

[54] **PROCESS AND SOLUTION FOR REMOVING
TITANIUM AND REFRACTORY METALS
AND THEIR ALLOYS FROM TOOLS**

[75] **Inventor: Dolphus L. Coggins, Berkeley, Mo.**

[73] **Assignee: McDonnell Douglas Corporation, St. Louis, Mo.**

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[63] **Continuation-in-part of Ser. No. 269,133, July 5, 1972, abandoned.**

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[58] **Field of Search 156/7, 18; 252/79.2, 79.3, 252/79.4; 148/6.15; 134/3, 41**

[56]

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Primary Examiner—William A. Powell
Attorney, Agent, or Firm—Gravely, Lieder & Woodruff

[57]

ABSTRACT

Titanium and refractory metals and their alloys are removed from tools, usually made from steel or carbides, without deleterious effects on the tool, by immersing the coated tool in an acidic solution including fluoride ions, a source of COOH radical such as formic acid, and one or more of the hydroxylated carboxylic acids such as gluconic acid.

7 Claims, No Drawings

PROCESS AND SOLUTION FOR REMOVING TITANIUM AND REFRACTORY METALS AND THEIR ALLOYS FROM TOOLS

REFERENCE TO OTHER APPLICATIONS

This application is a continuation-in-part of my co-pending application Ser. No. 269,133, filed July 5, 1972 now abandoned.

BACKGROUND OF THE INVENTION

One of the primary reasons titanium and other refractory metals are difficult to machine is that they tend to fuse to and coat the tools used for machining, thereby rendering the cutting edges ineffective. Furthermore, the effect is cumulative with the deposit of a thin coat compounding the coating tendency and leading to complete sizing and galling of that portion of the tool which engages the workpiece. Once coated, the tools are either discarded or the coated portion is mechanically cut off and a suitable cutting edge is ground onto the end of the remaining portion. In the case of drill bits, often as much as one inch must be removed to rid the bit of the titanium fused to it. The cost of tool bits for machining titanium is, accordingly, a significant factor in the cost of the machined product.

Heretofore, solutions have been developed for dissolving titanium and refractory metals from the tool steel, but these solutions are selective to only a limited extent and do etch the steel, although only slightly. This tends to reduce the diameter of the tool, and in some cases the diameter is reduced to the point that the tool no longer falls within prescribed tolerances. Moreover, current solutions tends to leave a deposit, commonly called smut, on the tool.

SUMMARY OF THE INVENTION

One of the principal objects of the present invention is to provide a novel process and composition for removing titanium, refractory metals, and their alloys from tools without affecting the surface or other physical characteristics of the tool. Another object is to provide a process and composition for removing titanium fused to tool bits made of steel or carbides without destroying portions of the bits. A further object is to provide a process of the type stated which consumes little time and does not require continued surveillance.

The present invention comprises a solution for removing refractory metals and titanium and their alloys from tools made from ferrous metals and carbides and a process employing said solution. The solution is acidic and includes a source of fluoride ions, a source of COOH radical, and a hydroxylated carboxylic acid selected from the group of hydroxylated mono, di or tricarboxylic acids of 1 to 6 carbon atoms and containing from 1 to 5 hydroxyl groups.

DETAILED DESCRIPTION

In practicing the present invention, titanium covered tools are immersed in a hydrofluoric acid solution containing constituents for preventing the acid from attacking the tool metal or otherwise adversely affecting its surface, and constituents for accelerating the dissolution of the titanium by the acid. While hydrofluoric acid is a wellknown etchant for titanium and titanium alloys, it alone is not suitable for removing titanium from steel inasmuch as it also attacks the steel, leaving a pitted surface thereon. Moreover, hydrofluoric acid

alone requires considerable time to remove the last traces of titanium which are in intimate contact with the steel and, in addition, leaves a heavy black deposit, often called smut, on the steel. This smut is actually a metal precipitate, and its appearance and growth inhibits the effect of the solution on the titanium.

The term refractory metals includes columbium, molybdenum, tungsten, and tantalum. The term alloys includes alloys of these metals as well as alloys of titanium.

The foregoing disadvantages are eliminated and hydrofluoric acid is rendered suitable for removing titanium in intimate contact with steel by the addition of formic acid and gluconic acid to the hydrofluoric acid. The composition for removing refractory metals, titanium, and alloys of refractory metals and alloys of titanium from tools is actually a solution which broadly speaking contains a source of fluoride ions, a source of the COOH radical, and in addition, a hydroxylated carboxylated acid selected from the group of hydroxylated mono, di or tricarboxylic acids of 1 to 6 carbon atoms and containing from 1 to 5 hydroxyl groups.

The composition contains a source of fluoride ions, preferably hydrofluoric acid (HF). Other suitable sources include fluoride salts, such as sodium or potassium fluoride. The weight percent of fluoride calculated as undiluted hydrofluoric acid is at least about 0.7%. The weight percent of hydrofluoric acid may be increased up to about 17.5%, but extremely high concentrations may attack the tool, and the upper limit is dependent on the type of material from which the tool is made, the temperature of the reaction, and the nature of the other constituents of the solution, in addition to the concentration of the fluoride ions.

Hydrofluoric acid (70% concentration by weight) is ideally suited for the source of fluoride ions and when employed should constitute 1% to 25% by weight of the removal solution. When fluoride salts are employed, the amount of salt should provide an equivalent concentration of fluoride ions. In any event, the weight percent of fluoride calculated as undiluted hydrofluoric acid should range between about 0.7% and about 17.5%, which is the weight percent afforded by 1% to 25% hydrofluoric acid (70% concentration).

For removing titanium from tool steel, the removal solution should preferably contain 10% of hydrofluoric acid (70% concentration) by weight, and this corresponds to approximately 10% by volume of hydrofluoric acid (70% concentration). A concentration of this magnitude can be used safely without danger of pitting or otherwise disturbing the surface of the tool. This concentration is also satisfactory for other tool material.

The source of the COOH radical in the removal solution preferably is formic acid (HCOOH) but oxalic acid and acetic acid or a mixture thereof can be substituted in whole or in part for formic acid. Oxalic and acetic acids are somewhat less effective than formic acid, and other sources of COOH radical such as maleic, adipic, malonic, etc., can also be used. Mono and dicarboxylic acids of 1 to 6 carbon atoms are suitable for use in this invention.

The formic acid accelerates the dissolution of the titanium and, furthermore, effects removal of the last traces of titanium in intimate contact with the tool surface. This results by reason of the fact that the formic acid acts as a chelating agent in that it prevents the

metal from precipitating and forming a coating over the surface of the remaining titanium. Such a coating would of course inhibit the hydrofluoric acid from attacking the titanium and dissolving the same. To a limited extent the formic acid also prevents the removal solution from attacking the steel. When formic acid (90% concentration by weight) is used as the source of the COOH radical, that acid should constitute 1% to 25% by weight of the removal solution. Where other sources of the COOH radical are employed, their concentration should be such that they produce an equivalent amount of COOH ions. Thus, the COOH radical calculated as undiluted formic acid constitutes about 0.9% to about 22.5% by weight of the composition.

The preferred amount of formic acid (90% concentration) in the removal solution composition is 9.8% by weight which is equivalent to 10% by volume.

A hydroxylated carboxylic acid selected from the group of hydroxylated mono, di or tricarboxylic acids of 1 to 6 carbon atoms and containing from 1 to 5 hydroxyl groups such as gluconic acid, succinic acid, citric acid, etc., forms the remainder of the removal solution. Although, the other materials may be used, gluconic acid $C_5H_6(OH)_5COOH$ is preferred. This gluconic acid (50% concentration) may constitute from about 50% to about 98% by volume of the removal solution, depending on the amount of hydrofluoric acid and the amount of formic acid employed. When the preferred amounts of hydrofluoric acid and formic acid are used, the gluconic acid is 79.9% by weight of the refractory metal removal solution.

The gluconic acid also serves as a chelating agent inasmuch as it prevents the dissolved metal from precipitating out of the removal solution and forming a protective coating over the titanium remaining on the tool. In addition, the gluconic acid prevents the hydrofluoric acid from attacking the tool. Indeed, the combination of formic acid and gluconic acid produces a synergistic effect, for the ability of the combination to retard the formation of metal precipitates and inhibit attack of the tool steel exceeds the ability of either one of those constituents to do so.

Thus, the solution of this invention calculated on weight percent is about 0.72% to about 17.91% HF, about 0.88% to about 22.03% HCOOH, about 49.00% to about 24.97% gluconic acid, and about 49.40% to about 35.09% water.

The temperature of the solution in use is not particularly critical with highly satisfactory results being obtained in the neighborhood of about 70°F. A practical temperature range is about 50°F. to about 90°F. Higher temperatures than indicated tend to produce some attack on the tool steel and at lower temperatures the titanium removal rate becomes too slow to be practical.

Prior to introducing the titanium covered tool into the removal solution, the tool is degreased in a suitable solvent such as trichloroethylene. 1 to 5 minutes in such a solvent is adequate. Thereafter, the tool is dried.

Once immersed in the removal solution composition, the titanium covered steel should remain in the solution until all of the titanium has dissolved. Thus, the duration of the immersion is dependent on the amount of titanium in contact with the steel. For conventional twist drills having moderate amounts of titanium seized and galled on their working surfaces, an immersion of from about 10 to about 30 minutes in the solution is sufficient. For reamers, about 3 to about 10 minutes

immersion is adequate. Slight agitation of the tool or solution is desirable while the tool remains in the solution.

After the tool is removed from the refractory metal removal composition it is rinsed clean with tap water and then immersed in a phosphoric acid solution for 1 to 2 minutes. This solution by weight should contain about 1% to about 25% phosphoric acid (75% concentration). The phosphoric acid solution prevents rusting of the chemically cleaned tool and helps the steel hold oils. Thereafter, the tool is dried with compressed air. If the cutting edges are dull they may be resharpened at this point, although it is important to note that it is the cutting and not the removal solution which dulls the cutting edges. After a light oiling, the tool is in condition for use again.

The tool materials to which this invention is applicable include: carbon steels, alloy steels, stainless steels, tool steels and tool materials known as carbides. The term 'carbides', as used here, covers iron carbides, chromium carbides, tungsten carbides, and any other types of carbides.

While the foregoing solution readily dissolves the refractory metals and titanium, including even that material in intimate contact with the steel, it does not pit or otherwise adversely affect the surface of the steel, nor does it alter the mechanical properties of the steel.

In summary, a tool covered with refractory metal, titanium, or alloys thereof, after being degreased, is immersed in a composition of the following constituency by weight:

About 1% to about 25% hydrofluoric acid (70% concentration)

About 1% to about 25% formic acid (90% concentration)

Remainder gluconic acid (50% concentration)

Once the titanium was dissolved, the tool is removed from the solution, rinsed in tap water, and immersed in a solution of the following constituency by weight.

About 1% to about 25% phosphoric acid (75%)

Remainder water

After remaining in the phosphoric acid solution for about 1 to 2 minutes, the tool is removed and dried. Thereafter, it is oiled lightly and again placed in use.

SPECIFIC EXAMPLE

A one-fourth-inch twist drill manufactured from M-36 tool steel had been used to drill holes in a titanium alloy designated as Ti-6Al-6V-2Sn. This alloy as its name implies contains about 6% aluminum, 6% vanadium and 2% tin, with the remainder being mostly titanium. The alloy had fused to the cutting edges and adjacent surface areas at the leading end of the drill. It was estimated that the titanium layer in places exceeded 0.005 inch. The drill so coated was immersed in trichloroethylene solvent for 5 minutes to remove grease therefrom and then was immersed in a titanium removal solution of the following composition by weight:

Hydrofluoric acid (70% concentration) 10.24%

Formic acid (90% concentration) 9.82%

Gluconic acid (50% concentration) 79.94%

After 20 minutes in the removal solution the titanium alloy had dissolved, and the drill was thereupon removed and rinsed in tap water. Next, the drill was immersed in a solution of the following composition by weight for 1 to 2 minutes:

5

Phosphoric acid (75% concentration) 3.12%
Water 96.88%

Immediately upon removal from the phosphoric acid solution, the drill was dried with compressed air and oiled with a light oil. The drill did not require sharpening. It further bore no pitting or other evidence of etching, nor did it have even a slight layer of so-called smut.

Thus, it is seen that this invention provides a process and composition for removing titanium and refractory metals and alloys containing refractory metal or titanium from tools and achieves all of the objectives and advantages sought therefor.

This invention is intended to cover all changes and modifications of the example of the invention herein chosen for purposes of the disclosure which do not constitute departures from the spirit and scope of the invention.

What is claimed is:

1. A composition for removing refractory metals, titanium and alloys of refractory metals and alloys of titanium from a metallic based tool without attacking the metal base, said composition being acidic and comprising: about 0.7% to about 17.5% by weight of a source of fluoride ions calculated as hydrofluoric acid; from about 0.9% to about 22.5% by weight of COOH radical provided by a COOH supplying material selected from the group consisting of mono and dicarboxylic acids of 1 to 6 carbon atoms; about 49% to about 24.97% by weight of a hydroxylated carboxylic acid selected from the group of hydroxylated mono, di or tricarboxylic

6

acids of 1 to 6 carbon atoms and containing from 1 to 5 hydroxyl groups, and the remainder being water.

2. The composition of claim 1 wherein the source of fluoride ions is hydrofluoric acid.

3. The composition of claim 1 wherein a hydroxylated carboxylic acid selected from the group of hydroxylated mono, di or tricarboxylic acids of 1 to 6 carbon atoms and containing from 1 to 5 hydroxyl groups is in solution and the solution thereof constitutes substantially the remainder of the composition.

4. The composition of claim 1 including hydrofluoric acid as a source of fluoride ions; and wherein the source of COOH radical is selected from the group consisting of formic acid, oxalic acid and acetic acid, and mixtures thereof.

5. The composition of claim 1 wherein the hydroxylated carboxylic acid is gluconic acid.

6. A process for removing titanium, refractory metals, alloys of titanium, and alloys of refractory metals from metallic based tools comprising the steps of immersing a tool coated with refractory metal or alloy thereof in the composition of claim 1, and removing the tool from the solution after the coating has been dissolved by the composition without affecting the surface of the tool.

7. A process according to claim 6 and further characterized by immersing the tool in a phosphoric acid solution after it is removed from the composition.

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