CORROSION BEHAVIOUR OF ALUMINIUM ALLOY METAL MATRIX COMPOSITE JOINTS OBTAINED BY FSW

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Abstract

It was studied the corrosion behaviour of two joints, obtained by Friction Stir Welding (FSW), of aluminium alloy metal matrix composites (MMCs), reinforced with alumina particles. W6A20A and W7A10A composite joints were examined. Corrosion tests were performed in EXCO or 3.5% NaCl solutions. The corrosion rates of MMCs and joints were compared. Corrosion tests were performed on both the nugget and the thermally affected zones of the joints. Pitting potentials were measured on electrodes prepared by isolating the different zones. Short-circuit currents were measured between the nugget, the thermally affected zone and the base. The results indicated the different behaviour of the two joints: the corrosive attack on the W7A10 joint was concentrated on the nugget and in its adjacent zones both in EXCO and 3.5% sodium chloride solution; in the case of W6A20A, the nugget remained protected while the adjacent zones and the base material were corroded. Electrochemical measurements confirmed these results. However, FSW, which produces welds without the formation of a fused zone, causes structural modifications in zones near the nugget, due to the higher temperature produced by the presence of the reinforcement. This negatively affects the corrosion resistance of the composite, also in relation to the base alloy composition.

Riassunto

E' stato studiato il comportamento a corrosione di due giunti, ottenuti con tecnica Friction Stir Welding (FSW), di compositi a matrice metallica in lega di alluminio, rinforzati con particelle di allumina. Sono stati esaminati giunti di compositi W6A20A (matrice AA6061, rinforzo Al_2O_3, 20% in volume) e W70A10A (matrice AA7005, rinforzo Al_2O_3, 10% in volume). Le prove di corrosione sono state eseguite in soluzione EXCO ed in NaCl 3,5%. Sono state confrontate le velocità di corrosione dei compositi e dei giunti. Si sono eseguite prove di corrosione sul nocciolo e sulla zona termicamente alterata della saldatura. Sono stati misurati i potenziali di pitting su elettrodi preparati isolando le diverse zone. Sono state misurate correnti di corto circuito fra il nocciolo, la zona alterata termicamente e la base. I risultati hanno messo in evidenza il diverso comportamento dei due giunti: sul giunto W70A10 l'attacco corrosivo sia nella soluzione EXCO che in cloruro di sodio 3,5% si concentra sul nocciolo e sulle zone ad esso adiacenti; sul giunto W6A20A il nocciolo rimane protetto mentre si corrodono le zone ad esso adiacenti e la base. Le misure elettrochimiche confermano questi risultati. La tecnica FSW, che produce giunti senza la formazione di una zona fusa, provoca comunque modifiche strutturali nelle zone prossime al nocciolo, a causa della maggior temperatura dovuta alla presenza del rinforzo, che influiscono negativamente sulla resistenza a corrosione del composito, anche in relazione alla composizione della lega base.

INTRODUCTION

The most commonly used metallic matrix composites (MMC) are those with an Al alloy base matrix. These are chosen for their light weight, ductility, low melting temperature and because their mechanical properties can be improved by thermal treatments. Alloys of the 7XXX (Al-Zn) series, along with those of the 2XXX (Al-Cu) series, are the most commonly used in aeronautic field due to their high mechanical resistance and to weight ratio. The reinforcement consists of ceramic materials, such as silicon carbide (SiC), alumina (Al2O3), titanium diboride (TiB2), graphite. The most common MMCs contain reinforcements in the form of particles, both for reasons of cost and to improve isotropy.

To expand the use of MMC, the problem of their weldability must be solved. The conventional welding methods with metal melting cause alterations in the distribution and features of the reinforcement, with substantial modifications of weld joint resistance. Therefore, these methods are difficultly applicable.

Recently, there have been obtained MMC welds by FSW [1,2]. The technique consists in welding without material melting by exploiting the frictional heat. During FSW, a rotating tool, consisting of a conical part and a shoulder, is forced between two plates and moves along a contact line. The frictional heat created by the contact of the shoulder against the workpieces produces a plastic zone on the edges to be welded.

A rotating probe produces continuous hot work transporting the plasticized metal from the leading to the trailing edge of the shoulder, where consolidation produces a continuous joint.

Nearly flaw-free weld joints are thus obtained. Indeed, mechanical strength and fatigue behaviour tests have demonstrated the excellent quality of the weldings.

Changes in the corrosion behaviour of the nugget, in the thermally and/or mechanically affected zones adjacent to it with respect to the base alloy have been found on different types of Al alloys welded by this technique. Corrosion tests yield different results. Thus, the altered microstructures around the FSW AA5083 joints appear more resistant to pitting and intergranular corrosion than the base material [3]. Frenkel and Xia [4] studied the pitting resistance of FSW AA5454 joints and found that pitting resistance of the joint was higher than that of the base alloy. Hu and Maletis [5] evaluated corrosion and stress corrosion behaviour of FSW AA2195 and AA2219 joints.

The welded joints showed a corrosion behaviour better than that of the base alloy. Davenport et al. [6-8] demonstrated that the nugget and the thermally affected zones of the FSW AA2024 and AA7010 joints were more susceptible to pitting than the base material. Lumdsen et al. [9,10] indicated that in FSW AA7050-T7651 and AA7075-T6 joints, the nugget and its adjacent zones were more sensitive to corrosion. Also the pitting potential of the nugget and thermally affected zone was respectively 75 and 50 mV lower than that of the base alloy. SSR tests in 0.6 M NaCl solution showed that the joints were susceptible to stress corrosion.

Cracking appears on the interface between nugget and thermally affected zone. Buchheit and Paglia [11] found that in FSW AA7075-T651 and AA7050-T7451 alloy joints, the welding zones were more susceptible to corrosion as compared to the base alloys. In the case of AA7075-T651 alloy, the thermally affected zones were more susceptible to corrosion and stress corrosion, while for the AA7050-T7451 alloy the region between the nugget and the thermo-mechanically altered zone showed maximum susceptibility to corrosion. In SSR tests, the FSW AA7075-T651 joint in general demonstrated a better resistance to cracking than 7050-T7451 joint, with reversed performance in comparison to that of the base alloys.

Pao et al. [12] found that the fatigue crack growth rate in FSW AA7050 joints in air was slightly higher than that of the base alloy. Both in air and in 3.5% NaCl, the fatigue crack advancement rate in the thermally affected zone was significantly lower and Kth was significantly higher than that of the base alloy. Gan and Meletis [13], examining the stress corrosion behaviour of FSW AA2195 joints, did not find any reduction in ductility in SSR tests under constant immersion in NaCl solutions. A certain degree of susceptibility to SCC appeared on specimens which, prior to the SSR tests, were subjected to alternating immersion in NaCl solutions. In this case, cracking developed in the thermally affected zones.

The object of this paper is to examine the corrosion behaviour of joints obtained by FSW of Al alloy based MMCs reinforced with Al2O3 particles. As far as we know, no studies have been published on FSW aluminium alloy MMC corrosion. The presence of reinforcement should increase the temperature and cause higher thermal gradients, with greater influence on alloy microstructures in the zones around the nugget.

EXPERIMENTAL PART

The following composites were tested: AA6061 aluminium alloy reinforced with 20% (by volume) Al2O3, and AA7005 aluminium alloy reinforced with 10% Al2O3. Both alloys were subjected to T6 thermal treatment: solubilisation, quenching and aging. The chemical composition of the two alloys, expressed as weight percentage, is shown in Table 1.

The corrosion tests were performed on specimens of the base material and on FSW joints, with an exposed surface of approximately 20 cm^2. In FSW joint specimens,the nugget was in central position. The tests for the evaluation of the weight losses due to corrosion were performed by dipping the specimens for 48 hours in an EXCO (Exfoliation Corrosion) solution (4.0 M NaCl + 0.5 M KNO3 + 0.1 M HNO3) or for 21 days in 3.5% NaCl solution, in both cases at room temperature.

Before immersion in the corrosive environment, the specimens were prepared to obtained perfectly flat surfaces. Grinding was performed using sandpaper with mesh progressively decreasing to N. 600. These specimen were then washed in distilled water, degreased in acetone, weighed with an accuracy of 0.01 mg, then immersed in the corrosive solution. At the end of the test, the corrosion products formed during the immersion were eliminated by 70% HNO_3 pickling for a few minutes. The weight loss was used to calculate the corrosion rate, expressed in mdd (mg/dm^2 day).

TABLE 1. - CHEMICAL COMPOSITION (%) OF THE MATERIALS USED

MMC	Si	Fe	Cu	Mn	Mg	Zn	Ti	Cr	Zr	Al
W6A20A	0.65	0.15	0.18	0.10	0.97	0.009	0.02	0.19	-	to 100
W7A10A	0.25	0.24	0.08	0.43	1.33	4.59	0.03	0.13	0.13	to 100

The tests in EXCO solution were performed on untreated base material and on welded specimens.
Coupons for weight loss tests and electrodes for pitting potential determinations were obtained from the three characteristic zones of the joints (nugget, thermally affected zone and base material), evidenced by 2.5% HF attack.
The electrodes were connected to a copper wire to ensures electrical contact and then incorporated in an epoxy resin.
The anodic polarisation curves were recorded with a scanning rate of 0.1mV/s, starting from the corrosion potential attained after one hour immersion in the solution.
For both alloys, short-circuit tests were also performed in EXCO solution between the nugget, the thermally affected zone (TAZ) and the base material.
Finally, the base materials were subjected to four different thermal treatments (375°C, 400°C, 450°C and 500°C, respectively) for two minutes.
Then, on the specimens thus obtained, corrosion tests in EXCO solution were carried out, as well as pitting potentials determinations in 3.5% NaCl solution.
All the tests were provided with photographic documentation, macrostructural and microstructural analysis by optical microscope.

Corrosion tests in EXCO solution

Table 2 collects the corrosion rate values, expressed in mdd, obtained from the weight losses of W7A10A and W6A20A base material specimens, not containing or containing the welding.
The tests lasted 48 hours. W7A10A composite corrodes faster than W6A20A composite, i.e. 921 mdd in the former case and 588 mdd in the latter case.
By analysing the coupons containing the welding, it was found that W7A10A weld joint showed a considerably higher corrosion rate than the corresponding base material, i.e. 1448 mdd for the former and 921 mdd for the latter, respectively (Table 2).
The difference appears even more evident if, as documented in Figure 1, it is considered that the corrosive attack is located on the nugget and in the thermally affected zone only. Corrosion rates higher than 2000 mdd were measured on specimens taken from the nugget or thermally affected zones (Table 3).
The behaviour of W6A20A joint is completely different.
In this case the corrosive attack develops on the base material and on the adjacent heat affected zones.
From EXCO solution tests, it is evident a variation of corrosion resistance of the welded materials with respect to the base materials not subjected to FSW. The temperature increase during welding indeed causes microstructural variations which influence the corrosion behaviour of the two materials. The corrosion resistance modification of the two composites caused by a temperature increase was confirmed by performing corrosion tests on the thermally treated composite specimens.
Lumsden et al [9] mapped the temperatures in the joint zone of 7075 alloy subjected to FSW.
They found that in these joints, the zones most susceptible to corrosion were the thermally and the thermomechanically affected zones, which reached temperatures from 375°C to 400°C.
Table 4 shows the corrosion rates determined on the base materials of the

Table 2. Weight losses in EXCO solution at room temperature, of base and welded materials

Aggressive environment	Test time (hours)	Material		Vcorr (mdd)
EXCO	48	W7A10A	base	921
			welding	1448
		W6A20A	base	588
			welding	440

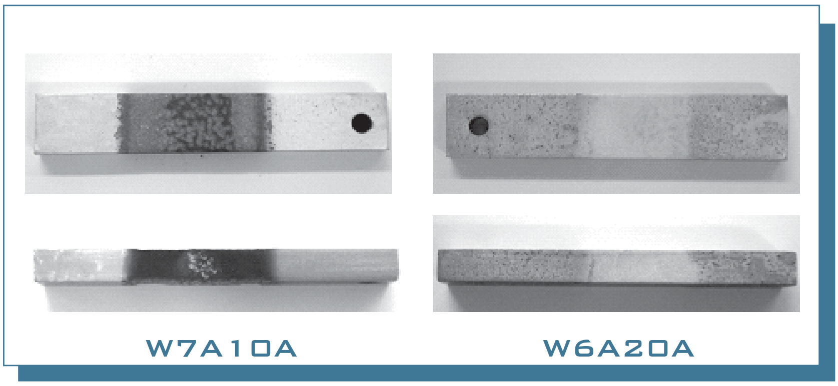


Fig. 1: Appearance of the FSW joints after soaking 48 hours in EXCO solution and pickling

two composites subjected for two minutes to thermal treatment at different temperatures.
The corrosion tests performed on W7A10A thermally treated specimens indicate an intergranular type corrosion, caused by the formation of copper-rich precipitates at grain boundaries.
The consequent copper depletion in the adjacent matrix causes the lower resistance of the W7A10A material.
The corrosion rate of the W7A10A composite increases as the thermal treatment temperature increases. Furthermore, the corrosion rate value of the material treated at 450°C (2199 mdd) is close that of the thermally affected zone of the corresponding welded joint.
AA6061 MMC shows a very similar behaviour to that above-described for AA7005 MMC, although, in this case, a corrosion rate comparable to that of joint TAZ is reached only after a thermal treatment at 500°C.
It is evident that the thermal treatment temperatures which caused higher corrosion rate, comparable to that of joint TAZs, are respectively 450°C for AA7005 MMC and 500°C for AA6061 MMC, both higher than those recorded by Lumsden [9].
This phenomenon is attributed to the presence of Al2O3 reinforcement, with a volumetric fraction of 10% in AA7005 MMC and of 20% in AA6061 MMC.

TABLE 3. WEIGHT LOSSES IN EXCO SOLUTION, AT ROOM TEMPERATURE, OF NUGGET AND TAZ IN W7A10A JOINT

Aggressive environment	Test time (hours)	Material	Zone	Vcorr (mdd)
EXCO	48	W7A10A	Nugget	2413
			TAZ	2092

TABLE 4. WEIGHT LOSSES IN EXCO SOLUTION AT ROOM TEMPERATURE FOR TWO BASE MATERIALS SUBJECTED TO DIFFERENT THERMAL TREATMENTS

Aggressive environment	Test time (hours)	Base Material	Vcorr (mdd) 375°C	400°C	450°C	500°C
EXCO	48	W7A10A	1631	1657	2199	-
		W6A20A	621	823	968	1207

Tests in 3.5% NaCl solution

It must be observed that in this solution, pitting is normally the corrosion attack and the low corrosion rates determined from weight losses give a very inaccurate indication of the entity of the attack.
In fact, the corrosion rates range from 0.32 mdd (FSW W6A20A) to 1.10 mdd (W7A10A base material).
After 21 days of exposure, the welded W7A10A specimen showed that the corrosive attack was concentrated on the nugget and in the immediately surrounding zones (Figure 2).
After pickling, a deep attack of the nugget was observed, while the adjacent zone was unaffected.
The base material specimen shows only a strip of corrosion products arising from the hole drilled to hang up the specimen.
After the same exposure time in the same solution, pitting was clearly evident on the surface of W6A20A specimen.
In this case, pits were distributed both on the horizontal side and on the transversal sections of the specimen.
In 3.5% NaCl corrosive environment, considerably less aggressive than the EXCO solution, only in the case of W7A10A joints, corrosion was localised in the nugget zone. The pitting of the W6A20A joint did not appear, indeed, particularly stimulated by the structural modifications occurring during welding; the corrosion points, not particularly deep, developed on the base material, while the nugget remained unaltered.

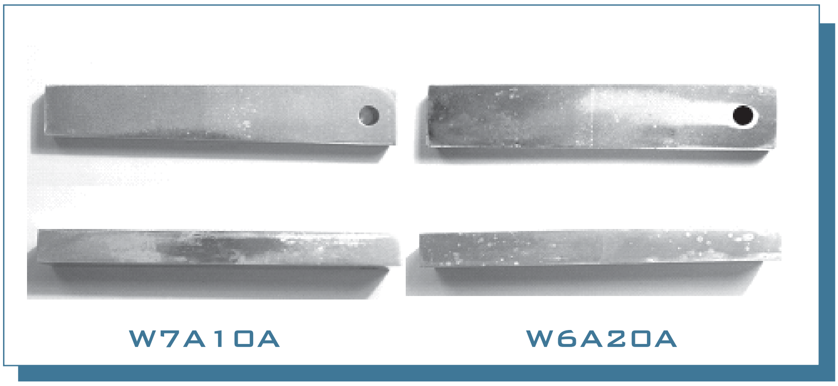


Fig. 2: Appearance of FSW joints after soaking 21 days in 3.5% NaCl solution and pickling

Pitting potential

Pitting potential values (Epit) of the two materials were obtained from the anodic polarisation curves performed in 3.5% NaCl.
The electrodes used were taken from the zones of most concern: nugget, TAZ, TAZvn (thermally affected zone near the nugget), TAZvb (thermally affected zone near the base), base, and thermally treated base material.
In the case of W7A10A base material, Epit was -820 mV/ECS, while the thermally affected zone and the nugget presented an Epit from -872 mV/ECS (nugget) to -880 mV/ECS (TAZ) (Figure 3).
Similar or slightly more negative pitting potential values were found on the electrodes made of the base material thermally treated from 375°C to 450°C.
These measurements confirm the observations in 3.5% NaCl corrosion tests performed on the welded material in which corrosion was concentrated in the central zone of the joint, the one subjected to a highest heating temperature.

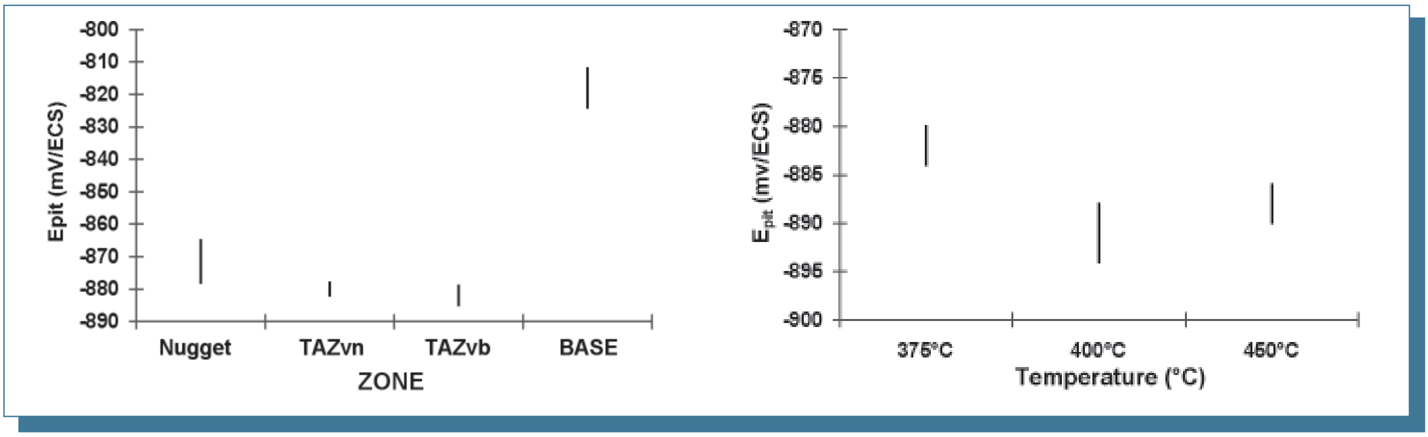


Fig. 3: Pitting potentials of the characteristic zones of the W7A10A joint and the base material after thermal treatment at different temperatures.

The Epit values of electrodes taken from the characteristics zones of W6A20A joint and of the thermally treated material are considerably more positive than the corresponding values measured on the first composite (Figure 4).
This aspect confirms a higher resistance to pitting corrosion of this alloy in this environment.
The pitting potentials decrease gradually from the nugget (-672 mV/ECS) to the thermally affected zone (-688 mV/ECS), to the base material (-730 mV/ECS).
The thermally treated specimens present an Epit value which tends to increase as the treatment temperature increases. The specimen treated at 500°C for two minutes shows a value of Epit close to that of the thermally affected zone.

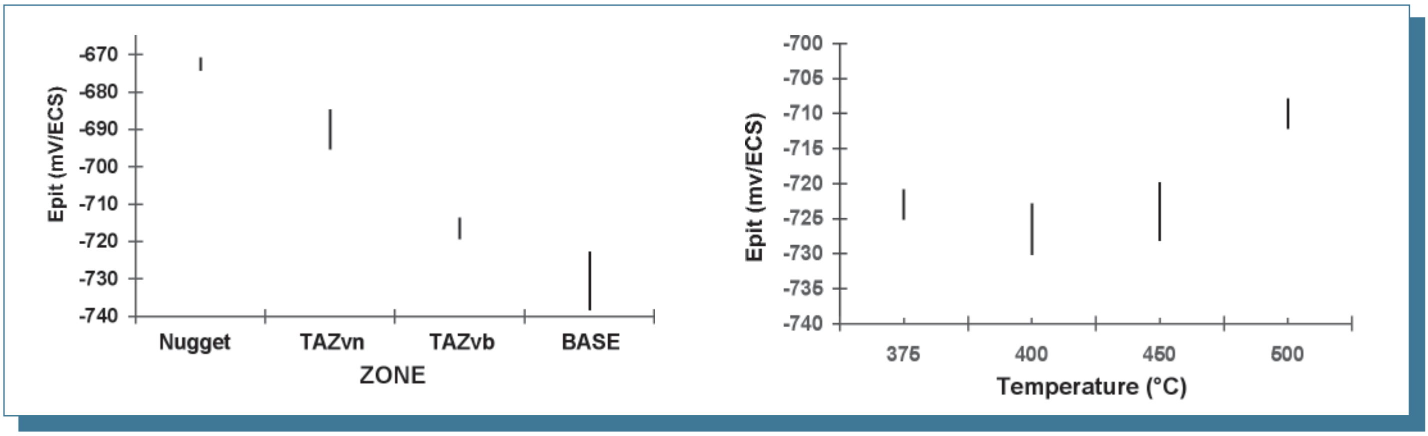


Fig. 4: Pitting potentials of the characteristic zones of the W6A20A joint and the base material after thermal treatment at different temperatures

Galvanic coupling measurements

From the galvanic coupling measurements in EXCO solution, the nugget-TAZ and nugget-base material short-circuit currents were obtained. The specimens were modelled to have exposed surfaces of equal area.
Figure 5 shows the corrosion currents related to W7A10A composite.
The behaviour of the nugget is anodic with respect to the base material.
In the nugget-base material galvanic coupling, after

a few minutes, the short-circuit current stabilises at $2.5x10^{-3}$ A/cm^2 and remains constant for the entire duration of the test.
The currents between the nugget and the thermally affected zone are considerably lower. The nugget behaves as an anodic area with respect to the TAZvb and for most of the time as cathodic area when in contact with TAZvn.
The corrosion potential (Ecorr) measurements in the same solution confirm the above-mentioned results.
Ecorr of the base material starts from -880 mV/ ECS, after ten minutes it reaches -820 mV/ECS, then it remains constant until the end of the test. For the nugget, the potential starts from -910 mV/ECS and stabilises at -890 mV/ECS after ten minutes. The Ecorr values of the thermally affected

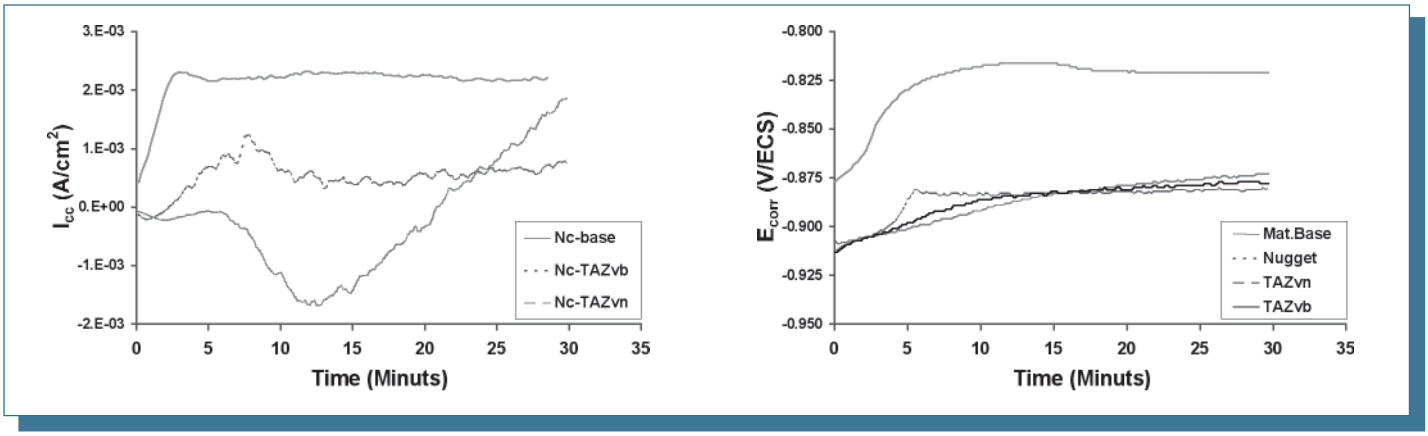


Fig. 5: Short-circuit currents and corrosion potentials of the characteristic zones of the W7A10A joint in EXCO solution

zones, initially equal to that of the nugget, increase more slowly. Furthermore, at the end of the test, Ecorr of the TAZvn was slightly more positive than that of the nugget.
Figure 6 shows the trends of short-circuit currents and potentials of the single zones for W6A20A composite. After the first minutes in which the short-circuit currents show an anodic behaviour of the nugget, with respect to both the base material and the thermally affected zone, an inversion is observed, in which the nugget behaves as a cathode.
The corrosion potentials confirm this trend. The nugget potential after the first moments stabilises at approximately -750 mV/ECS, while the base material and the thermally affected zone potentials nearly coincide and are equal to approximately -780 mV/ECS. The short-circuit currents are reduced and, at the end of the 24 hour test, they reach a value not greater than $2.5x10^{-4}$ A/cm^2.

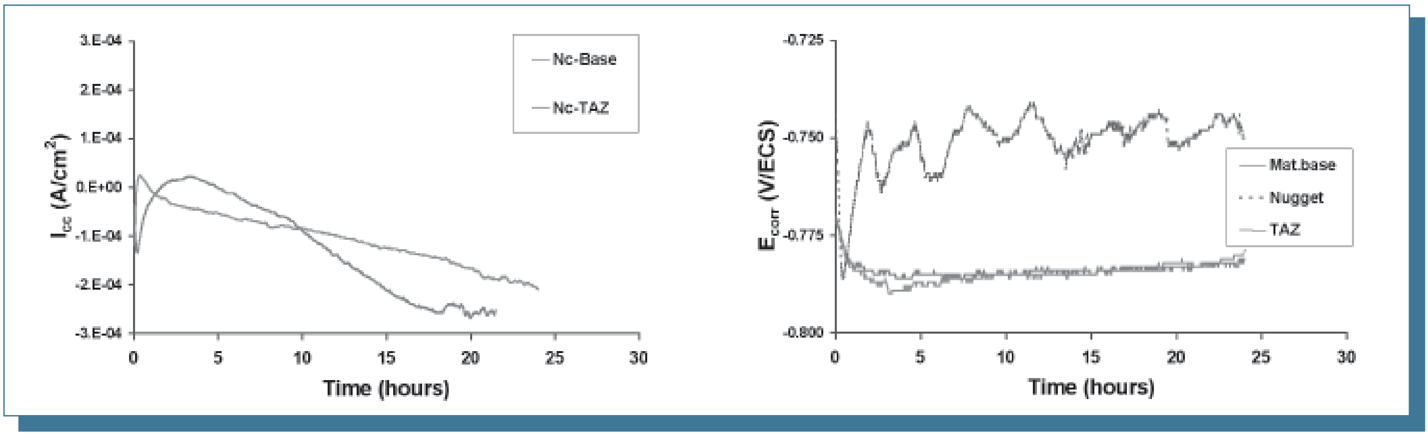


Fig. 6: Short-circuit currents and corrosion potentials of the characteristic zones of the W6A20A joint in EXCO solution

DISCUSSION

The tests show the considerably different corrosion behaviour in FSW joints obtained from the two MMCs.
In W7A10A joints, corrosion in the EXCO solution is concentrated in the nugget and in the adjacent zone. The attack is enhanced by the contact with the base material, which is more noble and works as a cathode.
Similar results were obtained in 3.5% NaCl tests. The thermally affected zones and the nugget are those which show lower corrosion resistance.
The electrochemical measurements (pitting potential, short-circuit currents, corrosion potential) confirm the corrosion test results.
Since no studies have been found on the corrosion behaviour of FSW joints of aluminium alloy MMC, the results could not be compared. In agreement with [9-11], concerning the corrosion behaviour of FSW 7XXX series alloys, we can affirm that in this type of alloy, FSW causes decaying in the corrosion resistance of the joint. This decrease can be attributed to the increase of precipitates in the zone adjacent to the nugget, with consequent variation

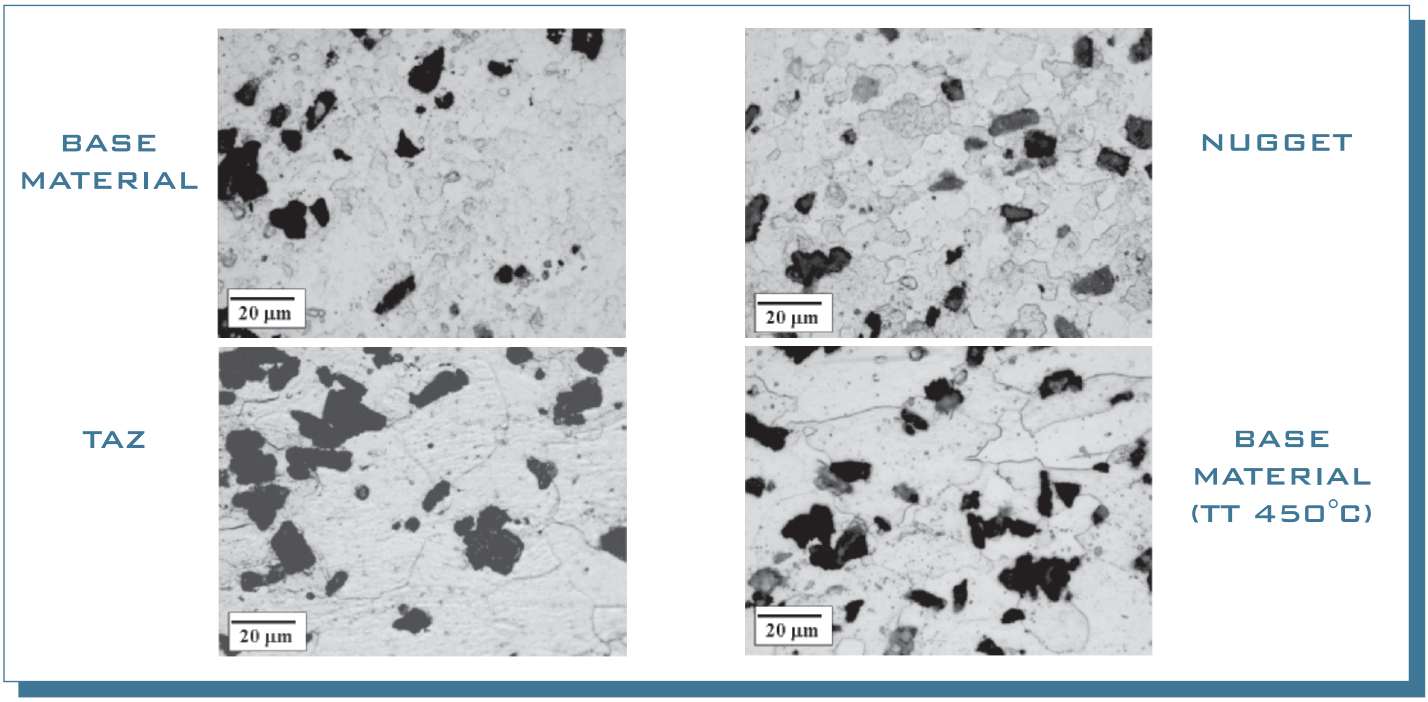


Fig. 7: Optical microscope micrographs of the base material, the nugget, the TAZ of the W7A10A joint and the base material after thermal treatment at 450°C

of the composition in the grain boundaries, thus making them more susceptible to intergranular corrosion and pitting.

The tests performed on the thermally treated W7A10A base material validate this conclusion.

Indeed, the W7A10A specimens, treated for two minutes at 450°C, show a corrosion rate in EXCO similar to that of the thermally affected zones of the joints, approximately double that of the W7A10A base material. Also the pitting potentials of the thermally treated material are similar to those of the welded zones and lower by around 60 mV than those of the base alloy.

The micrographs in Figure 7 show the most interesting structure of the W7A10A specimens, i.e., the base material, the nugget, the TAZ and the 450 °C thermally treated base material.

It can be observed a considerable increase in the size of the grains in the TAZ, due to heating, with formation of a nearly continuous series of precipitates at the grain boundary. A similar structure was reproduced by the thermal treatment at 450°C for two minutes.

On the W6A20A joints, with an alloy notoriously

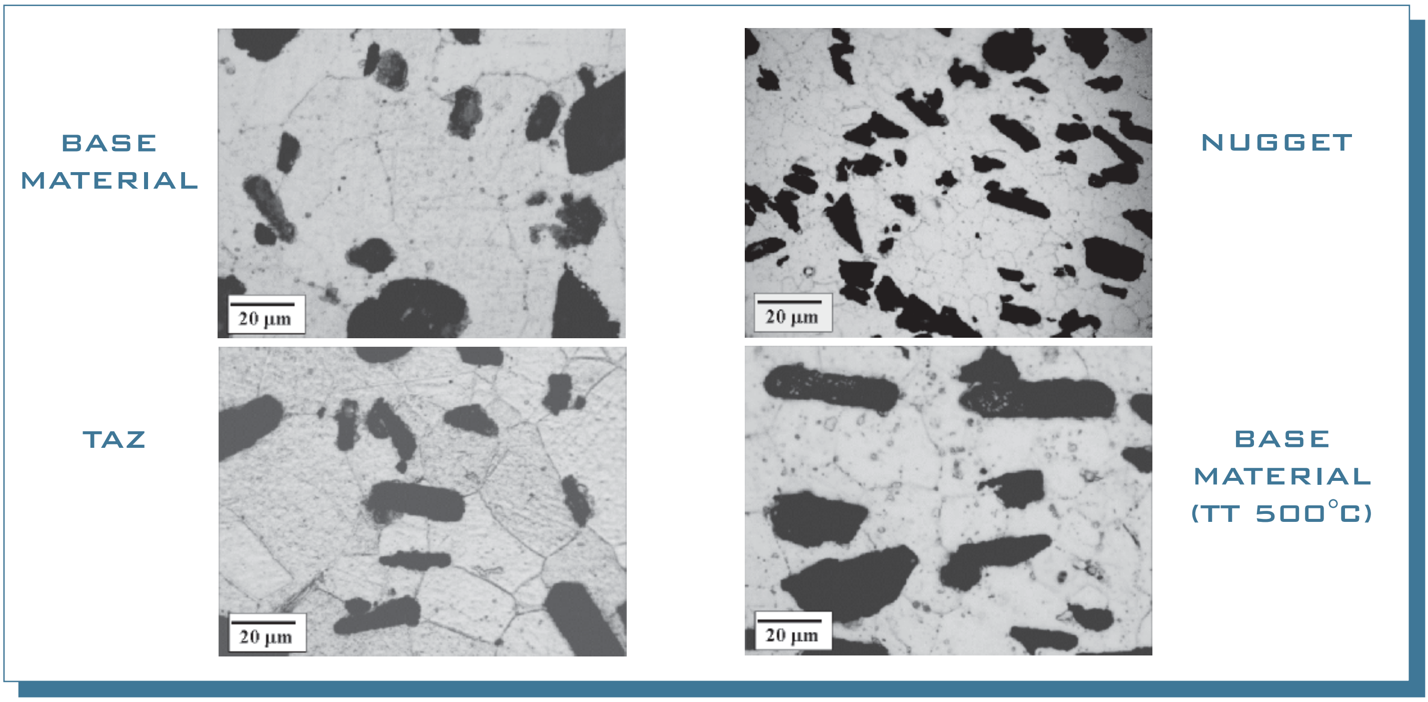
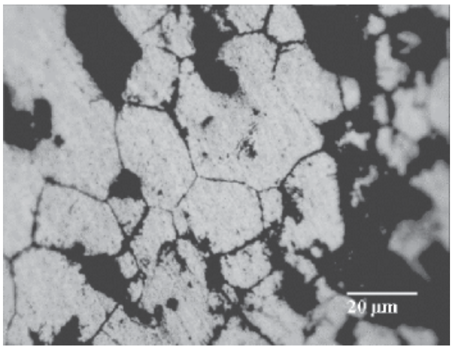


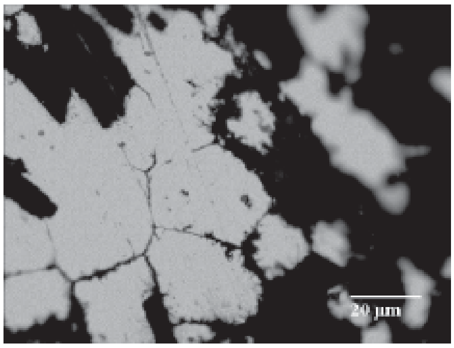
Fig. 8: Optical microscope micrographs of the base material, the TAZ of the W6A20A joint and the base material after thermal treatment at 500°C

more corrosion resistant than 7XXX alloys, the FSW process does not decrease so drastically the corrosion resistance, although the mechanical features of the joint are subjected to the same variations (hardness, fatigue strength, etc.) as the W7A10A joint. The micrographs in Figure 8 show the microstructure variations found in the TAZ and in the specimen thermally treated at 500°C as compared to the base alloy.

No modifications in the grain size were observed, but there was an increase of precipitates in the grain boundary zone of the thermally treated material. The nugget has grains of smaller size. The EXCO solution attack, as shown in the micrographs in Figure 9, is essentially intergranular. It can be hypothesized that the lower corrosion rate of the nugget.
Is linked to a complete recrystallisation, with formation of very small crystals. The extended grain boundary area prevents the formation of a continuous network of precipitates in the grain boundary zone, so that the material results much less susceptible to intergranular corrosion.

TAZ





BASE MATERIAL (TT 500°C)

Fig. 9: Optical microscope micrographs of the TAZ and of the base material of the W6A20A joint after thermal treatment at 500°C and exposure to EXCO solution

CONCLUSIONS

FSW is used to weld materials not weldable by other techniques. Both joints present a fatigue strength comparable to that of the base materials providing the welding technique is applied with correct parameters.
Resistance to intergranular corrosion and to pitting of the two MMCs welded by FSW is entirely different: lower in the W7A10A welds, better in the W6A20A welds.

The intergranular attack and the pits are concentrated in the nugget and in its adjacent zones in the W7A10A joint.
In the W6A20A joint, the nugget, entirely re-crystallised with very fine grains, corrodes at a lower rate than the base material and the both thermally and thermo-mechanically altered zones.
In both cases, it is evident the need to thermally treat the welded material to improve the corrosion behaviour.

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REFERENCES

[1] M. PONTE, G. GAMBARO, A.V. STROMBECK, L.M. MARZOLI and J.F. DOS SANTOS, Proc. 30° Convegno Nazionale AIM, Vicenza, November 2004, CD-ROM.

[2] L. CESCHINI, A. CASAGRANDE, G. MINAK, A. MORRI and F. TARTERINI, Proc. 30° Convegno Nazionale AIM, Vicenza, November 2004, CD-ROM.

[3] F. ZUCCHI, G. TRABANELLI, V. GRASSI, Mat. Corros., 52 (2001), p.853-859.

[4] G.S. FRANKEL and Z. XIA, Corrosion 55 (1999), p.139.

[5] WUSHENG HU and E.I. MELETIS, Materials Science Forum 331- 337 (2000), p.1683.

[6] R. AMBAT, M. JARIYABOON, S.W. WILLIAMS, D.A. PRICE, A. WESCOTT and A.J. DAVENPORT, Proc. Conference Aluminium Surface Science and Technology, Bonn (2003).

[7] A.J. DAVENPORT, R. AMBAT, M. YARIYABOON, P.C. MORGAN, D. PRICE, A. WESCOTT and S. WILLIAMS, Proc. Conference UMIST, Manchester 2003.

[8] A.J. DAVENPORT, R. AMBAT, M. YARIYABOON, B.C. CONNOLLY, S.W. WILLIAMS, D.A. PRICE, A. WESCOTT and P.C. MORGAN, Proc. Electrochemical Society 2004, 2003-23, p.403-412.

[9] J.B. LUMSDEN, M.W. MAHONEY, G. POLLOCK and C.G. RHODES, Corrosion 55, (1999), p. 1127-1135.

[10] J.B. LUMSDEN, M.W. MAHONEY, G. POLLOCK and C.G. RHODES, Corrosion 59, (2003), p.212-219.

[11] R.G. BUCHHEIT and C.S. PAGLIA, Proc. Electrochemical Society 2003, 2002-24.

[12] P.S. PAO, S.J. JILL, C.R. FENG and K.K. SANKARAN, Scripta Materialia 45, (2001), p.605-612.

[13] L. GAN and E.I. MELETIS, J. of Mechanical Behaviour of Materials 14, (2003), p.163-172.