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2,942,954

NON-HAZARDOUS ETCHING SOLUTIONS

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4 Claims. (Cl. 41-42)

This invention relates to an etchant solution and more particularly to a non-hazardous composition capable of obtaining a rapid etch having sufficient detail to enable micrographic analysis.

The use of a hydrofluoric acid etching solution such as Kroll's Reagent (1% HF, 2% HNO₃, 97% H₂O) is a well-known expedient in the art. Though such solutions are effective in bringing out the grain structure of such metals as titanium, the hazards of using such a corrosive solution are indeed apparent and well known in the art.

It is therefore an object of my invention to provide a non-hazardous etching solution. It is another object of my invention to provide an aqueous etching solution for titanium which is both safe to handle and is free from the evolution of gas during the etching process. It is another object of my invention to provide a titanium etching solution adapted to bring up the intergranular detail to an extent required for micrographic analysis.

These and other objects of my invention, apparent from the description thereof hereinafter following, are achieved by utilizing an aqueous solution of a safe yet powerful oxidizing agent and a complexing agent capable of forming a stable and soluble complex with the metal ions.

Inasmuch as the well-known hydrofluoric-type etchants such as Kroll's Reagent are known to be hazardous by reason of its acidic composition, elevated temperature and evolution of gas during the reaction in the etching process, especially to untrained personnel as are commonly used in any production operation, an active search was conducted for a titanium etchant which was both safe and at least as effective as the known etchants.

After considerable experimentation, a suitable composition was found using persulfate and fluoride salts in aqueous solution. The persulfates and fluorides of sodium, potassium and ammonium have been found to be entirely suitable for use in the composition of my invention and have been found to be capable of producing an etch with titanium specimens which is brighter and exhibits better grain definition than that which may be readily obtained with the known etchants.

The preferred embodiment of my invention comprises the use of the following aqueous solution:

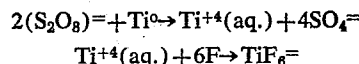
Ammonium persulfate.....	(NH ₄) ₂ S ₂ O ₈	0.5 M.....	114 gm./lit.
Sodium fluoride.....	NaF.....	0.5 M.....	21 gm./lit.

I have found that the use of such a solution, when heated to a temperature of from 190 to 205° F., will produce a good etch upon subjecting the specimen to treatment therewith for a period of about ten minutes. This solution was found to etch both fusion and spot weld specimens of titanium with a resultant quality of etch at least comparable to that obtained with the known etchants. Reheating and/or prolonged treatment has been found to increase the quality of the etch. A satisfactory etching procedure comprises the steps of bringing the etchant solution to a boil and immersing the metal sample therein for the desired period of time.

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While I have described my invention thus far in terms of a preferred embodiment, it should be noted that the persulfate may be used in a concentration of from about 68 gm./l. to a saturated solution at 25° C., and the fluoride from about 13 gm./l. to a saturated solution at 25° C. I have found that a concentrated solution, 0.5 M or above in each reagent is the most satisfactory. Likewise, I have found that the temperature of the etchant used for treating the specimen may be from about 170° to 212° F., it being understood that the rate and quality of the etch are directly related to the temperature. Similarly, the length of time during which the specimen is subjected to the treating solution may vary from the ten minute period stated above as preferred since it is dependent both upon the concentration of the solution, the temperature thereof and the quality of etch desired. The time element may therefore be best described as being that short but effective period of time necessary for obtaining an etch of the desired quality.

While I do not intend to be bound thereby, it is believed that the chemical reactions involved in the etching process are as follows:



The persulfate ion is believed to oxidize the metallic titanium to the plus 4 state. Though hydrolysis of the titanium ions would normally occur and result in the formation of Ti(OH)₄ with subsequent dehydration to TiO₂ and partial hydrates, the presence of the fluoride ions is presumed to block such normal reaction by the formation of the stable and soluble TiF₆³⁻ complex.

It is apparent from the foregoing description that I have provided an etchant solution which is non-hazardous in nature and may be readily handled in production operations by unskilled personnel. The persulfate etchant of my invention evolves no gas during the etching process and the solution is substantially neutral.

While I have described my invention in terms of a preferred embodiment, it should be understood that other modifications as may be apparent to those skilled in the art are within the intended scope of my invention as defined by the claims which follow.

I claim:

1. In a method for etching a titanium specimen, the step of treating the specimen with a hot aqueous etching solution comprising a water soluble persulfate salt as a safe yet powerful oxidizing agent and a water soluble fluoride salt as a complexing agent capable of forming a stable and soluble complex with the titanium ions for a short but effective period of time necessary for obtaining an etch of the desired quality, the concentration of said oxidizing agent being from about 68 gm./l. to saturation at 25° C. and the concentration of said complexing agent being from about 13 gm./l. to saturation at 25° C.

2. A method for etching titanium comprising the steps of heating the etchant comprising an aqueous solution of an oxidizing agent chosen from the group consisting of the persulfate salts of sodium, potassium and ammonium, and of a complexing agent chosen from the group consisting of the fluoride salts of sodium, potassium and ammonium to a temperature of from about 170 to 212° F., and treating the metal specimen with said etchant for a period sufficient to obtain an etch of the desired quality, the concentration of said oxidizing agent being from about 68 gm./l. to saturation at 25° C. and the concentration of said complexing agent being from about 13 gm./l. to saturation at 25° C.

3. A method for etching titanium comprising the steps of heating an aqueous etchant consisting essentially of about 114 gm./l. ammonium persulfate and about 21

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gm./l. sodium fluoride to a temperature of from about 190 to 212° F., and treating the metal specimen with said etchant for a period of about ten minutes.

4. In a method for etching titanium the steps of heating the etchant comprising an aqueous solution of a constituent chosen from the group consisting of the persulfate salts of sodium, potassium and ammonium and of a constituent chosen from the group consisting of the fluoride salts of sodium, potassium and ammonium to an elevated temperature, and treating the metal specimen with said etchant for a period of time sufficient to obtain an etch of the desired quality, the concentration of each of said constituents being, respectively, from about 68 gm./l. to

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saturation at 25° C. and from about 13 gm./l. to saturation at 25° C.

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