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CORROSION RESISTANCE OF AZ31 MAGNESIUM ALLOY INFLUENCED BY CONVENTIONAL **CUTTING FLUID**

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Resume

This paper deals with the evaluation of cutting fluid impact on corrosion resistance of AZ31 magnesium alloy in aggressive environment containing chloride ions supported by photo documentation. Ground samples were immersed in the standard commercial cutting fluid for 5 minutes to simulate conditions during machining process at the temperature of 22 \pm 2 °C and subsequently cleaned and immersed in 0.1M NaCl solution at the temperature of $22 \pm 2^{\circ}$ C in order to measure electrochemical corrosion characteristics. Cyclic potentiodynamic polarization (CPP) tests were chosen as a testing method. The measured CPP curves of immersed samples and ground samples were analysed by Tafel extrapolation method. The values of obtained electrochemical characteristics show that the chosen cutting fluid has negative effect on corrosion resistance of AZ31 magnesium alloy in sodium chloride solution.

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1. Introduction

In the modern world engineering, there is a need to reduce the weight of the components and machines (cars, aircrafts, ships, etc.) with the aim to lower operational costs, fuel consumption and also limits the carbon footprint. Magnesium and its alloys represents one of the few possibilities to accede this requirement. These alloys belong to the category of progressive materials used in automotive and aircraft industry due to the many outstanding properties, e.g. low weight, high specific strength, high dumping capacity and good machinability. From the ecological point of view, they are recyclable and after the end of their lifetime they could be used as a sacrificial anode to protect another metal [1 - 6, 13]. The Mg-Al-Zn alloys exhibit good combination of mechanical properties, castability, biocompatibility, workability and because of that they are extensively used by the engineers. The AZ31 alloy shows good plasticity, weldability, corrosion resistance, can withstand small loads and such that is often used in aircraft industry for exemplatory brackets and small components. According to the various authors alloy also provides very good biodegradable properties [7 - 9]. Despite of these pros, there is problem with high reactivity of Mg alloys which leads to the lower corrosion resistance compared to the aluminium alloys or steels and limits their wider usage [10, 11]. The Mg alloys reacts briefly when they are exposed to corrosive environment (aerial or aqueous) and the Mg oxides (MgO) hydroxides $Mg(OH)_2$ formed or are on the surface. These substances are not stable in the acidic or neutral conditions and such that do not protect the magnesium parts [12 - 14]. During the most of the machining processes, the magnesium workpiece is in contact with cutting fluid. The the components

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of the conventional cutting fluid could react with the alloy which may lead to the decrease of corrosion resistance.

This contribution is focused on the evaluation of the conventional cutting fluid impact on the corrosion resistance of the AZ31 magnesium alloy.

2. Experimental material and methods

The AZ31 magnesium alloy prepared continual casting and homogenized by at the temperature of 420 °C for 6 h has been used as an experimental material. Its chemical composition given by the material list is mentioned in the Table 1. The samples used for the metallographic observation have been prepared according to the standard metallographic procedures used for the Mg alloys. Subsequently, the samples have been etched by the etchant consists of acetic acid, picric acid, demineralised water and ethanol [15]. The microstructure of AZ31 samples has been observed using light microscope ZEISS Axio Imager.Z1M.

The samples have been ground before immersion to the cutting fluid by an emery paper p1000 to ensure the same surface roughness [16]. In the next step, they have been submerged to the conventional cutting emulsion with pH 9 for the 5 minute to simulate the conditions during the machining process. After that, the samples were cleaned by the demineralised water, ethanol and dried by the steam of air. The used cutting fluid consists of mineral oils, additives and dangerous components which are listed in the Table 2. For the better interpretation of the results, the photo documentation of the samples surfaces before and after the immersion has been done on the stereomicroscope OLYMPUS SZX16.

The cyclic potentiodynamic polarization (CPP) tests have been chosen for evaluation of the electrochemical corrosion characteristics. The measurements have been performed in the 0.1M NaCl (aggressive aqueous environment containing chlorides) with pH 7.2 at the temperature of 22 ± 2 °C using laboratory potentiostat VSP Biologic SAS [17]. The three electrode cell system has been used including AZ31 sample with the exposed area of 1 cm^2 set as working electrode, platinum electrode set as a counter and saturated calomel electrode which served as a reference electrode (+0.242 V vs. SHE). The CPP tests start after 5 minute of potential stabilization between the AZ31 sample and testing electrolyte. The applied potential ranged from -150 mV to +400 mV in order to record pitting potential area. The range of potentials has been set with respect to open circuit potential (OCP) and the scan rate was 1 mV.s⁻¹. The measured data in form of cyclic potentiodynamic curves have been analysed by the Tafel extrapolation method and owing to that values of corrosion potential Ecorr and corrosion current density icorr have been obtained using EC Lab V10.34 software. From the E_{corr} and i_{corr} values the corrosion rate r_{corr} has been calculated.

Table 2

Chemical composition of AZ31 magnesium alloy.							
Component	Al	Zn	Mn	Si	Cu	Fe	Mg
wt. %	2.96	0.82	0.43	0.004	0.004	0.002	balance

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Dangerous component of conventional cutting fluid								
Component	Amine soap	Methylene dimorpoholine	Alcohol C16-18, C18	Polyglycoether	Boracic Acid	Neutralized KOH		
wt. %	10 - 20	1 - 5	1 - 5	1 - 5	1 - 5	0.002		

3. Results and Discussion

The microstructure of AZ31 magnesium alloy (Fig. 1) consists of polyedral grains of solid solution of aluminium, zinc and other alloying elements in magnesium. There are visible twins and areas of Al₁₂Mg₁₇ intermetallic phase.



Fig. 1. Microstructure of AZ31 magnesium alloy. (full colour version available online)

The surface of the ground AZ31 sample and sample after immersion is depicted in the Fig. 2. It can be seen that the immersion in cutting fluid leads to the creation of corrosion products layer due to the reaction of Mg sample with components contained in fluid. Another components are MgO and Mg(OH)₂ probably formed on the surface due to the aqueous character of the fluid [18].

Measured CPP curves of AZ31 tested samples in 0.1M NaCl are shown in Fig. 3. The values of electrochemical characteristics obtained by the Tafel extrapolation method for both states are listed in Table 3. The samples in ground state have reached (in direct polarization) the corrosion potential Ecorr value of -1561 mV and value of corrosion current density of 5.3 µA.cm⁻². It can be seen that after the backward polarization, ground AZ31 samples exhibit more negative corrosion potential and higher corrosion current density due to the breakdown of the surface film probably consisting $Mg(OH)_2$ of occurred at the pitting potential E_{pt} (-1429 mV). During the exposition in aqueous environment following reaction takes place: MgO + H₂O \rightarrow Mg(OH)₂. According the EpH diagram for magnesium in water environment, Mg(OH)₂ is stable only in strongly alkaline environments. The ground samples tented to corrode rapidly after the breakdown of the surface film due to its interaction with aggressive chloride ions Cl⁻ contained in the testing electrolyte [12]. As can be seen from electrochemical characteristics mentioned in Table 3. the samples influenced by the immersion in cutting fluid have reached more positive value of E_{corr} (-1391 mV) compared to the ground samples. On the other hand, the corrosion current density increased to the value of 90.6 μ A.cm⁻². This value is more than 17-times higher in comparison with the i_{corr} of ground AZ31 samples. The part of CPP curve measured during the backward polarization shows the shift of E_{corr} to the more negative value and higher i_{corr} . It has to be noted that this backward E_{corr} is still more positive compared to the direct E_{corr} of the ground samples. The fact that the influenced samples exhibit more positive values of corrosion potential means that the presence of film created on surface during immersion in cutting fluid leads to the thermodynamically nobler behaviour of these samples. In terms of corrosion kinetics, the significantly higher corrosion current density values of influenced samples means that corrosion rate is higher compared to non-influenced ones as it is shown in Table 3. This fact is probably caused by the non-protective and highly soluble layer of corrosion products consisted of MgCl₂ and Mg(OH)₂ created on the AZ31 surface which are unstable when exposed to the Cl⁻ ions and such that provide poor corrosion protection to the magnesium substrate.



Fig. 2. Surface of the AZ31. (full colour version available online)

Table 3

Electrochemical characteristics of the ground samples and samples influenced by the immersion in cutting fluid measure in 0.1M NaCl.

	E _{corr} (mV)	i _{corr} (µA/cm ²)	$\beta_a (mV/dec.)$	$\beta_c (mV/dec.)$	r _{corr} (mm/year)
Ground	-1561±21	5.3±0.1	121±7	119±6	$0.12{\pm}0.01$
Influenced by cutting fluid	-1391±10	90.6±3.6	131±11	233±21	2.1±0.2



Fig. 3. Cyclic potentiodynamic polarization curves for the ground and influenced AZ31 Mg alloy in 0.1M NaCl. (full colour version available online)

4. Conclusions

According to the experiments and analysis that have been done, it can be concluded that the immersion in conventional cutting fluid leads to the creation of surface film on the AZ31 Mg alloy samples due to the interaction of fluid components with Mg substrate. The performed CPP measurements in 0.1M NaCl shows that the cutting fluid positively influenced thermodynamic stability of samples as the values of corrosion potential have been more positive to the values

of the ground samples and it means that influenced samples are thermodynamically more stable. However, the corrosion current density increased 17-times after impact of cutting fluid. From the corrosion kinetics point of view, it means that the corrosion rate is higher after the immersion in cutting fluid as the corrosion current density is in direct with proportionality corrosion rate. This negative influence on corrosion behaviour in environment containing Cl⁻ could be overcome by the using of cutting fluid with more suitable chemical composition that does not react with the Mg surface or by the usage of proper removing technique of the created surface film.

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References

- J. Drábiková, F. Pastorek, S. Fintová, P. Doležal, J. Wasserbauer: Koroze a ochrana materiálu 60(5) (2016) 132-138.
- [2] J.E. Gray, B. Luan: J. Alloys Compd. 336(1) (2002) 88-113.
- [3] J. Liao, M. Hotta: Corros. Sci. 100 (2015) 353-364.

- [4] Y. Zhao, G.Wu, H. Pan, K.W.K. Yeung, P.K. Chu: Mater. Chem. and Phys. 132(1) (2012) 187-191.
- [5] Y. Gu, S. Bandopadhyay, Ch. Chen, Ch. Ning, Y. Guo: Materials and Design 43 (2013) 66-75.
- [6] B. Hadzima, P. Palček, M. Chalupová, R. Čanády: Kovové materiály 41 (4) (2003) 257-269.
- [7] H. Feng et al.: J. Alloys Compd. 695 (2017) 2330-2338.
- [8] S.S. Jamali: Corros. Sci. 86 (2014) 93-100.
- [9] A. Dziubinska, A. Gontarz, K. Horzelska, P. Piesko: Proceedia Manufacturing 2 (2015) 337-341.
- [10] Y. Su et al.: Surface and Coatings Technology 307(A) (2016) 99-108.
- [11] M. Mhaede, F. Pastorek, B. Hadzima: Mater. Sci. Eng. C 39 (2014) 330-335.
- [12] G.L. Song: Advanced Materials Engineering 7(7) (2005) 563-586.
- [13] Y. Yang, F. Scenini, M. Curioni: Electrochimica acta 198 (2016) 174-184.
- [14] M. Esmaily et al.: Progress in Materials Science 89 (2017) 92-193.
- [15] G.F.V. Voort: ASM Handbook: Metalography and Microstructures, 9th edition, ASM International, Almere 2004.
- [16] F. Pastorek, B. Hadzima: Mater. Eng. Mater. Inž. 20(2) (2013) 54-63.
- [17] K. Arakami, T. Shimura: Corros. Sci. 52(4) (2010) 1464-1471.
- [18] M. Danaiae, R.M. Asmussen, P. Jakupi, D.W. Shoesmith, G.A. Botton: Corros. Sci. 77 (2013) 151-163.