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SURFACE PREPARATION OF MARAGING STEEL FOR ELECTROPLATING

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ABSTRACT OF THE DISCLOSURE

An improved method of preparing maraging steels for subsequent metal deposition by utilization of a combined nitric acid pickle-mechanical abrasion descaling step in conjunction with a low current density acidic electropolishing step to produce a scale free, activated surface for deposition of a very adherent electrodeposit.

The invention described herein may be manufactured, used and licensed by or for the Government for governmental purposes without the payment to us of any royalty thereon.

BACKGROUND OF THE INVENTION

Maraging steels are well known to the art. Their structural properties afford substantial toughness together with high strength. The development of 18% nickel maraging steel, in particular, has provided rocket designers with a material possessing a yield strength as high as 350,000 p.s.i. Fabrication of tankage from maraging steel increases the payload/total weight ratio of a missile and hence improves its performance. The hydrazine family of fuels both liquid and slurry have been found to be very efficient for use in liquid propellant rockets. Since maraging steel provides such favorable physical characteristics for use with rockets, inevitably an attempt was made to use this steel in conjunction with these fuels. It is well known that many metals cause catalytic decomposition of hydrazine and its derivatives and that many non-metals either react with or are dissolved by such propellants.

It was found that the hydrazine fuels undergo catalytic decomposition when stored in maraging steel vessels. This decomposition produces gaseous reaction products which in turn increase the pressure inside the tank to unsafe levels. The desired storage life of prepackaged liquid rockets is five years. Therefore it was necessary to run tests to determine hydrazine compatibility in maraging steels.

The tanks designed for these compatibility tests could tolerate a safe maximum of 500 p.s.i., which maximum should not be reached until after a projected five year storage period. It was established that hydrazine and certain hydrazine mixtures placed in an unprotected maraging steel tank produced 500 p.s.i. within two days. Therefore it was necessary to develop a means of preventing contact between the maraging steel and hydrazine or in fact any medium which produces corrosion in the steel or decomposition of the medium.

The best method of accomplishing this protection was found to be by plating the steel with a coating of certain

selected metals. Therefore, an investigation of metal deposition procedures was pursued.

One of the most important aspects of metallic deposition is production of high strength adherence between the substrate and the plate. The efficacy of a coating as a means of protecting the underlying substrate from contact with a corrosive or reactive medium is closely related to the condition of the surface of the substrate. Poor preparation of the substrate results in porosity of the plate and incomplete coverage of the basis metal. Also, it results in poor adhesion and thus separation of the plate and substrate when the composite is subjected to temperature cycling or mechanical stress. Such separation causes blisters, cracks and buckling in the plate and subsequent contact between the medium and metal.

Nickel maraging steels, because of their high content of Ni, Co and Mo are inherently passive and require special preplating processing to remove oxide films that otherwise prevent adhesion of a deposit and to smooth and activate their surface. This inherent problem of adhesion is known to the art as evidenced in the International Nickel Company Inc. data bulletin on this type of steel. In addition, since this steel is obtained by heat treatment and is normally covered with a heavy heat treating scale, scale removal is necessary. Improper or incomplete scale removal results in the imperfections in the coating mentioned above. It therefore is necessary to remove all heat treating scale as a part of the pre-deposition treatment.

Scale removal is always difficult. In the case of Ni maraging steel the procedure becomes even more critical because of the necessity of removing the scale without excessive thinning of the metal. As was previously specified, one of the major advantages in the use of this metal is that it can be used to effect a weight saving in rockets. Because of its great strength it can be used in a thinner state that normally would be employed. In the descaling operation great caution must be exercised to prevent excessive thinning of the metal. Therefore a somewhat specific scale removal process is needed.

A pre-plating process as described in the above-mentioned International Nickel Co. Inc. data bulletin was attempted but it was established that in the recommended anodic etch step for scale removal, passivity was not obtained at the stated current density on both parts of the welded specimens or in the weld zones for about ¼ inch from the weld. These areas etched preferentially and a sufficiently high current density could not be obtained in all cases to achieve passivity. For this reason and also because the recommended current density was too high to be practical in a scale-up operation the recommended method was discarded as inadequate.

It is therefore, an object of this invention to provide an improved method of surface preparation for subsequent electroplating of maraging steels.

Another object is to provide an effective method of passivating the basis metal for scale removal from maraging steels without excessive basis metal removal.

A further object is to furnish a pre-plating method which will effectively and uniformly activate the descaled surface of maraging steel tanks for subsequent metal deposition without selective etching on and around the welds.

Yet another object is to provide a method of surface preparation of maraging steel tanks utilizing a low cur-

rent density electropolish to minimize localized thinning of complex shaped tanks and be practical for use inside the tanks.

A still further object is to provide an activated surface free from scale and pits to promote the formation of a continuous coating and good adhesion between the basis maraging steel and subsequent deposited metals.

Other objects and many of the attendant advantages of this invention will be readily appreciated as the same become better understood by reference to the following detailed description.

These objects are attained and the prior art deficiencies are overcome by the use of a high nitric acid pickle-mechanical descaling step in conjunction with a low current density electropolish step incorporated into a conventional pre-plating procedure.

The use of our novel method permits production of a nickel deposit heretofore unattainable on 18% Ni maraging steel tanks of complex shape with the advantage that the adhesion and quality of this deposit are improved, that a low current density electropolish can be used yielding a substantially smooth surface free from excessive etching and in addition that welded surfaces can be successfully prepared for deposition.

The improved coatings obtainable by the present invention permit the design of rockets with an extremely advantageous payload/weight ratio, thus substantially advancing the science of rocket design.

The improved method of our invention can be outlined as follows:

(1) Descaling using a high nitric acid pickle-mechanical abrasion combination
(2) Subsequent descaling if necessary using concentrated nitric acid at elevated temperatures
(3) Water rinse
(4) Electropolish using low current density in acidic solution
(5) Water rinse
(6) Nickel strike

The steps which are considered to be the improvement of our invention are 1 and 4. In order to find a proper method of descaling within the thickness and etching limitations imposed by practical rocket design it was necessary to formulate and test a number of solutions and methods.

Heavily scaled blocks of maraging steel were obtained and tested for proper scale removal. The results were judged by visual observation. The standard used was good scale removal without severe etching or excessive removal of the steel substrate.

It is necessary to completely remove such scale before electroplating and indeed before other preplating surface treatment. The problem here was intensified by the presence of thicker layers of scale in some areas that were deeply embedded into the basis steel.

The following table illustrates a number of descaling formulations used in an attempt to achieve proper descaling without excessive attack on the substrate metal. The concentrations and specific gravity of the acids used in Table 1 as furnished by the supplier are as follows:

	Percent by weight	Specific gravity
Sulfuric	96	1.84
Nitric	70	1.42
Hydrochloric	38	1.19
(Ortho) phosphoric	85	1.69
Hydrofluoric	49	[1] 1.05

[1] Estimated.

It was found that mechanical descaling in combination with the sulfuric/nitric mixture described in #11 was most effective in maximizing scale removal while minimizing loss of substrate by etching metal. The other solutions listed in Table 1 with the accompanying treatment described were less effective or unsatisfactory.

It is theorized that descaling proceeds as follows: the high nitric acid content of the pickle passivates the basis steel with the result that it is dissolved very slowly, at a rate of about 0.1 mil/hr. However, the acid solution is also expected to dissolve the scale. Preliminary experiments showed that it dissolved the scale very slowly, but did soften it so that it could easily be removed by abrasion. Hence, the combination high nitric pickle-abrasion technique was indicated.

The preferred ranges of nitric acid, sulfuric acid and water in the scale-removing pickling solutions that can be used with our invention are as follows:

	Percent by weight
100% sulfuric acid	35 to 55
100% nitric acid	20 to 40
Water	20 to 35

A high nitric acid content must be maintained to insure passivity of the exposed steel as scale is removed during the descaling process. Up to one-half the sulfuric acid can be replaced with phosphoric acid in the pickling solution but because of the extra cost of H_3PO_4 this would normally not be practical.

In some cases, if the scale is not completely removed by the prior process an additional soaking period may be employed using concentrated (70% by weight) nitric acid as the soaking solution at about 45 to 50° C.

TABLE #1

Formulation	Descaling solutions: Solution	Treatment	Result
1	Concentrated sulfuric acid 50% by volume; concentrated phosphoric acid 50% by volume.	Soak 2 hours at 60° C	Very little scale removed.
2	Concentrated hydrochloric acid 50% by volume in water.	(a) Soak 2 hours at room temperature, (b.) Soak 2 hours at 60° C.	Very little scale removed.
3	Concentrated hydrochloric acid 5% by volume in water.	10 minutes anodic at 60° C. 5 amps/dm.[2]	Scale not removed, steel etched where exposed.
4	Concentrated sulfuric acid 20% by weight; water 15% by weight; concentrated phosphoric acid 60% by weight; chromic acid 5% by weight.	10 minutes anodic at room temperature 15 amps/dm.[2]	Uneven removal of scale.
5	Concentrated sulfuric acid 70% by volume	10 minutes anodic at room temperature 15 amps/dm.[2]	No apparent scale removal.
6	Concentrated nitric acid 50% by volume	Soak 30 minutes room temperature	Scale removal slow; steel attacked.
7	Sulfuric acid 90 g./l.; nitric acid 38 g./l.	Soak 15 minutes at 40° C. then 10 minutes anodic at room temperature 15 amps/dm.[2]	Scale removed but 7 mils of steel also removed.
8	Sulfuric acid 90 g./l. Nitric acid 38 g./l. Thiourea 2.2 g./l. (inhibitor).	Soak 15 minutes at 40° C. then 10 minutes anodic at room temperature 15 amps/dm.[2]	Scale removed but approximately 7 mils of steel also removed.
9	Concentrated sulfuric acid 500 ml.; concentrated nitric acid 430 ml.; concentrated hydrofluoric acid 110 ml.; Water 200 ml.	Soak 90 minutes at 40-50° C.; 10 minutes anodic at room temperature 15 amps/dm.[2]	Addition of hydrofluoric acid increased attack on basis steel.
10	(a) Concentrated hydrochloric acid 333 ml., Water 233 ml.; (b) concentrated nitric acid 125 ml.; concentrated hydrofluoric acid 25 ml., Water 350 ml.	Soak 40 minutes in (a) at 70° C. followed by 5 minutes in (b) at room temperature.	Scale removed but 5 mils of basis steel also removed.
11	Concentrated nitric acid, 430 ml.; concentrated sulfuric acid, 500 ml.; Water, 200 ml.	Combine with mechanical method, 1 liter of ¼" granite chips, agitate 6 hours.	Excellent scale removal.

The following specific example will illustrate the method of descaling preparatory to the preplating treatment.

Example 1

A cylindrical tank of 18 Ni 250 maraging steel was employed, which possessed a height of 26 in. and a dia. of 3½ in. I.D. and an axial ¾" threaded hole in one end. (Maraging steels are alloys developed by the International Nickel Co. Inc. The alloy used had the following nominal composition (percent by wt. Ni, 18; Co, 9; Mo, 5; Ti, 0.6; balance Fe.) Through the ¾" hole it was possible to examine the interior surface which was found to be generally covered with a heavy forming scale, especially in the dome area near the opening.

The tank was charged with 1 liter of a pickling solution as described in #11 Table 1, i.e. from 500 ml. concentrated sulfuric acid, 430 ml. concentrated nitric acid and 200 ml. water, together with 1 liter of granite chips of about ¼ inch sieve size. The tank was plugged, clamped at the center of its axis to a gear motor spindle and rotated end over end at about 6 r.p.m. for 6 hours. The tank was periodically rotated about 45° on its longitudinal axis during this time. After the agitation was finished the tank was rinsed, dried and inspected. A few small spots of scale remained in depressions but were so softened that they would be easily removed by the preplating process.

After maraging steel has been descaled, whether or not a substantial time has elapsed since descaling, subsequent cleaning and activating is required before plating. The method of cleaning 18% Ni maraging steel specified in the above-mentioned International Nickel data bulletin and U.S. Pat. 3,338,803 was attempted, found unworkable when applied to welds, and discarded.

A new method employing an acidic electropolish step was necessary in order to preserve the welds, rather than etch them, and low current density (about 7 amps/dm.^{2}) was used because of restrictions on electrode size due to the small opening and to limit the rate of gas evolved. Several prior art electropolishing solutions were selected for trial and are set forth in examples A through E.

(A)

Sulfuric acid (percent by vol.)	40–60
Phosphoric acid (percent by vol.)	60–40

(B)

Phosphoric acid (percent by wt.)	70–80
Chromic acid (percent by wt.)	8–15
Water (percent by wt.)	4–8

(C)

Hydrochloric acid (percent by vol.)	20–30
Glycerol (percent by vol.)	70–80

(D)

Sodium citrate (g./l.)	50–150
Citric acid (g./l.)	2–50
Sodium chloride (g./l.)	5–20

(E)

Perchloric acid (percent by wt.)	5–15
Glacial acetic acid (percent by wt.)	80–95

These electropolishing solutions were rejected either because they required too high a current density or resulted in an unsatisfactory finish on the maraging steel surface.

A treatment that was found to give excellent results is described in the following specific example.

Example 2.—Electropolishing procedure

200 grams of 96% by wt. sulfuric acid, 600 grams of 85% by wt. phosphoric acid and 50 grams of CrO_3 were mixed and diluted up to one liter to prepare the electropolish solution. A number of welded 18% Ni maraging steel specimens were successfully electropolished in this solution. A bare, copper electrode was centered in the tank. The tank was filled with the electropolish solution and partially immersed in a cooling bath to maintain a temperature of 35 to 50° C. The tank was made anodic and the copper electrode cathodic. Electropolishing was begun and continued at a current density of 7 amps./dm.^{2} for 10 minutes or until the required degree of smoothness was reached.

The range of constituents of electropolish solutions that may be used to advantage with our invention are indicated by the following table

TABLE 2.—PREFERRED CONCENTRATION LIMITS FOR ELECTROPOLISH SOLUTION

	Percent (wt.)
100% sulfuric acid	20–30
100% phosphoric acid	40–55
CrO_3	3–10
Water	10–20

The current density may be varied between about 6 and 8 amps/dm.^{2} and the time for electropolish may vary between about 3 and about 20 minutes depending on the initial condition of the surface and the smoothness desired. If the current density used is substantially outside of the limits specified the surface treatment will be inferior. Rough etching occurs if this current density is too high and the time factor necessary to produce a smooth surface is impractical if the current density is too low. The limits delineated in Table 2 indicate preferred concentrations of components to produce a satisfactory surface.

Visual observation which included microscopic viewing of electrodeposits plated on maraging steel surfaces using the novel process of our invention showed little or no tendency toward flaking, cracking or blistering in deposited nickel coatings. Maraging steel tanks treated by the method of our invention had no etching around the welds and subsequent nickel strikes applied by conventional methods had excellent adhesion. In the case of maraging steels having a high nickel content a nickel strike is necessary to activate the surface. It was found that any conventional electroplating metal can be deposited with excellent results over this nickel strike. Hydrazine and its derivatives and mixtures thereof have been stored in maraging steel tanks plated with certain metals by use of this invention for more than two years with no significant degradation of the liquid and negligible corrosion of the tanks.

Examples of some typical fuels are hydrazine, monomethyl hydrazine, aerozine-50 (50% hydrazine+50% unsymmetrical dimethyl hydrazine) and mixtures thereof, which undergo decomposition when in contact with maraging steel or cause corrosion of the steel, as well as fuels containing a substantial amount of hydrazine or its derivatives either alone or slurried with such powdered metals as aluminum, magnesium, beryllium, boron and mixtures thereof.

Indeed, the surface preparation of our invention is useful in any case where it is desired to deposit a protective metal coating on maraging steels to protect the steel from corrosion by any medium or the medium from decomposition by the maraging steel. Such protective coatings are particularly desirable for use in rocket tankage systems for hydrazine fuels.

The basis metals which can be treated according to this invention are maraging steels containing substantial proportions of nickel and either cobalt or molybdenum or both and mixtures thereof, e.g. nickel from about 11 to 19% by weight, molybdenum from about 2 to 6% by weight, cobalt from about 7 to 10% by weight.

The abrasive chips which may be used with our invention are any materials which may be produced in small sieve size such as granite, quartz, flint and other com-

mercial abrasive materials. They must be essentially non-reactive with the acidic descaling medium to preserve their abrasive characteristics. The size used is dependent on the size of the work piece.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

We claim:

1. A process for descaling and preparing the surface of maraging steel for deposition of metal thereon, said maraging steel containing from about 11 to about 19% by weight nickel, from about 2 to about 6% by weight molybdenum and from about 7 to about 10% by weight cobalt, which comprises:

(a) intimately contacting said surface with an agitated aqueous mixture effective to remove scale and minimize removal of steel, said mixture consisting essentially of about 35 to 55% by weight H_2SO_4, about 20–40% by weight HNO_3 and about 20 to 35% by weight water and solid abrasive particles and

(b) electropolishing the descaled surface in an aqueous solution consisting essentially of from about 20 to 30% by weight H_2SO_4, from about 40 to 55% by weight H_3PO_4, from about 3 to 10% by weight CrO_3 and from about 10 to 20% by weight water at a current density of from about 6 to 8 amps/dm.^{2}.

2. A process as defined in claim **1** wherein said surface is the inner surface of a welded maraging steel tank.

3. A process as defined in claim **2** wherein said electropolishing of said descaled inner surface of said tank is accomplished at a current density of from about 6 to 8 amps/dm.^{2} for about 3 to 20 minutes at a temperature from about 35 to 50° C.

4. A process as defined in claim **2** wherein said abrasive chips are granite chips.

5. A process as defined in claim **4** wherein said granite chips are of about ¼ inch sieve size.

6. A process as defined in claim **2** for preparing the inner surface of complex-shaped, welded, scale-coated maraging steel tanks, said maraging steel containing from about 11 to about 19% by weight nickel, from about 2 to about 6% by weight molybdenum and from about 7 to about 10% by weight cobalt, for subsequent electrodeposition comprising:

partially filling said tank with a mechanico-chemical descaling slurry consisting essentially of a mixture of about 35 to 55% by weight H_2SO_4, about 20 to 40% by weight HNO_3, about 20 to 35% by weight of water and an effective amount of abrasive chips,

agitating said descaling slurry in said tank to insure intimate contact of said mechanico-chemical descaling slurry with the inner surface of said tank to remove the scale,

removing said descaling slurry from said descaled tank,

rinsing said tank with water, and

electropolishing said descaled tank with an electropolishing solution consisting essentially of a mixture of from about 20 to 30% by weight H_2SO_4, from about 40 to 55% by weight H_3PO_4, from about 3 to 10% by weight CrO_3 and from about 10 to 20% by weight water at a current density of from about 6 to 8 amps/dm.^{2}.

7. A process as defined in claim **6** wherein said electropolishing step is carried out for about 3 to 20 minutes at a temperature from about 35 to 50° C.

8. A process as defined in claim **6** wherein said tank is additionally descaled by treating said tank with a solution of about 70% by weight HNO_3 at a temperature from about 45 to 50° C. for about 20 minutes to remove any residual scale from said tank subsequent to said removing step and prior to said rinsing step.

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