Materials Science-Poland, 29(4), 2011, pp. 305-311
http://www.materialsscience.pwr.wroc.pl/
DOI: 10.2478/s13536-011-0050-4

Influence of grain boundaries misorientation angle on intergranular corrosion in 2024-T3 aluminium

A. Bałkowiec[1]*, J. Michalski[2], H. Matysiak[1], K. J. Kurzydlowski[1]

[1]Warsaw University of Technology, Faculty of Materials Science and Engineering, Woloska 141, 02-507 Warsaw, Poland

[2]Materials Engineers Group, Woloska 141, 02-507 Warsaw, Poland

The special attention has been paid to the influence of misorientation angle of a random grain boundary (GB) on susceptibility to intergranular attack. The detailed observations of the microstructure of the intergranular corrosion (IGC) in 2024-T3 aluminium alloy (AA2024-T3) subjected to galvanic corrosion tests in two different solutions containing chloride ions (0.1 M and 0.5 M NaCl) were carried out using Scanning Electron Microscopy (SEM). The Electron Backscattered Diffraction (EBSD) technique was used to determine the grain boundary character distribution (GBCD) in the initial sample and a GBCD of corroded grain boundaries on a sample subjected to the corrosion test. The results are discussed in terms of the influence of the misorientation angle on the susceptibility of the grain boundaries to corrosion.

Keywords: *EBSD 2024, intergranular corrosion, grain boundaries*

1. Introduction

It is well known that grain boundaries in polycrystalline materials play a crucial role as preferential sites of corrosion and crack nucleation. This defines grain boundaries as “weak links” in material microstructure. The general concept of improving polycrystalline materials properties can be realized not only by so called grain boundary engineering but also by developing the models that would enable one to predict the properties of a microstructure. From this point of view, the estimation of a relationship between the resistance to intergranular degradation of a polycrystalline microstructure, expressed in terms of the grain boundary misorientation distribution, is essential for understanding the properties of grain boundaries.

The presented investigations are focused on 2xxx aluminium alloy, which is widely used as a structural material, i.e. in aerospace industry. For these applications, the 2xxx alloys have to fulfill the strict requirements regarding the corrosion resistance. Thus, a lot of efforts are made to reduce their corrosion rate, which can significantly decrease the lifetime of structural components in service. An important type of corrosion in aluminium alloys is an intergranular corrosion (IGC), which can lead to reduction of mechanical strength and failure. Although this type of corrosion was the subject of extensive research, the understanding of the intergranular (IG) attack is still far from being complete. Many questions regarding the nature of the intergranular corrosion in Al alloys are still unclear. Two types of corrosion mechanisms are considered; however, both of them are based on nonuniform chemical composition along the grain boundaries. This causes the differences in electrochemical potentials between the grain interior and the grain boundaries, where intermetallic phases precipitate. In aluminium alloys, two different situations may occur: the precipitation of an anodic phase or precipitation of a cathodic phase [1]. Precipitation of the cathodic phase, such as Al_2Cu, leads to the formation of copper depleted zone along the grain boundaries. The copper depleted regions are anodic with respect to both the precipitates (Al_2Cu) and

*E-mail: abalkowi@inmat.pw.edu.pl

grain interiors, which makes the grain boundaries susceptible to localized galvanic corrosion [2]. Such mechanism was described by Zhang and Frankel, who showed that IGC can be regarded as a special kind of pitting corrosion occurring preferentially at the grain boundaries for Al alloys since the mechanism of IGC was found to be of the same nature as the process of pitting [3]. Compatible results were presented by Guillaumin, who has shown that the main effects are connected to chemical composition differences [4].

It is believed that a new insight into this process can be obtained via systematic microscopic observations, in particular with the use of Scanning Electron Microscopy combined with Electron Back Scattering Diffraction (EBSD), as shown, for example, in a series of papers co-authored by Palumbo [5–10]. In these studies it has been shown that the grain boundaries in polycrystalline materials (like aluminium or alloy 600) differ in their susceptibility to the intergranular corrosion. In particular, the so called low angle grain boundaries proved to be resistant to the corrosion whereas the twin boundaries showed higher resistance to the corrosion than so called random boundaries [5]. It should be noted that such classification of the grain boundaries is based on the concept of coincidence site lattices (CSL), which is formed by atoms having the equivalent positions in the crystal lattices of the neighboring grains. A fraction of such atoms is described as Σ. This parameter is equal to 1 for dislocation boundaries, which divide crystals regarding to lattice positions of the atoms. For the twin boundaries the fraction is $\Sigma 3$, i.e. every third atom is in the CSL position. A number of the grain boundaries have been identified with Σ expressed by odd numbers from 1 to 29. The grain boundaries with $\Sigma > 29$ are considered random in this sense that an order exists in the neighbouring grains. It should be noted that each $\Sigma \leq 29$ grain boundary is characterized by a specific misorientation angle ($\Delta\Theta$). In polycrystalline materials, in contrast to bicrystals, the grain boundaries tend to deviate from such angles. In this situation, a criterion proposed by Brandon [11] that a given boundary can be considered as the fulfilling misorientation requirements completely if the deviation, $\Delta\Theta \leq \frac{15^\circ}{\sqrt{\Sigma}}$, is used.

The Brandon criterion, later modified by Palumbo [9], who categorizes the population of the grain boundaries into the special – slightly deviated, assuming low CSL and the random ones. Such classification of GBs is useful in explaining their differential resistance to intergranular corrosion in a number of alloys [5, 6, 8–10].

Considerable evidence exists suggesting that the concept of chemical differences as the main driving force for intergranular corrosion in 2xxx aluminum alloys cannot be limited to microstructural phenomena but should be complemented by the factors such as crystallographic structure of grain boundaries and their properties.

The aim of this paper is to supplement the existing body of the experimental evidences with the data obtained on 2024-T3 aluminium alloy. Also, an original procedure for microscopic observations has been used, which provides a complementary description of the properties of the grain boundaries.

2. Experimental

The sheets of AA2024 after T3 heat treatment were ground with SiC abrasive paper to 1200 grit and polished with diamond suspension of 3 µm and 1 µm. Galvanostatic polarization tests were performed using a PGSTAT100 potentiostat Autolab. The working cell was a standard three-electrode one with Pt wire as the counter and a calomel electrode (SCE) as a reference electrode. The tests were carried out in aerated 0.1 M and 0.5 M NaCl solutions. During the galvanostatic scans, the specimens were held at a current of 1 mA. The corrosion test was terminated after 24 h, when intergranular attacks were observed to avoid grain dropping and general surface dissolution, which would preclude EBSD observations. Such conditions were based on the findings reported by Galvele and co-workers [12] that IGC occurrence in the studied material takes place over a narrow potential range.

The EBSD analysis was performed using scanning electron microscope (SEM) Hitachi 3500 SEM equipped with EBSD system of HKL at 20 kV. The scatter level was in the range between 70% and 83%. To obtain the maximum signal intensity, the samples were tilted to 70 degrees.

The preparation of samples for EBSD measurements requires special procedures to avoid generation of artefacts. In the current study, the surface was etched with Keller etchant to remove the mechanically deformed layer after each step of grounding and polishing, in order to obtain the best quality of diffraction patterns. After each polishing step, the surface was examined under the light microscope to assure that the etching artefacts were completely removed.

The final step was polishing with a 1 μm diamond suspension. A mixture of glycerol and ethanol was used as the lubricant. Immediately before the EBSD mapping, the samples were polished using SiO_2 suspension of pH 4.5 and 0.12 mm gradation for 2 minutes to remove the corrosion products.

The orientation imaging microscopy (OIM) was used to determine the misorientation angle of the grain boundaries emerging on the examined surface. The population of such grain boundaries was characterized in terms of the character distribution function (GBCD).

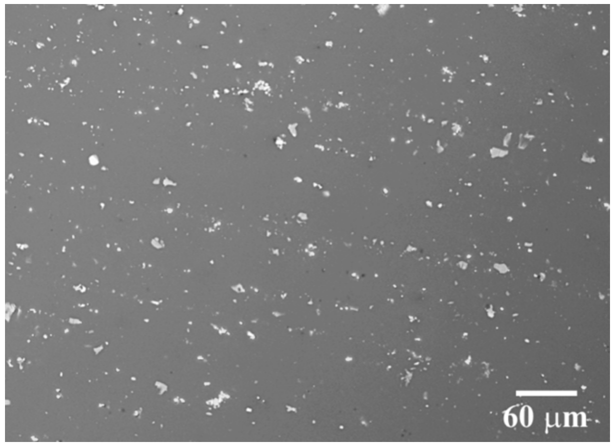

Fig. 1. SEM image of the as-supplied material after polishing with 1 mm diamond suspension prior the corrosion test.

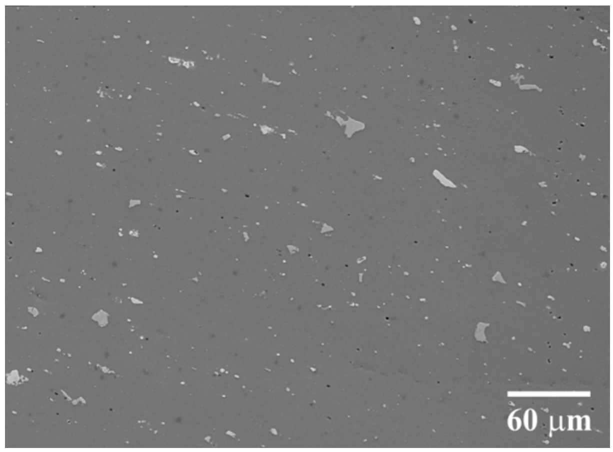

Fig. 2. SEM image of the as-supplied material after polishing with acidic SiO_2 suspension.

3. Results

3.1. EBSD analysis

The surface of the investigated samples before the corrosion test is shown in Fig. 1. There are no visible polishing artefacts in the form of scratches or pits. The surface after polishing with acidic silica suspension is shown in Fig. 2. The SEM observations did not reveal any IG attack, which proves that SiO_2 suspension of 4.5 pH does not affect further observations.

An EBSD map for an initial sample is shown in Fig. 3. Different colours of grains indicate different orientations of their crystal lattices. The surface of the samples which were polished with acidic silica after the electrochemical test, is shown in Fig. 4a. Not all of the observed IG corroded areas were suitable for the EBSD observations, as the surface was not planar. Examples of the analysed IGC attack areas are shown in Fig. 4 (b–d). The OIM maps with superimposed SEM image of IGC attack are shown in Fig. 4 (e–f). The location of corroded grain boundaries in the SEM image corresponds to the location of the grain boundaries determined via OIM analysis.

The GBCD function for the as-supplied material was estimated from the measurements

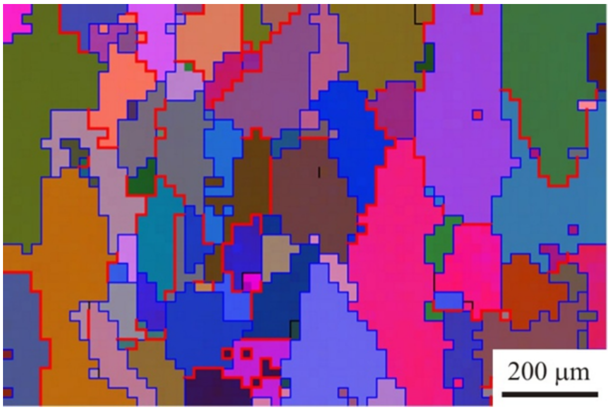

Fig. 3. An OIM map for as-supplied material, different colors of grains indicate orientation of their crystal lattices.

carried out for 273 GBs. The misorientation angles of the corroded grain boundaries were determined by comparing OIM and SEM images of the corroded areas (Fig. 4 e–f). In total, 59 and 72 corroded GBs were characterized for 0.1 M and 0.5 M NaCl solution respectively.

The GB misorientation angles were classified into the following three categories:

1. low misorientation (misorientation angle from 3 to 15 degrees)
2. medium misorientation (from 15 to 35 degrees)
3. highly misorientation (from 35 to 60 degrees).

The frequency function of GBCD for the samples representative of the materials as-supplied and subjected to the corrosion tests are shown in Fig. 5. The distribution function for the as-supplied material describes all the grain boundaries emerging on the surface of the AA2024-T3 sheets used in this study. On the other hand, the experimental distribution function obtained for the samples subjected to the corrosion tests describes the population of the grain boundaries prone to IGC. The results presented in Fig. 5 indicate that these two populations significantly differ in terms of the percentage of grain boundaries with low, medium and high misorientation angles. In the as-supplied material, 3% of the grain boundary population is made up by low misoriented GBs, while 32% and 65% are of medium and high misorientation, respectively.

In the case of the grain boundaries visibly corroded in 0.1 M NaCl, the percentage of highly misoriented ones is much higher and amounts to 73%. This percentage is even higher for the samples tested in 0.5 M NaCl solution, for which it is equal to 78%.

The results presented in Fig. 5 clearly demonstrate that the medium misoriented GBs are more resistant to IGC attack than the highly misoriented ones. One may also argue that the data collected indicate different dependence of the medium and high misoriented grain boundaries to the concentration of chlorine ions. For the medium misoriented GBs, the higher the concentration of chloride ions the lower the fraction of corroded GBs. The opposite relationship was observed for the highly misoriented GBs, where the higher Cl^- concentration generated the higher fraction of grain boundaries revealing IGC attack.

As the resistance of the grain boundaries to IGC depends also on their chemistry, STEM observations were carried out to reveal the presence of the fine second phase particles. These observations revealed small precipitates uniformly distributed in the grain interiors and at the grain boundaries. An EDS line scan revealed no chemical composition gradient at GBs (Fig. 6). This does not preclude the possibility of grain boundary segregation, which might have been beyond the resolution limit of the EDS technique.

4. Discussion

For the lower concentration of chloride ions (0.1 M NaCl) the lower intensity of corrosion attack is observed. This statement can be made based on the number of the observed corroded GBs on the samples immersed in different solutions. For the lower content of chloride ions, fewer corroded GBs were observed in comparison to the sample corroded in the solution containing higher concentration of chloride ions. This can be explained by the higher possibility of breakdown

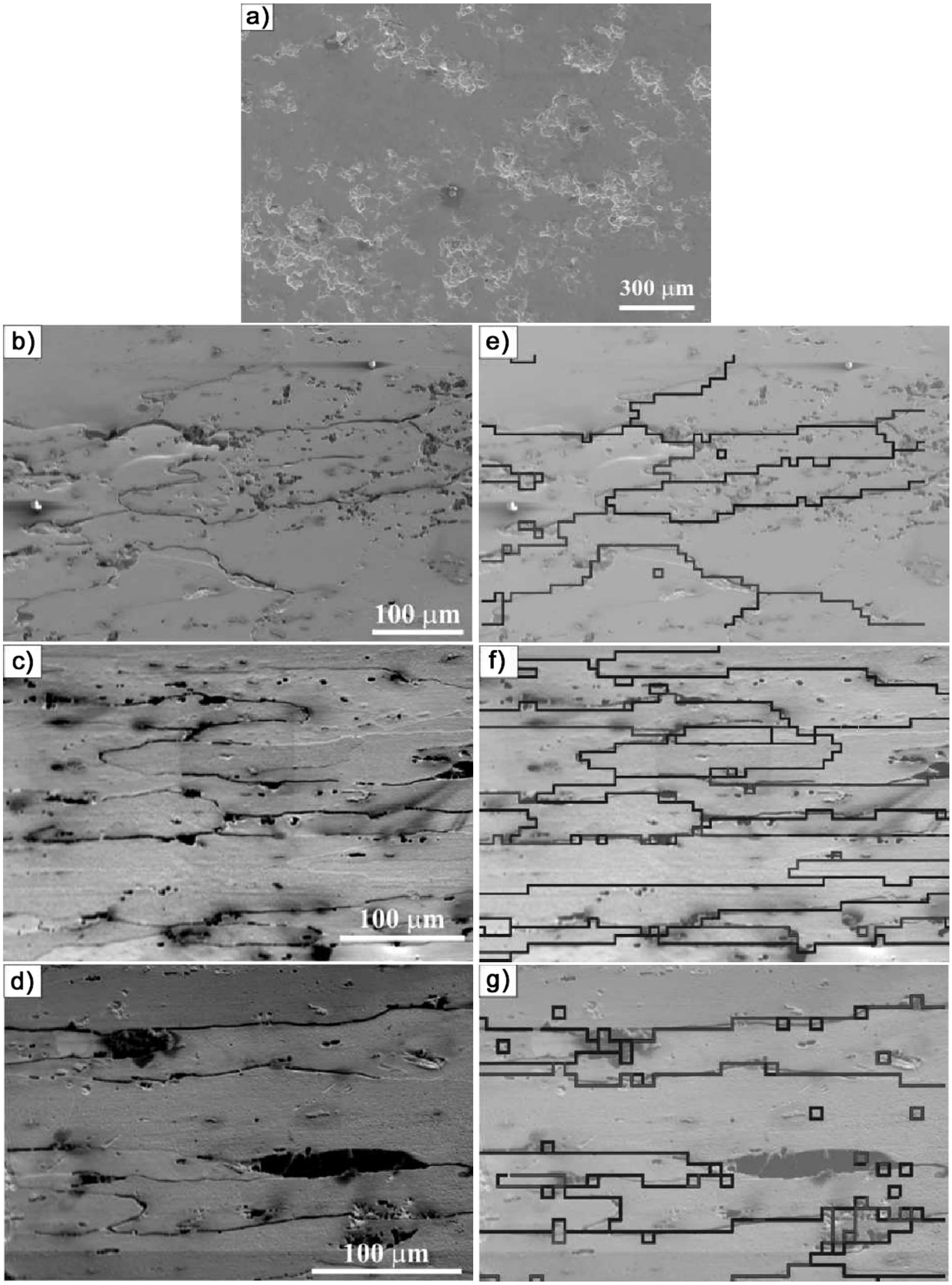

Fig. 4. SEM images of the surface of samples subjected to the IGC: (a) areas suitable for the OIM analysis (b–d), combined SEM images and OIM maps with grain boundaries marked according to the misorientations angle (black - higher than 3°, dark > 15°, light > 35°) (e-g).

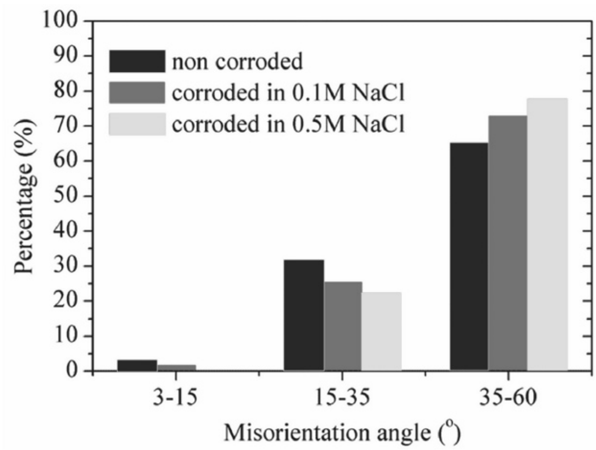

Fig. 5. The experimental GBCDs for the grain boundaries revealed in the as-supplied sheets of AA2024-T3 and in the samples subjected to the corrosion tests.

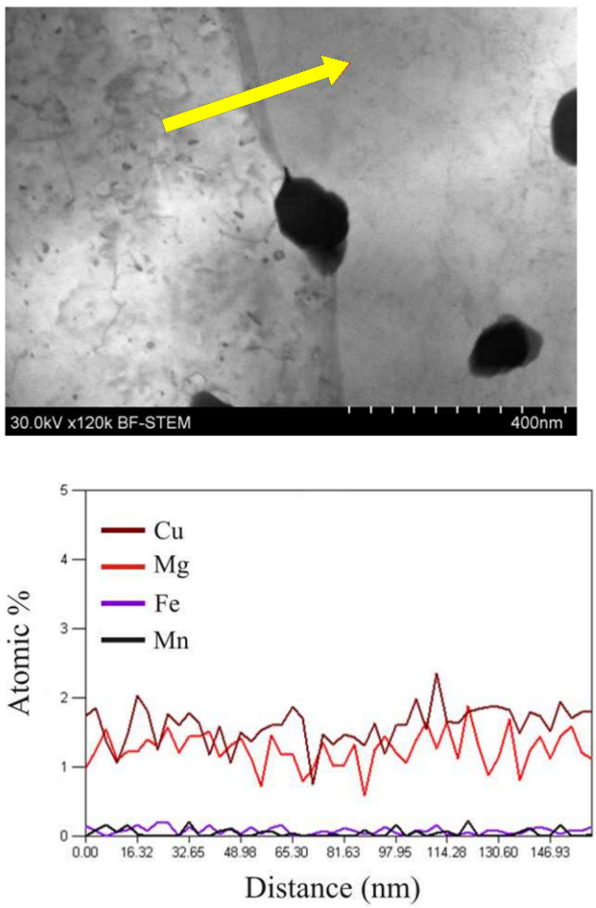

Fig. 6. STEM image and EDS lines scan of the areas in a close distance to the examined grain boundary.

with the higher concentration of chloride ions. This would confirm the theory of similar mechanism of intergranular corrosion and pitting corrosion described by Zhang and Frankel [3].

The results obtained in the present study for random grain boundaries clearly show that under the conditions employed in this study, both the medium and high misorientation GBs undergo IGC in AA2024-T3. However, the data collected here indicate that the grain boundaries of high misorientation angle are more prone to the corrosion attack. This is manifested by a higher proportion of such grain boundaries in the population of the corroded GBs in comparison to GBCD of all GBs occurring in the initial sample. Also, it has been found that the percentage of medium misorientation among the corroded GBs decreases with the increasing Cl^{-} concentration, which can be explained by more severe attack of corrosion to the highly misoriented GBs. As grain boundaries are often defined as the defects in the crystal structure, the passive film which is formed on them is also suspected to be more defected than the passive film which is formed on grain interior surface. This can lead to a higher breakdown propensity and intergranular corrosion initiation.

The low angle misoriented GBs seem to be immune to the corrosion attack. However, only few low misoriented GBs were observed, which is statistically inconclusive.

The result in correspondence with the theory of chemical decomposition on grain boundaries leads to the conclusion that it is impossible to determine one main cause of intergranular corrosion initiation. The mechanism of intergranular corrosion is a complex phenomenon and should be considered as a combination of microstructural and crystallographic factors.

5. Conclusions

1. It has been shown that the misorientation angle of the random grain boundaries of AA2024-T3 has a significant influence on their resistance to IGC.

2. GBs with higher misorientation angle are more prone to intergranular attack than GBs of medium misorientation angle.

3. Driving forces for the intergranular degradation process are more destructive for the highly misoriented GBs with increasing chloride ions concentration than for the medium misoriented GBs.

4. The other finding is that the higher concentration of chloride ions influences to a higher degree the susceptibility of the high angle grain boundaries to the localized intergranular attack.

Acknowledgements

This work was carried out within a SICOM Project (Simulation Based Corrosion Management) financed under the 6th Framework Programme of European Commision.

References

[1] VARGEL Ch., *Corrosion of aluminium*, Elsevier, 2004

[2] DAVIES J.R., *Corrosion of Aluminum and Aluminum Alloys,* ASM International, 1999

[3] ZHANG W., FRANKEL G.S., *Electrochimica Acta*, 48 (2003), 1193

[4] GUILLAUMIN V., MANKOWSKI G., *Corrosion Science*, 41 (1999), 421

[5] KIM S.H., ERB U., AUST K.T. and PALUMBO G., *Scripta mater.*, 44 (2001), 835

[6] LIN P., PALUMBO G., ERB U. and AUST K.T, *Scripta Metall. Mater.*, 33 (1995), 1387

[7] PALUMBO G., AUST K.T., LECHOCKEY E.M., ERB U. and LIN P., *Scripta Mater.*, 38 (1998), 1685

[8] LECHOCKEY E.M. , PALUMBO G. , LIN P. and BRENNENSTUHL A.M. , *Met. Mater. Trans.* 29A (1998), 387

[9] PALUMBO G., AUST K. T., *Acta Metall. Mater*. 38 (1990), 2343

[10] LECHOCKEY EM., PALUMBO G., LIN P. and BRENNENSTUHL A.M., *Scripta Materialia* 36 (1997), 1211

[11] BRANDON D.G., *Acta Metall*. 14 (1966), 1479

[12] GALVELE J.R., DE MICHELI S.M., *Corros. Sci*. 10 (1970), 795

Received 2010-07-08
Accepted 2012-04-11