

# A NOVEL SURFACE TREATMENT FOR TITANIUM ALLOYS

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## INTRODUCTION

High-speed commercial aircraft require a surface treatment for titanium (Ti) alloy that is both environmentally safe and durable under the conditions of supersonic flight. A number of pretreatment procedures for Ti alloy requiring multi-stages have been developed to produce a stable surface. Among the stages are, degreasing, mechanical abrasion, chemical etching, and electrochemical anodizing. These treatments exhibit significant variations in their long-term stability, and the benefits of each step in these processes still remain unclear. In addition, chromium compounds are often used in many chemical treatments and these materials are detrimental to the environment. Recently, a chromium-free surface treatment for Ti alloy has been reported [1], though not designed for high temperature applications. In the present study, a simple surface treatment process developed at NASA/LaRC [2] is reported, offering a high performance surface for a variety of applications. This novel surface treatment for Ti alloy is conventionally achieved by forming oxides on the surface with a two-step chemical process without mechanical abrasion. This acid-followed-by-base treatment was designed to be cost effective and relatively safe to use in a commercial application. In addition, it is chromium-free, and has been successfully used with a sol-gel coating to afford a strong adhesive bond after exposure to hot-wet environments. Phenylethynyl containing adhesives were used to evaluate this surface treatment with sol-gel solutions made of novel imide silanes developed at NASA/LaRC [3]. Oxide layers developed by this process were controlled by immersion time and temperature and solution concentration. The morphology and chemical composition of the oxide layers were investigated using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and Auger electron spectroscopy (AES). Bond strengths made with this new treatment were evaluated using single lap shear tests.

## EXPERIMENTAL

The adherends of primary interest in this study were Ti-6Al-4V alloy. There were two types: shiny and dark Ti-6-4. The former was cleaner and processed with shorter annealing time (15 min at 788°C) than the latter (45 min at 788°C). Other metals studied included aluminum and stainless steel. Acetone and methanol were used as solvents for degreasing for all the metals. Alumina grit-blast and alkaline peroxide solution (1M H<sub>2</sub>O<sub>2</sub>-0.5M NaOH) were used to prepare reference specimens. The materials for the new acid-base process were sulfuric acid solution (9M H<sub>2</sub>SO<sub>4</sub>) and alkaline perborate solution (0.5M NaBO<sub>3</sub>·1M NaOH) as the acid etchant and oxidizing agent, respectively. Sol-gel solutions were prepared prior to acid-base treatment [3]. PETI-5-APEIS/TEOS and PPEIDS were used as the sol-gel solutions. Dipping was used for each treatment. First, after solvent degreasing, the sulfuric acid was used to generate a fresh Ti surface. Next, an alkaline perborate solution was used to form an oxide on the surface. Ultrasonic washing in distilled water was used between each treatment. Dipping time for each acid and base treatment was varied in order to develop various surface morphologies. The principal dipping time was 10 min. The sequence of the acid and base treatment was also

varied, for examples, acid-base and base-acid-base sequences were tried. A sol-gel solution was applied to the pretreated metals for 3 min immediately after drying them in an oven at 100°C for 10 min. The sol-gel coated metals were placed in the oven at 110 and 220°C for 30 min each.

Single lap shear specimens were bonded at 371°C under 50 psi for an hour using a phenylethynyl containing imide adhesive tape (FM-X5, Cytec). Bond strengths of the lap shear specimens were tested using ASTM D1002. An SEM (JMS-6400), XPS (5400-XPS), and AES (610 scanning Auger system) were used to analyze the surface morphology and chemical composition. Polished sections of the Ti-6-4 alloys in an epoxy molding resin were used for EDX and X-ray mapping study using the SEM.

## RESULTS AND DISCUSSION

Fig. 1 shows lap shear strengths for the specimens treated with the alkaline peroxide (RT for 10 min) subsequent to the mechanical abrasion. While the RT strength with only grit-blast did not exhibit resistance in the hot wet environment, those with additional alkaline peroxide treatment raised both initial and hot-wet strengths significantly. This helps to prove the efficacy of using an oxidizing agent (alkaline peroxide) to develop a durable oxide layer against hostile environments. Although mechanical abrasion is desirable to produce a rough and fresh surface, there is a limit for this application to complex substrates, so that mechanical abrasion was replaced by sulfuric acid etching. In addition, alkaline peroxide was replaced by alkaline perborate to produce a safe and stable oxidizing agent. Perborate, eventually liberates hydrogen peroxide at temperatures up to 60°C. Lap shear strengths with grit-blast/alkaline peroxide and sulfuric acid/alkaline perborate treatments are compared in Fig. 2. The strengths are almost the same for both treatments, although the new acid-base treatment exhibits slightly better resistance in the hot-wet environment. Lap shear strengths for grit-blast/Pasa-Jell treatment with a phenylethynyl containing adhesive (PETI-5) have also been reported, which were 7110 psi RT strength and 5950 psi RT strength after a 3-day water-boil [4].

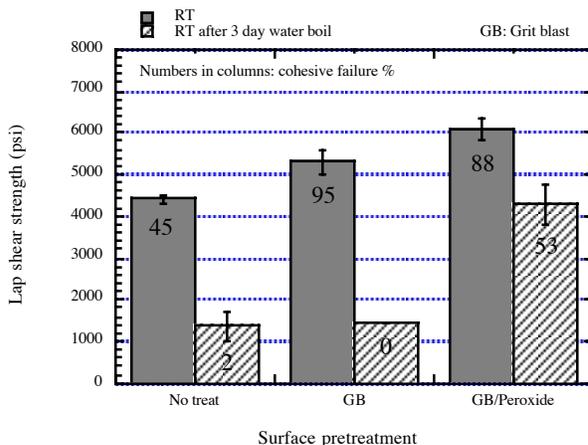


Figure 1. Lap shear strength for various surface pretreatments with 2% PPEIDS sol-gel solution.

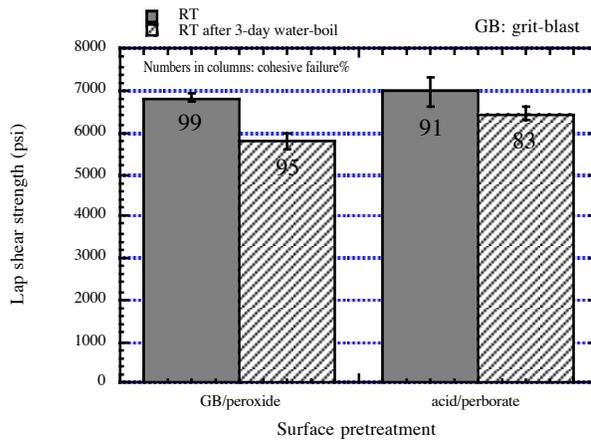


Figure 2. Lap shear strengths for GB/peroxide and acid/perborate using 15% PETI-5-APEIS/TEOS.

Fig. 3 shows lap shear strengths for various alkaline treatments, indicating that the acid-base is more effective than the base-acid-base sequence. The specimens treated with only NaOH are also shown for comparison. Base treatment before acid etching probably reduces the acid etching effect due to neutralization between acid and base.

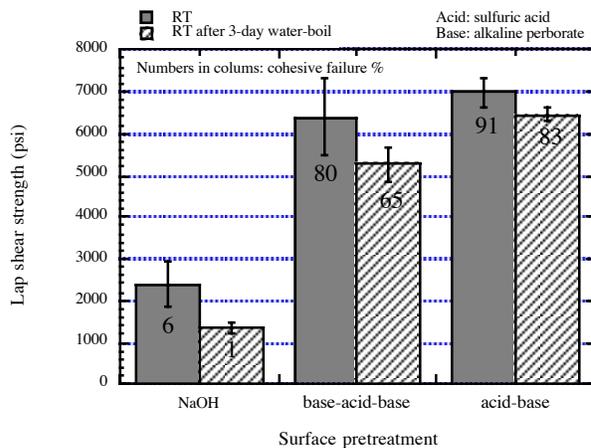


Figure 3. Lap shear strengths for various alkaline treatments.

Ti-6-4 alloy specimens subjected to the acid-base treatment with a variation in time and temperature were analyzed using microscopy. Acid etching was fairly effective in degreasing tacky contaminants, and the degree of degreasing was proportional to etching time according to optical microscopy examination. It was difficult, however, to quantify the degree of etching due to the intrinsic non-uniform contamination of the metal. On the other hand, base treatment as an oxidizing agent was very successful in developing a fresh oxide layer. The thickness of the oxide layer increased with both time and temperature. Round platelets ( $< 2\mu\text{m}$  in diameter) with a broad size distribution were developed during the base treatment. The shape and size of the platelets were most likely dependent on the processing conditions of the Ti alloys such as heat treatment, rolling, and cleaning. The shiny Ti-6-4 treated with the alkaline perborate at RT 10 min produced what appeared to be a single layer of the platelets with the periphery being more angular

compared to the dark Ti-6-4, which formed thicker and more round platelets. The role of the shape, size, and thickness of the platelets remains unknown. A surface having a thick oxide layer usually affords a thinner sol-gel coating compared to a nominal mono-layer oxide surface. This thicker oxide layer results in lower strengths. Essentially, the same trend was observed with temperature variation. Higher temperature (60°C) tended to develop a non-uniform, multi-layer oxide because perborate dissociates very rapidly into hydrogen peroxide at 60°C to become more reactive than at 125 RT. A 60°C treatment of the dark Ti-6-4 afforded 4254 psi RT strength and 4034 psi RT strength after a 3-day water-boil. This was almost 40% lower strength than for the shiny (cleaner) Ti-6-4. Analyzing these data, a 10 min exposure at RT in the perborate/base was selected as an optimum condition.

AES depth profile revealed an oxygen peak at the interface between the metal and sol-gel layer, probably representing a fresh oxide layer developed during base treatment. The thickness was less than 200 nm based on AES, which corresponds to the value from SEM (ca. 150 nm). This oxygen peak was also observed at an EDX line map of a metal treated by the alkaline perborate solution at RT for 10 min as shown in Fig. 4. X-ray mapping of a metal treated by an acid-base process (RT for 10 min) illustrated that the aluminum composition slightly increased while the titanium and vanadium vanished rapidly at the outermost metal surface. This is seen in Fig. 5, from which the interface of the Al map appeared distinct compared to the diffusive interfaces of the rest of the sample. This observation was further supported by EDX line mapping. It is speculated that an oxide layer developed by the alkaline perborate has aluminum compounds such as aluminum oxides which may provide a more durable interface after being chemically bonded with silane groups of the sol gel layer.

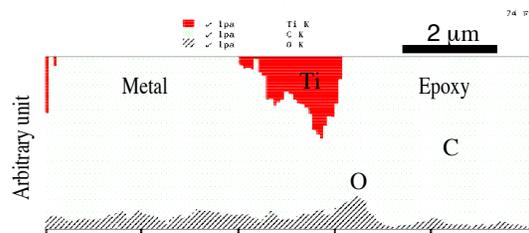


Figure 4. EDX line map of Ti-6-4 alloy treated by acid/base (RT for 10 min) chemical process.

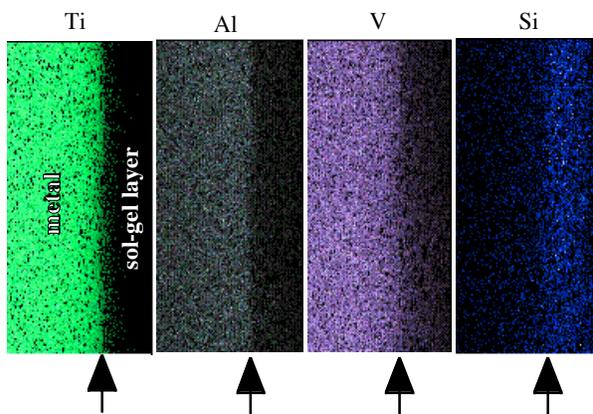


Figure 5. X-ray maps of Ti-6-4 treated by acid/base with a sol-gel solution (Arrows: the metal surface boundary).

The acid-base pretreatment was also employed for other metals including aluminum and stainless steel again using the 15% PETI-5-APEIS/TEOS primer/coupling agent. Single lap shear specimens were prepared and tested. An example of the tested aluminum specimen is shown in Fig. 6. Failure occurred in the metal rather than in the joint, giving 3314 psi with significant, permanent joint deformation.



Figure 6. A tested aluminum lap shear specimen showing deformed joint after metal failure.

## CONCLUSIONS

A simple surface pretreatment process for Ti-6-4 alloy was developed at NASA/LaRC to meet requirements of high-speed commercial aircraft application. This process may offer both environmentally safe and durable bonding at low cost under the conditions of supersonic flight. This novel surface treatment for Ti alloy is conventionally achieved with a two-step chemical process without mechanical abrasion. In addition, it is chromium-free and has been successfully used with a sol gel coating to afford a strong adhesive bond. It exhibits excellent durability for hot wet environments with approximately 90% retention of initial strengths. An oxide layer developed by this base treatment can be controlled by time, temperature, and concentration. The morphology and chemical composition of the oxide layer was investigated which revealed formation of aluminum oxide compounds. It is expected that this process will establish a low cost and high performance surface for not only high-speed commercial aircraft but also for other commercial applications with any metal adherend.

## REFERENCES

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## ACKNOWLEDGEMENTS

We thank Professor John G. Dillard for his help in experiments for the XPS and AES depth profile data.