POLYTECHNIC UNIVERSITY OF BUCHAREST
FACULTY OF MATERIALS SCIENCE AND ENGINEERING

Author: Eng.LAZĂR (NATRĂ) CLAUDIA ALINA

PHD THESIS SUMMARY

STUDIES AND EXPERIMENTAL RESEARCH ON THE MECHANICAL AND CORROSION RESISTANCE OF ALUMINUM BRAZED ALUMINUM ALLOYS FOR HEAT EXCHANGES IN THE AUTOMOTIVE INDUSTRY

PhD supervisor: Prof. habil. dr. eng. Brânduşa GHIBAN

BUCHAREST 2022

THANKS

First of all, I would like to thank the scientific director, Mrs. Prof. Ph.D. **Brânduşa GHIBAN**, for the guidance, support and help provided during the entire research period, as well as the successful completion of the entire doctoral thesis. I also thank him for the good mood and sincerity with which he guided me on this path.

Special thanks to Mr. Prof.univ.dr.ing. **Cristian PREDESCU**, from the Faculty of Materials Science and Engineering, from the Materials Processing and Ecometallurgy department, who was my mentor during my years of study and guided my steps towards my current professional career.

Secondly, I thank the management of ALRO S.A. Slatina, especially to the general manager dr.eng. **Gheorghe DOBRA** for the trust and support received during the elaboration of this thesis, for the special possibility to carry out and complete the experimental researches. I would also like to thank Mrs. **Luxandra MARIN**, Head of Physical-Mechanical Testing Laboratory, at ALRO S.A. Slatina, for the relentless help in achieving and interpreting the results of the complex statistical analysis.

My thoughts are directed to Mrs. Prof.dr.ing. **Ioana CSAKI**, a chosen man, who directed my steps towards the realization of this doctoral thesis.

I also send respectful thanks to Prof. **Ionelia VOICULESCU,** PhD, from the Faculty of Industrial Engineering and Robotics, from the Polytechnic University of Bucharest, for the unconditional support provided in the structural investigation of the scanning electron microscope and for the help granted in the interpretation of structural analyzes.

I thank the staff of the Department of Metallic Materials Science, Physical Metallurgy - UPB, professors **Florin MICULESCU**, **Dan GHEORGHE**, **Mihai BRÂNZEI**, **Marian MICULESCU**, for the good collaboration and expertise in the investigation of metallic materials based on aluminum.

I thank the distinguished professor of scientific references for their kindness in accepting this work and for their appreciation of the doctoral thesis.

And, last but not least, dear thanks to my wonderful family, husband and child, as well as parents, for their support, trust and motivation, and also for their time.

CONTENT

INTRODUCTION

The progress made in the development of humanity has always been based on spectacular discoveries in the field of materials and their performance, each stage of which is marked by a major leap in the field of materials in general, metallic materials in particular. In the automotive industry, the competition of materials is constantly intense, meeting the requirements for improving passenger safety being in balance with concerns related to global warming, respectively reducing emissions from vehicles. One material in constant attention is aluminum and its alloys. The use of aluminum in automotive applications has increased by over 80% in the last 5 years. Modern high-performance cars use heat exchangers made of aluminum alloys, whose market share has grown dramatically, the brazed sheet being the main point in niche products. Research over the last decade has focused mainly on the development of so-called "long-life" alloys, in order to increase the reliability of these components.

Looking at these aspects, namely aluminum alloys and the possibility of exploring their properties, this doctoral thesis is part of current concerns.

The general objectives of the doctoral thesis consist in the following aspects:

• Identification of the possibilities to improve the mechanical behavior and corrosion resistance of the plated sheets of aluminum alloy type 3003, with different alloys from the 4xxx series by optimizing the applied heat treatments, respectively:

• Temporal, statistical analysis of the evolution of the mechanical characteristics for the products of aluminum alloy type 3003 plated with 4xxx alloy depending on the manufacturing characteristics

• Identification of the main structural characteristics of type 3003 aluminum alloy sheets, in different structural states, plated with different alloys from the 4xxx series

• Determining the corrosion behavior of aluminum alloy plated sheets type 3003, with different alloys from the 4xxx series, respectively:

In order to meet the proposed objectives, both statistical analyzes and structural investigations were performed on specimens from ALRO Slatina, sheets of aluminum alloys type 3003, in different structural states, dimensions and types of joints by brazing with alloys from series 4xxx . The thesis includes 6 chapters, as follows:

Chapter 1, entitled "Current state of research in the field of aluminum alloys for heat exchangers" is intended to present the main aspects related to the development of aluminum alloys in the automotive industry. The main applications of aluminum alloys in the automotive field are presented, respectively car body applications, applications for interior or exterior panels, ending with the applications of brazed sheets. Future trends in lightweight materials in the automotive industry are presented. A subchapter is intended to present the most important brazing elements of aluminum alloys, brazing processes, the properties of brazed joints, ending with examples of applications of heat exchangers for automobiles. The chapter ends with the main elements related to the corrosion behavior of heat exchangers.

Chapter 2 is intended to present the experimental materials and procedures used during the experimental research, which ended with the presentation of the experimental program.

Chapter 3 is entitled 'Studies and experimental research on the evolution of mechanical properties for 3003 aluminum alloy products plated according to their manufacturing characteristics'. After the presentation of the theoretical starting elements, a statistical analysis of the products made of 3003 plated aluminum alloy is performed according to thickness, plating alloy, plating percentage, finally presenting the evolution of mechanical characteristics for 3003 plated aluminum alloy products in different structural states, in a presentation also through a complex statistical analysis. The statistical analysis used in the quality control of the products was performed with the help of two types of diagrams: a control diagram of the variables (X-Chart) and a control diagram of the amplitudes (variations between determinations) (R-Chart), being presented diagrams for tensile strength, yield strength and elongation corresponding to type 3003 alloy sheets, in different structural states and material thicknesses. Finally, CPK capability and PPK performance indices are used, which allow a complete and reliable evaluation of the mechanical characterization of the performance of 3003 alloy plated products, from the production of ALRO Slatina. The chapter ends with obtaining a regression equation, which is valid for Si ϵ [0.07 0.60%], Fe ϵ [0.10 - 0.70%], Cu ϵ [0.05 - 0.75 / 0] Mn ϵ (0.18 1.5%).

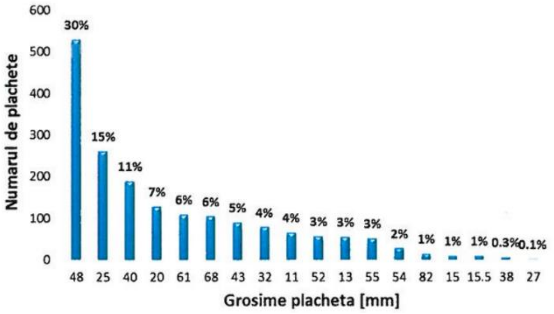
Chapter 4 is entitled "Experimental research on the optimization of heat treatments applied to 3003 alloy plated products". After the presentation of the motivation that determined the start of these experiments, the experimental researches on the possibilities of lowering the temperature of the intermediate heat treatment are presented, in order to decrease the specific consumptions. The experiments in laboratory conditions were confirmed by tests in industrial regime, which determined the obtaining of values of mechanical characteristics with approximately 5MPa higher than those for which the heat treatment was performed in laboratory conditions. For elongation, the values for which the heat treatment was performed industrially are lower by approx. 6%. The last subchapter is intended for experimental research on the possibilities of improving the performance indicators of heat treatment furnaces.

Chapter 5 is entitled "Experimental research on the structural characterization of type 3003 aluminum alloy sheets coated with 4xxx series alloys." The complex structural analysis allowed the identification of structural changes of 3003 aluminum alloy products (in different layers), brazed with different types of aluminum alloys from the 4xxx series, respectively: determining the grain size before and after simulating the brazing process, determining the distribution phases, determining the thickness of the cladding layer and identifying the “brown band” area, ie quantitative and qualitative structural elements that define this area. Finally, a comparative analysis of the grain size values of the 3003 alloy sheets plated with different alloys from the 4xxx series is performed, which shows that after simulating the brazing process at 600°C / 10 minutes in all situations the grain size of was up to 80□m (ie class 4.5 according to ASTM E112), and by increasing the maintenance time to 1 hour the grain size is finished, having values over 80μm (class 4 according to ASTM E112).

Chapter 6 is entitled "Corrosion behavior of aluminum alloy sheets type 3003 brazed with 4xxx series alloys". Preliminary research includes investigations into the corrosion potentials of different classes of aluminum alloys, highlighting the influence of copper and zinc content on corrosion potential values. Research on the determination of corrosion potentials of alloy type 3003 plated with 4xxx series alloys, in different states of the sheet surface have highlighted the influence of potential values depending on the delivery state, the state of chemical surface cleaning or post-brazing state. Finally, a case study on the structural investigation of the fins of a radiator from a decommissioned tractor after 6 years is presented.

CHAPTER 3
STUDIES AND EXPERIMENTAL RESEARCH ON THE EVOLUTION OF MECHANICAL CHARACTERISTICS FOR 3003 PLATED ALUMINUM ALLOY PRODUCTS ACCORDING TO MANUFACTURING CHARACTERISTICS

3.2. Statistical analysis of products made of 3003 plated aluminum alloy by thickness, plating alloy, plating percentage



The analysis regarding the products made of 3003 plated aluminum alloy was performed for the period 01.11.2016 ÷ 31.10.2017. Data for this analysis were extracted from the Centralizer application. Figure 3.4 shows the structure of the plates made according to their thickness. Thus, most of the plates made (528) had a thickness of 48 mm and correspond to a cladding percentage of 10%.

FIG. 3.4. The structure of the platelets made during 01.11.2016 ÷ 31.10.2017 depending on the thickness

The distribution of the quantity delivered by the LTB section according to the type of alloy for the analyzed period is represented in fig. 3.5.

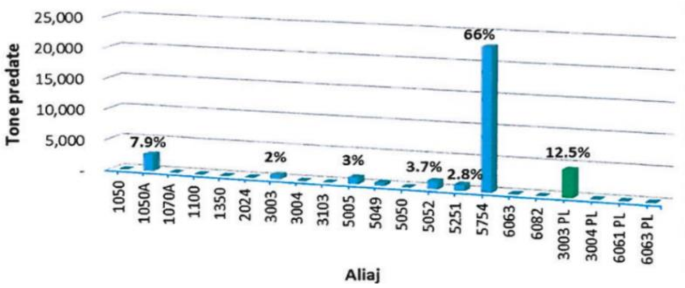


Figure 3.5. The structure of the delivered quantity takes the LTB section depending on the type of alloy for the period 01.11.2016 - 31.10.2017

For the analyzed period (01.11.2016-31.10.2017), for each plated product delivered, the quantity represented by the plating alloy was calculated according to the plating percentage. The data obtained are presented in table 3.4. Thus, for the analyzed period (01.11.2016 -31.10.2017) the most used plating alloys for obtaining plated products were the alloys 4004 (214 t - 39%) and 4045P1 (202 t - 37%). depending on the quantity delivered for the plated products, base alloy 3003, were: 0.8 mm; 2.5 mm; 0.6 mm; 1.5 mm.

3.3. Evolution of mechanical characteristics for 3003 aluminum alloy products plated in different structural states

In the European standard EN 485-2 [4] for coated products there are no values imposed for the mechanical characteristics (breaking strength - Rm, yield strength - Rp0.5 and elongation - A50mm), most often for these products it is required by customers the classification of plated products within the values imposed for the 3003 alloy specified in the standard. It should be noted that in the American standard ASTM B209 [5] are specified values imposed for the mechanical characteristics for both alloy 3003 and plated alloys (Table 3.6).

Table 3.6. Mechanical characteristics for alloy products 3003 and 3003 PL, state 0, standard EN vs. ASTM

EN 485-2	ASTM B209

3003, Temper 0						3003, Temper 0						Alclad 3003, Temper 0					
Thickness [mm]		**Rm** [MPa]		**Rp** [MPa]	**A** [%]	**Thickness** [mm]		**Rm** [MPa]		**Rp** [MPa]	**A** [%]	**Thickness** [mm]		**Rm** [MPa]		**Rp** [MPa]	**A** [%]
0.2	0.5	95	135	35	15	0.15	0,2	96.5	131	34	5	0.15	0.2	90	124	31	4.5
0.5	1.5	95	135	35	17	0.2	0.3	96.5	131	34	5	0.2	0.3	90	124	31	4.5
1.5	3	95	135	35	20	0.3	0.8	96.5	131	34	5	0.3	0.8	90	124	31	4.5
3	6	95	135	35	23	0.8	1.3	96.5	131	34	5	0.8	1.3	90	124	31	4.5
6	12.5	95	135	35	24	1.3	6.3	96.5	131	34	5	1.3	6.3	90	124	31	4.5
12.5	50	95	135	35	23	6.35	76.2	96.5	131	34	5	6.35	12.7	90	124	31	4.5
												12.7	76.2	96.5	131	34	

There are minor differences of the two standards between the values imposed for Rm and Rp0,2 for alloy products 3003, state 0, instead for elongation the minimum value imposed in the EN standard is 15% and in the ASTM standard 5%.

For 3003 PL alloy products the required values for mechanical properties are lower (3 ÷ 7 MPa) than for 3003 alloy products.

The statistical analysis used in product quality control was performed using two types of diagrams: a variable control diagram (X-Chart) and an amplitude control diagram (variations between determinations) (R-Chart), being the most commonly used within the industrial statistical control. The control diagram of the variables is a graphical representation of the variation between the means of the subgroups, and the diagram of the variations between the determinations, analyzes the variability within these subgroups. The variation within the subgroups is represented by the interval. The range of values for each subgroup is plotted on the Y axis of the R diagram. The center line is the mean or mean of the interval. The control limits on the graphs are given by the following formulas: The results of the complete statistical analysis are presented comparatively in table 3.8.

Table 3.8. Summary of mechanical properties (Rm, Rp0.2, A50) of 3003 alloy plated sheets, in different states and thicknesses

Valori	Stare O/ 0,5mm			Stare H14 / 0,5mm			Stare O/ 0,5mm			Stare O/ 2,5mm			Stare H14 / 0,5mm		
	Rm	$Rp_{0,5}$	A_{50}	Rm	$Rp_{0,5}$	A_{50}	Rm	$Rp_{0,5}$	A_{50}	Rm	$Rp_{0,5}$	A_{50}	Rm	$Rp_{0,5}$	A_{50}
Limita inferioară specificată (LSL)	95	34	15	145	125	2	95	35	17	95	35	20	145	125	3
Limita superioară specificată (USL)	130	-	-	185	-	-	135	-	-	135	-	-	185	-	-
Min	95	49	15	146	126	2,8	98	45	28	101	58	30,5	149	144	5
Max	121	80	49,5	173	164	12,5	130	84	49,5	112	72	50,5	174	163	10,5
Mean	107,97	58,04	32,72	159,34	147,62	7,04	108,16	58,18	41,68	105,95	63,29	45,57	159,93	152,5	6,73
Median	107	56,5	32,5	158	147	7,00	108	57	42,5	106	62	46	160	154	6,5
Mode	107	55,00	29	158, 157	143	5,5	110	57	45	101	61	46	159	158	6,5
Stdev	4,53	6,28	5,36	6,84	8,91	1,97	5,03	6,77	4,22	2,98	4,33	3,79	6,96	5,59	1,47
Cpk	3,15	4,27	3,15	2,7	3,66	2,19	4,92	3,69	4,83	6,78	9,31	6,12	6,55	7,24	3,57
Ppk	0,95	1,28	1,10	0,7	0,85	0,85	0,87	1,14	1,95	1,23	2,18	2,25	0,71	1,64	0,84

- The detailed analysis of all the data regarding the statistical behavior of the values of the mechanical characteristics of the 3003 alloy sheets in different delivery states (state O and state H14) and different sheet thicknesses (0.5mm / 0.97mm / 2.5mm) shows that the processes considered are stable (in control) in the sense that all X and R values in the control sheets are within the control limits and there are no specific trends. The stability of a process is particularly important, because a stable process today is very likely to remain stable in the future, if there are no major changes in its evolution. Thus, if a process is stable, it is very likely that its capability will also be predictable based on previous performance.

- Analyzing the data in terms of CPK performance index values, it is noted that in all situations (fig.3.57) this index is much higher than 1.33 / /, which means that the processes are stable with a normal distribution of values.
- • PPK capability index values are much lower than CPK.
- • The distribution of elongation values (in state O, at thickness 0.97- with the value of PPK capability index 1.95 and state O thickness 2.5- with the value of PPK capacity index 2.25 mm) has a value higher than 1.67, which indicates that this characteristic is in a state of statistical control (ie PPK ≥ 1.67 and Cpk≥ 1.33).
- • The fact that for the other characteristics the value of the PPK≤ capability index 1.67, and yet the process is stable, means that there must be improvements in the process through various corrective measures until continuous stability is achieved.
- The complete statistical analysis performed on the values of the mechanical characteristics of the 3003 alloy plated sheets, in different delivery states and different thicknesses showed that the applied technological processes led to obtaining appropriate mechanical characteristics, without deviating from the tolerance limits, with high reproducibility and stability. At the same time, the additional use of the CPK capability and PPK performance indices allowed a complete and reliable evaluation of the mechanical characterization of the performances of the 3003 alloy plated products, from the ALRO Slatina production.

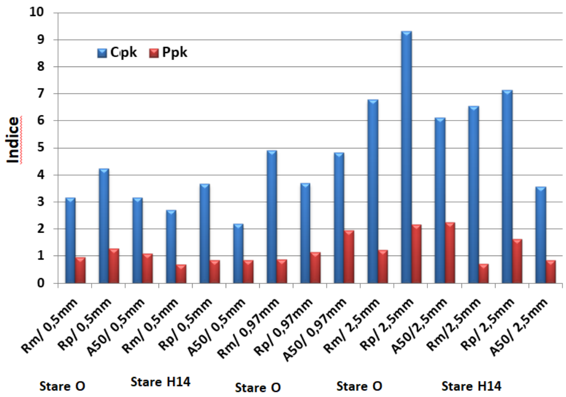


FIG. 3.57- The values of the capacity and performance indices for the mechanical characteristics of the products from 3003, after the statistical processing (in state O and state H14, and different thicknesses of the plated sheets)

Finally, to determine a correlation between a dependent value (respectively breaking strength Rm, in this case) and a lot of independent values (chemical composition, process parameters, etc.) we used the method of least squares [6].

Depending on the value of the coefficient of determination obtained, it can be determined whether or not there is a correlation between the main manufacturing characteristics and the mechanical properties. Thus, its value is in the range from 0 to 1. If it is 1, there is a perfect correlation in the sample. At the other extreme, if the coefficient of determination is 0, the regression equation obtained will not be useful.

For this analysis we considered the products obtained from aluminum alloy 3003 PL for the period January 2016 - October 2017 (approx. 700 lots), state O. For the products from alloy 3003 PL, state 0, we have:

$Rm = 90.81 + 9.15 \cdot Si + 6.37 \cdot Fe + 60.26 \cdot Cu + 5.48 \cdot Mn$ (3.1)

with a value of the coefficient of determination of 0,90, without excluding data from the analysis.

Equation (3.1) is valid for Si ϵ [0.07 0.60%], Fe ϵ [0.10 - 0.70%], Cu ϵ [0.05 - 0.75 / 0] Mn ϵ (0, 18 1.5%).

CHAPTER 4
EXPERIMENTAL RESEARCH ON THE OPTIMIZATION OF HEAT TREATMENTS APPLIED TO PLATED ALLOY PRODUCTS TYPE 3003

In order to increase the productivity of the heat treatment furnaces within the LTB section, tests were initially performed in laboratory conditions in order to optimize the heat treatments for the 3003PL alloy sheet rolls. Table 4.1 shows the annealing treatments that are currently used in the LTB section for obtaining 3003PL alloy sheets and strips, depending on the metallurgical conditions. Also for each state were presented the limits imposed for the mechanical characteristics, according to the standard EN 485-2: 2009.

Temper	Intermediate heat treatment	Final heat treatment	Rm [MPa]	$Rp_{0,2}$ [MPa]	A* [%]
O	-	415 °C/ 3h	95 — 135	35	23
H12	415 °C/ 3h	190 °C/ 3h	120 — 160	90	6
H14	415 °C/ 3h	190 °C/ 3h	145 — 185	125	4
H16	415 °C/ 3h	190 °C/ 3h	170 — 210	150	2
H22	415 °C/ 3h	190 °C/ 3h	120 — 160	80	9
H24	415 °C/ 3h	190 °C/ 3h	145 — 185	115	6

Table 4.1. Annealing treatments used in the LTB section and the characteristics required by the standard for different states of alloy products 3003

*** Only values for thicknesses greater than 3 mm have been entered. These values are also implicitly checked for smaller thicknesses**

In order to obtain the soft state (O), a single final treatment of total annealing is performed, respectively at the parameters 415 ° C / 3h. In order to obtain states H12, H14, H16, H22 and H24, the following is performed:

• a partial annealing treatment at parameters 415 ° C / 3h which has the role of relaxing the laminated material in order to be subjected to new cold rolling passes, as well as to obtain the mechanical characteristics according to the specifications in the customer's standards or requirements;

• a final drying heat treatment at 190 ° C / 3h.

The detailed analysis of the mechanical properties in Table 4.1 allows the formulation of two relevant observations:

- on the one hand, the study of the possibilities of lowering the temperature of the intermediate heat treatment (from 415 ° C / 3h to lower values), in order to reduce the specific consumptions, the lower temperature being sufficient to obtain the soft state,
- on the other hand, since the limits imposed for the mechanical properties (Rm, Rp0.2 and A_{50mm}) imposed for states H12 and H24 are identical, to study the possibility of using a single heat treatment of partial annealing (for example at 275 ° C / 3h).

4.2 Experimental research on the possibilities of lowering the temperature of intermediate heat treatment, in order to reduce specific consumptions

The experiments were performed in the Laboratory of Physico-Chemical Tests of Processed Aluminum. For this, samples were taken from the roll no. 2175, lot no. 46001, alloy 3003P7 plated with 4343P2, 4%, 1 side, thickness 0.5 mm, Before the final heat treatment of total annealing. The sampling was performed at the Salico slider. The chemical compositions of the casting batches used to obtain the roll no. 2175 are shown in table 4.2.

At the thickness of 1.50 mm the cutting operation was performed at the edges, and at the thickness of 0.50 mm the roller was subjected to the operation of straightening by stretching, followed by the operation of files in strips with a width of 96.7 mm during the operation of files with samples measuring 0.5x30x250mm were taken to determine the mechanical characteristics and simulate the annealing treatment in the laboratory at different parameters.

Alloy	Standard	Limits	Si	Fe	Cu	Mn	Mg	Cr	Ni	Zn	Ti
3003P7	SP 13 Rev. 13/2016	min.	-	-	0,05	1,0	-	-	-	-	-

		max.	0,6	0,7	0,20	1,5	0,01	-	-	0,10	-
	51503523/5 - Achieved		0,29	0,43	0,08	1,23	0,003	0,004	0,007	0,007	0,015
4343P2	SP 13 Rev. 13/2016	min.	6,8	-	-	-	-	-	-	-	-
		max.	8,2	0,8	0,25	0,10	0,05	-	-	0,20	-
	S15090904/5 - Achieved		6,99	0,25	0,005	0,024	0,002	0,007	0,007	0,005	0,012

Table 4.2. Chemical compositions of batches used to obtain material 433P7 plated with 4343P2

Operation technological	Input thickness [mm]	Output thickness [mm]	Reduction per step [%]	Total reduction [%]
Lamination step 1	7,50	4,50	40	40
Lamination step 2	4,50	2,50	44,44	66,67
Lamination step 3	2,50	1,50	40	80
Lamination step 4	1,50	1,00	33,33	86,67
Lamination step 5	1,00	0,70	30	90,67
Lamination step 6	0,70	0,50	28,57	93,33

Table 4.3. The discounts applied to the roll no. 2175, for obtaining the alloy 3003P7 plated with 4343P2, 4%, 1 side, thickness 0.5mm, condition O

The mechanical characteristics of the samples taken before the final heat treatment of total annealing and to which different heat treatments were performed in the laboratory are shown graphically in Fig. 4.4, 4.5, and 4.6.

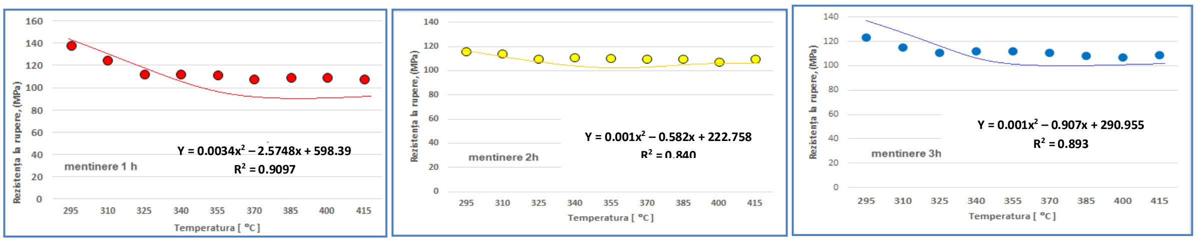


Fig.4.4- Variation of breaking strength depending on temperature and heat treatment time applied to 3003 alloy sheets plated with 4343, thickness 0.5mm, 1 side

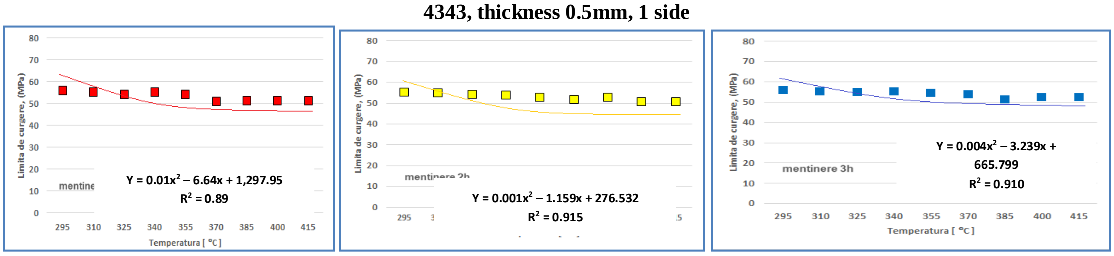


Fig.4.5- Variation of the flow limit depending on the temperature and time of the heat treatment applied to the 3003 alloy sheets plated with 4343, thickness 0.5mm, 1 side

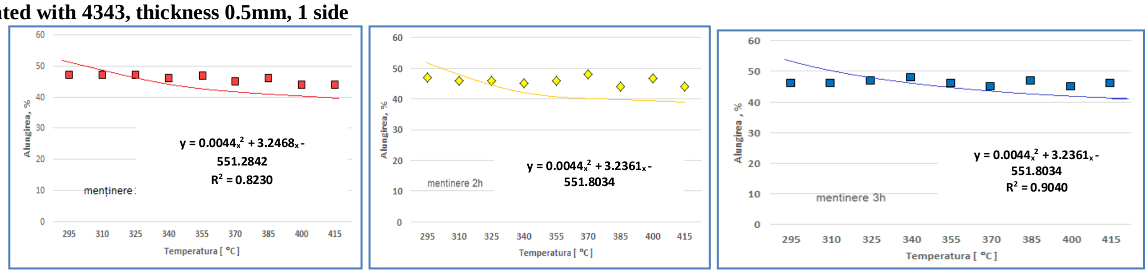


Fig.4.6- Elongation variation depending on temperature and heat treatment time applied to 3003 alloy sheets plated with 4343, thickness 0.5mm, 1 side

From the analysis of the results (Fig. 4.4, fig. 4.5 and fig.4.6) it is observed that almost all the values obtained for the mechanical characteristics, except those recorded for the treatment performed at a temperature of 290 ° C, fall within the limits imposed by the EN 485 standard. : 2-2009 for alloy products 3003 state O, respectively for Rm values were obtained between 95 ÷ 135MPa, for Rp0.2 the values are strictly higher than 35MPa, and for elongation the values obtained were strictly higher than 23% . It should be noted that the regression analysis performed to determine the influence of temperature on the values of mechanical properties determined the second degree equations, which were inserted for each case. The statistical analysis performed to verify the correctness of the heat treatments was performed excluding the extreme values, ie the values of the mechanical characteristics corresponding to the holding temperature of 290 ° C. The results of the statistical analysis are presented in table 4.7. It is observed that the values obtained for the mechanical characteristics are concentrated around the average values, the difference between the maximum and minimum value determined for Rm, respectively Rp0.2 being 6MPa. Also for elongation the amplitude of the values is 7.5%. The concentration of the mechanical characteristics determined around the mean values is also indicated by the low values obtained for the standard deviation: 1.7 for each of the characteristics Rm, Rp0.2 and A50 rnm which represents a measure of the dispersion of the values around the mean. For alloy 3003PL4343, the annealing treatment was simulated in the laboratory at 340 ° C / 4h, taking into account the fact that for 6063PL alloy products this treatment is performed industrially and the rollers could be loaded in the same batch, thus avoiding the creation of a new treatment. annealing. The results obtained (Table 4.6) are within the limits imposed by the standard EN 485: 2-2009 for alloy products 3003, state O.

Indicator statistic	Rm [MPa]	$Rp_{0.2}$[MPa]	$A_{50\ mm}$ [%]
Min	107	50	41
Max	113	56	48,5
Medie	109,9	53,1	46,0
Abaterea standard	1,7	1,7	1,7
Amplitudinea	6	6	7,5

Table 4.7. Statistical indicators for the mechanical properties obtained for the alloy 433 plated with 4343, 1 side, thickness 0.5mm, following the simulations performed in the laboratory, except for the treatment performed at a temperature of 290^0 C

The metallographic results regarding the determination of the grain size resulted by the application of the two heat treatments in laboratory conditions, respectively 415°C / 3h and 340°C / 4h are summarized in table 4.8.

Proba	Mărimea medie de grăunte [μm]	Clasa conform ASTM E 112
recoacere la 415 °C/3h	35,56	6.5
recoacere la 340 °C/4h	33,01	7.0

Table 4.8. Average grain size for alloy samples 3003PL 4343, 4%, 1 side, thickness 0.5mm, subjected to different heat treatment parameters

The samples were prepared on the L-LT (flat) section. The results indicate a slightly finer granulation (class 7.0) for the material subjected to the annealing heat treatment at parameters 340 ° C / 4h compared to the material subjected to the heat treatment at parameters 415 ° C / 3h, where the class 6.5 was obtained according to ASTM E 112 .

INDUSTRIAL TESTING

In order to validate the laboratory results, the values obtained in the laboratory at the parameters 415°C / 3h were compared with those obtained industrially at the same parameters. Roll no. 2175, lot no. 46001, alloy 3003P7 plated with 4343P2, 4%, 1 side, thickness 0.5 mm was subjected to the final heat treatment of total annealing in the SecoWarwick furnace no. 3.

Material status	Mechanical characteristic					
	Rm, [MPa]		$R_{p0,2,}$ [MPa]		$A_{50\ mm}$ [%]	
annealing 415°C/3h – in industrial conditions	112	114	55	57	38,5	42,5
annealing 415°C/3h – under laboratory conditions	109	109	53	52	46	45,5

Table 4.9. Mechanical characteristics for the same material (3003PL4343) In different final heat treatment conditions

According to the results in table 4.9, no major differences were obtained between the two determinations for the same material. Thus the values obtained for Rm and Rp0.2 in industrial conditions are approx. 5 MPa higher than those for which the heat treatment was performed in laboratory conditions. For elongation, the values for which the heat treatment was performed industrially are lower by approx. 6%.

4.3. Experimental research on the possibilities of improving the performance indicators of heat treatment furnaces

The research experiments were performed in the Laboratory of Physico-Chemical Testing Aluminum Processed. For this, samples were taken from an experimental roll, alloy 3003P8 plated with 4343P2, 4%, 1 face, thickness 0.5 mm, before performing the final heat treatment of total annealing. The sampling was performed at the Salico slider. The chemical compositions of the casting batches used to obtain the experimental roll are given in Table 4.10.

Alloy	Standard	Limits	Si	Fe	Cu	Mn	Mg	Cr	Ni	Zn	T
3003P8	SP 13 Rev. 13/2016	min.	-	-	0.05	1.0	-		-	-	-
		max.	0,6	0,7	0,20	1,5	0,05	-	-	0,10	-
	experimental		0,25	0,43	0,09	1,30	0,002	0,001	0,01	0,008	0,016
4343P2	SP 13 Rev. 13/2016	min.	6,8	-			-		-		-
		max.	8,2	0,8	0,25	0,10	0,05	-	-	0,20	-
	experimental		6,99	0,25	0,005	0,024	0,002	0,007	0,007	0,005	0,012

Table 4.10. Chemical compositions of batches used to obtain the material 433P8 plated with 4343P2

The roll obtained from hot rolling was subjected to the following cold reductions, as illustrated in Table 4.3.

At a thickness of 1.50 mm, the cutting operation was performed at the edges, and at a thickness of 0.50 mm, the roller was subjected to the stretching straightening operation, followed by the operation of striping into strips with a width of 96.7 mm. During the strip operation, samples with dimensions of 0.5x30x250mm were taken to determine the mechanical characteristics and simulate the annealing treatment in the laboratory at different parameters.

In order to simulate the industrial conditions in the laboratory, a 100 ° C / h ramp was used for the annealing treatment.

The mechanical characteristics of the samples taken before the industrial realization of the final heat treatment of total annealing and to which different thermal treatments were performed in the laboratory are graphically in Fig. 4.9. From the analysis of the results it is observed that only the values obtained for 260 ° C / 3h, 260 ° C / 4h and 270 ° C / 2h fall within the limits imposed by the standard EN 485: 2-2009 for alloy products 3003, state H14 and state H24.

Increasing the annealing temperature causes a decrease in breaking strength by:

- 1.61 MPa / ° C for a holding time of 2h;
- 1.34 MPa / ° C for a holding time of 3h;
- 1.28 MPa / ° C for a holding time of 4h.

It should be noted that the regression analysis performed to determine the influence of temperature on the values of mechanical properties determined the first degree equations, which were inserted for each case.

Thus, following the industrial researches, the following assessments can be made:

o The tests involved the simulation in the laboratory of the annealing heat treatment at different parameters, respectively the holding temperature varying from 290 ° C to 415 ° C, and the holding time from 1 hour to 4 hours.

o Following the tests performed, it is observed that almost all the values obtained for the mechanical characteristics, except those recorded for the treatment performed at a temperature of 290 ° C, fall within the limits imposed by the standard EN 485: 2-2009 for alloy products 3003 state O .

o The annealing treatment was also simulated in the laboratory at 340 ° C / 4h, taking into account the fact that for 6063PL alloy products this treatment is performed industrially and the rollers could be loaded in the same batch, thus avoiding the creation of a new annealing treatment. The mechanical characteristics obtained were within the limits imposed by the standard. For the grain size, a slightly finer granulation was obtained, class 7.0, than for the material subjected to the parameters 415 ° C / 3h, for which class 6.5 was obtained according to ASTM E 112.

o In order to validate the laboratory results, the values obtained in the laboratory at the parameters 415 ° C / 3h were compared with those obtained industrially at the same parameters. No major differences were obtained between the two determinations for the same material. Thus, the values obtained for Rm and Rp0,2 in industrial conditions are approximately 5 MPa higher than those for which the heat treatment was performed in laboratory conditions. For elongation, the values for which the heat treatment was performed industrially are lower by approx. 6%.

CHAPTER 5
EXPERIMENTAL RESEARCHES REGARDING THE STRUCTURAL CHARACTERIZATION OF ALUMINUM ALLOY TABLES TYPE 3003 PLATED WITH 4XXX SERIES ALLOYS

The purpose of this study is to identify structural changes in 3003 aluminum alloy products (found in different layers), brazed with different types of aluminum alloys from the 4xxx series, respectively: determining the grain size before and after simulating the brazing process, determining the distribution phases, determining the thickness of the cladding layer and identifying the “brown band” area, ie quantitative and qualitative structural elements that define this area. The following chapter will present the most important structural aspects, on different joints by brazing.

5.1 Microstructural analysis of 3003 aluminum alloy plating layers with 4045 aluminum alloy

This subchapter presents the results of the structural analysis on brazed welded joints of alloy 3003 with alloy 4045, which has a silicon level close to the eutectic concentration level of about 9 ÷ 11%. In order to determine the grain size, samples were prepared from brazing of sheet metal 3003 plated with 4045, both in longitudinal section and in cross section, before brazing. The analyzed samples showed a texture with elongated grains, with diffuse grain boundaries, of the "pancake" type.

Zona	Microcompozitie locală, % masic				
	Mg	Si	Mn	Fe	Zn
20	1,69	13,53	1,15	8,68	1,72
25	1,55	13,49	1,14	5,62	1,65
30	1,55	12,65	1	1,74	1,67
40	1,55	3,3	1,32	0,31	1,55
50	1,47	2,1	4,75	2,38	0,25
60	1,33	2,42	6,04	3,09	0,36
70	1,52	1,05	5,81	0,87	0,32

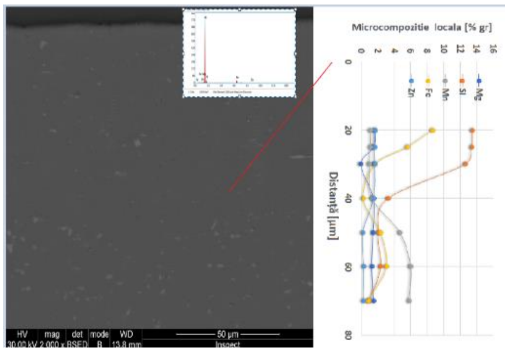


FIG. 5.6- Scanning electron microscopy (SEM) analysis of 30045-plated 3003 alloy specimens, indicating the local microcomposition and its distribution in cross section

Identification of the “brown band” area - after simulating the brazing process was highlighted by microstructural analysis, with spectacular results presented in fig. 5.8 and FIG. 5.9. Thus, on 3003 alloy specimens plated with 4045, in H24 state, with a thickness of 0.6 mm, aspects of the brazing simulation process were highlighted, at a temperature of 600˚C, for 10 minutes, to identify the area, , brown band ”(fig. 5.8). The maximum size of the “brown band” area was approximately 43.82µm (face A) and 48.08µm (face B), (fig. 5.9). The intergranular precipitated eutectic is noticeable in the brazing layer.

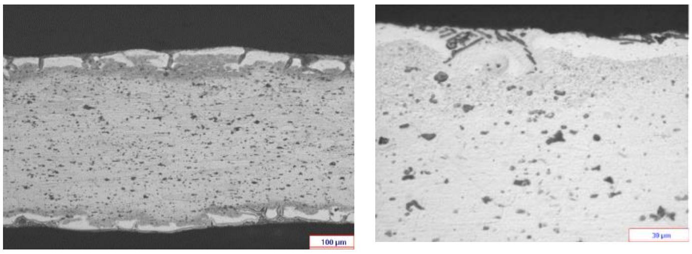


FIG. 5.8 Microstructural appearance of 3003 aluminum plated specimens with 4045 aluminum, condition H24, subjected to 600□ / 10 minutes (a- x100, b- x500)

After applying a brazing simulation process at a temperature of 600˚C, for 1 hour on specimens in the same state H24 with a thickness of 0.6mm, it was found that the thickness of the “brown band” area increased to 78.89µm (face A) and 83.26µm (face B).

The microstructural analysis performed on 3003 alloy plates plated with 4045, in state O, with a thickness of 0.6 mm, to identify the “brown band” area, after it has been subjected to the brazing simulation process is shown in fig. 5.10 for brazing at a temperature of 600˚C, for 10 minutes, respectively fig. 5.11 for brazing at 600˚C for 1 hour. Thus, if after brazing at 600˚C, for 10 minutes the maximum size of the “brown band” area was approximately 37.15µm (face A) and 41.52µm (face B) (fig. 5.10), after brazing at 600˚C, for 1 hour, the maximum size of the “brown band” area was approximately 74.31µm (face A) and 90.71µm (face B). It is thus noted that the simulation process performed on O-shaped specimens leads to unequal dimensions on both sides of the board in both simulation variants, either 10-minute maintenance or one-hour maintenance.

The analysis regarding the determination of the grain size, after the simulation of the brazing process is presented comparatively in table 5.1. Thus for the 3003 alloy specimens, plated with 4045, in H24 state, with a thickness of 0.6 mm, after applying the brazing simulation process, at a temperature of 600˚C, for 10 minutes, the average grain size was 79.25 µm (class 4.5, according to ASTM E112).

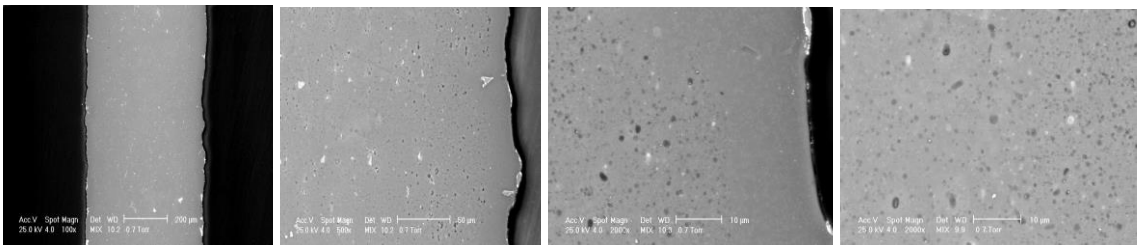
The same analysis for the determination of the grain size of the sheets from 3003, plated with 4045, but in state O, after the process of simulating the brazing, at the temperature of 600˚C, for 10 minutes, showed an average grain size was 79.10µm (class 4.5, according to ASTM E112), (fig. 5.14) and a grain size of grain was 87.27µm (class 4.0, according to ASTM E112), after increasing the duration of the brazing process at 1 hour, fig. 5.15.

Stare	Proces de simulare a brazării	Mărime medie de grăute, µm	Clasa ASTM E112	Figura
H24	600°C/10 minute	79,25	4,5	5.12
	600°C/1 oră	83,15	4	5.13
O	600°C/10 minute	79,10	4,5	5.14
	600°C/1 oră	87,27	4	5.15

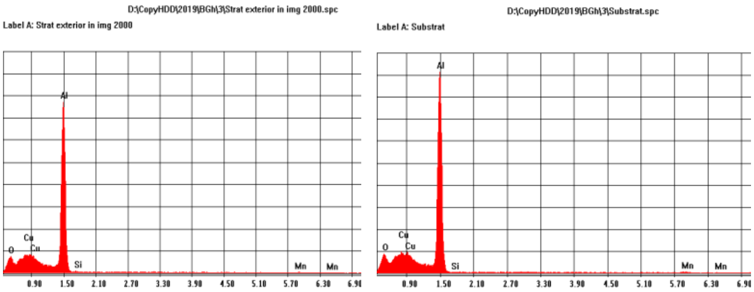
Table 5.1 Results of grain size analysis of 3003 alloy plated sheets with 4045 alloy, in different states and different holding times at 600°C

The observation can be noted after simulating the brazing process at 600°C / 10 minutes, regardless of the condition of the alloy 3003 (H24, or O) grain size of about 79µm (class 4.5), and by increasing the maintenance time at one hour, the grain size is finished, reaching about 85µm (class 4).

The analysis with the scanning electron microscope of the specimens after the simulation of the brazing process confirmed the change of the local microcomposition in the “brown band” area. Thus, in figure 5.16 we can see either the macroscopic aspect (fig.5.16a), or microstructural aspects in cross section at high magnification powers (fig. 5.16 b, c, d), with the highlighting of the change of the local microcomposition.



a b c d



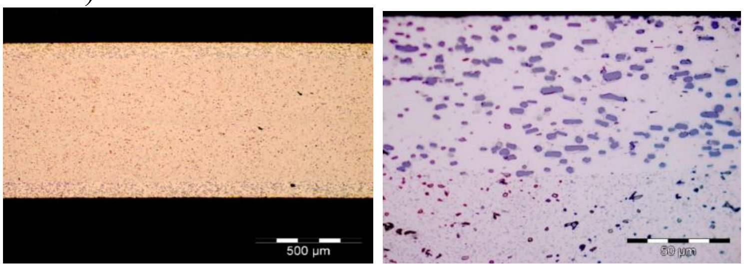
Zona	Microcompozitie locala % gr				
	Mg	Si	Mn	Fe	Al
1	1,11	12,09	0,85	13,36	72,59
2	1,00	14,42	1,27	6,65	76,69
3	1,22	2,3	1,24	6,50	88,75

Fig.5.16- Analysis by scanning electron microscope of the 3003 alloy specimen plated with 4045, after brazing, at 600 / 1h, indicating the local microcomposition

5.1 Microstructural analysis of 3003 aluminum alloy plating layers with 4343 aluminum alloy

In this subchapter are presented the results regarding the structural analysis on the welded joints by brazing of alloy 3003 with alloy 4343, which has a lower silicon level than the eutectic one, respectively of about 6.8 ÷ 8.2%.

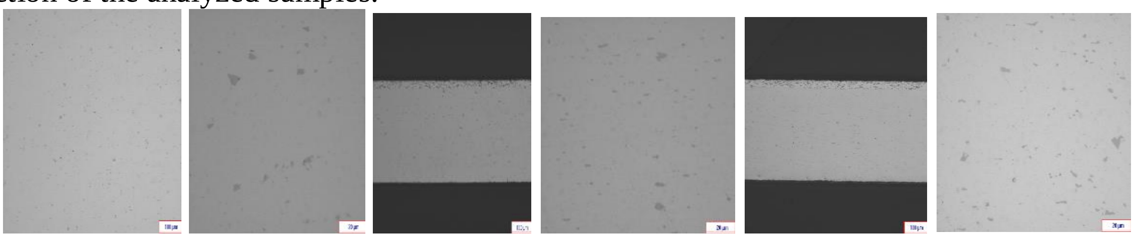
Figure 5.17 shows the microstructural aspect of alloy 3003 brazed with 4343, in cross section. There is a uniform distribution of precipitates both in the base material (respectively alloy 3003) and in the plating layers, alloy 4343 (upper and lower of similar thicknesses, of about 80□m).



a **b**

FIG. 5.17- The microscopic aspect of the cross section of alloy 3003 plated with 4343, in state O

The detailed microstructural analysis of the prepared samples from alloy 3003, plated with 4343, thickness 0.3 mm, is compared in figure 5.18. It is noted that both in the flat direction and in the longitudinal and / or transverse direction, there is a uniform distribution of the phases of MnAl6 and α (AlMnSi), most of the phases of MnAl6 and αAlMnSi are spherical, distributed relatively evenly, the precipitate (of Mn) is finely and uniformly distributed throughout the section of the analyzed samples.



a b c d e f

FIG. 5.18- The microstructural aspect of the specimens from 3003 plated with 4045, in state O, unattached, sections and magnifying powers (a, c, e x100; b, d, f- x500; a, b- flat section; c, d, cross section; e, f- longitudinal section)

The analysis under the scanning electron microscope (SEM) of the specimens of alloy 3003 plated with alloy 4045 is shown suggestively in figure 5.19. It is noted that the silicon content in the layer can reach up to 13.38% and can suddenly decrease in section over a distance of 30µm to 4.78%, reaching in the base material the content of alloy 3003, of about 1 -2% Yes.

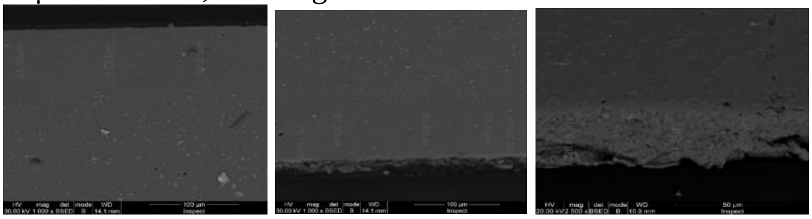


FIG. 5.19- Scanning electron microscope (SEM) analysis of 30043 alloy specimens plated with 4343, indicating the local microcomposition and its distribution in cross section

Detailed microstructural analysis of samples plated from alloy 3003, with alloy 4343, in state O, at a thickness of 0.3 mm, after the electrolytic attack showed in the base alloy, 3003 a structure with strongly elongated grains, strongly deformed in both directions (longitudinal and transverse), with diffuse grain boundaries.

By applying the different simulation parameters of the brazing process, according to the Behr specification, as indicated in table 5.3, the “brown band” areas could be identified. The microstructural aspect of the “brown band” areas is suggestively shown in fig. 5.22. The outer plating layer is noticeable, which consists of eutectic, with dendritic appearance and islands of solid solution , with a thickness of about 80µm. The “brown band” size for 3003LL alloy samples plated with 4343 thickness 0.3mm - cross section (LT-ST), subjected to brazing, according to Behr specification and electrolytically attacked, was between 27.37µm and 49.25 µm, with an average , made on 17 measurements of 38.43 µm, which represents 12.81% of the total thickness of the sheet of 0.3 mm, as shown in Figure 5.23.

The thickness of the plating layer (for the plated face) for the prepared samples (cross section, LT-ST) from sheet 433 plated with 4343, thickness 0.3 mm, is given in table 5.4, The value required for the thickness of the plating layer for the plated face is 8.5% ± 1.5%. It is found that the thickness of the plating layer (for the plated face) for all samples in the roll was within the required value of 8.5% ± 1.5%.

Table 5.3 Heat treatment parameters for simulating the brazing process applied to alloy plates 3003 plated with alloy 4343

Temperature – Duration of maintenance				
Heating		Brazing		Cooling
RT-300^{0}C	300-577^{0}C	›577 ^{0} C	T_{max}	T_{max}-RT
$10^{+/-2}$ min,	$9^{+/-2}$min,	$6^{+/-2}$min,	$600^{+/-5}$ °C	$12^{+/-2}$min,

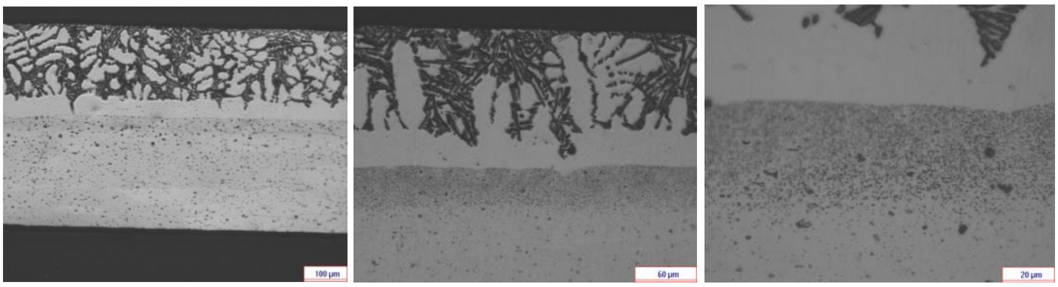


FIG. 5.22- The microstructural aspect of the brazing layer of alloy 3003 with alloy 4343, at different magnifying powers

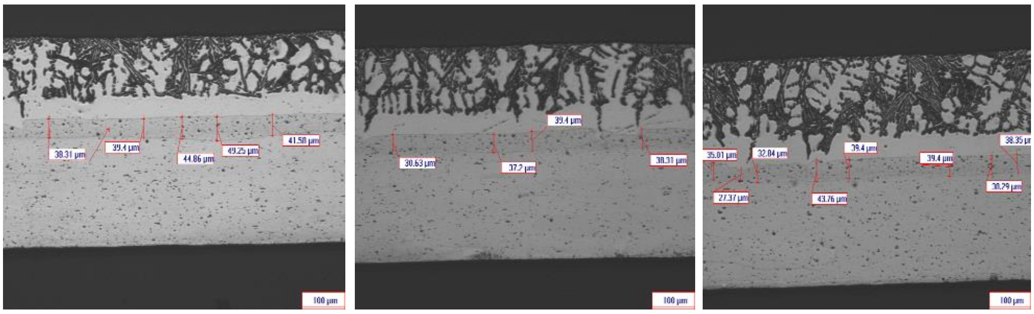


FIG. 5.23- Measurement of the "brown band" thickness of the plating layer of alloy 3003 with alloy 4343, at magnification of x100

Thus for the 3003 alloy specimens, plated with 4343, in H24 state, with a thickness of 0.3 mm, after applying the brazing simulation process, at a temperature of 600˚C, for 10 minutes, the average grain size was 78.65µm (class 4.5, according to ASTM E112), and after increasing the holding time to 600°C for one hour, the average grain size was 84.19µm (class 4, according to ASTM E112). The same observation can be made as for the plating of alloy 3003 with alloy 4004, that also for the plating with alloy 4343, by increasing the holding time to one hour, the grain size is finished, from class 4 to class 4.5.

Table 5.5 Results of grain size analysis of 3003 alloy plates with 4343 alloy, in H24 state and different holding times at 600□C

Temper	Brazier simulation process	Medium grain size, µm	Class ASTM E112	Figure
H24	600°C/10 minutes	78,65	4,5	-
	600°C/1 hour	84,19	4	5.2

5.4 Microstructural analysis of 3003 aluminum alloy plating layers with 4004 aluminum alloy

This subchapter presents the results of the structural analysis on brazed welded joints of alloy 3003 with alloy 4004, which have a lower level of silicon than eutectic, respectively of about 9.0 ÷ 10.5%. There is a uniform distribution of precipitates both in the base material (respectively alloy 3003) and in the plating layers, alloy 4004 (upper and lower of similar thicknesses, of about 80µm). Analysis by scanning electron microscopy (SEM) of the 3003 alloy specimens plated with 4004 alloy is shown suggestively in Figure 5.28. It is noted that in the layer the silicon content can reach up to 14% and can suddenly decrease in section over a distance of 20-30□m to 3%, reaching the base material to the content of alloy 3003, about 0.5 ÷ 2% Si.

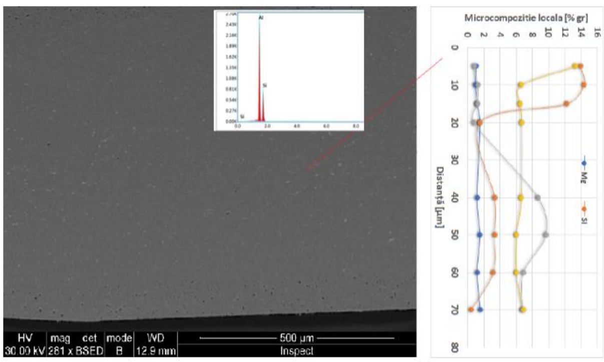


FIG. 5.28- Analysis by scanning electron microscope (SEM) of the 3003 alloy specimens plated with 4004, indicating the local microcomposition and its distribution in cross section

Area	Local microcomposure, % by mass			
	Mg	Si	Mn	Fe
5	1,11	14,02	0,85	13,36
10	1,00	14,42	1,27	6,65
15	1,22	12,3	1,24	6,50
20	1,56	1,58	0,83	6,73
40	1,25	3,39	8,74	6,68
50	1,54	3,39	9,68	6,08
60	1,25	3,23	6,92	6,04
70	1,59	0,50	6,81	6,91

The analysis regarding the determination of the grain size, after the simulation of the brazing process is presented comparatively in table 5.6. Thus for the 3003 alloy specimens, plated with 4004, in H24 state, with a thickness of 0.98 mm, after applying the brazing simulation process, at a temperature of 600˚C, for 10 minutes, the average grain size was 76.29µm (class 4.5, according to ASTM E112) .When the temperature of the brazing simulation process increased to 600˚C for 1 hour, the average grain size became 88.57µm (class 4.0, according to ASTM E112). The same analysis for the determination of the grain size of the sheets from 3003, plated with 4004, but in state O, after the brazing simulation process, at the temperature of 600˚C, for 10 minutes, showed an average grain size was 76.66µm (class 4.5, according to ASTM E112) and a grain size of grain was 84.31µm (class 4.0, according to ASTM E112), after increasing the duration of the brazing process to 1 hour.

Temper	Brazier simulation process	Average grain size , µm	Class ASTM E112	Figure
H24	600°C/10 minutes	76,29	4,5	5.29
	600°C/1 hour	88,57	4	5.30
O	600°C/10 minutes	76,66	4,5	5.31
	600°C/1 hour	84,31	4	5.32

Table 5.6 Results of grain size analysis of 3003 alloy plated sheets with 4004 alloy, in different states and different holding times at 600°C

The same observation can be noted as in the case of plating 3003 with 4045, and in this situation, respectively plating the sheets from 3003 with 4004 after simulating the brazing process at 600°C / 10 minutes, regardless of the state of the alloy 3003 (H24, or O) the grain size of about 79µm (class 4.5), and by increasing the maintenance time to one hour, the grain size is finished, reaching about 85µm, (class 4).
A comparative analysis of the grain size values of the 3003 alloy sheets plated with different alloys from the 4xxx series, respectively of the results from table 5.1, table 5.5 and table 5.6 shows that after simulating the brazing process at 600°C / 10 minutes in all situations the grain size was up to 80µm (ie class 4.5 according to ASTM E112), and by increasing the maintenance time to 1 hour the grain size is finished, having values over 80µm (class 4 according to ASTM E112). This behavior is summarized in Figure 5.33.

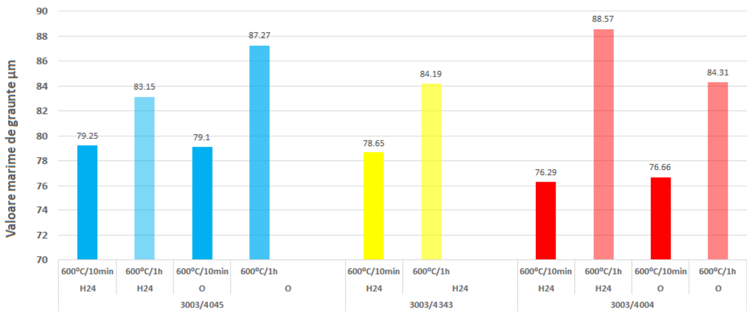


Fig.5.33- Distribution of grain size values determined on 3003 aluminum plated alloys, in different structural states, with different types of 4xxx series aluminum alloys

CHAPTER 6
CORROSION BEHAVIOR OF ALUMINUM ALLOY TABLES TYPE 3003 STRIPED WITH 4XXX SERIES ALLOYS

6.2.Research on the determination of corrosion potentials of alloy 3003 plated with 4000 series alloys, in different states of the sheet surface

The samples were prepared similarly to the preliminary research, respectively according to PO-043 and analyzed according to ASTM G69 and PO-042. The investigated samples were alloy 3003/4045, 3003/4004 and 3003/4343, at which the potentials were determined. corrosion in delivery condition, chemically cleaned condition and post-brazing coating. The values of the corrosion potentials obtained after the investigations are shown in table 6.3, and the variations of the corrosion potentials thus obtained are shown comparatively in figures 6.6, 6.7 and 6.8.
The analysis of the values of the corrosion potentials allows the formulation of the following conclusions:
• The condition of the material influences the value of the corrosion potentials, as follows: the lowest values are recorded for the delivery condition, then for the chemically cleaned condition and the highest values for the post-brazing condition, for all brazed alloys (in this hierarchical

order). This behavior is similar for both values of the brazing duration (respectively 30 and 60 minutes), with the mention that when the brazing duration increases, the values of the corrosion potentials increase;

• Through the different processes for processing the surface of the 3003 alloy plated with different alloys from the 4000 series, the values of the corrosion potentials change by approximately 20%, being located in the range -777 eV□ +698 eV. This change in corrosion potential does not remove these alloys from the corrosion resistance class, the value of the potential being relatively small;

• It is possible to make a hierarchy of the corrosion resistance of the 3003 brazed alloys with 4000 series alloys, as follows: the most resistant is the 3003/4045 alloy, followed by 3003/4004 and 3003/4343.

Table 6.3- Values of corrosion potentials of brazed sheets made of aluminum alloys

Material	Durata mentinere min	Valoare medie potential de coroziune, eV		
		Starea materialului		
		In stare de livrare	Curatat chimic	Post brazare
3003/4045	30	-777	-760	-703
	60	-766	-756	-698
3003/4004	30	-758	-748	-735
	60	-749	-740	-729
3003/4343	30	-757	-728	-716
	60	-741	-715	-703

6.2.2 Research on the determination of corrosion potentials of 3003 alloy sheets, of different thicknesses, depending on the size of the joints

These researches aimed to establish a possible correlation between the grain size of 3003 alloy sheets with different thicknesses and different states.

Table 6.4 summarizes the values obtained for the corrosion potential of the samples prepared from the strip samples, alloy 3003 plated with 4045, with a thickness of 0.6 mm, compared to the resulting values of grain size. It is noted that for the 3003 alloy plated sheets, the values of the corrosion potentials are similar, in the range - 721 ÷ - 742 (mV), and the grain size is in the range 79 µm ÷ 83µm (being in class 4.5 and 4, respectively, according to ASTM).

The detailed analysis of the values contained in table 6.5 allows the formulation of some interesting conclusions, ie a correlation can be established between the thickness of the 3003/4045 alloy plated sheet, the grain size and the values of the corrosion potentials. Thus, as the thickness of the sheet increases, an increase of the granulation is observed, respectively from 63µm (at a thickness of 0.3mm), to 200 µm (at 2.5mm), fact illustrated in figure 6.18. At the same time, as the thickness of the sheet increases, the potentials are sometimes more electronegative, as can be seen from the diagram in figure 6.19. The values of the average corrosion potentials are in the range -721 (mV) -766 (mV).

Table 6.4 - Corrosion potential and grain size values of plated alloy sheets 3003, post brazing, 0.6 mm thick

Temper	Alloy	E corr medie (mV)	E corr min. (mV)	E corr max. (mV)	Grain size
H24	4045	-742,57	-744,51	-739,81	79,25µm (class 4.5)/ post brazaing 600°C/10 min
	3003	-738,09	-739,92	-735,30	83,15µm (class 4.0)/ post brazaing 600°C/1 hour
O	4045	-743,53	-745,86	-741,07	79,10µm (clasa 4.5)/ post brazaing 600°C/10 min
	3003	-721,89	-724,09	-720,64	87,27µm (clasa 4.0)/ post brazaing 600°C/1 hour

Table 6.5 - Grain size and corrosion potential values of 3003 sheets in state O, post brazing, with different thicknesses

Tablă placată	Grosime (mm)	Mărime de grăunte		Potențial de coroziune		
		µm	clasa	$E_{corr\ med}$ (mV)	$E_{corr\ min}$ (mV)	$E_{corr\ max}$ (mV)
3003/4045 postbrazare 600^0 C/1h	0,3	63,17	5	730,14	727,58	732,7
	0,6	80	4,5	721,29	724,09	720,64
	1,2	107,02	3,5	748,02	745,02	751,02
	1,5	155	2,5	752,58	748,81	756,35
	2	171,02	2	760,17	755,23	765,11
	2,5	200,89	1,5	766,0	762,57	769,43

6.3 Case study on the structural investigation of the wings of a radiator

This study is performed on a tractor radiator, which was taken out of use after 6 years of operation.

Table 6.6 - Measurement of the dimensions of the brazed area of the radiator fins

Fin	lower fin		Superior fin		Average size of the brawled area	
	Length (µm)	Width (µm)	Length (µm)	Width (µm)	Length (µm)	Width (µm)
1	300	64,38	466,66	63,65	419,25	67,82
2	400	85,05	506,66	71,93		
3	453,33	71,12	Discontinuous			
4	453,33	74,34	380	65,1		
5	466,66	56,38	346,66	58,43		

Table 6.7 - Description of the structural aspects of the radiator fins

Fin	Lower	Superior
1	General corrosion of intergranular piping, intergranular cracks of about 80µm	General corrosion of intergranular-looking piping with cracks of about 50µm, partial destruction of the thickness of the fin
2	General corrosion of the piping with intergranular aspect, intergranular fissures of about 100µm	General corrosion of the intergranular duct with cracks of about 30µm, discontinuity in the wing of 50 µm
3	General corrosion of intergranular piping, numerous areas with intergranular cracks of about 100µm	Destruction of the brawled area, corrosion of the piping over long distances over 100 µm
4	General corrosion of the fin affecting over 50% of the thickness, intergranulary cracks of the piping of about 50 µm	Partial destruction of the defective fin over 100 µm
5	General corrosion of intergranular-looking piping	Intergranular cracks on the piping about 30-50 µm

CHAPTER 6
CONCLUSIONS, ORIGINAL CONTRIBUTIONS, DIRECTIONS AND PERSPECTIVES OF FUTURE RESEARCH

6.1 CONCLUSIONS

The researches carried out within the present doctoral thesis led to the obtaining of some results that allowed to reach the initially proposed objectives, respectively:

• Identification of the possibilities to improve the mechanical behavior and corrosion resistance of the plated sheets of aluminum alloy type 3003, with different alloys from the 4xxx series by optimizing the applied heat treatments, respectively:

o Determining the possibilities of lowering the temperature of the intermediate heat treatment, in order to decrease the specific consumptions;

o Determining the possibilities for improving the indicators of
performance of heat treatment furnaces

• Temporal, statistical analysis of the evolution of the mechanical characteristics for the products of aluminum alloy type 3003 plated with 4xxx alloy depending on the manufacturing characteristics

• Identification of the main structural characteristics of type 3003 aluminum alloy sheets, in different structural states, plated with different alloys from the 4xxx series

• Determining the corrosion behavior of aluminum alloy plated sheets type 3003, with different alloys from the 4xxx series, respectively:

o Establishing a relevant correlation between the delivery layer, the corrosion potential and the metallographic structure of aluminum alloys (series 2xxx, 3xxx, 5xxx, 6xxx, 7xxx),

o Determination of corrosion potentials of alloy 3003 plated with 4000 series alloys, in different states of the sheet surface,

o Highlighting the corrosion behavior in a case study of a tractor radiator, which was taken out of use after 6 years of operation.

6.1.1 Final conclusions from the research on the evolution of mechanical properties for aluminum alloy products of type 3003 plated with 4xxx series alloys according to their manufacturing characteristics

The analysis of the evolution of the mechanical properties of the products of aluminum alloy type 3003 coated with 4xxx series alloy, depending on the manufacturing characteristics, has been taken into account knowing, on the one hand, the multitude of factors that may influence the mechanical behavior of these products, and, on the other hand, to see the reproducibility of the results during the different processing periods of these products within ALRO Slatina. From the statistical analysis performed for the period 01.11.2016 - 31.10.2017, the following conclusions were formulated:S-au predat 4338 t de produse din aliaj de aluminiu 3003 placat, aprox. 12,5% din cantitatea totala predata la sectia LTB

• For the 3003 plated alloy, 58 combinations of base alloy, plating alloy and plating percentage were made.

• The main metallurgical state for the 3003 plated alloy products delivered during the analyzed period is represented by the soft state products, respectively 44.6% (1934 t).

• Most platelets made (528 pieces 30%) were 48 mm thick and correspond to a plating percentage of 10%.

• The most used plating alloys for obtaining plated products were alloys 4004 (39%) and 4045P1 (37%).

• In order to obtain plated products, for the analyzed period a load coefficient of 1.82 t / t was obtained.

• The most requested thicknesses depending on the quantity delivered for the plated products, base alloy 3003 were: 0.8 mm (13%); 2.5 mm (12%); 0.6 mm (11%) and 1.5 mm (10%).

• A regression equation was determined for the plated products, base alloy 3003, state O: respectively: Rm = 90.81 + 9.15 • .Si + 6.37 • Fe + 60.26 • Cu + 5.48 • Mn, with a value of the determination coefficient of 0.90. The regression equation is valid for a chemical composition of: Si ϵ [0.07 ÷ 0.60%], Fe ϵ [0.10 ÷ 0.70%], Cu ϵ [0.05 ÷ 0.75%] and Mn ϵ [0.18 ÷ 1.5%].

6.1.2 Conclusions from experimental research on the optimization of heat treatments applied to alloy plated products 3003

In order to increase the productivity of the heat treatment furnaces within the LTB section, tests were initially performed in laboratory conditions in order to optimize the heat treatments for the 3003PL alloy sheet rolls. Subsequently, tests were performed in industrial conditions to verify the results of laboratory investigations.

The experiments in laboratory conditions were performed before the final heat treatment of total annealing. The tests performed involved the simulation in the laboratory of the annealing heat treatment at different parameters, respectively the holding temperature varying from 290 ° C to 415 ° C, and the holding time from 1 hour to 4 hours.

Following the tests performed, it is observed that almost all the values obtained for the mechanical characteristics, except for those recorded for the treatment performed at a temperature of 290 ° C, fall within the limits imposed by the standard EN 485: 2-2009 for alloy products 3003 state O.

The annealing treatment was also simulated in the laboratory at 340 ° C / 4, taking into account the fact that for the 6063PL alloy products this treatment is performed industrially and the rollers could be loaded in the same batch, thus avoiding the creation of a new annealing treatment. . The mechanical characteristics obtained were within the limits imposed by the standard. For the grain size, a slightly finer granulation was obtained, class 7.0, than for the material subjected to the parameters 415 ° C / 3h, for which class 6.5 was obtained according to ASTM E 112.

In order to validate the laboratory results, the values obtained in the laboratory at the parameters 415 ° C / 3h were compared with those obtained industrially at the same parameters. No major differences were obtained between the two determinations for the same material. Thus, the values obtained for Rm and Rp0.2 under industrial conditions are approximately 5 MPa higher than those for which the heat treatment was performed under laboratory conditions. For elongation, the values for which the heat treatment was performed industrially are lower by approx. 6%.

6.1.3 Conclusions from *the experimental research on the structural characterization of aluminum alloy sheets type 3003 plated with 4xxx series alloys*

Particularly important complex structural analyzes were performed in establishing the reliability of the investigated metal products, as well as in forecasting an in-service behavior in accordance with the imposed requirements. The analyzes led to the identification of structural changes of aluminum alloy products type 3003 (in different layers), brazed with different types of aluminum alloys from the 4xxx series, respectively: determination of grain size before and after simulation of the brazing process, determination phase distribution, determining the thickness of the cladding layer and identifying the “brown band” area, ie quantitative and qualitative structural elements that define this area..

- ***Microstructural analysis of the plating layers of aluminum alloy 3003 with aluminum alloy 4045*** allowed the identification of a uniform distribution of precipitates both in the base material (respectively alloy 3003) and in the plating layers, alloy 4045 (upper and lower thicknesses similar, about 75μm). Scanning electron microscopy (SEM) analysis showed a drastic change in the local chemical composition, the silicon content in the layer can reach up to 14%, to suddenly decrease in section over a distance of 20-30μm to 8%, reaching in the basic material the content of the alloy type 3003, of about

1-2% Si. The analysis regarding the determination of the grain size before and after the simulation of the brazing process showed that regardless of the condition of the alloy 3003 (H24, or O) the grain size is about 79µm (class 4.5, according to ASTM E112), and by increasing the duration of maintenance at one hour, the grain size is finished, reaching about 85µm, (class 4, according to ASTM E112).

- ***Detailed microstructural analysis of plating layers of alloy type 3003, with aluminum alloy type 4343***, thickness 0.3 mm showed that both in the flat direction and in the longitudinal and / or transverse direction, there is a uniform distribution of phases of $MnAl_6$ and α (AlMnSi), most phases of $MnAl_6$ and αAlMnSi are spherical, relatively evenly distributed, The precipitate (of Mn) is fine and evenly distributed throughout the section of the analyzed samples. Scanning electron microscopy (SEM) analysis showed that the silicon content in the layer can reach up to 13.38% and can suddenly decrease in section over a distance of 30µm to 4.78%, reaching the material of base to the content of alloy 3003, of about 1-2% Si. The "brown band" size for 3003LL alloy samples plated with 4343 thickness 0.3mm - cross section (LT-ST), subjected to brazing, according to Behr specification and electrolytically attacked, was between 27.37µm and 49.25 µm, with an average , made on 17 measurements of 38.43 µm, which represents 12.81% of the total thickness of the sheet of 0.3 mm. The thickness of the plating layer (for the plated face) for the prepared samples (cross section, LT-ST) was within the required value of 8.5% ± 1.5%. The analysis on the determination of the grain size before and after the simulation of the brazing process showed that after the 600˚C simulation, for 10 minutes, the average grain size was 78.65µm (class 4.5, according to ASTM E112), and after increasing the holding time to 600°C for one hour, the average grain size was 84.19µm (class 4, according to ASTM E112).
- ***Detailed microstructural analysis of plating layers of alloy type 3003, with aluminum alloy type 4004,*** thickness 0.98 mm showed that the precipitates have a uniform distribution both in the base material (respectively alloy 3003) and in the plating layers , alloy 4004 (upper and lower of similar thicknesses, about 80µm). Scanning electron microscopy (SEM) analysis showed that the silicon content in the layer can reach up to 14% and can suddenly decrease in section over a distance of 20-30µm to 3%, reaching the base material at the content of alloy 3003, of about 0.5 ÷ 2% Si. The analysis regarding the determination of the grain size, after the simulation of the brazing process at the temperature of 600˚C, for 10 minutes, showed an average grain size of 76.29µm (class 4.5, according to ASTM E112), and at the increase of the duration of maintenance at 600°C for 1 hour the average grain size became 88.57µm (class 4.0, according to ASTM E112). The same analysis for the determination of the grain size of the sheets from 3003, plated with 4004, but in state O, after the brazing simulation process, at the temperature of 600˚C, for 10 minutes, showed an average grain size was 76.66µm (class 4.5, according to ASTM E112) and a grain size of grain was 84.31µm (class 4.0, according to ASTM E112), after increasing the duration of the brazing process to 1 hour.
- ***Comparative analysis of the grain size values of the 3003 alloy sheets plated with*** different alloys from the 4xxx series showed that after simulating the brazing process at 600°C / 10 minutes in all situations the grain size was up to 80µm (class 4.5 according to ASTM E112), and by increasing the holding time to 1 hour the grain size is finished, having values over 80µm (class 4 according to ASTM E112).

6.1.4 Conclusions regarding the corrosion behavior of aluminum alloy sheets type 3003 brazed with 4xxx series alloys

Experimental research was performed in order to establish a relevant correlation between the delivery layer, the corrosion potential and the metallographic structure of aluminum alloys (2xxx, 3xxx, 5xxx, 6xxx, 7xxx series). In this sense, the following were observed:

• For the alloys from the 2xxx series, the lowest Xmean = -618.8mV was obtained.

• In alloy 3003, a stability is observed in terms of corrosion potential, the analyzed samples, both those made of sheet metal and those from plates (regardless of whether it is a milled or laminated face) have approximately the same values, the samples being corresponding to ASTM G69.

• For 5xxx series alloys as well as for 3003 the potential values are close, both between the milled and the laminated face and between the measuring intervals of 30 or 60 minutes.

• For the alloys from the 6xxx series, the highest Xmean = -988.8mV was obtained. Also, in these alloys, the biggest differences are observed between alloys with the same delivery conditions but also in the alloys with different delivery conditions (both on the laminated and on the milled surface).

• For 7xxx series alloys, there are quite large differences between alloys with the same delivery condition but different chemical composition between the milled and laminated face. Only in the 7075 alloy are there no noticeable differences between the milled and the laminated face.

Research on the determination of corrosion potentials of alloy 3003 plated with alloys of series 4000, in different states of the surface of the sheets showed that:

- The condition of the material influences the value of the corrosion potentials, as follows: the lowest values are recorded for the delivery condition, then for the chemically cleaned condition and the highest values for the post-brazing condition, for all brazed alloys (in this hierarchical order). This behavior is similar for both values of the brazing duration (respectively 30 and 60 minutes), with the mention that when the brazing duration increases, the values of the corrosion potentials increase;
- Through the different processes for processing the surface of the 3003 alloy plated with different alloys from the 4000 series, the values of the corrosion potentials change by approximately 20%, being located in the range -777 eV ÷ +698 eV. This change in corrosion potential does not remove these alloys from the corrosion resistance class, the value of the potential being relatively small;
- It is possible to make a hierarchy of the corrosion resistance of the 3003 brazed alloys with 4000 series alloys, as follows: the most resistant is the 3003/4045 alloy, followed by 3003/4004 and 3003/4343.
- The researches regarding the determination of the corrosion potentials of the 3003 alloy sheets, of different thicknesses, depending on the hollow size, allowed the formulation of some interesting conclusions:
- as the thickness of the sheet increases, an increase of the granulation is observed, respectively from 63μm (to 0.3mm thickness), up to 200μm (to 2.5mm), as the thickness of the sheet increases, the potentials are sometimes more electronegative, the values of the average corrosion potentials being in the range -721 (mV) ÷ -766 (mV).
- The case study performed on a tractor radiator, which was taken out of use after 6 years of operation, allowed the formulation of the following conclusions:

  • both the dimensions of the brazed area of the fins, respectively an average length of the fins of about 410μm and a width of about 65-70μm were highlighted,

  • the phenomenon of general corrosion of the piping with intergranular aspect was identified, both on the lower part and on the upper part of the fins, with the highlighting of the partial destruction of the brazed area on portions included in the range 50-100μm..

6.2 ORIGINAL CONTRIBUTIONS

- Carrying out a complex analysis of the statistical mechanical characteristics for the products of aluminum alloy type 3003 plated with 4xxx series alloy, depending on the manufacturing characteristics, considering knowing, on the one hand the multitude of factors that can influence the mechanical behavior of these products , and, on the other hand, to see the reproducibility of the results during the different processing periods of these products within ALRO Slatina;
- Determination of a regression equation for plated products, base alloy 3003, state O: respectively: $Rm = 90.81 + 9.15 \cdot .Si + 6.37 \cdot Fe + 60.26 \cdot Cu + 5.48 \cdot Mn$, with a value of the coefficient of determination of 0,90, the regression equation valid for a chemical composition of: Si ϵ [0,07 ÷ 0,60%], Fe ϵ [0,10 ÷ 0,70%], Cu ϵ [0.05 ÷ 0.75%] and Mn ϵ [0.18 ÷ 1.5%];
- Carrying out experiments in laboratory conditions for the optimization of heat treatments applied to products plated in alumina alloy type 3003, which allows the reduction of production costs, without endangering the values of mechanical characteristics of heat treated products
- Carrying out a complex structural analysis that led to the identification of structural changes of aluminum alloy products type 3003 (in different layers), brazed with different types of aluminum alloys from the 4xxx series, respectively: determining the grain size before and after the simulation brazing process, determining the phase distribution, determining the thickness of the cladding layer and identifying the “brown band” area, ie quantitative and qualitative structural elements that define this area;
- Highlighting the corrosion behavior of aluminum alloy sheets type 3003 brazed with 4xxx series alloys by establishing a relevant correlation between the delivery layer, corrosion potential and metallographic structure of aluminum alloys (series 2xxx, 3xxx, 5xxx, 6xxx, 7xxx);
- Comparative determination of the corrosion potentials of type 3003 aluminum alloy plated with 4000 series alloys, achieving a hierarchy of strength on different thicknesses, depending on the size of the joints, so that as the thickness of the sheet increases, the granulation increases , respectively from 63µm (0.3mm thick), up to 200µm (2.5mm), and at the same time as the sheet thickness increases, the potentials can sometimes be more electronegative, the values of the average corrosion potentials being is in the range -721 (mV) ÷ -766 (mV).
- Carrying out a case study on a tractor radiator, which was taken out of use after 6 years of operation, highlighting both the dimensions of the brazed area of the fins, respectively an average length of the fins of about 410□m and a width of about 65-70□m, as well as the identification of the phenomenon of general corrosion of the piping with intergranular aspect, both on the lower and on the upper part of the fins, with the partial destruction of the brazing area in a range of 50-100µm.

6.3 DIRECTIONS AND PERSPECTIVES OF FUTURE RESEARCH

□ During the research within the doctoral thesis were identified some aspects, new or current, that can be considered or improved.

□ Aluminum alloys are still sources of future experimental research on exploring their performance in the field of corrosion resistance of various structural components.

□ At the same time it is possible to promote the analysis of complex statistics extended over different periods, or different classes of aluminum alloys, in order to identify the reproducibility of the industrial results within the company ALRO Slatina.

 It may also be proposed to use techniques specific to stereomicroscopy in assessing the condition of surfaces or plastic deformation, or interim or final heat treatment performed on products plated with other types of aluminum alloys.

LIST OF PAPERS PUBLISHED IN THE FIELD OF DOCTORAL THESIS
Claudia Alina LAZAR (NATRA)

1. **PUBLISHED ARTICLES - in recognized international journals of ISI listing or indexed in field-specific international databases**

[1.1] Ghiban, B, **Natra, CA**, Popescu, G- **CORROSION POTENTIALS OF THE ALUMINUM ALLOYS** , UNIVERSITY POLITEHNICA OF BUCHAREST SCIENTIFIC BULLETIN SERIES B-CHEMISTRY AND MATERIALS SCIENCE , Volume: 79 , Issue: 4 , Pages: 39-244 , Published: 2017

[1.2] Ghiban, B, Popescu, G, **Lazar, C**, Rosu, L;Constantin, I.,Olaru, M;Carlan, B.) **- Corrosion Behaviour in Human Stimulation Media of a High Entropy Titan-Based Alloy**, Volume: 374,Conference: EUROINVENT International Conference on Innovative Research (ICIR), Iasi, ROMANIA, 17-18 MAI, 2018

[1.3] Ghiban, B, **Natra, C. – Brown band characteristics of aluminum cladding alloys,** Volume 572, Issue 1, 2 August 2019, Article number 0120342019 International Conference on Innovative Research, ICIR EUROINVENT 2019; Palace of CultureIasi; Romania; 16 May 2019 through 17 May 2019; Code 150123

[1.4] Ghiban, B., **Natra, C**., Cernea, A., Raiciu, A.D.,Odagiu, O., Balkan, I.-**Structural investigations concerning Al 3003/Al 4xxx clad materials,** UPB Scientific Bulletin, Series B: Chemistry and Materials Science, Volume 81, Issue 4, 2019, Pages 281-290

[1.5] **C. Lazar (Natra),** D Istrate, O P Odagiu, A M Demian, A D Buzatu, B Ghiban-**Evaluation of mechanical characteristics of 3003 aluminum alloy plated sheets**, IOP Conference Series: Materials Science and Engineering, an open-access proceedings journal, with abstracting and indexing in ISI Web of Science (Conference Proceedings Citation Index), 2022 (lucrare recenzată și aprobată spre publicare).

2. **Articles presented as part of a scientific event**

[2.1]. B. GHIBAN, **C. NATRA**, - **Structural investigations of brown band of Aluminum 3003/Al 4xxx clad materials 11th International Conference on Materials Science and Engineering** – BraMat 2019, prezentare orală, I.PO.11. 11th International Conference on Materials Science and Engineering – BraMat 2019

[2.2]. B. Ghiban, **C. NATRA -Structural investigations concerning Al 3003/Al 4xxx clad materials**, poster, ROMAT 2018

[2.3]. **C. Lazar (Natra),** D Istrate, O P Odagiu, A M Demian, A D Buzatu, B Ghiban-**Evaluation of mechanical characteristics of 3003 aluminum alloy plated sheets**, ACME, 9-10 iunie 2022- Iași

BIBLIOGRAFIE SELECTIVĂ

- G. Cole, A. Glove, R. Jeryan, G. Davies, Steel World 2 (1)(1997) 75–83.
- Morita, Aluminium alloys for automobile applications, in:Proc. of ICAA-6, Toyohashi, Japan, 5–10 July 1998, in: Aluminium Alloys, vol. 1, 1998, pp. 25–32.
- C.T.W. Lahaye, W.C. Emmens, J. Bottema, F. Schoepen, G.Verhoeven, Influence of substrate texture on forming and paint appearance of aluminium sheet material, in: Conf. Proc. IBEC'97, 1997, pp. 107–114.
- C.T.W. Lahaye, J. Soderlund, G. Koelewijn, Development of an aluminium bonnet for SAAB 9-3, in: Conf. Proc. of 32nd ISATA, SAE Technical Paper Series 99NM065, 1999.
- R.K. Bollingbroke, A. Gray, D. Lauzon, Optimisation of nocolok brazing conditions for higher strength brazing sheet, VTM 3 Conf., Indianapolis, USA, SAE Paper 971861, 1997.
- N.D.A. Kooij, J. Sontgerath, A. Burger, K. Vieregge, A. Haszler, New high strength alloys for brazing with long life corrosion properties, VTMS 3 Conf., Indianapolis, USA, SAE Paper 971862, 1997.
- T.J. Hurd, A. Burger, N.D.A. Kooij, K. Vieregge, A. Haszler, New alloy development in aluminium brazing sheet, in: Proc. of ICAA-6, Toyohashi, Japan, 1998, pp. 1979–1984.
- N.D.A. Kooij, T.J. Hurd, A. Burger, K. Vieregge, A. HaszlerHigh strength heat-treatable aluminium alloys for CAB brazing, VTMS 4 Conf., London, UK, SAE Paper C543/014/99, 1999.
- El-Sayed, M.H.; Naka, M.: Structure and Properties of Carbon Steel-Aluminium Dissimilar Joints. Science and Technology of Welding and Joining, 2005, vol. 10, no. 1.
- Agudo, L.; Jank, N.; Wagner, J.; Weber, S.; Schmaranzer, C.; Arenholz, E.; Bruckner, J.; Hacki, H.; Pyzalla, A.: Investigation of Microstructure and Mechanical Properties of Steel-Aluminium Joints Produced by Metal Arc Joining. Steel research int., 2008, vol. 79, no. 7.
- Ghiban, B,Natra, CA, Popescu, G- CORROSION POTENTIALS OF THE ALUMINUM ALLOYS , UNIVERSITY POLITEHNICA OF BUCHAREST SCIENTIFIC BULLETIN SERIES B-CHEMISTRY AND MATERIALS SCIENCE , Volume: 79 , Issue: 4 , Pages: 39-244 , Published: 2017
- Ghiban, B, Popescu, G, Lazar, C, Rosu, L;Constantin, I.,Olaru, M;Carlan, B.) - Corrosion Behaviour in Human Stimulation Media of a High Entropy Titan-Based Alloy, Volume: 374,Conference: EUROINVENT International Conference on Innovative Research (ICIR), Iasi, ROMANIA, 17-18 MAI, 2018
- Ghiban, B, Natra, C. - Brown band characteristics of aluminum cladding alloys, Volume 572, Issue 1, 2 August 2019, Article number 0120342019 International Conference on Innovative Research, ICIR EUROINVENT 2019; Palace of CultureIasi; Romania; 16 May 2019 through 17 May 2019; Code 150123
- Ghiban, B., Natra, C., Cernea, A., Raiciu, A.D.,Odagiu, O., Balkan, I.-Structural investigations concerning Al 3003/Al 4xxx clad materials, UPB Scientific Bulletin, Series B: Chemistry and Materials Science, Volume 81, Issue 4, 2019, Pages 281-290
- Bordo K. et al - Electrochemical profiling of multi-clad aluminium sheets used in automotive heat exchangers. Corrosion Science, 131: 28–37, 2018.
- Donatus U et al - Corrosion pathways in aluminium alloys. Transactions of Nonferrous Metals Society of China, 27: 55−62, 2017.
- Ghiban B, Natra C - Brown band characteristics of aluminium cladding alloys. IOP Conference Series Materials Science and Engineering. 572:012034. 2019.
- Hirsch J - Aluminium in innovative light-weight car design. Proc Innovative Development for Lightweight Vehicle Structures. Wolfsburg, Germany: VW, 2009: 101.
- Kim HW et al - Mechanical Properties of Al/Al-Mg/Al Clad Sheets Fabricated by Roll Bonding Process. Proceedings of the 12th International Conference on Aluminium Alloys. Pp. 1978-1983. 2010.
- Kucharikova L et al - Role of Chemical Composition in Corrosion of Aluminium Alloys. Metals - Open Access Metallurgy Journal . 8(8):581. 2018.

- Zhang X et al - Microstructure and Properties of Cladding Layers Prepared by Argon-Shielded Arc Cladding of CuZn40-WC Powders on Pure Aluminium Substrate. Coatings. 8(11):382. 2018.
- M.A. Pech-Canul, J.C. Guía-Tello , M.I. Pech-Canul , J.C. Aguilar , J.A. Gorocica-Díaz , R. Arana-Guillén , J. Puch-Bleis, Electrochemical behavior of tube-fin assembly for an aluminum automotive condenser with improved corrosion resistance, Results in Physics , Volume 7, 2017, Pages 1760-1777
- M. Melander , R. Woods, Corrosion Study of Brazed Aluminum Radiators Retrieved from Cars After Field Service, CORROSION, vol 66, nr. 1 2010, 0150005-1-14
- ASTM G85-09, “Standard Practice for Modified Salt Spray (Fog) Testing” (West Conshohocken, PA: ASTM International, 2009).
- ASTM B117-09, “Standard Practice for Operating Salt Spray (Fog) Apparatus” (West Conshohocken, PA: ASTM International, 2009).
- ASTM B368-09, “Standard Test Method for Copper-Accelerated Acetic Acid-Salt Spray (Fog) Testing (CASS Test)” (West Conshohocken, PA: ASTM International, 2009).
- Gray, C. Pargeter, “Waterside Corrosion Testing of Aluminum Heat Exchangers—Will There Ever Be A Globally Accepted Test?,” AFC-Holcroft Invitational Seminar (Wixom, MI: AFC-Holcroft, 2007).
- M. Melander, R. Woods, “A Corrosion Study of Field-Retrieved CAB-Brazed Automobile Condensers,” Vehicle Thermal Management Systems (VTMS)-8 Conference Proc., paper no. C640/076/ 2007 (London, U.K.: Institution of Mechanical Engineers, 2007).
- M. Melander, “A Corrosion Study of Field-Retrieved Automobile Evaporators,” 5th Int. Congress on Aluminum Brazing (Dusseldorf, Germany: Aluminum-Verlag, 2006).
- M.A. Pech-Canul, J.C. Guía-Tello, M.I. Pech-Canul, J.C. Aguilar, J.A. Gorocica-Díaz, R. Arana-Guillén, Puch-Bleis- Electrochemical behavior of tube-fin assem bly for an aluminum automotive condenser with improved corrosion resistance, Results in Physics Volume 7, 2017, Pages 1760-1777
- 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.
- Hirsch J. Recent development in aluminum for automotive applications. Trans Nonferrous Met Soc China 2014;24:1995–2002.
- 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.
- Yoon S, Kim H, Lee Ch. Fabrication of automotive heat exchanger using kinetic spraying process. Surf Coat Technol 2007;201:9524–32.
- Parundekar, G, Chavan, A. Corrosion life improvement of all aluminum micro channel heat exchangers (MCHX) in HVAC&R industry, Paper CSD-01, International Corrosion Conference and Expo CORCON2015. NACE International Gateway India Section; 2015.
- Sugiura S, Toyama T, Mutou S, Matsuura S, Yamaguchi H. Development of a Cooling Module Containing a Radiator and a Condenser. Part 2 Alloy Development. Warrendale, PA: Society of Automotive Engineers [SAE]; 2001. SAE Technical Paper 2001-01-1019.
- Mundt R, Koblenz H. Introduction to Brazing of aluminum alloys. European Aluminum Association; 1994. TALAT Lecture 4601.
- ASTM G85-09. Standard practice for modified salt spray (Fog) testing. West Conshohocken, PA: ASTM International; 2009.
- Afshar FN, de Wit JHW, Terryn H, Mol JMC. The effect of brazing process on microstructure evolution and corrosion performance of a modified AA4XXX/ AA3XXX brazing sheet. Corros Sci 2012;58:242–50.
- Meijers S. Corrosion of aluminum brazing sheet [Ph.D. thesis]. Delf University of Technology; 2002. [19] Vander Voort GF. ASM handbook volume 9: metallography and microstructures. ASM International; 2004.
- Sekulic´ DP, Galenko PK, Krivilyov MD, Walker L, Gao F. Dendritic growth in AlSi alloys during brazing. Part 1: experimental evidence and kinetics. Int J Heat Mass Transfer 2005;48:2372–84.

- Zhao H, Woods R. Controlled atmosphere brazing of aluminum. In: Sekulic´ DP, editor. Advances in brazing, science, technology and applications. Woodhead Publishing Ltd.; 2013.
- Lacaze J, Tierce S, Lafont M-C, Thebault Y, Mankowski G, Blanc C, Robidou H, Vaumousse D, Pébère N, Daloz D. Study of the microstructure resulting from brazed aluminum materials used in heat exchangers. Mater Sci Eng A 2005;413–414:317–21.
- Tierce S, Pébère N, Blanc C, Mankowski G, Robidou H, Vaumousse D, Lacaze J. Solidification and phase transformations in brazed aluminum alloys used in automotive heat exchangers. Int J Cast Met Res 2005;18:370–6.
- Davoodi A, Pan J, Leygraf C, Norgren S. The role of intermetallic particles in localized corrosion of an aluminum alloy studied by SKPFM and integrated AFM/SECM. J Electrochem Soc 2008;155:C211–8.
- Marshall GJ, Bolingbroke RK, Gray A. Microstructural control in an aluminum core alloy for brazing sheet applications. Metall Trans A 1993;24A:1935–42.
- Schäuble K. Silica passivation layer on aluminium brazing sheets [Doctoral dissertation]. University of Köln; 2010.
- Brett CMA. The application of electrochemical impedance techniques to aluminum corrosion in acidic chloride solutions. J Appl Electrochem 1990;20:1000–3.
- Lenderink HJW, Linden MVD, de Wit JHW. Corrosion of aluminum in acidic and neutral solutions. Electrochim Acta 1993;38:1989–92. [29] 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.
- 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.
- 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.
- Bessone J, Mayer C, Jüttner K, Lorenz WJ. AC-impedance measurements on aluminum barrier type oxide films. Electrochim Acta 1983;28:171–5. [33] Harrington DA, Conway BE. AC-impedance of faradaic reactions involving electrosorbed intermediates-I. Kinetic theory. Electrochim Acta 1987;32:1703–12.
- Harrington DA, Van den Driessche P. Stability and electrochemical impedance of mechanisms with a single adsorbed species. J Electroanal Chem 2001;501:222–34.
- Córdoba-Torres P, Mesquita TJ, Devos O, Tribollet B, Roche V, Nogueira RP. On the intrinsic coupling between constant-phase element parameters a and Qin electrochemical impedance spectroscopy. Electrochim Acta 2012;72:172–8.
- Aoki IV, Bernard M-C, Cordoba de Torresi SI, Deslouis C, de Melo HG, Joiret S, Tribollet B. AC-impedance and Raman spectroscopy study of the electrochemical behavior of pure aluminum in citric acid. Electrochim Acta 2001;46:1871–8.
- Lee S, White HS. Dissolution of the native oxide film on polycrystalline and single-crystal aluminum in NaCl solutions. J Electrochem Soc 2004;151: B479–83.
- Shi Q, Liang F, Cheadle B. Electrochemical behaviors of quad-layer aluminum brazing sheet composite for automotive applications. Corrosion 2004;60:492–500.
- Afshar FN, Ambat R, Kwakernaak C, de Wit JHW, Mol JMC, Terryn H. Electrochemical depth profiling of multilayer metallic structures: an aluminum brazing sheet. Electrochim Acta 2012;77:285–93.
- Flatoy Jarl Erik Morsund, *Process- and Alloy Development of Recyclable Aluminium Alloys: Recovery and Recrystallization Behavior of a Selection of AlMn-model* Alloys, master thesis, 2011, Norwegian University of Science and Technology.