (Ref. 61). Wear-test data illustrating results are presented in Table XVIII.

A recent detailed discussion of finishes that lubricate, particularly the properties and applications of bonded-solid-lubricant coatings, is given in a recent paper by Di Sapio and Goldie (Ref. 62). They state that bonded solid lubricants are increasingly being specified for all manner of bearing surfaces of machine parts and that they have been used for some time now in aircraft applications and special mechanisms where liquid lubricants are unsuitable.

Many finely divided, inorganic solids are used as lubricants in one way or another. Classic examples are graphite and molybdenum

TABLE XVIII. WEAR DATA OBTAINED ON A FALEX WEAR TESTER

Pin	V-Block	Weight Loss on Pin, mg[a]				
		Mineral Oil MIL-0-6082[b]	Silicate Ester MLO-8200	Plexol 201[c]	Phenyl Methyl Silicone	Halogenated Hydrocarbon
Steel	Steel	1.2	2.0	1.7	Welded	0.6
Steel	Ti-2.8Cr-1.5Fe	3.6	9.4	6.3	Welded	2.0
Ti-2.8Cr-1.5Fe	Ti-2.8Cr-1.5Fe	403.8	362.5	391.6	391.0	0.2
Ti-2.8Cr-1.5Fe	Cyanided Ti-2.8Cr-1.5Fe	444.8	--	--	--	--
Cyanided Ti-2.8Cr-1.5Fe	Ti-2.8Cr-1.5Fe	297.2	--	--	--	--
Cyanided Ti-2.8Cr-1.5Fe	Cyanided Ti-2.8Cr-1.5Fe	0.5	--	0.2	--	0.0
Cyanided Ti-2.8Cr-1.5Fe	Steel	0.2	0.3	0.1	0.2	0.1
Steel	Cyanided Ti-2.8Cr-1.5Fe	3.2	--	--	--	1.7
Steel	Ti-4Al-4Mn	2.4	--	8.3	--	2.1
Ti-4Al-4Mn	Ti-4Al-4Mn	286.5	203.3	278.4	208.6	0.2
Cyanided Ti-4Al-4Mn	Cyanided Ti-4Al-4Mn	1.1[d]	--	0.3	--	0.3
Cyanided Ti-4Al-4Mn	Steel	0.2[d]	0.2	0.2	0.2[d]	0.3
Steel	Cyanided Ti-4Al-4Mn	4.6	12.1	6.5	383.7	1.3
Steel	Ti-3Al-5Cr	--	--	10.1	--	0.9
Ti-3Al-5Cr	Steel	526.4	--	506.8	--	0.3
Ti-3Al-5Cr	Ti-3Al-5Cr	330.6	0.0	0.1	264.8	0.1
Cyanided Ti-3Al-5Cr	Cyanided Ti-3Al-5Cr	216.9	--	0.5	--	0.2[d]
Cyanided Ti-3Al-5Cr	Steel	162.3	0.3	0.4	58.1[d]	0.3
Steel	Cyanided Ti-3Al-5Cr	4.3	--	21.2	--	--

(a) Conditions of tests: load, 250 lb; time, 30 min; room temperature.

(b) Military specification for a lubricating oil, aircraft-engine grade.

(c) Di-2-ethylhexyl sebacate.

(d) One run only.

disulphide, which provide effective lubrication in a wide variety of applications. Molybdenum disulphide is especially effective at high bearing pressures. These lubricants are available in powder form, as greases and grease-consistency concentrates, in liquid dispersions, and, more recently, as bonded-solid-lubricant coatings.

These coatings are commonly supplied as a suspension of finely divided powder in a lacquer or thermosetting resin, thinned with various solvents. Both are one-part systems, packaged ready for use. The film is applied to the bearing surface and cured in place as a thin, but long-lasting, lubricative coating.

Resin binders may be of several types; air-drying lacquers, air-curing resins, and thermosetting resins are the most common, although inorganic binders are sometimes used. The solvent used varies with the nature of the binder and, to a lesser degree, with the application method. Three most common methods of applying a coating are: spray, dip, and tumble. Brushing and flow coating can be used, but do not give uniform results. For the greatest uniformity, thickness control, and endurance, spray coatings are much to be preferred. Tumbling offers economic advantages when large numbers of small, simple parts are processed.

Alloys of titanium may be pretreated either by abrasive blasting or a commercial phosphate-fluoride conversion coating. Parts must be thoroughly rinsed in water after the chemical treatment.

No specific examples of the application of bonded-solid-lubricant finishes on titanium were given by Di Sapio and Goldie. Solid lubricants have some effectiveness at very low loads on bare titanium surfaces but no strong bonding takes place. Heavy loads cause breakthrough and metal-to-metal contact (Ref. 1).

PAINTS

Paints are used on military aircraft both as a functional finish and for appearance and identification. Dissimilar metals appear on the surfaces of these aircraft with aluminum and magnesium used in low-temperature areas and titanium in the high-temperature areas. The combination of metals necessitates the best corrosion protection available, particularly since many of the aircraft are used in the salt-laden atmospheres of carriers and beaches. Elsewhere, runway deicing salts can be the source of corrosion problems. Since engine oil for jet engines is an effective stripper of most paints, formulation of effective paints presents a challenge. Bentinck and Hohman (Ref. 63) report that the Navy Bureau of Aeronautics has developed an acrylic-lacquer system which performs well on most exterior areas of aircraft. One of the problems in its use has been loss of adhesion from glass laminates, aluminum, magnesium, and titanium. Most difficulty has been encountered in its use with magnesium.

The sequence of operations used by manufacturers in painting aircraft is (1) preclean, (2) steam clean, (3) treat surface, (4) apply paint, (5) apply markings, (6) apply stencils, (7) touch up, and (8) final inspect. Since many of the problems only incidentally involve titanium, the cleaning process and primer and finish coat formulations are not presented here. See the paper of Bentinck and Hohman (Ref. 63) for the composition of "Wash primer" MIL-C-8514(AER) with major ingredients of polyvinyl butral, resin, zinc chromate, magnesium silicate, n-butyl and ethyl alcohols, and an acid component of phosphoric acid; the tie coat of cellulose-nitrate modified alkyd primer, MIL-P-7962, and the finish coat of acrylic-nitrocellulose resin, MIL-L-19537.

CERAMIC COATINGS

Titanium and its alloys, as well as other metals, often are subjected to heat treatments to improve properties. Since the operation is carried out at high temperatures, the problems of oxidation and scale formation on a reactive metal such as titanium are formidable. They can be circumvented by use of inert-gas atmosphere or vacuum furnaces, but this often is more complicated and expensive than is desired. Recently Rolls-Royce, Ltd., developed (Ref. 64) a variety of coatings that protect titanium during heat treatment. These coatings are available from F. W. Berk & Company, Ltd., of Berk House, 8 Baker Street, London W1, under the name of Berkatekt, as described in Metallurgia (Ref. 64).

Berkatekt is supplied in liquid form, and its application to a clean metallic component results in a thin impervious film on the surface of the metal, which reduces oxidation and scale formation with the attendant problems of pickling and machining.

Berkatekt coatings fall into two broad classes: the four grades of thin-film, non-self-descaling, nonfusing coatings, incorporating bentonite materials which can be used from 1110 to 2100 F, and the three grades of self-descaling coatings which incorporate ceramics and are used in high-temperature annealing in the range 1560 to

2190 F. Of the four non-self-descaling grades, two have toluene and two have trichloroethylene as a solvent. In the case of the self-descaling grades, the solvent is toluene in each case.

The Berkatekt preparations may be applied by spraying or dipping, but whichever technique is used, the metal surface to be coated must be free from paint, dirt, oxide, scale, and grease, and should be bright - preferably polished - to obtain the best results. Dipping probably produces the better coating, but this method can only be used for simple shapes, such as flat plates, and spraying must be regarded as the universal method of application. Fortunately, the coatings do not run in the wet state, so that, provided the liquid is well stirred, it is not difficult to achieve a uniform coating. In the case of the non-self-descaling grades, a coating of 1 to 1.5 microns thick usually gives better results than a thicker film.

The safety precautions to be observed depend on whether the solvent is the inflammable toluene or the toxic trichloroethylene, and whether the dipping or spraying technique is used. Adequate fire precautions are necessary with toluene, and efficient fume-extraction facilities with trichloroethylene. There is no fire risk from the dried coating.

While dealing with the application of this coating, reference may be made to its removal in the case of the non-self-descaling grades. As this thin film is inert and not abrasive (the self-descaling coating is) there may be no need to remove it. Where its removal is desirable, this can be effected simply by a short pickling operation.

The properties of titanium and zirconium alloys are markedly affected by their content of gases such as oxygen, nitrogen, and hydrogen, and the barrier provided by this coating against pickup of such gases, even at high temperatures, is said to result in little or no deterioration of mechanical properties.

SURFACE TREATMENTS AND THEIR RELATION TO THERMAL RADIATIVE PROPERTIES

The rapid development of space and missile technology has created an increased and specific need for data on radiant heat transfer and thermal-radiation properties. There is special interest in these properties of titanium and its alloys since they are favored for space applications because of their low density, high strength, and relatively high melting points. The thermal-radiative properties of titanium, titanium alloys, and other selected materials have been collected by W. D. Wood, H. W. Deem, and C. F. Lucks (Ref. 65). In a series of curves and supporting tables, they present data on total emittance (normal or hemispherical) and total reflectance as a function of temperature, and normal spectral emittance and spectral reflectance as a function of temperature and wavelength. The effects of polishing, vacuum heating, and surface oxidation in air at various temperatures and times are shown. Figure 15 shows a typical curve which presents the normal spectral emittance of Ti-6Al-4V alloy. The curves for oxidized and polished surfaces also are shown.

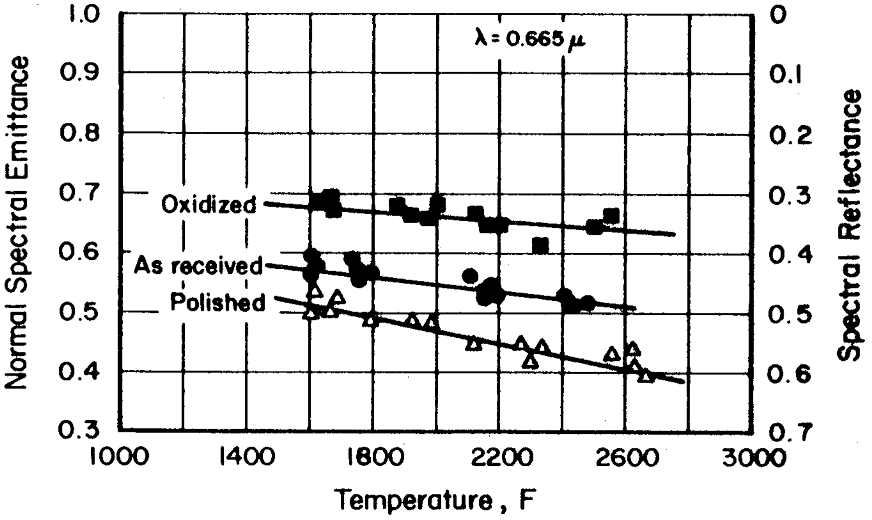

FIGURE 15. NORMAL SPECTRAL EMITTANCE OF ALLOY Ti-6Al-4V

Symbol	Composition and Surface Condition	Test Method	Remarks
△	Polished	Normal spectral emittance. Modified hole-in-tube method. Drilled black-body hole. Temperatures measured with thermocouples.	Measured in vacuum (λ = 0.665 μ). Data taken from curves.
●	As received or wiped clean		
■	Oxidized		

Wood, Deem, and Lucks (Ref. 65) have also presented thermal radiative properties of various coatings on titanium and titanium alloys. These coatings include enamels and paints, oxide coatings (other than oxidized or anodic), and metallic coatings. The coatings cited are listed in Table XIX.

Janssen, et al. (Ref. 43), in a study of reflectance of anodic films found that the sodium hydroxide anodizing process (see p 23) worked well on Ti-5Al-2.5Sn, but produced no coating on the Ti-3Al-11Cr-13V alloy. The sulfuric acid process produced a very thin, transparent, deep-blue film on titanium. However, it was so fragile that it could be easily wiped off.

The reflectance values for the sulfuric acid, sodium hydroxide, and the phosphoric acid anodizing processes on the Ti-5Al-2.5Sn alloy are compared in Figure 16 along with the unanodized metal. These three processes gave approximately the same reflectance values beyond about 4 μ except for an absorption band from 7 to 15 μ with the phosphoric acid process. The sodium hydroxide process on Ti-5Al-2.5Sn (Figure 16) produced a spectral reflectance almost identical to that of the phosphoric acid process on Ti-3Al-11Cr-13V. The sulfuric acid process gave almost identical results on both alloys.

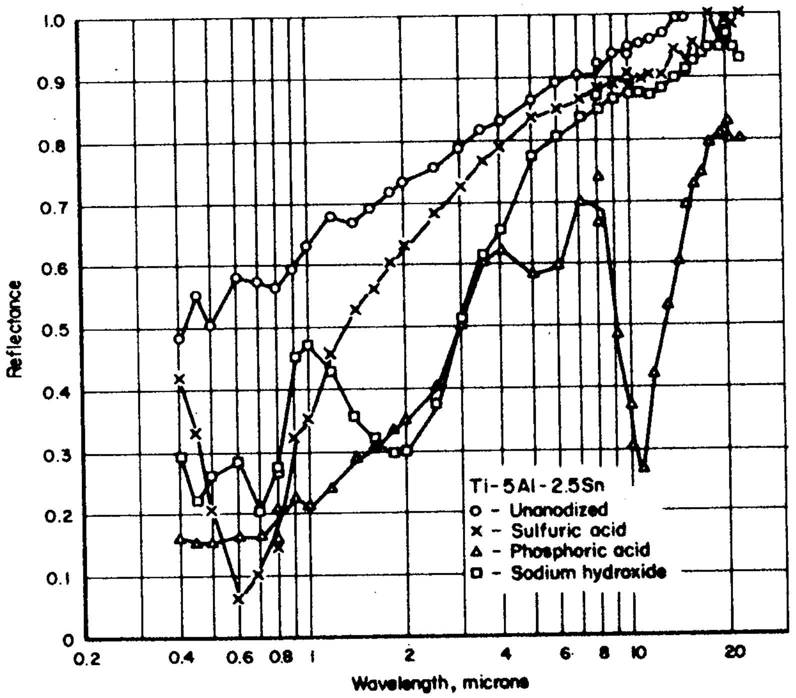

FIGURE 16. EFFECT OF ANODIZING PROCESS ON REFLECTANCE OF Ti-5Al-2.5Sn ALLOY (REF. 43)

TABLE XIX. COATINGS FOR THERMAL-RADIATION STUDIES OF TITANIUM AND Ti-6Al-4V

Coating	Baking Treatment	Titanium Material
	Enamel or Paint	
Chem Industries, high-temperature, silicone-base aluminum paint	Measurements at 800 F	Ti-6Al-4V
Corning XP-310, aluminized - silicone paint	To 300 hr at 870 F	Unalloyed
DuLite 3-0, an oxide conversion coating of the base metal	Measurements at 400 to 1800 F	Unalloyed
Vita Var PV100, a white paint with silicone vehicle and TiO_2 pigment, 0.7-mil coating.	Ditto	Unalloyed
Pratt and Lambert 91-1524, butyl titanate paint with aluminum pigment, 0.5 to 1.0-mil coating	"	Unalloyed
Rinshed-Mason, J 15934, a silicone paint with aluminum pigment, 1.0-mil coating	"	Unalloyed
Rinshed-Mason Q36K802, a silicone paint with carbon-black pigment, 0.9-mil coating	"	Unalloyed
	Oxide	
Norton LA-9683, a refractory oxide, not identified, flame sprayed on 12-mil Nichrome V undercoat	Measured at 800 F	Unalloyed
Norton LN 9684, a very dark nickel oxide, flame sprayed on Nichrome V undercoat	Ditto	Ti-6Al-4V
Norton LA-9696, a tan Alundum, 92 per cent Al_2O_3, flame sprayed on Nichrome V undercoat	Measured at 800 F and 1800 F	Ti-6Al-4V
Norton Rokide A, white 98.5 per cent alumina, flame sprayed on 12-mil Nichrome V undercoat	Measured at 800 F	Ti-6Al-4V
Norton Rokide Z, stabilized ZrO_2	Measured at 800 F and 1800 F	Ti-6Al-4V
	Metal Coat	
Engelhard Industries Bright Gold No. 6854, applied by spray	Fired at 1110 F, 5 min, measured at 480, 930, and 1380 F	Unalloyed

The reflectance values obtained with the phosphoric acid process on Ti-5Al-2.5Sn were somewhat higher beyond 7 microns than those for the same process on Ti-3Al-11Cr-13V. This effect apparently is the result of a thicker oxide coating on the Ti-3Al-11Cr-13V alloy. The thickness measurements indicated that the oxide film was built up more rapidly on the Ti-3Al-11Cr-13V.

Measurements at elevated temperatures in vacuum had little effect on the reflectance of sodium hydroxide anodized Ti-5Al-2.5Sn. However, for the phosphoric acid process on both titanium alloys, a marked decrease in reflectance at elevated temperatures was observed at wave lengths less than 10 microns.

The effect of anodizing time on the reflectance of the coatings was investigated for the sodium hydroxide process on Ti-5Al-2.5Sn and the phosphoric acid process on both alloys. In all three cases investigated, the reflectance for the short anodizing time was nearly identical to that for the standard time, indicating that the anodizing process was essentially completed in one-third of the standard anodizing time. In the case of the phosphoric acid process, voltage rather than time was the controlling parameter.

Reflectance measurements on unanodized specimens of Ti-5Al-2.5Sn indicated that electropolishing increased the reflectance about 10 per cent. All the titanium specimens that were not electropolished were pickled. It appeared that the effect of pickling was similar to that of electropolishing in all cases, except for Ti-3Al-11Cr-13V anodized by the phosphoric acid process. In this case, the electropolished specimen gave considerably lower reflectance, especially beyond 12 microns. It appeared that, in this case, electropolishing activated the surface so that the coating formed more rapidly. This same effect has been noted on hydrochloric acid etched anodized magnesium alloy, Mg-3.25Th-0.7Zr.

The effect of prior heat treatment at 1500 F in air was investigated only for the phosphoric acid anodizing process on Ti-3Al-11Cr-13V, and the same decrease in reflectance, as that produced by heating in vacuum, was noted. Since this happened both in vacuum and air, it would appear that it was due to diffusion of metal atoms from the substrate into the coating. A sodium hydroxide anodized titanium specimen heat treated in this manner changed so greatly in appearance that it was considered unusable.

The estimated solar absorptance to infrared emittance ratios (α_s/ϵ) for titanium were generally high and varied from about 3.5 to 7. The sodium hydroxide process on Ti-5Al-2.5Sn gave a solar absorptance of about 0.7 and an infrared emittance of about 0.1, making this an attractive combination for a solar collector. It also withstood a temperature of 1300 F, in vacuum, with little change in reflectance.

Since most of the anodized titanium specimens had relatively low reflectance at the short wavelengths and high reflectance at the longer wavelengths, they are attractive for use as solar collector surfaces. The choice of material and process for a solar collector, however, would depend on the operating temperature of the collector surface and the radiant-energy density incident on the surface. The sodium hydroxide process on Ti-5Al-2.5Sn would probably be attractive for most applications.

CONCLUSIONS AND RECOMMENDATIONS

Among the problem areas that require further investigation in the surface treatment of titanium and titanium alloys are the coating of these materials (a) to improve frictional properties and (b) to provide stable, specific radiative properties.

If titanium alloys are to be used in bearing applications, there needs to be improvement in the adherence of metallic and other coatings applied to lessen seizing and galling of bearing surfaces and improvement in lubricability. To date, success is confined to rather moderate loads. Under heavy loads, platings and hard coatings break down and bearing properties and wear resistance are lost. Both improvement of coating techniques and application of postcoating mechanical treatment and/or heat treatment of coatings to improve performance should receive further investigation.

In the area of radiative properties, there is a general need for more data on coated titanium and titanium alloys. Measurements vary among investigators, probably because the method of application of a given film is critical. Techniques leading to reproducible coatings should be demonstrated.

There also is need for development of coatings with specific properties for particular applications. For example, a solar-orbiting spacecraft may require use of heat from the sun. In this case, some components of the craft would require a high-solar-absorptance coating with low infrared emittance so as not to lose heat back to space. In another component or craft, diametrically opposite radiative properties may be called for. Here, the need may be to remove as much heat as possible, as from an atomic-powered spacecraft. Hence, the craft may have a coating with low solar absorptance so as not to pick up heat from the sun and have coated fins of high infrared emittance to dissipate excess heat.

It also appears that considerable more work could be devoted toward the study of coatings capable of protecting titanium alloys from atmospheric contamination during heat treatment. Very little information was found regarding the protective qualities of presently available coatings. Increasing interest in the use of titanium alloys in solution-heat-treated and aged tempers should greatly increase the need for coatings that will minimize contamination. Methods of applying coatings, the degree of protection which can be expected, and methods of removing the coating after heat treatment should be thoroughly examined.

Finally, there is need for a more general dissemination of information regarding the behavior of coated titanium components in service. Much of the data presently available is the result of laboratory work. No doubt, these studies have been applied, with success in many cases, to various production parts. This information is not available, however.

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SURFACE TREATMENTS FOR TITANIUM ALLOYS

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The information in this report has been reviewed for security classification. Review of any information concerning Department of Defense or Atomic Energy Commission programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

This document has also been reviewed and approved for technical accuracy.

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