Influence of the corrosive environment on the Portevin–Le Chatelier plastic instability phenomenon in Al–1Mg and Al–3Mg model alloys

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The aim of this work was to indicate the influence of changes on the surface of materials caused by the corrosive medium (3.5% NaCl solution) on the intensity and character of the Portevin–Le Chatelier effect in model aluminium alloys. For this purpose, two Al alloys, containing 1% and 3% of magnesium, were subjected to tensile testing in the as-cast state and after the exposition in NaCl solution for various time. Several electrochemical measurements were held to determine materials’ corrosive behaviour and microscopic observations to evaluate the surface character of the samples. High corrosion resistance of the materials resulted in a very slight alteration of their surface development, which didn’t lead into any significant variations in the plastic instability phenomenon PLC.

Key words: Portevin–Le Chatelier effect, aluminium alloys, plastic instability, corrosion.

1. INTRODUCTION

Portevin–Le Chatelier effect (PLC effect) is a well-known phenomenon occurring in many aluminium alloys during deformation [1], manifesting itself in a form of characteristic serrations on the stress–strain curve, caused by rapid changes of force in small extensions. It can lead to inhomogeneous deformations in materials microstructure, resulting in the deterioration of its mechanical properties [2]. Apart from the most commonly analysed structural factors, like grain size, precipitations or texture, there are some extrinsic ones which can also strongly influence materials vulnerability to PLC effect [3].

Abduluyahed in his research [4, 5] compared serrated flow in 316 and 316L austenitic steels during tensile testing in air and in vacuum. He reported a considerable decrease in serration frequency in vacuum conditions, which can be subjected to the fact that there is no oxygen layer on the surface, which could crack during deformation and work as a stress concentration. Temperature was considered as a factor influencing PLC effect, by Yilmaz [6], who performed tensile testing of 1020 low-carbon steel in room temperature and in increased temperature ranging from 50 to 85°C, simultaneously registering potential variations on the sample surfaces. According to his results, in the tested steel which didn’t exhibit jerky flow in the room temperature, it occurred while heating and kept on intensifying until a certain value, when it disappeared again. There was also a noticeable relationship between the PLC effect in enhanced temperature and the values of potential on the surface of samples. In the same publication [6] the author describes the difference in serrations character depending on the roughness of surface, using polished and unpolished samples. For the unpolished samples the PLC effect was much more intensive, the curves less regular and the strain propagation twice slower. The same behaviour was observed by Abbadi [7] in 5000 aluminium alloy. Jerky flow did not occur in this material when the samples were properly polished before testing, but it was present when the surface of the samples was rough and unpolished. In both cases the explanation of this phenomenon is similar and analogical to that in materials exhibiting a brittle oxygen layer on the surface. All the irregularities on the rough surface work as tension concentrators, increasing the intensity of serrations.

Zdunek in her work [3] related the character of PLC oscillations with the strain rate during deformation, describing three types of the oscillations possible. Type A oscillations are observed at high strain rates and have a form of sudden, irregular changes of stress with low amplitude. Type B oscillations occur with medium strain rates, have irregular stress amplitude, but a cyclic character. Type C static oscillations are characterized by regular, cyclical stress variations with high amplitude and are observed at low strain rates only.

Corrosion resistance of aluminium alloys depends mostly on their ability to develop a passive layer on the surface. It forms easily in atmospheric conditions, but in many cases has low homogeneity and thickness or poor cohesion to the surface. This results in the pitting corrosion of the material, when subjected to the environment containing aggressive ions, halides in particular [8]. Moreover, alloying elements, such as magnesium, used to enhance mechanical properties of material, may deteriorate its corrosive performance. This is due to the fact that the formed intermetallic phases have different structure and electrochemical activity then the matrix and can become the centers of corrosion or lead to the further inhomogeneity of material [9]. Presence of magnesium can also cause the occurrence of stress cracking corrosion in aluminium alloys, because the precipitations have a tendency to form on the grain boundaries and have a strongly anodic character. This may in result influence mechanical properties and elongation of material during tensile testing [10].

2. EXPERIMENTAL

2.1. Materials

Two model aluminium alloys were used in the experiments. Al–1Mg alloy, containing app. 1 wt % of magnesium and Al–3Mg with app. 3 wt % of magnesium. Full composition of the materials is shown in the Table 1. Presence of silicon in the alloys is a result of fabrication method and they have a form of primary, insoluble precipitations. The materials were obtained with semi-continuous casting and extrusion, in the form of rods with 20 mm diameter, and subjected to subsequent annealing. Both alloys are dual phased with equiaxial microstructure and distinctive grain boundaries.
ing the experiments, all the samples were subjected to supersaturation by two hours of annealing in 300°C.

2.2. Tensile tests and PLC effect analysis

Tensile tests were held on standard flat specimens with the use of MTS QTest 10 machine. Low strain rate of 10^{-4} s^{-1} was chosen to obtain evident and easy to analyse serrations in both materials. Before testing, certain samples from each alloy were exposed to corrosive solution 3.5% NaCl for 1 or 7 days.

Based on the stress–strain curves obtained from each test, characteristic parameters of PLC effect were calculated. These were: number of serrations, average serration amplitude \( A \), serration frequency \( f \), and \( RL \) parameter. \( RL \) parameter was created to quantitatively describe the intensity of PLC effect. It is defined as \( L / L' \) ratio, where \( L \) is the length of a given segment of the curve, and \( L' \) is the length of its projection [11], as pictured in Figure 1.

2.3. Corrosion tests

Various electrochemical tests were held to determine and compare the alloys resistance to corrosion in 3.5% NaCl solution. Electrochemical measurements were carried out using the FAS1 Gamry potentiostat, in a conventional three-electrode electrochemical cell, containing of a graphite electrode as a counter electrode, an Ag/AgCl electrode as a reference electrode and the aluminium alloy sample as a working electrode. Potentiodynamic test allowed to calculate corrosive current density and corrosion potential and determine the type of corrosion the material undergoes. Polarization curves were recorded at a constant sweep rate of 1 mV/s from –0.2 to 0.4 V with respect to the open circuit potential (\( E_{corr} \) vs Ag/AgCl). Electrochemical impedance spectroscopy results, in a form of Nyquist curves, were obtained for frequencies ranging from 5\times10^{-2} Hz to 2.5\times10^{-2} Hz and sinusoidal potential with amplitude of 10 mV. They enabled the calculation of polarization resistance and constant phase element admittance of the alloys.

2.4. Microstructural observations and surface development

Cross-sections of the samples in an as-cast state and after the exposition in corrosive medium for 1, 3 or 7 days were observed with scanning electron microscopy (SEM). TM 1000 microscope was used, operating with 15 kV voltage in SE mode, photographs were taken with 2000x magnification.

Based on the pictures of cross-sections, surface development of materials in each state was calculated. It can be useful to determine the level of degradation on the surface of materials with the increased time of exposition in NaCl solution. The value of surface development is calculated as the ratio between the length of the edge in a given picture of a sample and the length of its projection, as shown in Figure 2.

All the presented pictures of samples’ cross-sections are only cut parts of SEM photographs which were of interest during the analysis.

3. RESULTS

3.1. Corrosion resistance

Polarization curves for examined materials are shown in Figure 3. They have similar shape in a cathodic, as well as in an anodic part, although Al–1Mg curve is slightly shifted towards the positive potentials. Characteristic peaks in the anodic part for both alloys suggest the formation of a passive layer on the surface of materials.

Table 2 presents the calculated values of corrosion potential \( E_{corr} \) and corrosive current density \( i_{corr} \). Corrosion potentials for the alloys do not vary significantly, but there is a huge difference between the values of corrosive current density. For Al–1Mg alloys it is less than 0.9 μA/cm², while for the Al–3Mg it is almost twice as high, over 16 μA/cm². According to this values the corrosive reactions occur much faster on the surface of the latter material.

Nyquist plots obtained during EIS measurements are presented in the Figure 4. The model for an equivalent electrical circuit was a Simplified Randles Cell, so they have the shape of a semicircle for both materials.

![Fig. 2. Example of a picture used to calculate the surface development](image2)

![Fig. 3. Polarization curves for Al–1Mg and Al–3Mg alloys](image3)
Much bigger radius of the curve for Al–1Mg alloy is the evidence of higher polarization resistance, though. It indicates a lower flow of charge on the surface of this material, resulting in slower corrosive processes. It is in accordance with the values of constant phase element (CPE) admittance. A two times higher admittance for Al–1Mg suggests slower course of electrode reactions on the surface of this material. The values of the parameters calculated for both materials are shown in Table 3.

### 3.2. PLC effect analysis

The parameters of PLC effect calculated for samples in an as-cast state and after 1 or 7 days of exposition in corrosive medium are presented in Table 4. In both alloys the character of serration remains almost unchanged, irrespective of the state. In Al–1Mg alloy the number of serrations is high, but the amplitude relatively low, less than 1 MPa, while in the Al–3Mg the amount of serrations is almost 50% lower, but the amplitude significantly higher, over 3.3 MPa. The $R_p$ parameter stays on the same level in each material, though. The course of serrations for both alloys in each state is compared on sections of chosen stress–strain curves, presented in Figures 5 and 6.

### 3.3. Surface characteristic

Figures 7a to 7d and 8a to 8d show the cross-sections of Al–1Mg and Al–3Mg samples respectively, in an as-cast state and after 1, 3 and 7 days of exposition in the 3.5% NaCl solution. For both materials we can notice the presence of pits only after one day in the corrosive medium and their deepening with a longer time of exposition. For Al–1Mg the pits seem to be bigger and wider, while for the Al–3Mg deeper but less frequent. The relationship between the time of exposition and the surface development calculated for both alloys as described in Experimental section is presented in the form of a curve in the Figure 9, with the calculated results presented in Table 5. In each material it increases constantly for the whole time, but the increase is most intensive during the first days. The values of surface development
are higher for Al–3Mg alloy during the whole experiment, but they are relatively low for both materials, which is consistent with the results of corrosion tests.

4. DISCUSSION

Electrochemical measurements proved the high resistance of both alloys to corrosion in 3.5% NaCl solution. Because of the microstructure — less precipitations and grain boundaries — it is higher in Al–1Mg alloy. When exposed to the solution they develop a passive layer on the surface, preventing it from a rapid, uniform degradation. With the increased time of exposition some pits are present on the surface, though, enhancing slightly the surface development rate.

In case of both materials results of PLC effect analysis did not show any explicit differences between the samples in an as-cast state and exposed to the corrosive solution. Each alloy had its characteristic course of PLC effect, with more, much frequent serrations and lower amplitude for Al–1Mg and higher amplitude, but lower frequency and amount of serrations for Al–3Mg. This is a result of different microstructures of these alloys, grain size in particular. Within the same alloy but with various surface development the character of serrations did not change at all, though.
### 5. CONCLUSIONS

The passive layer created on the surface of Al–1Mg and Al–3Mg alloys after exposition to NaCl solution seems to have preserved the same level of roughness and development as the material in as-cast state, preventing the deterioration of plastic instability PLC effect.

Exposure to more aggressive media may give the answer whether there is a threshold value of changes in surface development in those alloys needed to intensify the serrations, as it would be expected based on studies of other materials.

What should also be considered is a question of the brittleness of passive layer. As mentioned in an introduction, cracks in the layer may work as concentrators of tension on the surface of a sample, leading to the intensification of PLC effect. This doesn’t seem to occur in this material, though. It suggests either a high homogeneity and low brittleness of a passive layer, or its very low thickness.

### REFERENCES

Wpływ środowiska korozjennego na niestabilność odkształcenia plastycznego Portevin–Le Chatelier w modelowych stopach Al–1Mg i Al–3Mg

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Słowa kluczowe: zjawisko Portevin–Le Chatelier, stopy aluminium, niestabilność odkształcenia plastycznego, korozja.

1. CEL PRACY

Efekt Portevin–Le Chatelier jest dobrze znany i szeroko opisany zjawiskiem pojawiającym się w wielu stopach aluminium. Objawia się on podczas odkształcania w postaci charakterystycznych ząbków na krzywej rozciągania wywołanych gwałtownymi zmianami naprężenia przy niewielkim odkształceniu. Wpływ na to zjawisko jest przypisywany głównie czynnikom wewnętrznym, wynikającym ze struktury materiału, takim jak: wielkość ziarna, obecność wydzieleń czy tekstury. Istotne mogą być jednak również czynniki zewnętrzne, m.in. szybkość odkształcania, środowisko czy stopień rozwinięcia powierzchni próbkii.

Celem pracy było zbadanie, jak zmiany na powierzchni materiału wywołane przez ekspozycję w środowisku korozyjnym (3,5% roztworze NaCl) wpłyną na intensywność i charakter zjawiska Portevin–Le Chatelier w dwóch modelowych stopach aluminium, Al–1Mg oraz Al–3Mg.

2. MATERIAŁ I METODYKA BADAN

Do badań wykorzystano dwa modelowe stopy aluminium z różną zawartością magnezu. Ich skład przedstawia tabela 1. Badania przedzieliło przesycanie próbek przez 2 h w temperaturze 300°C. Przeprowadzono statyczną próbę rozciągania standardowych próbek płaskich, z szybkością 10–4 s–1. Część próbek z obu stopów przed badaniem poddano działaniu środowiska korozjennego (3,5% roztworze NaCl) przez 1 lub 7 dni. Na podstawie uzyskanych wyników wyznaczono charakterystyczne parametry efektu PLC: liczbę ząbków, średnią amplitudę ząbkowania, częstotliwość ząbkowania oraz parametr $R_L$ określający w ilościowy sposób intensywność zjawiska. Wykonano pomiary elektrochemiczne w celu określania odpowiednio korozjowej biegunowości stopów metodą potencjodynamiczną oraz elektrochemicznej spektroskopii impedancji (EIS). Wyznaczono również zmianę rozwinięcia powierzchni materiałów w funkcji czasu ekspozycji w roztworze korozjennym na podstawie analizy SEM przekrojów próbek poddanych działaniu ośrodka korozjennego przez 1, 3 oraz 7 dni.

3. WYNIKI I ICH DISKUSJA

Pomiary elektrochemiczne wskazują na dobrą odporność korozjenną obu badanych stopów (rys. 3, 4). Pod działaniem roztworu zawierającego jony Cl– wytwarzają one warstwę pasywną zapobiegającą szybkiej degradacji. Rozwinięcie powierzchni w przypadku obu materiałów nie uległo w związku z tym znacznym zmianom, zaobserwowano jedynie powstawanie nielicznych wżerów, których liczba wzrosła z czasem ekspozycji w roztworze (rys. 7, 8).

Analiza pomiarów wytrzymałościowych również nie wykazała w przypadku obu podstawowych stopów znaczących różnic pomiędzy próbki w stanie wyjściowym a poddanymi oddziaływaniu środowiska korozjennego. Każdy ze stopów wykazywał charakterystyczny dla siebie przebieg zjawiska PLC, niemal niezmienny pod wpływem zmian wywołanych działaniem roztworu NaCl.

4. PODSUMOWANIE

Należy przypuszczać, iż warstwa pasywna wytworzone w war- pierszyny stopów Al–1Mg oraz Al–3Mg zapobiega zwiększeniu rozwinięcia powierzchni, przez co nie wystąpiła zmiana charak- terystyki zjawiska Portevin–Le Chatelier. Ekspozycja w bardziej agresywnym środowisku może określić, czy dla danego materiału istnieje krytyczna wartość rozwinięcia powierzchni, która wywołu- je intensyfikację ząbkowania, tak jak można wnioskować na pod- stawie analizy literatury.