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Multi-walled carbon nanotube reinforced polymer as a bonded repair for Al 2024-T3 fatigue crack growth

Crecimiento de grieta por fatiga en Al 2024-T3 reparado con polímero reforzado con nanotubos de carbono

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ABSTRACT

The influence on multi walled carbon nanotubes (MWCNT, or simply CNT) as a reinforcement material in an epoxy resin in order to decrease the fatigue crack propagation rate in the 2024 T3 aeronautical Al alloy was studied. CT samples were pre-cracked in a resonant fatigue machine until a 4 mm pre-crack length. Four groups of samples were considered: a non-repaired reference group, two groups repaired with epoxy resin reinforced with two CNT proportions (0.5 and 1 vol %) and a group repaired by the conventional “stop drill” technique. The crack was propagated until a length of 16 mm, measuring the number of cycles to this crack propagation. Resin Hysol EA9320 NA was used, mixing it with the CNT and the hardener, by ultrasonic stirring. S-N curves (stress *vs* number of cycles) were plotted obtaining an increment of 104% for a 0.5 vol% of CNT, 128% for 1 vol% of CNT and 400% for “stop drill” repairing. These results were referred to the non-repaired samples at the lower load level. These results showed that in repaired samples with CNT reinforced resin, the initiation and propagation of cracks would be delayed, constituting this method a reasonable and convenient repairing procedure useful for aeronautical cracked structures.

Keywords: Multi-walled carbon nanotubes (MWCNT), Al 2024, Fatigue.

RESUMEN

Se estudió la influencia de nanotubos de carbono multipared (MWCNT, o simplemente CNT) como material de refuerzo en una resina epóxica con el fin de disminuir la velocidad de propagación de grietas por fatiga en la aleación de uso aeronáutico Al 2024-T3. Se preagrietaron probetas CT en una máquina de fatiga resonante hasta lograr una pregrieta de 4 mm. Se separaron cuatro grupos de probetas: un grupo de referencia sin reparación, dos grupos que fueron reparadas con resina epóxica reforzada con dos dosificaciones de nanotubos de carbono de múltiples capas (0,5 y 1% en volumen) y un grupo reparado con la técnica convencional de “stop drill”. La grieta fue extendida hasta una longitud final de 16 mm, midiéndose el número de ciclos necesarios. La resina utilizada fue Hysol EA9320 NA, la que fue mezclada con agitación ultrasónica con los nanotubos de carbono y el endurecedor. Se trazaron las curvas esfuerzo versus número de ciclos (S-N) obteniéndose un incremento de 104% para el caso de probetas reparadas con polímero con 0,5% de CNT, de 128% en el caso de 1% de CNT y de 400% en el caso de “stop drill”, resultados respecto de las probetas sin reparar en el menor nivel de carga usado. Estos resultados muestran que en probetas reparadas con resina reforzada con CNT, se retardaría la iniciación y propagación de grietas constituyéndose de esta manera en un método alternativo en la reparación de estructuras aeronáuticas agrietadas.

Palabras clave: Nanotubos de carbono de multicapa, Al 2024, Fatiga.

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1. INTRODUCTION

Carbon NanoTubes (CNT), discovered by Iijima [1] in 1991, are carbon atoms with covalent bonds in a hexagonal configuration forming a monoatomic layer sheet coiled over itself forming a tube. Carbon nanotubes can be found in a single layer (SWCNT=Single Walled Carbon NanoTubes) or multilayer (MWCNT=MultiWalled Carbon NanoTubes) structure. Since they were discovered, considering their extraordinary properties, efforts were made to incorporate them to existing materials to improve their characteristics.

An example of this is the incorporation of CNT to reinforce Aluminum alloys [2,3] forming a composite material with a metallic matrix composite (MMC), which can be manufactured by different techniques: spark plasma sintering followed by hot extrusion [4,5] or just sintering followed either by hot extrusion [6,7] or compacted by hot rolling [2], using between 0.5% to 2 vol% CNT. The improvement of thermal properties of Al-12%Si alloys by incorporating 10 wt% MWCNT has been studied by Bakshi et al. [8], finding that the thermal conductivity depends on CNT cluster formation. Another aspect related to the present work that has been studied is the incorporation of CNT to epoxy resin, with the goal to improve its mechanical properties [9-13]. Several types of resin were subjected to testing, showing that it is possible to improve their elastic modulus and maximum tensile strength as the addition of CNT increases. The addition percentages studied vary, among the different authors, from 0.1% to 0.5wt% [10], 0 to 8.0 wt% [11], and 1.0% to 30.0 wt% [12]. In this last case a hybrid composite material with the addition of CNT and carbon fibers was also analyzed with relative success. The properties to fatigue and fracture of CNT doped resin [14,15] has been studied, finding that the resistance of crack propagation and fracture improves as the addition of CNT to the resin increases. The resistance to delamination in glass fiber composite materials doped with CNT has also been studied [16], resulting that delamination resistance improves as the quantity of CNT additions increases. Yu et al. [17], studied the effect of adding 0.5%, 1.0%, 2.0%, 3.5% and 5.0 wt% CNT to epoxy adhesives to join aluminum plates, finding that the bonding improved both in strength and durability. Nevertheless as the addition of CNT increases, fracture toughness decreases.

The idea of using CNT to reinforce composite materials is born due to their extraordinary mechanical properties as compared with the traditional fibers. The elastic modulus of CNT reaches 1 TPa (1,000 GPa) [7], and the ultimate tensile strength is 150 GPa [18]. One of the problems of CNT doped composite materials is the CNT powder manipulation, as it tends to form clusters [19, 20], phenomena that can be controlled through ultrasonic stirring.

The aim of this work is to investigate the influence upon the fatigue life of aluminum alloys repaired with a patch made of a resin doped with CNT.

2. MATERIALS AND METHODS

The efficiency to decrease crack propagation rate in Al 2024-T3 aluminum alloy samples was evaluated, using CNT doped epoxy resin repair patches. Also a traditional "stop-drill" repair was evaluated, this is, a hole drilled on the crack tip using a given diameter drill bit. The Al 2024-T3 alloy is normally used in aeronautics for airplane bodies. The main alloying elements are copper and magnesium, contributing to strength through aging phenomena. The T3 thermal treatment consists in homogenization, quenching, cold work and natural aging. Chemical analysis of 2024-T3 aluminum bare sheets are shown in Table 1.

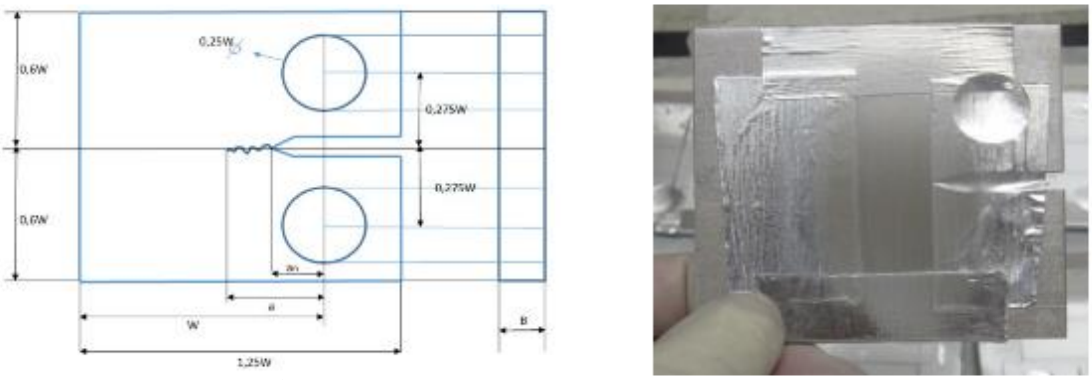
Table 1: Chemical composition of 2024-T3 aluminum bare sheet.

Al (%)	Si(%)	Fe(%)	Cu(%)	Mn(%)	Mg(%)	Zn(%)
93	0.06	0.19	4.5	0.66	1.6	0.16

Used CNT characteristics are: multilayer CNT (MWCNT) of 13 to 18 nm of external diameter, 1 to 12 μm length, 99% purity, bought at Cheap tubing Inc. USA. The epoxy resin used is denominated EA9320 NA and is normally used in the local aeronautic industry, with hardener included, products manufactured in Switzerland by Suter-Kunststoffe The resin is used mixed with a hardening agent in proportion 100 to 19. In the present work the CNT was added to the hardening agent and then the resin and the doped hardening agent were mixed. To evaluate the influence of the different addition quantities of CNT doped resin on the fatigue properties on the Al 2024-T3 samples, the following experimental design was elaborated: pre-cracking of the samples up to a crack length of 4 mm, fatigue crack growth up to a crack length of 16 mm, repair of the pre-cracked samples (0.5 vol%, 1 vol% CNT and "stop-drill"), and fatigue of the repaired samples.

2.1 Definition of samples to be used and pre-cracking tests

A CT fatigue type sample [21] was used, as shown in Figure 1a), with a thickness (B) of 3.55 mm, and a distance (W) between the loading line and bottom of the sample of 60 mm. Sample orientation was T-L (orientation of the crack growth parallel to de rolling direction). The samples were pre-cracked in a resonant fatigue machine until a crack length of 4 mm (measured from the bottom of the notch). To quantify the effect of the resin in the crack growth rate a number of pre-cracked samples were not repaired, while other two groups of samples were repaired with 0.5 vol% and 1 vol% CNT doped resin. The resin was applied over an area of 15 mm in the crack growth direction by 40 mm in the perpendicular direction, as shown in Figure 1b). Then the samples were divided in four groups. Group 1: non-repaired samples; Group 2: repaired samples with 0.5 vol% CNT doped resin, Group 3: repaired samples with 1 vol% CNT doped resin, and Group 4: samples that were repaired with the "stop-drill" method.



a) b)

Figure 1: a) CT test sample for fatigue testing and b) Masked test simple showing the repair area.

2.2 Preparation of the doped resin

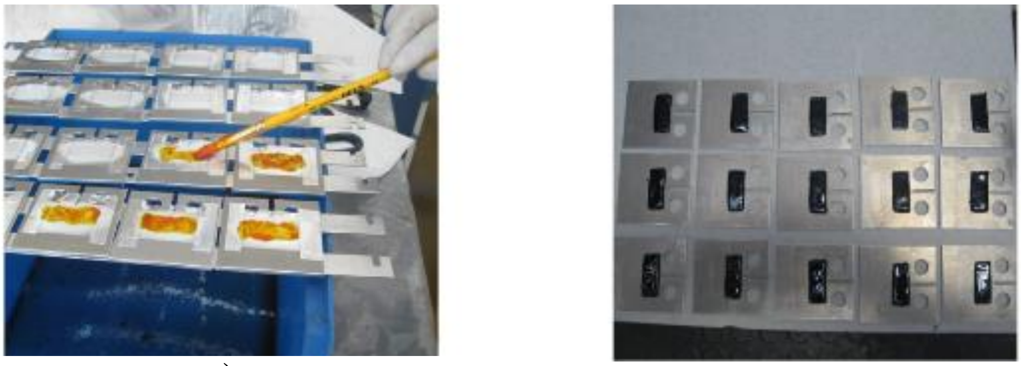
Two CNT proportions were prepared: 0.5 vol% and 1 vol%. The epoxy system utilized was Hysol EA 9320NA, of two components (resin and hardener), white colored translucent resin and the blue colored hardening agent. First, the hardening agent and the CNT proportions were mixed. Then the resin and the already doped hardening agent are manually mixed (Figure 2), and applied on the Al 2024-T3 already prepared surface as specified as follows.

Figure 2: Epoxy resin Hysol EA 9320NA with carbon nanotubes mixture.

2.3 Sample preparation and application of the patch

To have a good bond between the resin and the aluminum alloy, the sample surface was treated with Pasa-Jell 105 (Semco). This product activates the alloy surface facilitating the adherence between the resin and the aluminum alloy (Figure 3a). This product is a thixotropic gel of a reddish orange color, composed mainly by chromic and sulphuric acid, which can be applied to localized zones to provide improved surface adherence on aluminum alloys. Application of the resin patch is as follows:

- Application of Pasa-Jell 105.
- CNT mixing with the hardening agent (both 0.5 vol% and 1 vol%).
- Ultrasonic mixing of the MWCNT doped hardening agent.
- Mixing the hardening agent with resin.
- Application on the previously prepared repair zone (Figure 3b).



a) b)

Figure 3: a) Aplication of Pasa Jell-105 and b) Samples repaired with Hysol EA 9320NA+1 vol% MWCNT.

2.4 Fatigue testing and S-N curves

Considering that all samples were fatigue pre-cracked up to a length of 4 mm, measured from the bottom of the notch, and that the distance between that base line is 12 mm, the length of the pre-crack was 16 mm. Then the samples were subjected to fatigue testing until an increment of crack length of 15 mm was attained. The number of cycles needed to generate a crack growth from 16 to 27 mm from the loading line was measured. The curves were plotted using five different loading levels, using three samples per level, getting results on the four already indicated conditions. Table 2 shows the different loading conditions used, with a load ratio R of 0.5, and a cycling frequency of 96.7 Hz. A Rumul resonant fatigue machine, Mikrotron model, was used with a load control on both, repaired and unrepaired CT samples.

For those samples repaired by the “stop-drill” procedure, the cycle counting starts with the nucleation of a new crack to the growth up to a distance of 5 mm, distance which is equivalent to 27 mm measured from the load line. According to the repair instruction manual [22], the drilled hole size is of 0.1875” (4.76 mm) at a distance of 0.3” (7.62 mm) from the crack initiation, which with the 5 mm crack growth, adds up to 27 mm, as shown in Figure 4.

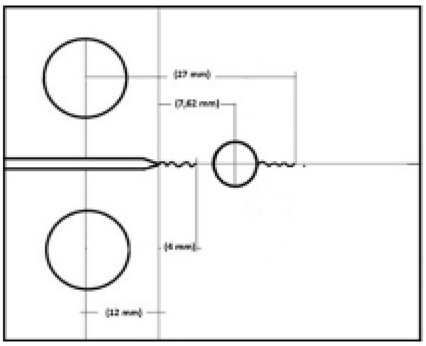


Figure 4: Diagram of the cycle counting for samples repaired by the “stop-drill” procedure.

Table 2: Load levels for fatigue testing.

LOAD LEVEL	MIN. LOAD (N)	MAX. LOAD (N)	AVERAGE LOAD (N)	LOAD RANGE (N)	LOAD RATIO
I	1,400	2,800	2,100	1,400	0.5
II	1,333	2,667	2,000	1,333	0.5
III	1,200	2,400	1,800	1,200	0.5
IV	1,100	2,200	1,650	1,100	0.5
V	1,000	2,000	1,500	1,000	0.5

2.5 Fracture surfaces

Fracture surfaces were studied with a Zeiss Evo MA-10 scanning electron microscope, with a 5KV electron acceleration potential, using primary and secondary electrons, as well as X-rays.

3. RESULTS

The results were presented in S-N diagrams (in this study, load versus number of cycles). A macroscopic stable crack propagation mechanism is observed, with symmetrical crack growing on both sides of the samples. As expected, as load increases, the number of required cycles for crack growth decreases.

Table 3 shows the numbers of average cycles obtained in the four study groups and the percentage difference with respect to the reference group and the Figure 5 also shows the S-N diagrams of the "stop-drill" repaired samples together with the rest of the repaired samples, as well as the reference ones.

Table 3: Numbers of average cycles obtained in the four study groups and the percentage difference with respect to the reference group.

LOAD LEVEL (N)	REFERENCE GROUP	0,5% CNT	% DIFFERENCE	1% CNT	% DIFFERENCE	STOP-DRILL	% DIFFERENCE
1,400	50,960	70,591	39	87,287	71	155,719	206
1,333	59,857	86,191	44	110,205	84	215,705	260
1,200	78,979	132,543	68	173,286	119	320,850	306
1,100	128,224	202,457	58	239,010	86	551,093	330
1,000	163,471	334,066	104	373,326	128	816,599	400

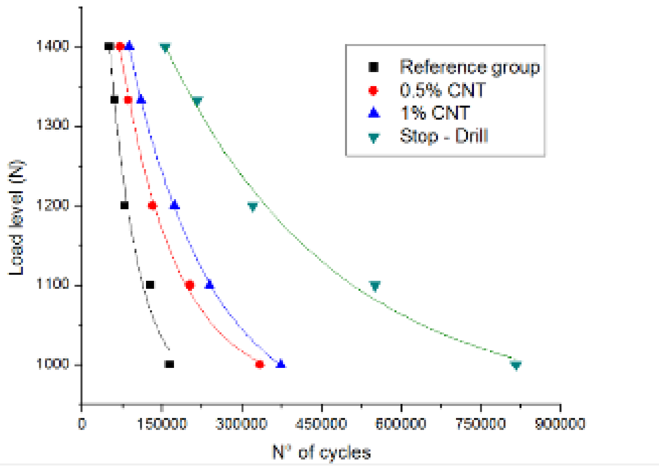
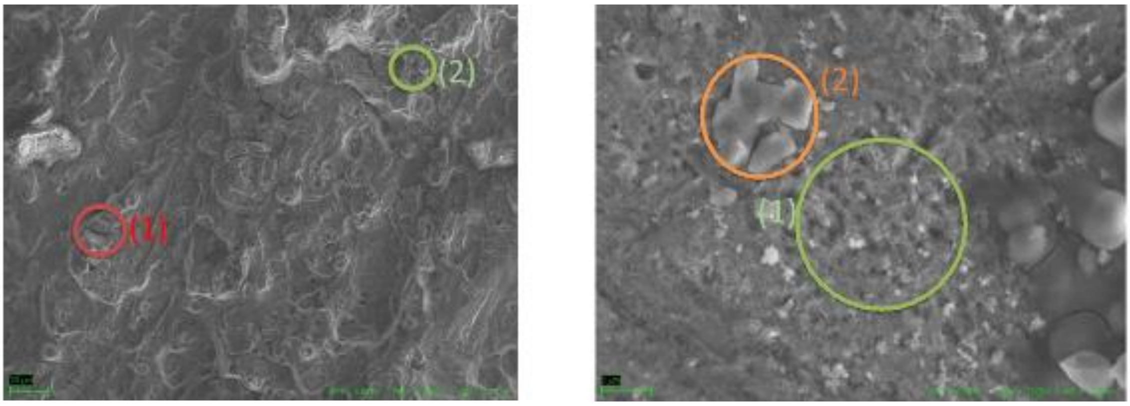


Figure 5: Fatigue S-N diagram of the repaired and unrepaired sample group.

The analysis of the fracture surfaces through scanning electron microscopy (SEM) was used to study the fracture mechanisms present in the cracks. The analysis of the repaired and the un-repaired samples with both CNT proportions was made. Another sample of an Al 2024-T3 treated with Pasa-Jell 105 was analyzed to appreciate the generated porosity on the surface.

Figure 6a) shows the fracture zone (1,000x), where are microcracks (1) due to the fatigue process can be seen, as well as decohesion of precipitates of the Al alloy (2), due to the same process. Even if these precipitates improve the mechanical properties of the material, they do act as weak points to fracture. The growing cracks do not fracture the precipitates, but generate its decohesion with the aluminum rich matrix. Some zones show localized plastic deformation that can be identified by their white coloring. In Figure 6b), it is possible to identify a wide area where porosity (1) can be observed, which corresponds to the surface preparation with Pasa-Jell 105, permitting the formation of adequate roughness to generate micro mechanical behavior where the adherence of the CNT doped polymer with the aluminum alloy was adequate. The presence of some particles in localized zones can be appreciated, probably debris (2) produced by the abrasion performed prior to the application of Pasa-Jell 105.



a) b)

Figure 6: a) Fracture surface 1,000x, repaired sample with 1 vol%. MWCNT doped resin, with (1) microcracks and (2) decohesion of the precipitates of aluminums alloy and b) Image at 25,000x of Al 2024-T3, zone prepared with Pasa Jell-105, with (1) porosity and (2) debris.

4. DISCUSSION

At all load levels, a better response to fatigue was obtained, an improvement that becomes more significant to a greater amount of reinforcement.

The utilization of two CNT proportions in the repairs, improves fatigue life of the pre-cracked samples in 104% and 128% for 0.5 vol% and 1 vol% CNT respectively, at the lowest load level. This improvement in the number of cycles is attributed to the reinforcing effect of the CNT in the epoxy resin used, probably because the initiation and propagation of cracks is interrupted by the presence of CNT.

Yu [15] shows a considerable increase in the number of fatigue cycles obtained in a reinforced resin with 0.5 wt% of NTC, when compared to the resin without reinforcement, an improvement that is attributed to the great interfacial bonding effect delivered by CNT, where they are strongly bound to the polymer matrix. The stresses are transferred from the resin to the CNT and the stiffness nature of the reinforcement will contribute to the improvement of the toughness of the material.

Other authors [23] explain the reinforcement obtained by adding CNT to polymer materials, according to the short fiber hardening mechanism. In this model, during the loading of a composite, the matrix and the fibers can be deformed in the same way because the modulus of elasticity of the short fibers is much greater than the modulus of elasticity of the matrix. In this case the CNT can limit the deformation of the matrix, implying that the polymer matrix does not reach the rupture directly when reaching its intrinsic fracture limit. The matrix will crack only when CNTs are no longer able to withstand the increase in applied load. Otherwise, short CNT fibers would favor the improvement of the non-uniform distribution of the stress and would reduce the shear stress at the end of the short fiber.

Improvement in fatigue life is not better than the obtained by the traditional “stop-drill” method which shows a 400% improvement as compared with the reference group, at the lowest load level. This result can be explained throughout the lower stress concentration due to the “stop-drill”. The traditional “stop-drill” repair is shown as a better option to improve fatigue life than the use of epoxy resin patches doped with different CNT proportions. However, in those cases where stop drill cannot be used, this repair reveals as a convenient, easy to apply and quick repair alternative.

Figure 7 shows the same zone as Figure 6a), but at 10,000x, showing a great number of fatigue striations (1), as well as numerous microcracks (2). It is also possible to observe cleavage which is related to flat fracture zones, phenomenon which corresponds to the decohesion of atomic planes (3). There are microbrittleness and microductility zones characteristic of the material (aluminum), as the macroscopic overall behavior of the crack growth zones is brittle fracture. The Figure 6a) and 7 described summarize the microstructural behavior both of the reference group and the repaired samples, mechanisms associated with fatigue crack growth phenomena.

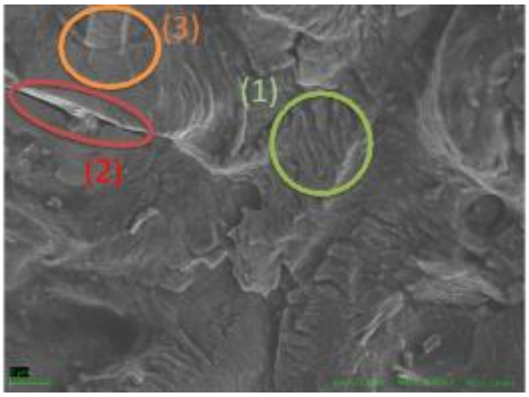


Figure 7: Fracture surface 10,000x, repaired sample with 1 vol%. MWCNT doped resin, with (1) fatigue striations, (2) microcracks and (3) cleavage.

5. CONCLUSIONS

Small volume fractions of MWCNTs reinforcing a polymer matrix is useful to enhance the fatigue crack growth life of aluminum alloy test specimens in a bonded repair concept.

Repairs with CNT reinforcing a polymer matrix in 0.5 vol% and 1 vol% showed an improvement in the fatigue life of 104% and 128% respectively, as compared with the unrepaired group, at the lowest load level. The adhesive patch helps to delay the crack propagation, this being more effective at higher CNT doping.

The repair through the "stop-drill" technique shows an improvement of 400% as compared with the cycles obtained on the reference group, at the lowest load level. This process is the one normally used in aircraft maintenance and still is more efficient than the MWCNT reinforcement of a polymer matrix.

Further analysis using scanning electron microscopy, shows that typical crack growth microstructural mechanisms are present in both repaired and unrepaired test specimens.

The analysis on the fracture surfaces permitted to verify the presence of localized microbrittleness and microductility mechanisms, precipitates, cleavage or atomic plane decohesion and microcracks in the fracture zone. These micromechanisms present in the different CNT doses and in the reference group samples showed that even if the adhesive patches delayed crack propagation, the typical fatigue crack growth morphology for these type of alloys was present.

Macroscopically it was verified that the repair fails due to the cracking of the matrix by fatigue crack propagation. The repair patches did not present adherence failure, showing that the surface preparation with Pasa-Jell 105 contributed to improve the mechanical behavior of the interfacial adhesion of the patch and the aluminum alloy sample.

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