STRUCTURAL INVESTIGATIONS CONCERNING Al 3003/Al 4xxx CLAD MATERIALS

Brandusa GHIBAN[1], Claudia NATRA[2], Alexandru CERNEA[3], Anca Daniela RAICIU[4], Ovidiu ODAGIU[5], Irina BALKAN[6]

Generally, Al 3003 material is Al−Mn alloy which has superior ductility, but the strength and hardness are low. Al series 4xxx material is Al−Si alloy which has high strength and hardness, but the ductility is low. Clad materials are a variant of the typical composites, which consist of two or more materials joined on their interface surfaces. Clad materials as metallic composite materials are developed for the needs of user because the single metal often cannot satisfy it application conditions. That is, the advantage of clad materials is that the combination of different properties of materials can satisfy both the need of good mechanical properties and the demand of users such as industrial consumer. The purpose of this study is to investigate structural aspect in aluminum 3003 clad material with 4004 and 4045 alloy, after different cladding time.

Keywords: clad aluminum alloys, metallography, heat treatments, automotive applications

1. Introduction

Aluminum is the most optimal material for the automotive field, especially for heat exchangers because it offers many advantages such as production cost, plasticity, low weight, good corrosion resistance and easy processing [1-4].

The heat exchanger industry is subject to continued pressure from the automotive industry to produce as low, light, efficient and inexpensive heat exchangers [5-8]. As the thickness of the material used decreases, materials are increasingly sensitive to pitting corrosion [9]. The structure of a shifter can be protected using a specific anticorrosive design, such as the use of high Zn material for fins that are part of the exchangers.

[1] Prof., Dept. of Metallic Materials Science, University POLITEHNICA of Bucharest, Romania, e-mail: ghibanbrandusa@yahoo.com
[2] PhD student, Dept. of Metallic Materials Science, University POLITEHNICA of Bucharest, Romania
[3] PhD student, Dept. of Metallic Materials Science, University POLITEHNICA of Bucharest, Romania
[4] *Titu Maiorescu* Univ, Fac Pharm, Bucharest, Romania
[5] PhD student, Dept. of Metallic Materials Science, University POLITEHNICA of Bucharest, Romania
[6] Lecturer, Processing Department, University POLITEHNICA of Bucharest, Romania

Increased corrosion protection can be achieved by introducing long life alloys. These are so produced so that at the surface of the material we have a much lower corrosion potential than the basic alloy [10-14].

To obtain such a gradient of corrosion potential, it is necessary to keep the manganese content in the solid solution as follows:

- maintaining the silicon content at the lowest level in the base alloy;
- the material is not homogenized;
- preheating at a lower temperature for hot rolling;
- intermediate treatments should be avoided and, if necessary, they should be done at a lower temperature.

Also, the copper content has a very important role in improving the mechanical post-brazing properties and because high content leads to an increase in corrosion potential.

Thus, through careful control of the chemical composition and processing conditions, a material with a lower corrosion potential on the surface of the center can be produced, with a much higher corrosion resistance.

2. Materials and Experimental Procedure

The elemental composition of the investigated samples was determined using an ARL sputter optical emission spectrometer. Table 1 shows the chemical compositions for the investigated samples.

Table 1

Chemical composition of the experimental alloys

Alloy	**Chemical Composition, %wt.**						
	Si	**Fe**	**Cu**	**Mg**	**Mn**	**H**	**Al**
3003	0,2	0,53	0,075	0,021	1,15	0,136	Rest
4004	10,37	0,54	0,006	1,25	0,06	-	Rest
4045	10,2	0,33	0,003	0,001	0,003	-	Rest

The experimental samples were obtained within the SC ALRO SA company following the milling, plating, preheating, hot rolling, cold rolling, heat treatment stabilization, straightening, cutting or fastening process. The experimental samples were made of alloy 3003 plated alloys 4004, 4045, subjected to the above-mentioned technological processes.

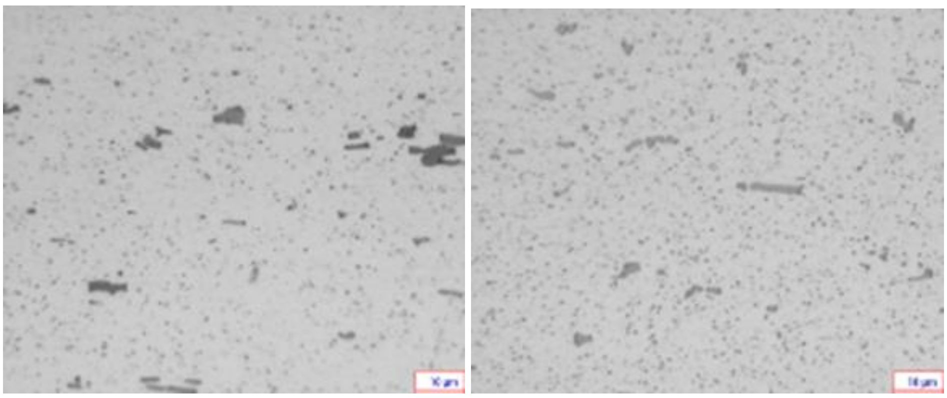
The two metals, both the base plate and the plate, are prepared to be welded with a longitudinal cord on one of the ends of the sleeve in the direction of rolling, and on the other end the plate platens the area. Then secure with steel strips to avoid loosening the base plate at the time of insertion into the deep furnace. After the milling and cladding operation, the billets are placed in the preheating furnaces (fixed furnace furnaces) for lamination. The working temperature depends on the nature of the alloy of origin. In the case of plated alloys, the range of temperature is 20-40 ° C lower than the melting temperature. From the metal obtained from the above production flow, samples of experimental aluminum alloys have undergone the chemical composite, morphological, mechanical and structural investigations.

Before performing the microstructural analysis and determining the degree of contamination, the samples were prepared metallographically. The metallographic preparation of the samples was carried out following the following operations: cutting, embossing, grinding, polishing, in order to research the structure of the material by optical and electronic microscopy. Optical microscopy images were acquired using an Olympus BX60M metallographic microscope with the KP-M1 camera.

3. Results and discussions

Knowing the structure of the material is essential in the evaluation of aluminum and aluminum alloys. The macroscopic examination highlights the inhomogeneities in the analyzed material, its compactness and the breakage mode. Depending on the shape of the mold, the surface analyzed provides information on the casting techniques used and the casting quality. Surface examination often reveals casting defects such as: macroporous, shrinkage, oxides, macro-inclusions, grain size differences, cracks, cracks, etc. Such an analysis makes it possible to identify defects, helping to eliminate the causes and to improve the properties of the material. The metallographic analysis was performed on samples of 3003 plated with 4045 and 3004 plated samples of 4004.

The metallographic analysis of plated alloys 3003 alloy 4045 is shown in Figs. 1 ÷ 3.

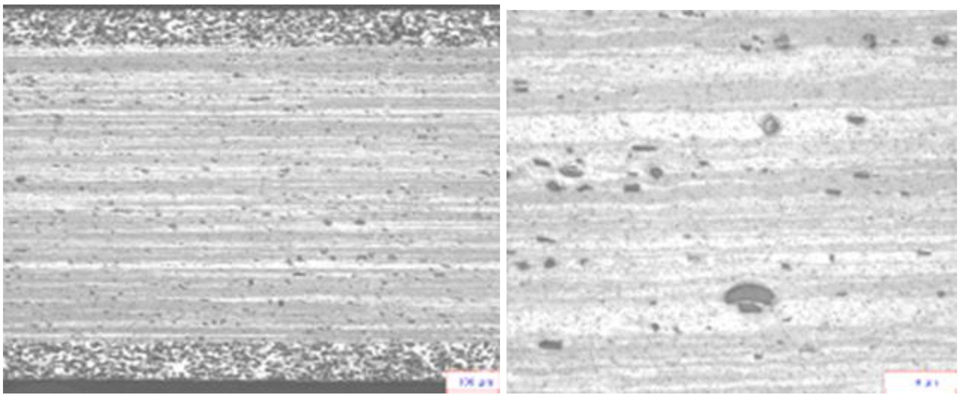


a b

Fig. 1. Optical microscopy for grain size measurements of the 3003 aluminum alloy coated with 4045 aluminum alloy (x1000): a- longitudinal cross section, b- transversal cross section

In the images from the Fig. 1 there are presented the structural aspects of the 3003 aluminum alloy coated with 4045 aluminum alloy, both in transversal and longitudinal cross-section, unattached and attacked state.

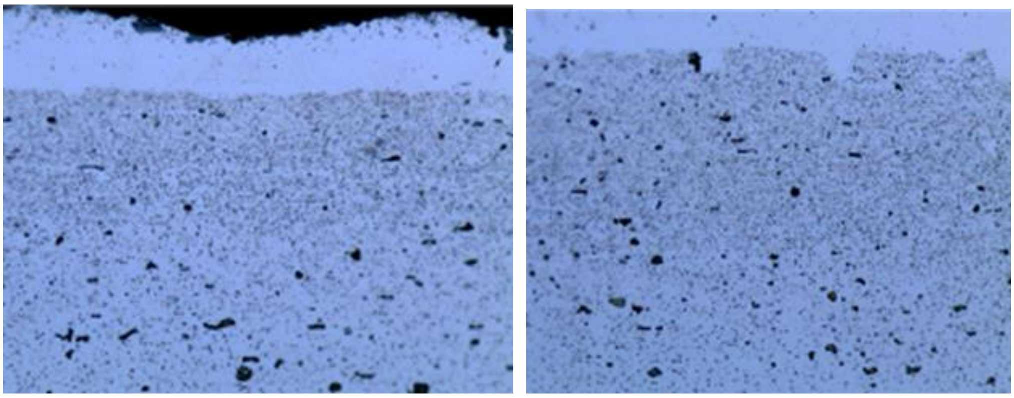
The analysis of the images in Fig. 1 indicates that the analyzed samples showed a uniform distribution of the MnAl6 and α (AlMnSi) phases. The precipitation is fine and uniformly distributed. For the determination of the grain size in the experimental sample, two samples were cut, as illustrated in Fig. 2. The analyzed samples revealed an elongated grain texture with "pancake" diffuse grain boundaries which induced mechanical properties improved to a standard 3003 alloy. This type of grain gives the material a mechanical strength and tear strength with 20 MPa units higher than the standard material. It also gives the structure a uniform distribution and good protection against intergranular corrosion.



a b

Fig. 2- Optical microscopy for grain size measurements of the 3003 aluminum alloy coated with 4045 aluminum alloy:
a- longitudinal cross section, b- transversal cross section

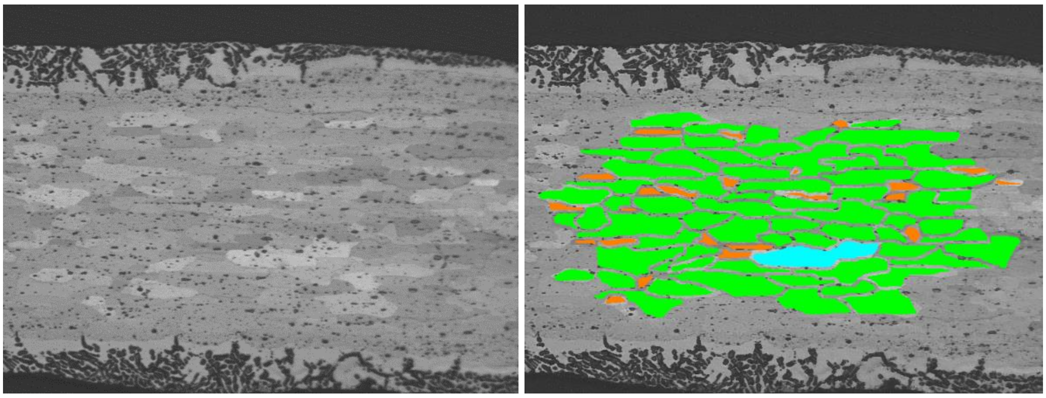
In order to identify the "brown band" area, two metallurgically prepared samples were prepared for the microstructural analysis after having undergone the brazing process at 600 ° C for 10 minutes and 60 minutes (Fig. 3). The maximum size of the brown band for the sample subjected to the brazing process for 10 minutes was about 58.78µm (face A) and 61.94µm (face B), representing approximately 20.12% of the total thickness of the plate (0.6mm) and about 24.79% of the total thickness of the base alloy (487µm).



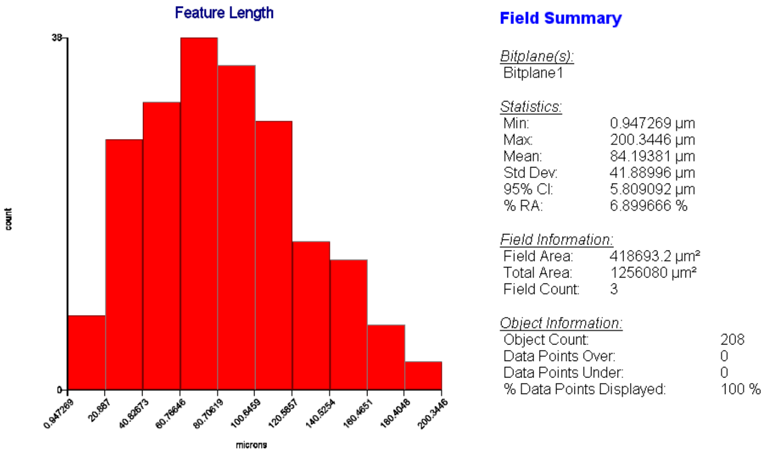
a b

Fig. 3. Optical microscopy images for "brown band" identification for the brazed sample after 10 minutes (a) and 60 minutes (b), 3003 alloy coated with 4045 aluminum alloy (500 x)

The maximum area of the brown band of the sample subjected to the brazing process for 60 minutes was approximately 73.95 µm (face A) and 81.53 µm (face B), representing approximately 25.91% of the total thickness of the sheet plated (0.6mm) and approximately 31.93% of the total thickness of the base alloy (487µm).



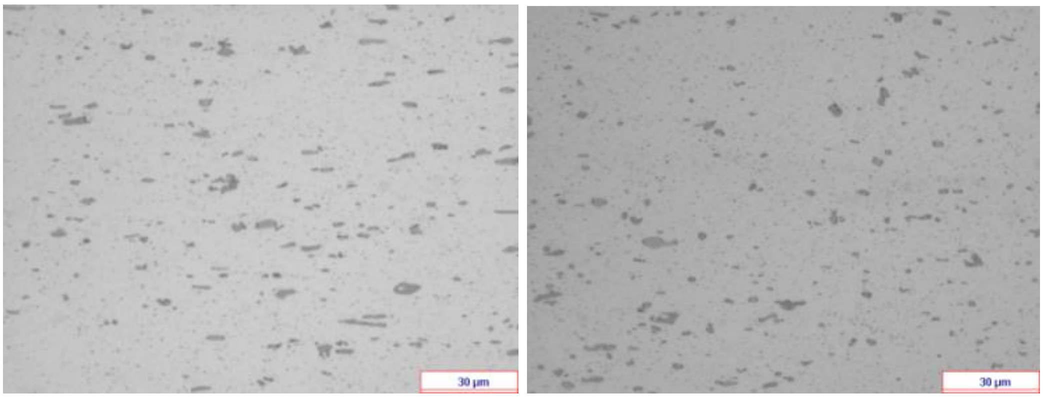
a b



c

Fig. 4. Grain size measurement 3003/ 4045 clad alloys:
a- captured image, b- detected image, c image Analysis Measurements

The metallographic analysis performed on plated alloy 3003 alloy 4004 alloy is shown in Figs. 5 and 6. Fig. 5 shows microstructures of 3003 aluminum alloy coated with 4004 aluminum alloy in longitudinal and transverse section. Metallographic analysis shows that most of the αAlMnSi and MnAl6 phases are spherical and uniformly distributed. Mn precipitation is fine and evenly distributed throughout the investigated sample. Grain size was relatively non-omogeneous, as shown in Fig. 6.



a b

Fig. 5- Optical microscopy images of 3003 aluminum alloy coated with 4004 aluminum alloy: a- longitudinal cross section, b- transversal cross section (x1000)

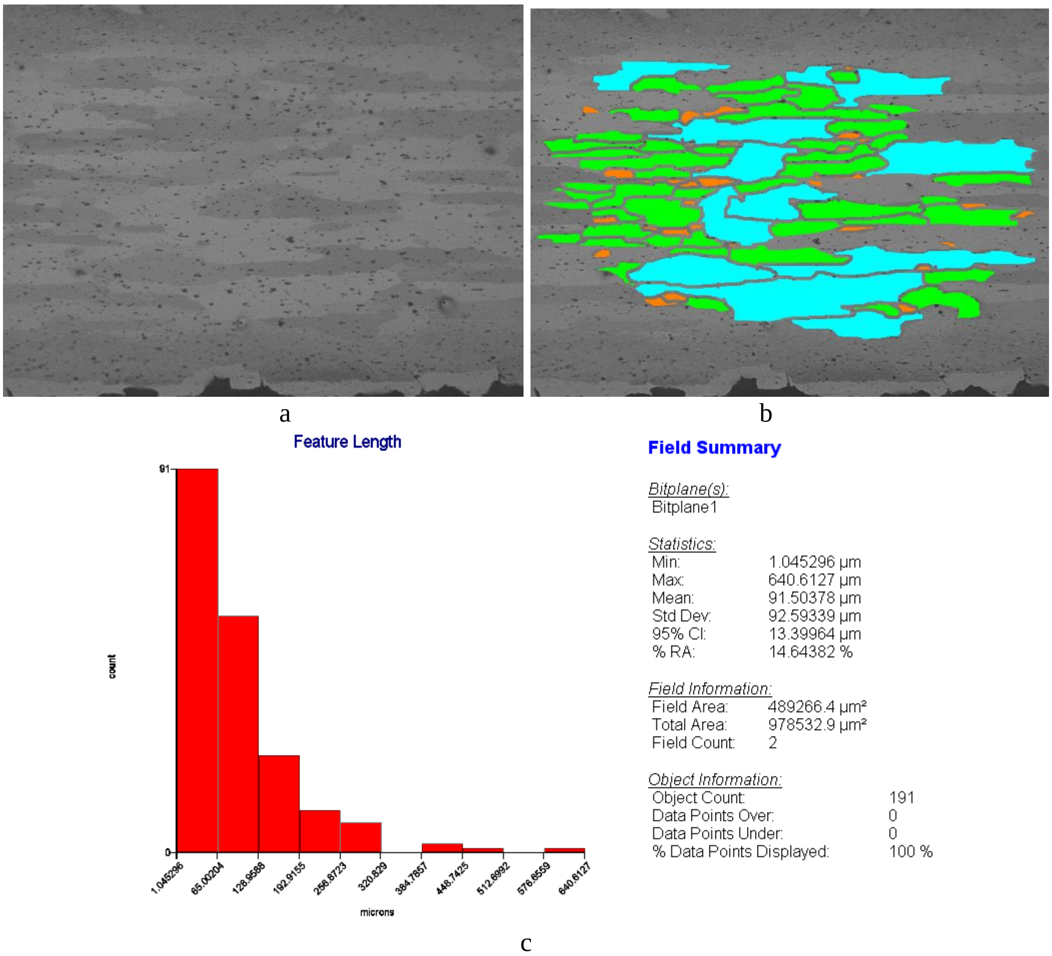


Fig. 6- Grain size measurement 3003/ 4004 clad alloys:
a- captured image, b- detected image, c- Image analysis measurements

4. Conclusions

In this paper, samples from 3003 aluminum alloy coated with 4045, respectively 4004 aluminum alloy were investigated at 600°, at two maintenance times, 10 minutes and 60 minutes.

The thickness of the cross-sectional plating layer was within the required value of 8.5% ± 1.5%.

The microstructural analysis of the samples prepared from the sheet metal samples, the 403, long life, 0.33 mm long, flat, longitudinal and transverse planar alloy 3003, reveals a uniform distribution of the MnAl6 and α (AlMnSi) phases. Most MnAl6 and αAlMnSi phases are spherical, distributed relatively uniformly. The precipitate (Mn) is finely and uniformly distributed throughout the analyzed sample section.

The samples analyzed from the sheet samples to determine the average grain size prior to brazing (electrolytic attack) revealed that the 3003C base alloy had a strongly elongated grain structure deformed in both directions (longitudinal and transversal) with grain diffusion limits.

R E F E R E N C E S

[1.] W.S. Miller, L. Zhuang, J. Bottema, A.J. Wittebrood, P. De Smet, A. Haszler, A. Vieregge, Recent development in aluminium alloys for the automotive industry, mater. Sci. Eng. A 280 (2000) 37–49,

[2.] V.C. Gudla, K. Rechendorff, Z.I. Balogh, T. Kasama, R. Ambat, In-situ tem investigation of microstructural evolution in magnetron sputtered Al-Zr And Al-Zr-Si coatings during heat treatment, mater. Des. 89 (2016) 1071–1078

[3.] F.N. Afshar, R. Ambat, C. Kwakernaak, J.H.W. De Wit, J.M.C. Mol, H. Terryn, Electrochemical depth profiling of multilayer metallic structures: an aluminum brazing sheet, electrochim. Acta 77 (2012) 285–293,

[4.] In-soo Son, Sang-Pill Lee, Jin-Kyung Lee, Woo-Cheol Kim, Ji-Seon Moon, Sangmok Lee, Jong-Sup Lee, Yong-Bae Kim, Geun-Ahn Lee, Dong-Su Bae - Effect of hydro co-extrusion on microstructure of duo-cast Al 3003/Al 4004 clad materials, trans. Nonferrous met. Soc. China 24(2014) s75−s80

[5.] Buzatu M; Geanta V; Stefanoiu R; Butu M; Petrescu Mi; Buzatu M; Antoniac I; Iacob G; Niculescu F; Ghica, Si; Moldovan H; Investigations into Ti-15Mo-W alloys developed for medical applications, materials, volume 12, issue 1, 2019.

[6.] Ghiban B; Antoniac I; Gheorghe D; Ghiban A; Ene R; Metallurgical failure analysis of intramedulary nail used for femoral fracture stabilization, Key Engineering Materials, volume 695, pages 178-182, 2016.

[7.] Antoniac IV, Stoia DI, Ghiban B, Tecu C, Miculescu F, Vigaru C, Saceleanu V. Failure analysis of a humeral shaft locking compression plate—surface investigation and simulation by finite element method. *Materials*. 2019; 12(7):1128.

[8.] Grecu D; Antoniac I.; Trante O; Niculescu N; Lupescu O; Failure analysis of retrieved polyethylene insert in total knee replacement, Materiale Plastice, volume 53, no.4, pages 776-780, 2016

[9.] Bane M; Miculescu F; Blajan Ai; Dinu M; Antoniac I; Failure analysis of some retrieved orthopedic implants based on materials characterization, solid state phenomena, volume 188, pages 114-117, 2012

[10.] Gheorghe, D., Pop D., et al., Microstructure development in titanium and its alloys used for medical applications, U.P.B. Sci. Bull., series B, 2019, **81**(1): 243-258.

[11.] Antoniac I; Sinescu C; Antoniac A; Adhesion aspects in biomaterials and medical devices, Journal of Adhesion Science and Technology, 2016, **30**(16):1711-1715.

[12.] Bita AI; Stan GE; Niculescu M; Ciuca I; Vasile E; Antoniac I; Adhesion evaluation of different bioceramic coatings on Mg-Ca alloys for biomedical applications, Journal of Adhesion Science and Technology, volume 30, issue 18, pages 1968-1983, 2016

[13.] Raiciu A.D., Popescu M., Manea S., et al., Antioxidant activity and phyto-therapeutic properties of gemmo-derivatives obtained from *rosmarinus officinalis, vaccinium myrtillus, salix alba*, *ribes nigrum*, and *betula pubescens* (2016) Revista de Chimie, **67**(10), 1936-1939.

[14.] Popescu M., Puiu D., Raiciu A.D., Comparative study of alpha and beta- pinene content in volatile oils of *abies alba, pinus sylvestris, juniperus communis, rosmarinus officinalis, salvia officinalis* and *coriandrum sativum*, (2018) Revista de Chimie, **69**(9), 2338-2342.

[15.] Cirstoiu, C., Ene, R., Panti, Z., et al., Particularities of shoulder recovery after arthroscopic bankart repair with bioabsorbable and metallic suture anchors, (2015), Materiale Plastice, 52(3), 361-363.

[16.] Ene, R., Panti, Z., Nica, M., et al., Chondrosarcoma of the pelvis - case report, (2018), Romanian Journal of Morphology and Embryology, **59**(3), 927-931

[17.] Ionescu R; Mardare M; Dorobantu A; Vermesan S; Marinescu E; Saban R; Antoniac I; Ciocan DN; Ceausu M; Correlation between materials, design and clinical issues in the case of associated use of different stainless steels as implant materials, Key Engineering Materials, **583**, 41-44, 2014

[18.] Ionescu R; Cristescu I; Dinu M; Saban R; Antoniac I; Vilcioiu D; Clinical, biomechanical and biomaterials approach in the case of fracture repair using different systems type plate-screw, Key Engineering Materials, volume 583, pages 150-154, 2014

[19.] Miller WS, Zhuang L, Bottema J, Witterbrood AJ, De Smet P, Haszler A, Vieregge A. Recent development in aluminum alloys for the automotive industry. Mater sci eng a 2000;280:37–49.

[20.] Von Zengen K-H. Aluminum in future cars-a challenge for materials science. Mater sci forum 2006;519–521:1201–8.

[21.] Hirsch J. Recent development in aluminum for automotive applications. Trans nonferrous Met Soc China 2014;24:1995–2002.

[22.] Shah RK, Sekulic´ DP. Fundamentals of heat exchanger design. John Wiley & sons inc.; 2003.

[23.] Tait RD, Rogers CJ, Cottone AJ, Henkes JP, Saperstein ZP. Corrosion resistance of the as brazed pf heat exchanger as achieved by alloy selection. Warrendale, Pa: Society of Automotive Engineers [SAE]; 1991. SAE technical paper 910594.

[24.] Meijers SD, Calcedo Martinez CE, Desikan S. Tube-fin interaction – a closer look at the corrosión mechanism. Warrendale, Pa: Society of Automotive Engineers [SAE]; 2005. SAE technical paper 2005-01-2027.

[25.] Ishikawa K, Kawase H, Koyama H, Hasegawa Y, Negura K, Nonogaki M. Development of pitting corrosion resistant condenser with zinc-arc-spray extruded multi-cavity tubing. Warrendale, Pa: Society of Automotive Engineers [SAE]; 1991. SAE technical paper 910592.

[26.] Shi Q, Liang F, Cheadle B. Electrochemical behaviors of quad-layer aluminum brazing sheet composite for automotive application. Corrosion 2004;60:492–500.

[27.] Yoon S, Kim H, Lee Ch. Fabrication of automotive heat exchanger using kinetic spraying process. Surf Coat Technol 2007;201:9524–32.

[28.] Schäuble K. Silica passivation layer on aluminium brazing sheets [doctoral dissertation]. University of Köln; 2010.

[29.] Brett CMA. The application of electrochemical impedance techniques to aluminum corrosion in acidic chloride solutions. J Appl Electrochem 1990;20:1000–3.

[30.] Lenderink HJW, Linden MVD, De Wit JHW. Corrosion of aluminum in acidic and neutral solutions. Electrochim Acta 1993;38:1989–92.

[31.] Metikoš-Hukovic´ M, Babic´ R. Impedance spectroscopic study of aluminum and Al-alloys in acid solution: inhibitory action of nitrogen containing compounds. J Appl Electrochem 1994;24:772–8.

[32.] Garrigues L, Pebere N, Dabosi F. An investigation of the corrosion inhibition of pure aluminum in neutral and acidic chloride solutions. Electrochim Acta 1996;41:1209–15.
[33.] Metikoš-hukovic´ M, Babic´ R, Grubacˇ Z. The study of aluminum corrosion in acidic solution with nontoxic inhibitors. J Appl Electrochem 2002; 32:35–41.