INTEGRATED BRAZING TECHNOLOGIES WITH ADVANCE PRECURSORS

Thesis designed to obtain the scientific title of PhD engineer
at
University "Politehnica" Timisoara
in INDUSTRIAL ENGINEERING-MMUT
by

BINCHICIU EMILIA FLORINA

ABSTRACT

Scientific coordinator:	Prof.Univ.PhD.Eng. FLEŞER TRAIAN
Scientific reviewers:	Prof.Univ.PhD. Eng. VOICULESCU IONELIA
	Prof.Univ.PhD.Eng. IOVĂNAŞ RADU
	Prof. Univ.PhD.Eng. ŞERBAN VIOREL-AUREL

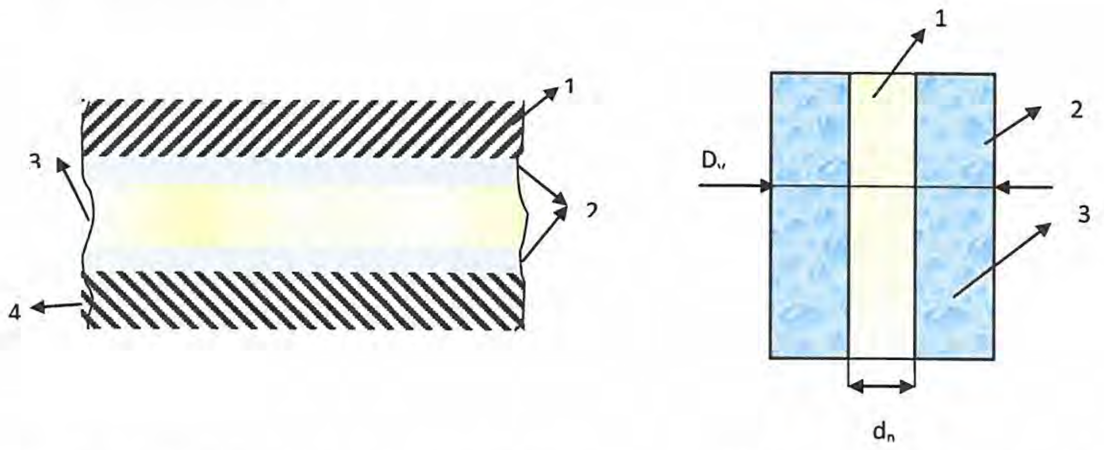
Presentation day: 23 September 2016.

The theme proposed for solving through the doctoral research program, fall within the area of new generation soldering processes, systematic and thorough by EABS [EABS 2014], through congresses and international projects.

Studies on the **current state** of manufacturing coated brazing rods were completed by these findings, namely:

- companies that manufacture, concurrently present a wide range of products that fall within international rules regarding oxidation alloys and fluxes;
- brazing materials with a wide range of uses, high coefficient of safety to failure, pollution or occupational diseases are quite expensive. The expensive materials is silver and assuring high purity to all material used;
- the technical, technological and operational safety proprieties of brazed joints are dependent on brazing materials features, which depend on the manufacturing process and brazing process parameters;
- Traceability methods for verifying brazed joints in the current stage are theoretical, based on entries in the quality assurance process without tangible evidence to merge

The innovative idea of the thesis (Figure 1.2), results from analysing the technological brazing condition when brazing with flame and coated rods and achieve the melting of the oxidising coat before the addition metallic bare rod [Onza, 1988], it consists in adding to the coating an additional alloying system that when it simultaneously melts, with the oxidiser, allow the deposition of a buffer layer which has required diffusion and oxidation proprieties, suited to the requirements of cost cuts when producing brazed joints.



a) Overlapped joint with the new material. 1-base material; 2-deposition accomplished by the alloying system (bumper layer); 3-deposit made by the new bare rod (filler layer); 4-base material

b) New generation coated rod. 1-bare rod; 2-oxidizer layer; 3-alloying system; D_v/d_n –coating coefficient

Figure 1.2. The innovative principle of the research theme.

In accordance with the conditions and trends reported in the brazing material industry, the doctoral program formulates the following main objectives:

1. Summary of the current stag of technology and guidelines of manufacture of brazing materials.
2. Develop processes for manufacturing bulk materials with compact grains that ensure improved diffusion processes and corrosion protection in / and base metals.
3. Experiments to develop coated rods containing chemically active brazing materials, with high efficiency and at reasonable cost.
4. Develop and qualification of brazing technology, applied industrial, that are technical and economic efficient, for homogeneous and heterogeneous joints.

In conjunction with these, specific objectives are defined, to ensure the pleasant conduct of activities under the doctoral program:

- ✓ develop recipes that generate brazing materials with enhanced fluidity of the alloy, which ensures easy penetration of gaps between metals to be joined;
- ✓ develop and implement, through studies and applied research, recipes and processes to obtain experimental brazing rods;
- ✓ optimizing production process of the functional model and product recipes, on the basis of cost-quality index supported by social needs;
- ✓ developing and characterising the functional model and its production process;
- ✓ implementing results in production and launching the dissemination and marketing strategies.

Experimental research has specific technological objectives to harness laboratory results by developing and qualifying economically efficient niche technologies of major importance for national economy, and not only, such as:

- ➢ develop and characterize joints type steel pipe in copper pipe;
- ➢ develop and characterize deep joints in the tungsten carbide reinforcement and the steel knife holder Routers used to strip asphalt;
- ➢ develop and characterize joints type steel pipe in brass pipe;
- ➢ develop and characterize overlapped and corner joints made of stainless steel.

Technical and economic objectives of the research stated:

- ❖ achieve, with reasonable costs, coated rods for brazing joints, with high efficiency, between stainless steels used in heat exchangers;
- ❖ develop coated brazing rods with high efficiency for heterogeneous joints with restriction requests like sintered metallic carbides reinforcement in steel brackets that allow simultaneous deposit when melting.

Ensuring the technical-material and scientific base to develop the rods. Worldwide there is scientific knowledge regarding manufacturing processes for coated rods, obtained by moulding / milling of precursor activity and achieving brazed.

Deficiencies were found in:

- methodology to elaborate product recipes for coated rods with composite coatings and chemically active precursors;
- the coatings extrusion process on the rod;
- develop and implement the coated rods with composite coatings;
- deficiencies in supply from current production with precursors assets.

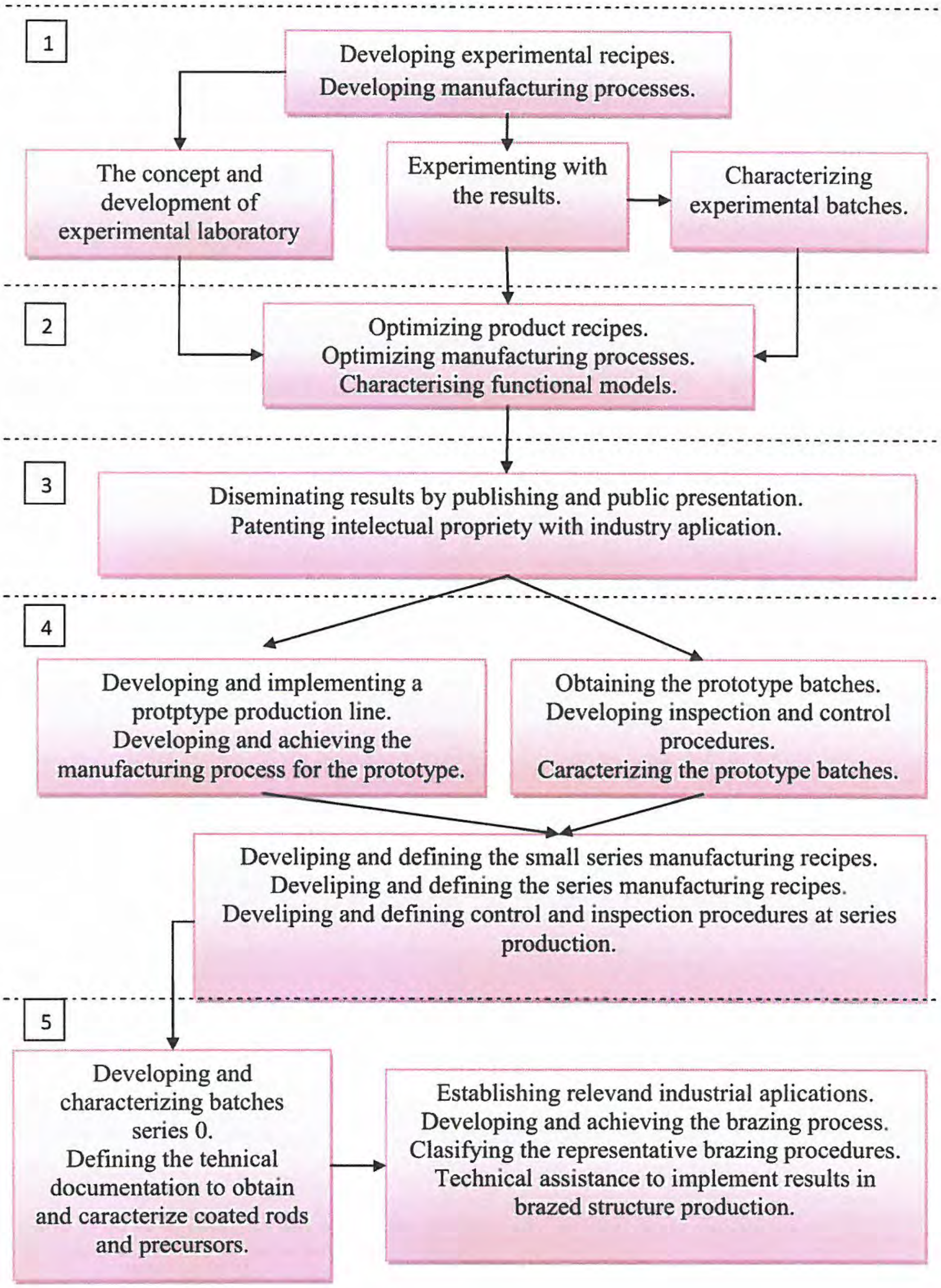


Figure 2.19. Strategic stages of the research

Projection models for product recipes take into consideration the materials count:

$$M_i = \sum_{i=1}^{n} a_i x_i + \sum_{j=1}^{m} b_j y_j + \sum_{k=1}^{r} d_k z_k \tag{2.2}$$

x_i - components, in mass participation, of substances of the oxidizing system, chemical substances described by SR EN 1045:1999 [SR 1045, 1999] or technical product norms;
y_j - components, in mass participation, of substances of the alloying system, chemical substances described by SR EN ISO 17672:2010 [SR 17672, 2010] ;
z_k - components, in mass participation, of substances of the bonding/ laminating;
$a_i;b_j;d_k$ – mixture participants.

The mass conservation law was extended in order to develop de global alloying system, which consists of the rod and the secondary coat alloying system.

$$ag_p = eg_{Mi} + fg_{VN} \tag{2.3}$$

α – global loss at brazing coefficient of the chemical element, in g;
g_p; g_{Mi}; g_{VN} – element coefficients, in g, thus: g_p-in deposition, g_{Mi}-in the coating, g_{VN}- in the bare rod;
e;f – correction coefficients of the participation of element „g” function to the participation concentrations of base materials in the mixture.

Homogeneity is determined by the mixing degree „I”

$$I = \frac{\frac{T_1}{T_{med}} + \frac{T_2}{T_{med}} + \ldots + \frac{T_n}{T_{med}}}{n} \tag{2.5}$$

where: I – mixing degree,
$c_1 \ldots c_n$ – concentrations in different measured points,
$T_1 \ldots T_n$ – temperature in different measured points,
c_{om} – homogenous concentration of the mixture,
T_{med} – medium temperature,
n – number of measured points.

When referring to producing materials to weld and braze there are no current fast procedures to determine the homogeneity. In order to eliminate the deficiencies two methods were developed that have impact in the domain.

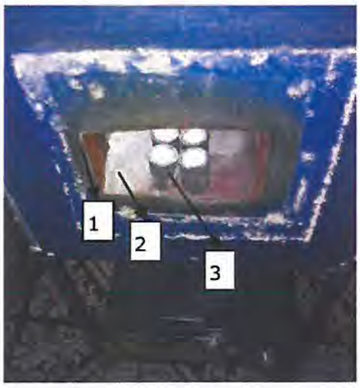
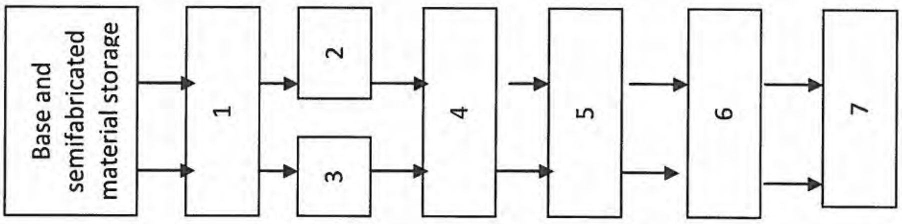


Figure 2.1. Test sample.
1-homogenus mixture; 2-grafitt calibrated chamber; 3-argon protection oven.

Figure 2.2. Test coated rods.
1-coated rod; 2-delimitating element from ceramic graphite; 3-vacuum oven.

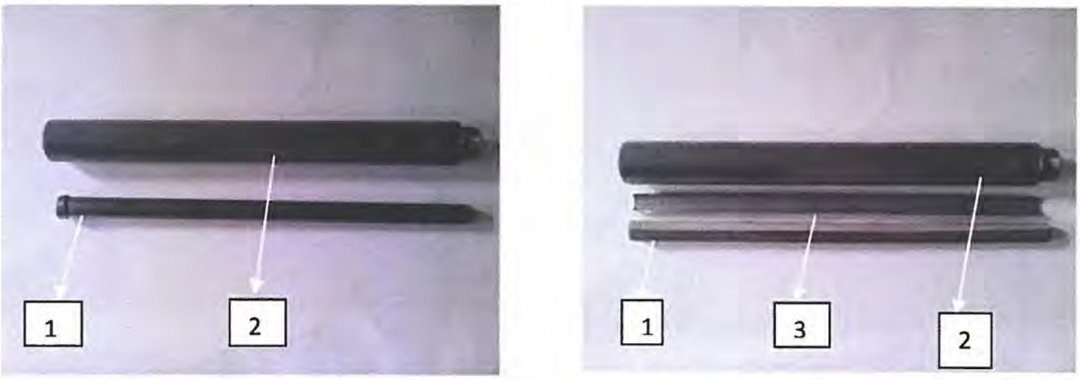
Manufacturing line block scheme:



- Machines, detection and dosage SDVs for components in the product recipe(1);
- Mixing installations for powders and paste mass(2);
- Rod straitening and debiting machines(3);
- Screw or piston extrusion equipped with rod feeder and coating calibration capacity(4);
- Calm air cooling chamber, with the possibility to control humidity and drying temperature(5);
- Calcinations oven(6);
- Laboratory specialized in testing and characterising brazing materials(7);

Deficiencies that may appear at manufacturing tools when extruding are:

1. The rods may get stuck in the guidance roll, innovatively solved by the elastic guidance system.

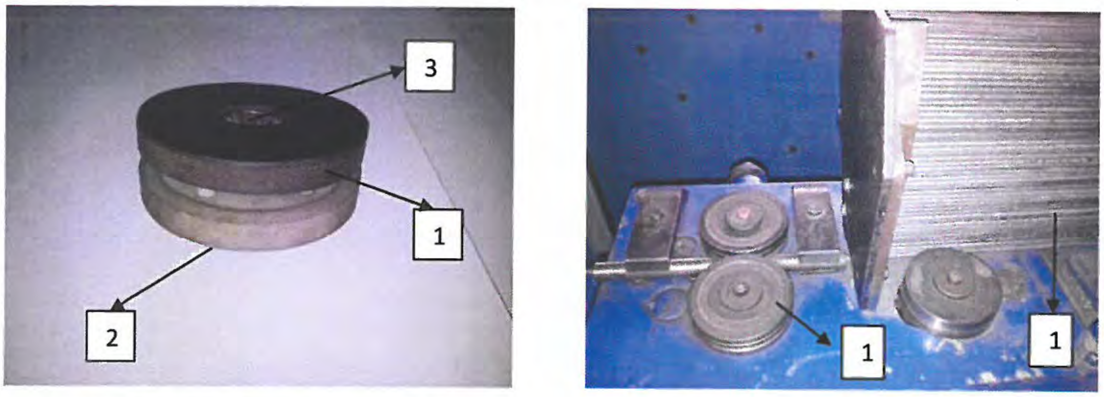


a)1-bare rod guide made from steel and calibrated inside; 2-guider support equipped with blocking system.

b) 1-bare rod guide made from extruded teflon pipe; 2- guide support equipped with block system; 3-steel semi elastic support.

Figure 2.8. Entrainment and guidance system.

2. The rods can be deformed under the action of the entrainment metallic rolls, innovatively solved by implementing double roles, one made from bakelite and second of teflon, with the possibility of controlling the pressing and pushing pressure by determining the space between them.



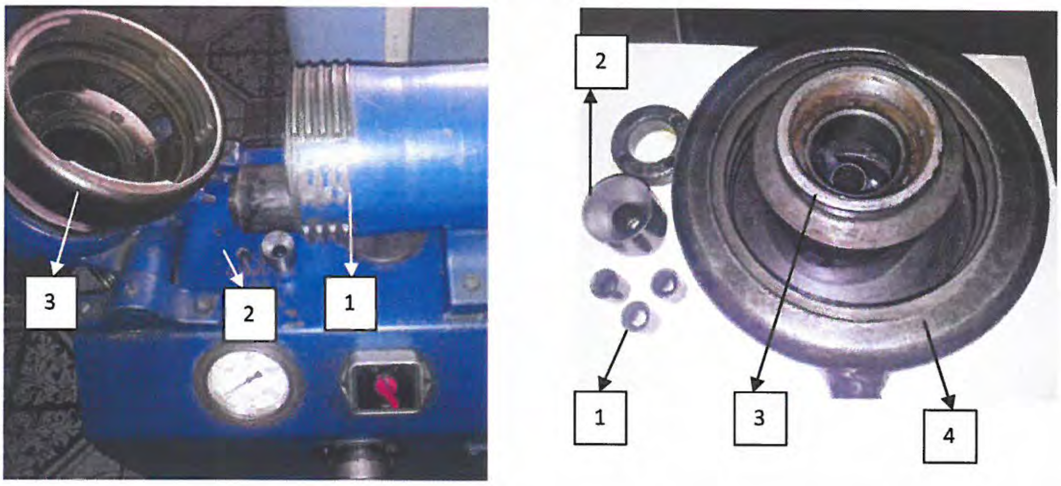
c) 1-backelote roll; 2-teflon roll; 3-gap adjustment system between rolls.

d) 1- entraining steel rolls; 2-rods in movement.

Figure 2.8. Guidance and entrainment system

Expriments regarding the coatings behaviour at extrusion, highlights the need to develop technical and technological compromises between the participants of the manufacturing process by extruding the coated rods for brazing.

To this end a platometer was built and used to develop research on extrusion phenomenas.



a)1-power cylinder; 2-coat calibration and lamination system; 3-coat extrusion space.

b) 1-calibrated extrusion nozzle; 2-nozzle designed support 1; 3-designed support to sustain the assemble 2; 4-locking system 3 extrusion space.

Figure 2.4. Experimental plasticizer, assembly (a), details (b).

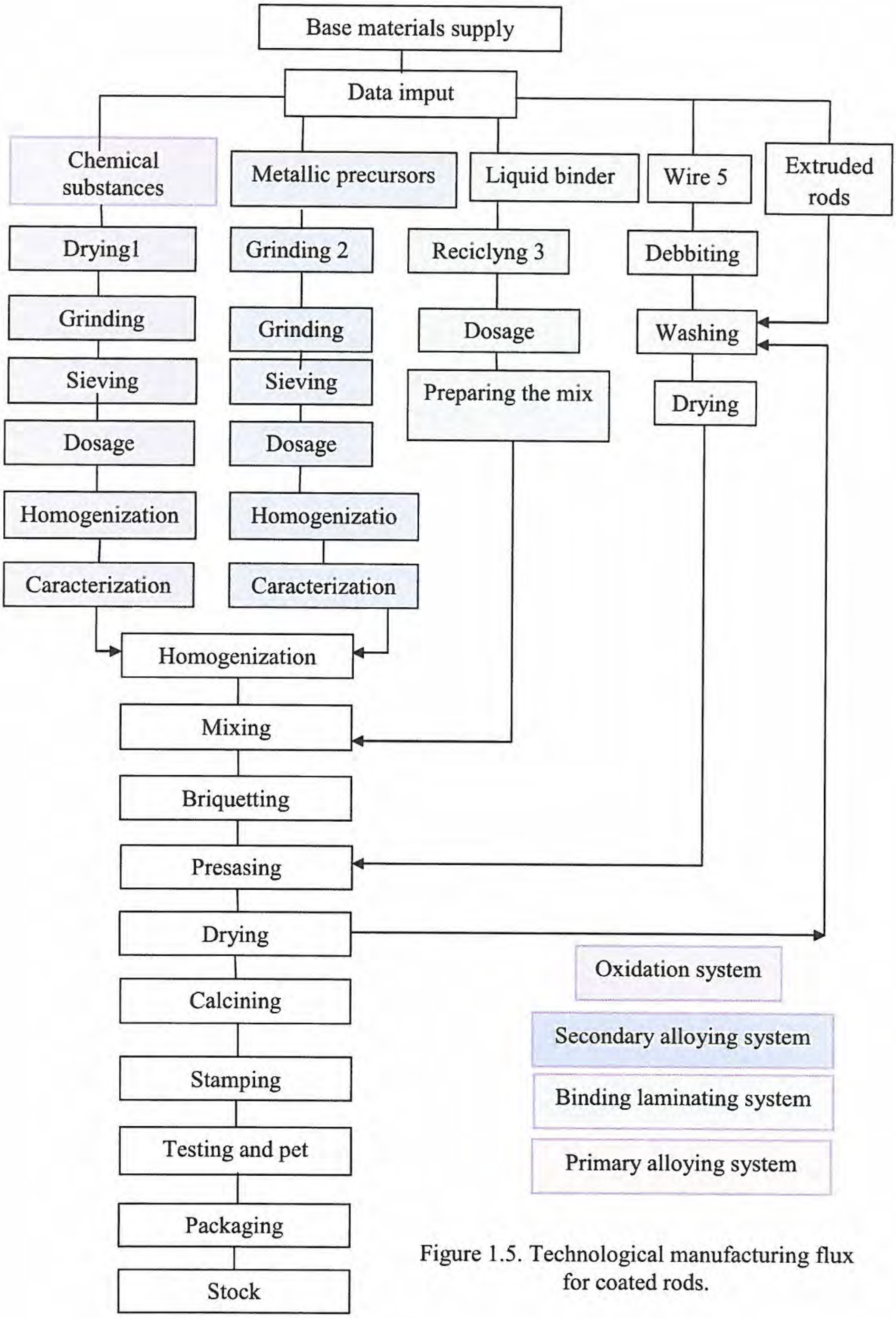


Figure 1.5. Technological manufacturing flux for coated rods.

The plasticity meter theus developed used to research the characteristics of **the generic recipe.**

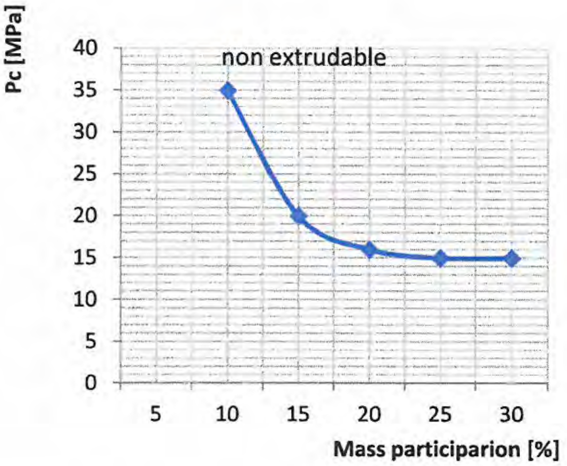
Table 2.2. Generic recipe of the coating mass.

Components	Difference of participation /%/		Investigation step /%/
	1a	1b	
Oxidation system type FH10 SR EN 1045:1999	65-85	70	5 (1a)
Alloying system	10	10	0
Laminating-plasticizing hydric system	5-25	20	5 (1a)

Two research scenarios were developed, the mutual influence of manufacturing parameters and coated rods, function to physical and morphological characteristics from the product recipe.

1.a – with variations in the participation of the oxidation and Laminating-plasticizing system.

1.b – on a representative recipe for the domain.



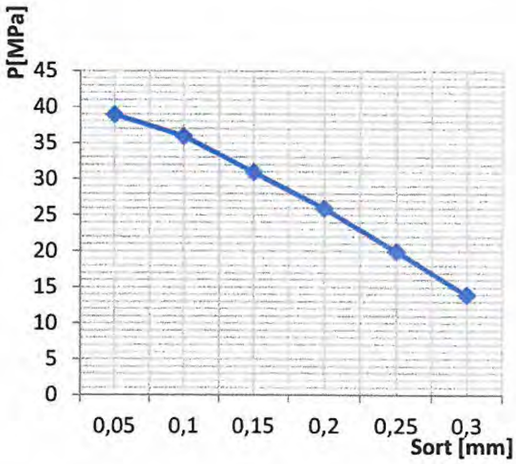


Figure 2.5. Dependency of the extrusion pressure on the participation ratio of the plasticizer binder system in the total coating mass.

Figure 2.6.Dependency of the extrusion pressure on grain size in the making of the alloying system.

Manufacturing stands for advances precursors. Stands used to melt base materials are consisted from machines and elements specific to each manufacturing process of the casted briquettes. Before melting, the base materials have been weighed and dosage according to the laboratory recipes, with or without flux.

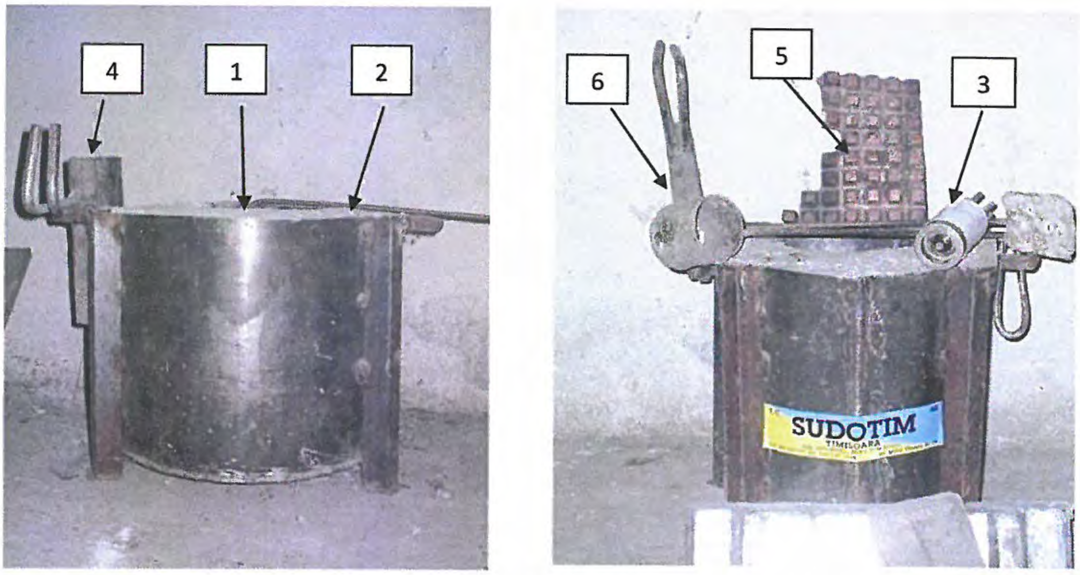


Figure 3.1. Melting stand with gas and compressed air flame.
1 – oven caster; 2 – isolating cylinder; 3 – burner with liquefied petroleum gas;
4 – casting shape; 5 – casted briquettes; 6 – casting pot.

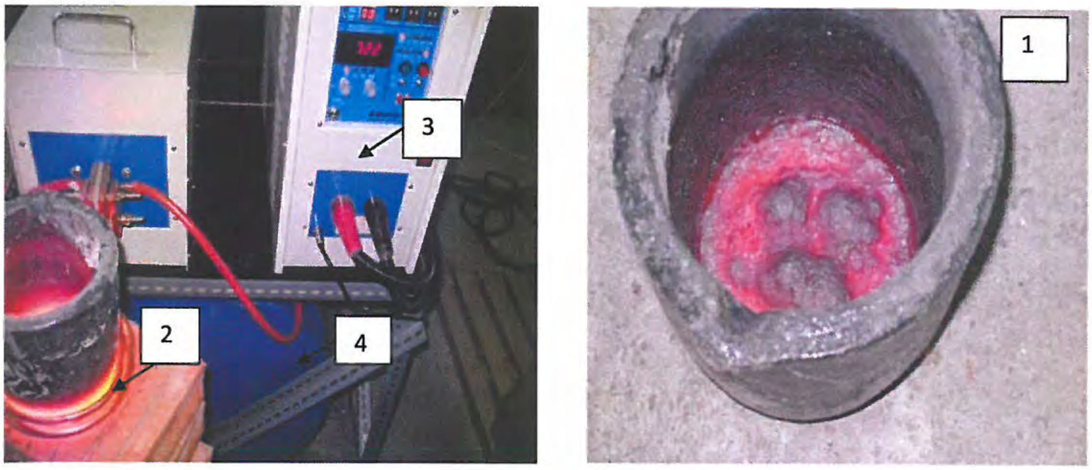


Figure.3.2. Melting stand in CIF.
1 – graphite pot; 2 - inductor; 3 – high frequency current generator;
4 – water cooling installation.

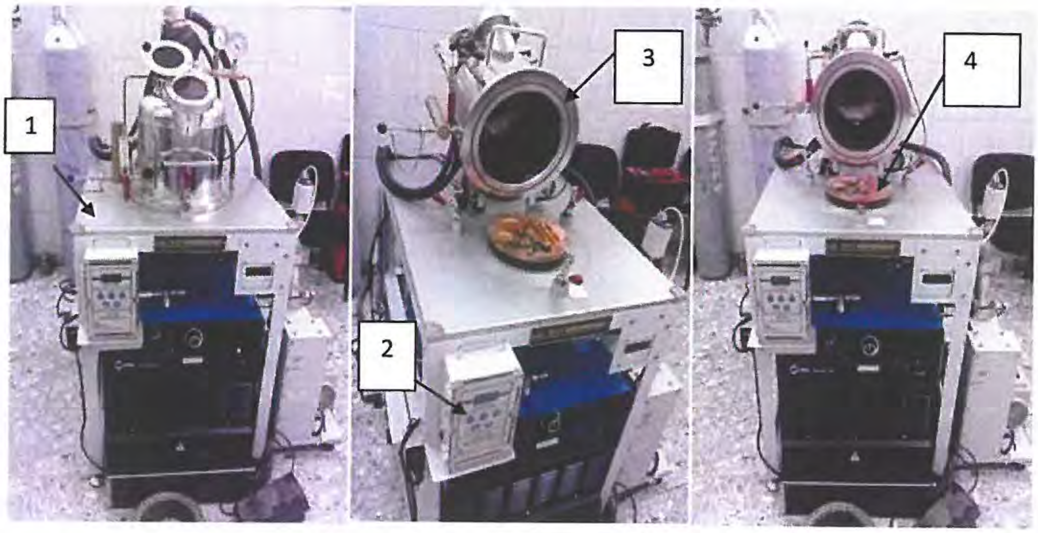


Figure 3.3. Re-melting installation with arc and vacuum MRF ABJ 900.
1 – installation support frame; 2 – command panel; 3 – vacuum work chamber;
4 – melting panel.

Developing batches of chemically active materials in CF and CIF ovens was made by direct melting copper, namely phosphorous copper, followed by dissolving the alloying elements in its melt. In the RAV case, melting is done simultaneous in the copper tray, cooled with water, and respecting the positions of loading components from the try to the surface of the electric arc attack, in ascending order to the specific weight, to rapidly form a melted bath of copper that includes elements that have a evaporating tendency (Zn).

When calculating metallic load, the RAV procedure kept into consideration the theoretic degrees of assimilation of the melt elements and eventual loss by evaporation during the vacuum metallurgic process or the controlled argon atmosphere procedure. These loses are reduced as the load is extremely clean (cleaned with ethanol and ultrasounds chamber for 30 min), the developing time is also short, that limited evaporation loss to the maximum during the electric arc procedure. Technological parameters and grain size established by minimum loss conditions dosed by batches of 25 grams/socket.

Table 3.5. Technological parameters for CF+CIF.

Alloy type	Melting procedure/ Planking characteristics	Load	Flux	Component order	Nature of the casting shape
50%Cu-50%Sn (1)	CF/acid magnesium - silicon	1000gCu +1010gSn	43% fluorspar +8%borax +24%criolit +27%ZnCl	1.Cu-lichid 2.Sn	Cast iron
50%Cu-48%Sn-2%Si	CF/acid magnesium - silicon	1000g Cu +970g Sn +40g Si	43% fluorspar +8%borax +24%criolit +23%ZnCl +4%alumina	1.Cu 2.Sn 3.Si	Cast iron
47%Cu-50%Sn-3%P [BinchiciuE, 2014c]	CF/acid magnesium - silicon	1000g CuP180 +1010g Sn	43% fluorspar +8%borax +24% cryolite +27%ZnCl	1.CuP180 2.Sn	Cast iron
50%Cu-45%Sn-5%P	CF/ magnesium - silicon	1100g CuP181 +900g Sn	43% fluorspar +8%borax +24% cryolite +27%ZnCl	1.CuP181 2.Sn	Cast iron
50%Cu-40%Sn-8%P-2%Si	CIF/ graphite	1020g CuP14 +880gSn +30g Si	43% fluorspar +8%borax +24% cryolite +21%ZnCl +6%alumina	1.CuP14 2.Sn 3.Si	Ceramic
25%Ag-45%Cu-20%Zn-1,5P-8,5%Sn	CIF/ graphite	1030g Ag156 +500g CuP180 +510g CuSn (1)	43% fluorspar +8%borax +24% cryolite +27%ZnCl	1.CuP180 +Ag156 2.CuSn	Ceramic
80%Cu-15%Sn-3%Si -2%P	CIF/ graphite	1600g CuP180 +380gSn +30gSi	43% fluorspar +8%borax +24% cryolite +23%ZnCl +4%alumina	1.CuP180 2.Sn 3.Si	Cast iron

Table 3.6. Load structure for RAV procedure.

Alloy type	Load
54%Cu-43%Sn-3%P	15g Phosphorous copper (CuP180)
	10g Tin 99,90
50%Cu-47%Sn-3%P	13g Phosphorous copper (CuP180)
	12g Tin 99,90
55%Cu-38%Sn-3%Ag-4%P	12g Phosphorous copper (CuP283)
	13g Tin 99,90
49%Cu-38%Sn-9%Ag-4%P	15g Phosphorous copper (CuP286)
	10g Tin 99,90
92%Cu-6%P-2%Si	25,4g Phosphorous copper (CuP181)+ 0,5g Metallic silicon
89%Cu-6%P-5%Si	23,75g Phosphorous copper(CuP181) +1,25gS Metallic silicon
85%Cu-5%P-10%Si	23,72g Phosphorous copper (CuP181) +2,5g Metallic silicon
80%Cu-5%P-15%Si	21,25g Phosphorous copper (CuP181) +3,75g Metallic silicon
75%Cu-5%P-20%Si	20g Phosphorous copper (CuP181)+ 5g Metallic silicon

Table 3.7. Chemical composition of the precursors developed with CF and CIF installations.

Precursor type	Elemental chemical composition in [mass%]					
	Cu	Sn	P	Si	Ag	Others
50%Cu-50%Sn(1)	50,66	48,32	---	---	---	1,2
50%Cu-48%Sn-2%Si	49,20	48,10	---	1,90	---	0,8
47%Cu-50%Sn-3%P [BinchiciuE, 2014c]	48,60	46,10	3,20	---	---	Cd+As+Pb= 0,04
50%Cu-45%Sn-5%P	50,31	44,82	4,73	---	---	0,14
50%Cu-40%Sn-8%P-2%Si	50,44	39,33	7,62	1,85	---	0,76
25%Ag-45%Cu-20%Zn-1,5P-8,5%Sn	45,38	8,35	1,48	---	24,75	Zn=18,93 Rest 1,11
80%Cu-15%Sn-3%Si-2%P	81,35	13,61	1,92	2,95	---	0,17

Table 3.8. Chemical composition of precursors developer by RAV installation.

Precursor type	Elemental chemical composition in [mass%]					
	Cu	Sn	P	Si	Ag	Others
54%Cu-43%Sn-3%P	53,7	42,8	3,4	---	---	0,1
50%Cu-47%Sn-3%P	50,3	46,8	2,8	---	---	0,1
55%Cu-38%Sn-3%Ag-4%P	55,6	37,5	3,7	---	3,1	0,1
49%Cu-38%Sn-9%Ag-4%P	48,7	37,4	4,4	---	9,4	0,1
92%Cu-6%P-2%Si	92,12	---	5,88	2,00	---	0,00
89%Cu-6%P-5%Si	89,28	---	5,72	5,00	---	0,00
85%Cu-5%P-10%Si	84,60	---	5,40	10,00	---	0,00
80%Cu-5%P-15%Si	79,88	---	5,12	15,00	---	0,00
75%Cu-5%P-20%Si	75,20	---	4,80	20,00	---	0,00

To determine structural and hardness conditions the developer precursors have been examined according to EN ISO 17639:2013 [EN17639, 2013], STAS 7626-79 [STAS7626, 79] and CR12361:2003 [CR 12361, 2003], on the optic microscope Olympus GX51 from LAMET Bucharest [Voiculescu, 2014]. Samples have been delivered under the form of casted tablets from which samples were taken. The mechanical polishing procedure was applied [Voiculescu, 2015] and shining with abrasive powder made of alpha alumina. Surfaces shined have been subjected to attack by emerging 3 minutes in metallographic reactive with the following recipe: 2gFeCl3, 5mlHCl, 30mlH2O, 60ml ethanol.

Detected structures on the representative precursors 50%Cu-47%Sn-3%P; 85%Cu-5%P-10%Si; 49%Cu-38%Sn-9%Ag-4%P; 80%Cu-15%Sn-3%Si-2%P; 50%Cu-45%Sn-5%P;50%Cu-50%Sn are shown in the table 3.9 and figure 3.7, 3.8, 3.9, 3.10, 3.11, 3.12.

Table 3.9. Microscope analysis results.

Sample composition	Microscope examination [100x;500x]		Fig. No.
	Constituents SR 5000-97	Defect STAS 5500-74	
50%Cu-47%Sn-3%P	Dual phase solid solution α+μ, rich in copper with fine oxides	unnoticeable	3.7
85%Cu-5%P-10%Si	Solid solution α rich in copper with fine oxide	unnoticeable	3.8
49%Cu-38%Sn-9%Ag-4%P	Solid solution α rich in copper with particles of unaligned oxides	unnoticeable	3.9
80%Cu-15%Sn-3%Si-2%P	Solid solution α rich in copper with particles of unaligned oxides	unnoticeable	3.10
50%Cu-45%Sn-5%P	Solid solution α rich in copper with fine oxide	unnoticeable	3.11
50%Cu-50%Sn.	Solid solution α rich in copper with fine oxide	unnoticeable	3.12

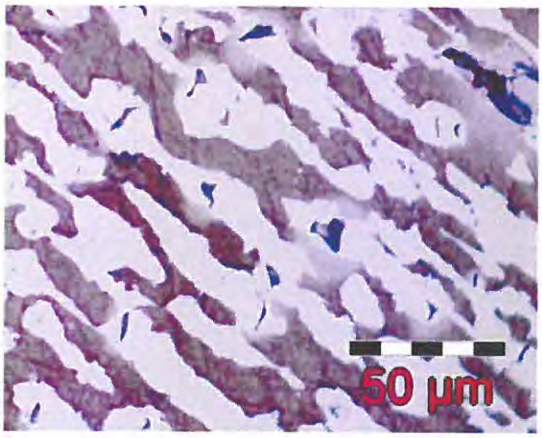


Figure 3.7. Microstructure of the dual phase alloy 50%Cu-47%Sn-3%P casted. Growth 500x.

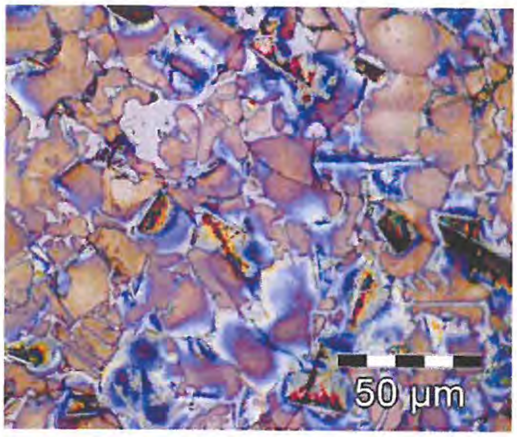


Figure 3.8. Alloy microstructure 85%Cu-5%P-10%Si casted. Growth 500x.

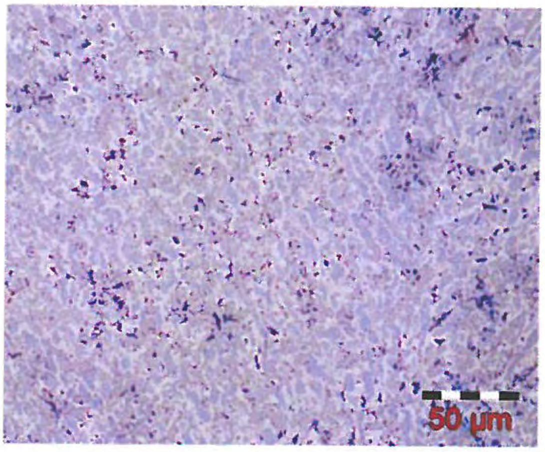


Figure 3.9. Microstructure of the dual phase alloy 49%Cu-38%Sn-9%Ag-4%P. Growth 500x.

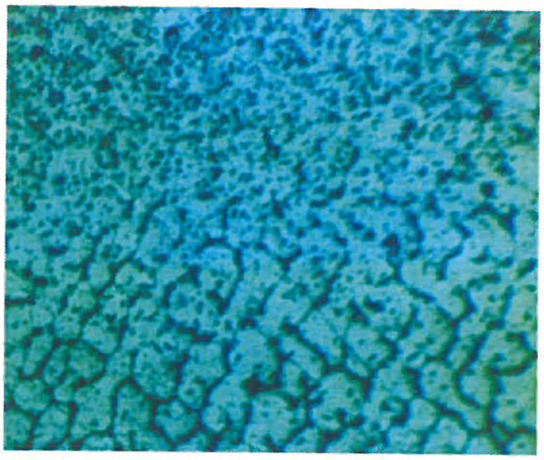


Figure 3.10. Microstructure of the dual phase alloy 80%Cu-15%Sn-3%Si-2%P. Growth 100x.

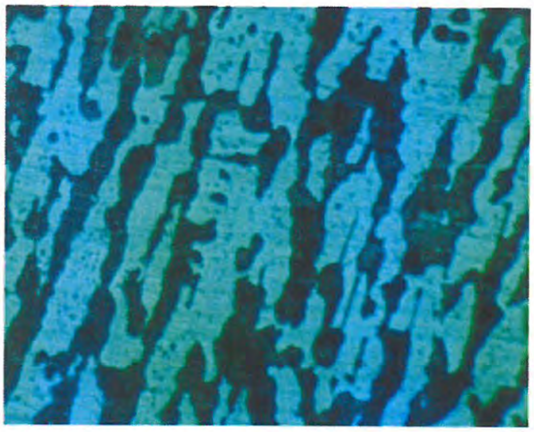


Figure 3.11. Microstructure of the dual phase alloy 50%Cu-45%Sn-5%P. Growth 500x.

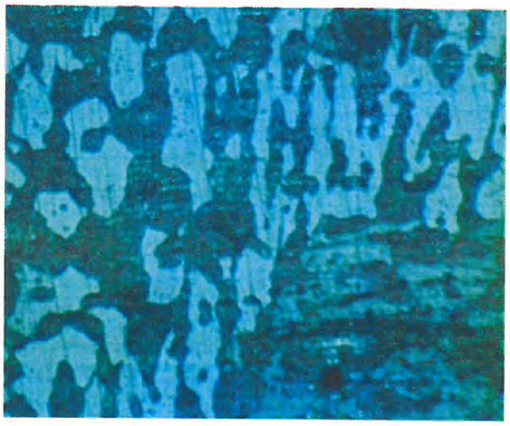


Figure 3.12. Alloy microstructure 50%Cu-50%Sn. Growth 500x.

Manufacturing procedure for precursors by grinding

Figure 3.23. Planetary mill with load in the nest.

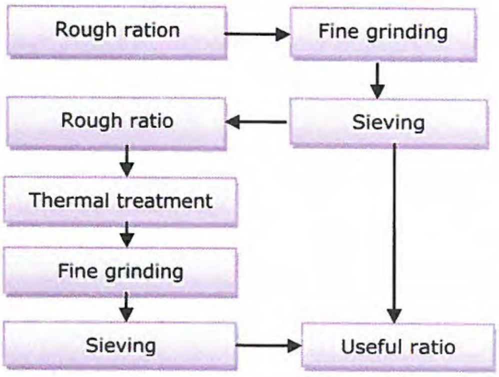


Figure 3.24. Technological manufacturing flux for chemically active powders.

Table 3.13. Technological parameters at grinding.

Alloy/Mark	Filling coefficient [%]	Nest rotation [rot/min]	Grinding time [ore]	Exiting coefficient [%]
50%Cu-47%Sn-3%P/1	0,5	4350	65	99,2
		5800	1	
85%Cu-5%P-10%Si/2	0,5	4350	58	98,9
		5800	1	
49%Cu-38%Sn-9%Ag-4%P/3	0,3	4725	183	83,2
		6300	2	
80%Cu-15%Sn-3%Si-2%P/4	0,3	4725	122	89,8
		6300	1	
50%Cu-45%Sn-5%P/5	0,5	4350	63	98,3
		5800	1	
50%Cu-50%Sn/6	0,5	4350	56	99,6
		5800	1	

Elemental chemical composition of deposits with VIAg25SnSiPR

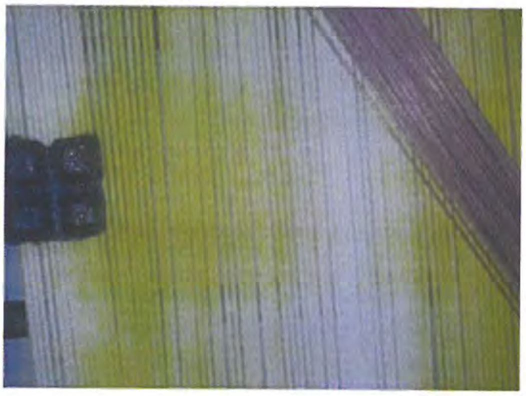


Figure 4.4.Coated rods VIAg25SnSiPR, precursors and nude rods.

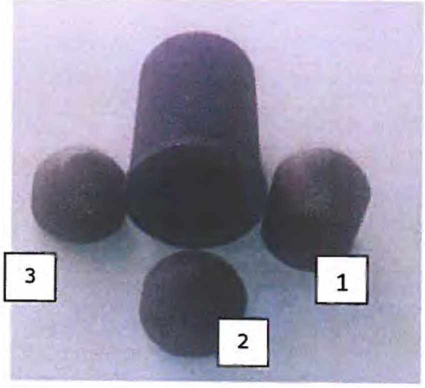


Figure 4.5. Graphite caster and deposited metal (DM) using coated rods.

Figure 4.6. Chemical analysis MV and DM.

Figure 4.7. Deposited metal (DM) analysed.

Table 4.6.Chemical composition on DM and MV.

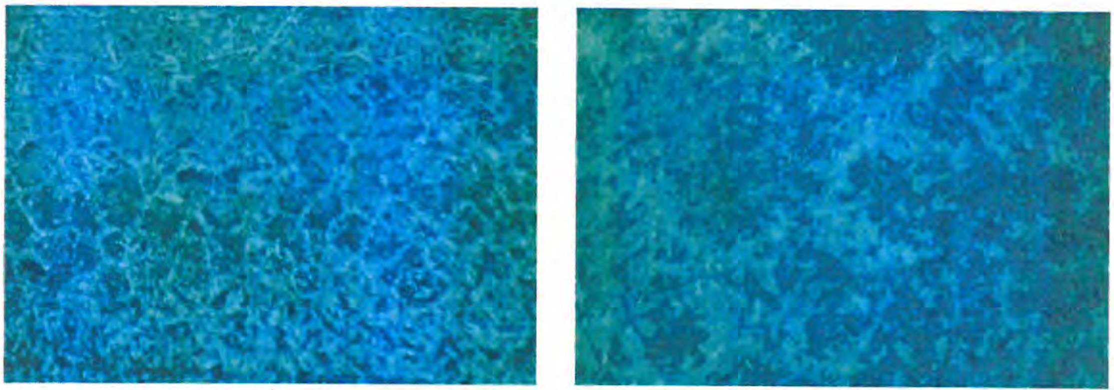
Sample mark	Composition [mass %]							
	Ag	Cu	Zn	Cd	Sn	Si	P	Pb
MV Ag125 SR EN ISO 17672/2010 prescribed	24,0 26,0	39,0 ... 41,0	31,0 ... 35,0	-/ 0,010	1,5 ... 2,5	-//-	max. 0,008	max. 0,025
MV determined	25,2	40,5	32,7	0,008	1,8	0,12	0,006	0,015
DM	25,6	40,7	31,2	0,007	2,1	0,25	0,02	0,011

Structural and hardness characterisation of the load with VIAg25SnSiPR

Table 4.7. Metallographic examination results of DM with VIAg25SnSiPR.

Sample	Microscopic examination SR EN 12797 : 2002		
	Constituents SR 5000-97	imperfections STAS 5500-74	Nr. figure
Deposited metal (DM)	Fine melting structure	undetected	4.8, 4.9

In figure 4.8 we can see dual phases structures, soloed substances α – pale and solid solutions β - darker. No micro-fissures are detected or imperfections type hydrogen disease or/and oxygen pores.



a) b)

Figure 4.8. DM dual phase solutions, solid solutions α – pale and solid β – darker -[100X], b-[500X].

Table 4.9. Hardness values HB.

Product	Hardness values HB	Media
New	160; 167; 160; 167; 160	162,8
Standard	143; 152; 157; 143; 143	147,4

Recipe and manufacturing process for VIAg30SnR

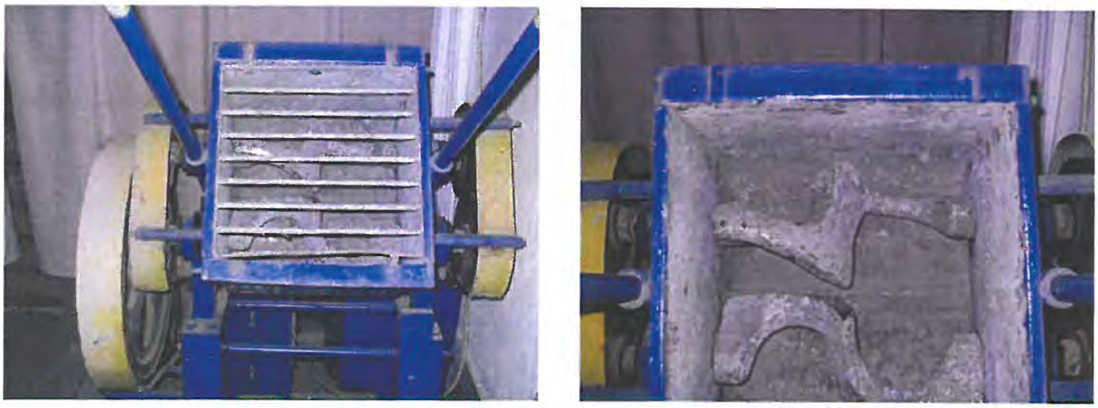
Table 4.12. Experimental recipe for VIAg30SnR.

Base materials	Product participation [mass%]	Constituents [mass%]
Bare rods SR EN ISO 17672:2010	50-80%	Ag130; Φ2x500mm
Oxidizing flux FH EN 1045:1999	49-10% max.size 0,2	• 25% mechanical mixture[2/3acid boric+1/3(borax+trioxide de bore)] • 35% potassium phosphate • 25% (1/2florură de potassium +1/2tetraborat de potassium) • 15%(binder plasticizer)
Active precursor	1-10% nano-powders	Ag156 EN ISO17672:2010

Table 4.15. Process parameters used to develop VIAg30SnR rods.

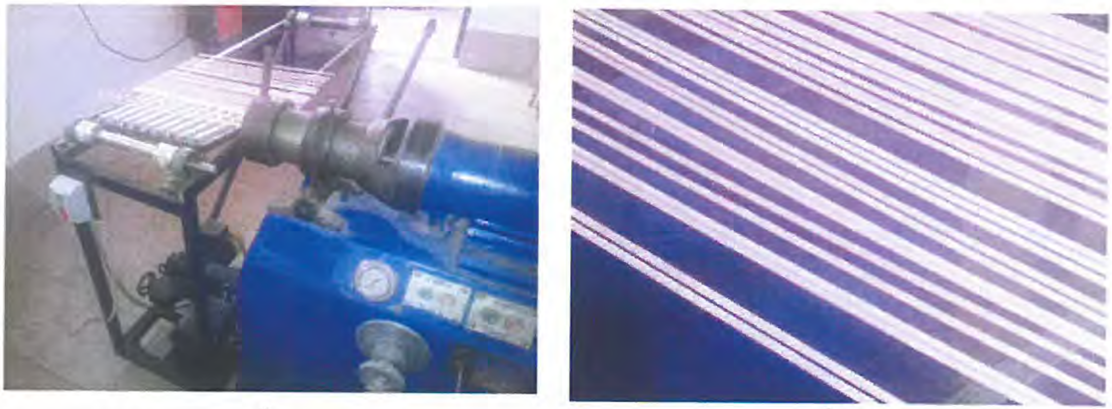
Process parameters	Experimental results
Briquetting temperature	Min. 40°C
Briquetting pressure	20 ±0,1 MPa
Extrusion pressure	25±0,1 MPa
Rods mass debit	approx. 4,5 kg/hour
Coat mix mass debit	approx. 3,5kg/hour
Coated rods takeaway tape speed	approx. 8,0 kg/hour

Heat manufacturing process



a. b.

Figure 4.11. Snail mixer, a) mixer b) snails in nest.



a. b.

Figure 4.13. Production line, a) pressure multiplication line and takeaway tape with one way, b) brazing rods.

Deposition characteristics with VIAg30SnR

Table 4.16. Chemical composition of the analysed materials

Code	Composition [mass%]							
	Ag	Cu	Zn	Sn	Si	Cr	Mo	V
Ag130 prescribed	29-31	35-37	30-34	1,5-2,5	-/0,05	-/0,1	-/0,1	-/0,1
Ag130 determined	30,2	35,8	31,4	2,1	0,01	0,06	0,08	0,02
Ag156 prescribed	55-57	21-23	15-19	4,5-5,5	-/0,05	-/0,1	-/0,1	-/0,1
Ag156 determined	56,2	22,4	16,3	4,8	0,03	0,08	0,04	0,04
MD VIAg30SnR	30,5	35,3	30,1	2,6	0,01	0,08	0,07	0,03

Table 4.17. Metallographic analysis results when brazing with VIAg30SnR.

Sample	Microscopic examination SR EN 12797 : 2002		
	Constituent SR 5000-97	Imperfections STAS 5500-74	Figure
Deposited metal (DM)	Fine casting structure	unnoticeable	4.16

Table 4.18. Hardness values/micro-hardness measured on the deposited metal when brazing with VIAg30SnR.

Hardness values HB/DM	Micro hardness VICKERS - HV0,1/DM	Media
175; 180; 180; 172;179	195; 205; 198; 201; 187 Measurement uncertainty 2,14%	177,2 HB 197,2 HV0,1

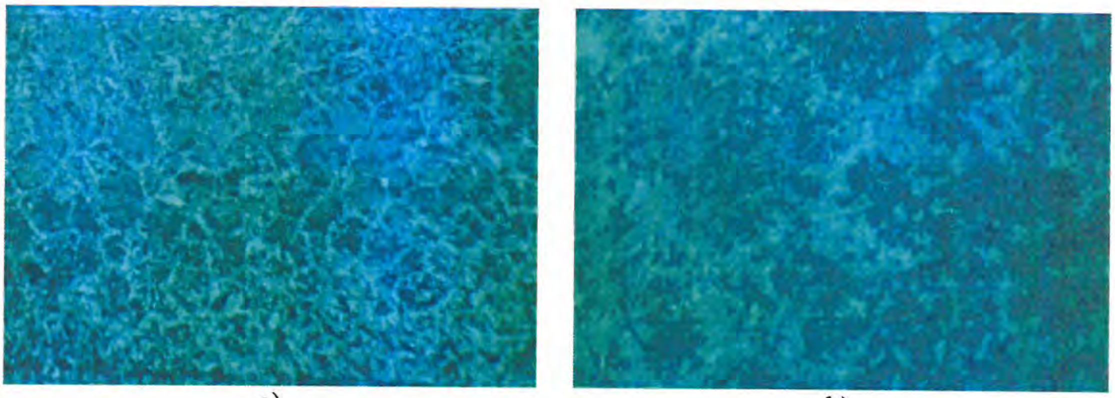

a) b)

Figure 4.15.Structural characteristics of DM. a- [100X], b – [500X].

Recipe and manufacturing process for VIAg40SnR

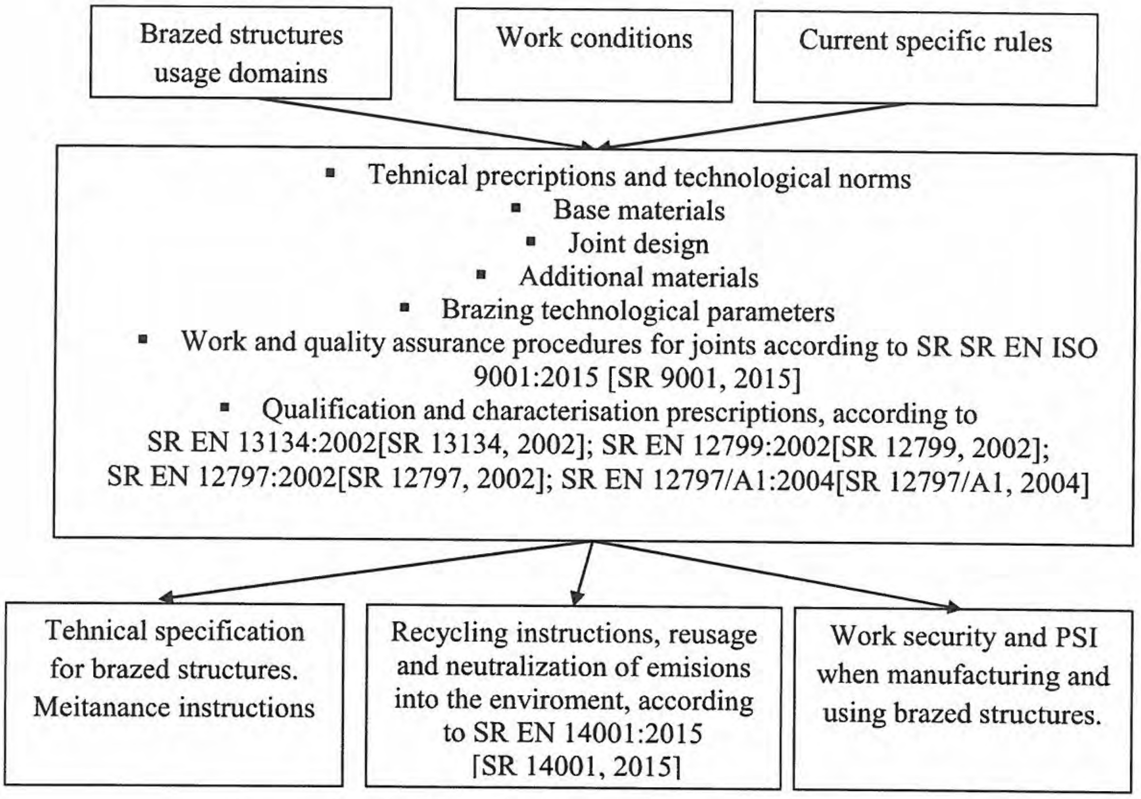
Table 4.21. Experimental recipes for rods type VIAg40SnR.

Base materials	Product participation [mass%]	constituents, [mass%]
Nude rods SR EN ISO17672:2010	45-75%	Ag140; Φ2x500mm
Oxidizing flux FH SR EN 1045:1999	30-15%	• 25% mechanical mixture (2/3 boric aid+1/3borax) • 35% potassium hydroxide • 25% [1/2florides in homogenous mixtures de(potassium+calcium+criolit+Na_2SiF_6) +1/2tetraborat de potassium] • 15%(binder plasticizer)
Active precursors, nano-powders	25-10%nano-powders	10%Ag156+5%(Cu50-Sn48-Si)

Table 4.24. Process parameters to manufacture VIAg40SnR.

Process parameters	Experimental results
Briquetting pressure	25±0,1 MPa
Extrusion pressure	25±10 MPa
Rods mass debit	cca. 7 kg/hour
Coat mass debit	cca. 4 kg/hour
Coated rods takeaway tape speed	cca. 11 kg/hour

Brazing methodology



Brazed structures usage domains

Work conditions

Current specific rules

- Tehnical precriptions and technological norms
- Base materials
- Joint design
- Additional materials
- Brazing technological parameters
- Work and quality assurance procedures for joints according to SR SR EN ISO 9001:2015 [SR 9001, 2015]
- Qualification and characterisation prescriptions, according to SR EN 13134:2002[SR 13134, 2002]; SR EN 12799:2002[SR 12799, 2002]; SR EN 12797:2002[SR 12797, 2002]; SR EN 12797/A1:2004[SR 12797/A1, 2004]

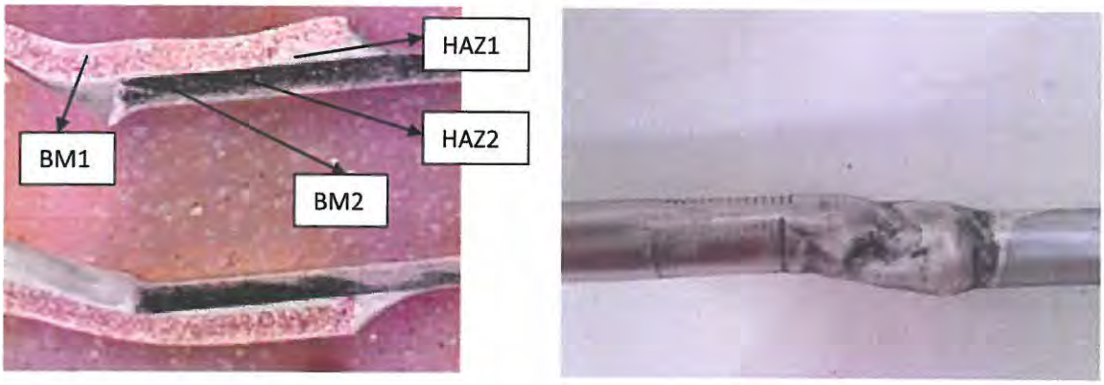
Tehnical specification for brazed structures. Meitanance instructions

Recycling instructions, reusage and neutralization of emisions into the enviroment, according to SR EN 14001:2015 [SR 14001, 2015]

Work security and PSI when manufacturing and using brazed structures.

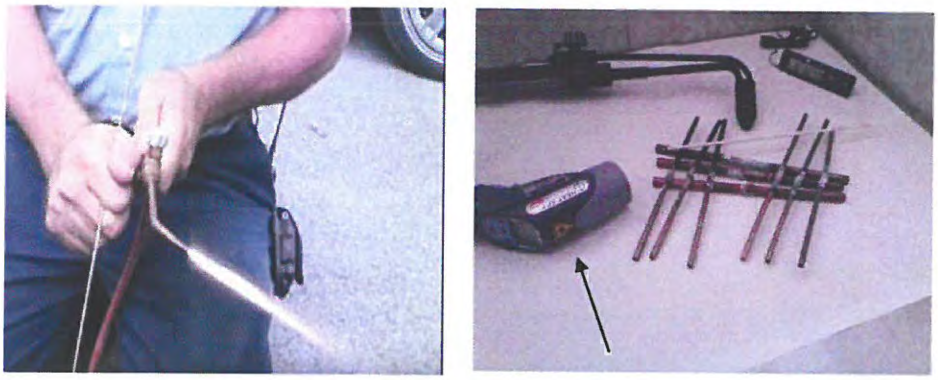
Figure 5.1. The logical structure of the brazing procedure.

Developing steel pipe in copper pipe joints



a. b.

Figure 5.2. Steel pipe in copper pipe joint.
a) Joint projection; b) heterogeneous joint.



a. b.

Figure. 5.3. adjusting the oxi-acetylene flame:
a) Oxi-acetylene flame b) brazed joints and work equipment

Characterizing heterogeneous joints, type pipe in pipe

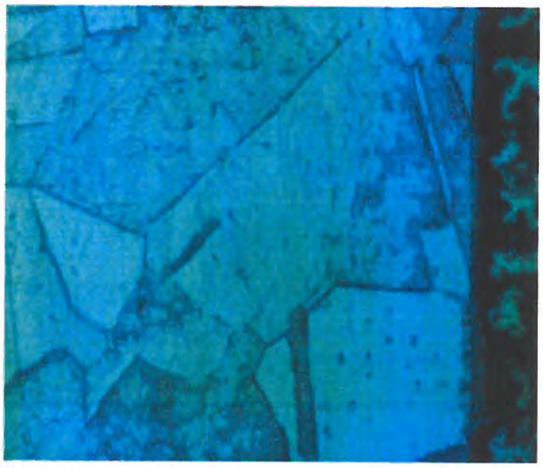


Figure 5.5 HAZ-Copper [attack E1, 500X].

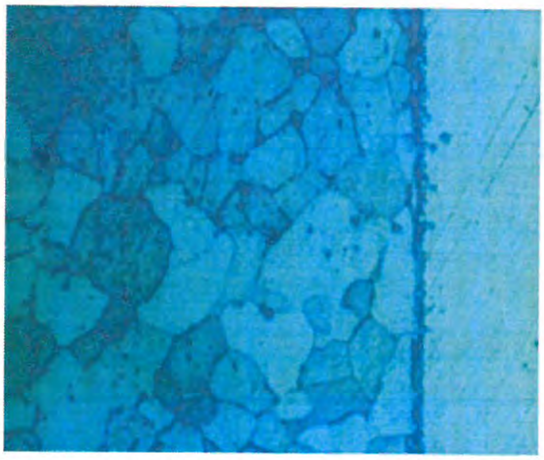


Figure 5.6 HAZ2-Steel[attack Nital2%,500X].

Table 5.3. Hardness tests.

Tested zone	BM$_1$	HAZ$_1$	SUD	HAZ$_2$	BM$_2$
Micro-hardness Vickers HV0,1	113	92	160	128	143
	122	94	160	132	139
	128	92	181	126	151

Table 5.4 Traction tests.

Sample mark	Initial diameter d_0 [mm]	Maximum force F_{max}[N]	Breaking zone	No. figure
Cu-OL	6	890	MB (OL)	5.12

Figure 5.8. Sample broke by applying traction.

Developing heterogeneous joints in deep joints

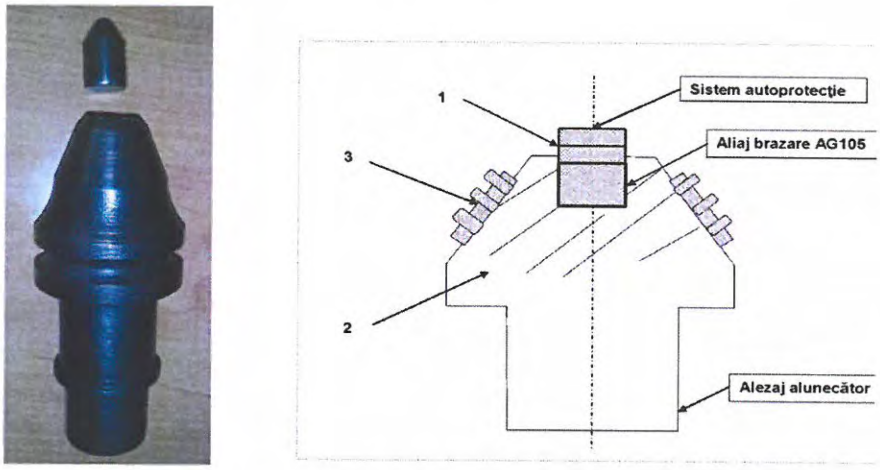
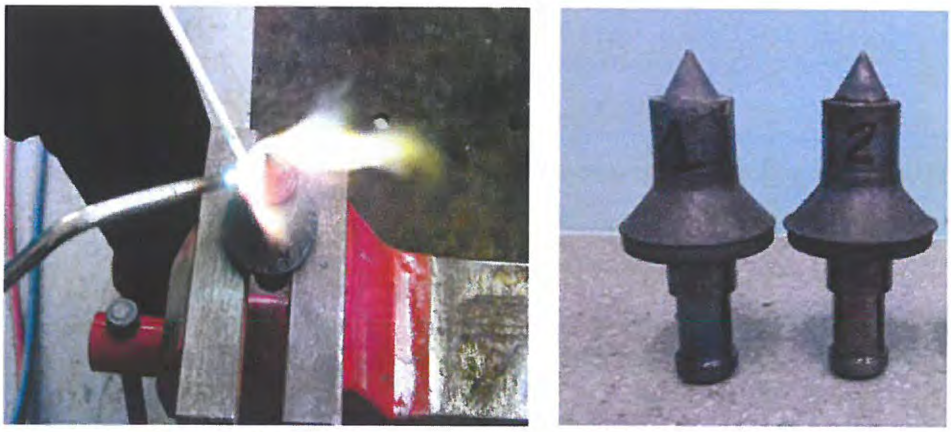


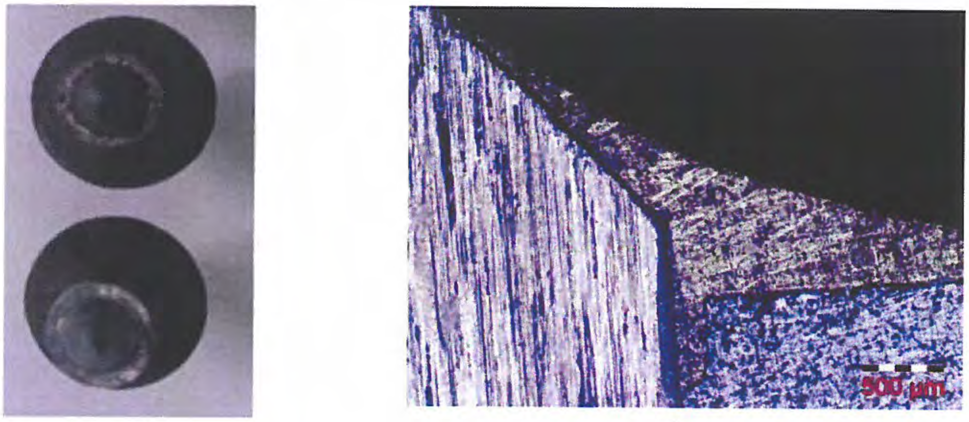
Figure 5.10. mill knife for asphalt stripping machines:
1) reinforcement-cutting body equipped with self-protection system to wear; 2) knife support from low alloyed steel with chromium; 3) spin self-blocking system.



a. b.

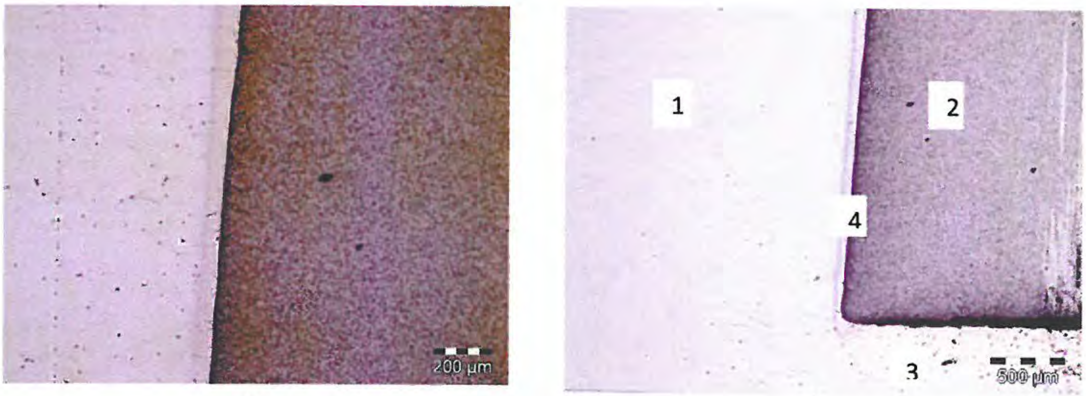
Figure 5.11 gas flame brazed joints:
a) adding brazing layers and filling the joint; b) brazed mill teeth.

Characterising brazed joints



a. b.

Figure 5.12 Brazed joint:
ı) a) visual examination; b) metallographic analysis of the joining area in transversal section, 50X.



a. b.

Figure 5.13 Metallographic analysis images;
a) transition zones 200X; b) transition zones 500X. 1-MB support; 2-BM reinforcement; 3-brazing alloy; 4-thermic influenced area.

Table 5.8.Hardness tests results (HV0, 1).

Tested zone	BM_1-support	HAZ_1-support	DM	CW	Matrices
Micro-hardness Vickers HV0,1	680	550	160	1480	352
	700	515	160	1560	339
	710	535	181	1410	351

Developing homogenous joints with stainless steels

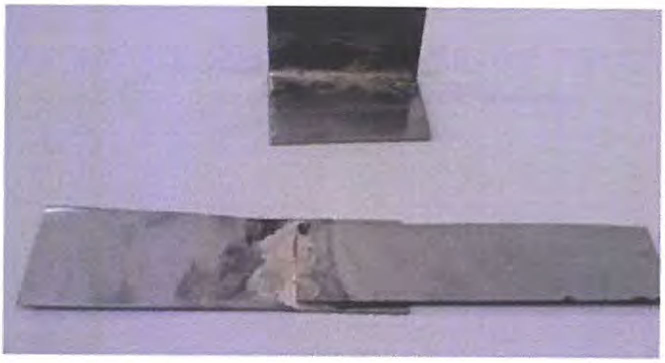


Figure 5.23. Brazed joints made from 304AISI steel.

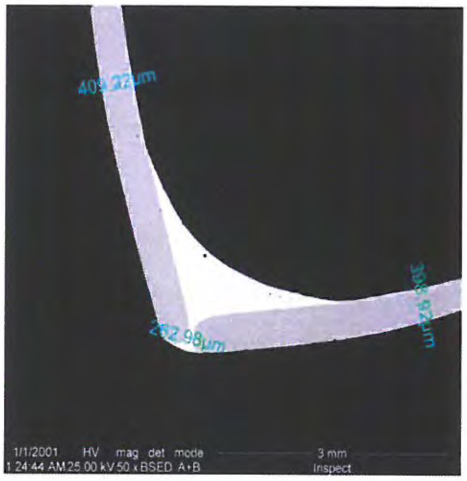


Figure 5.24 Macro-graphic transversal section aspect for brazed corner sample (sample „L")
50X.

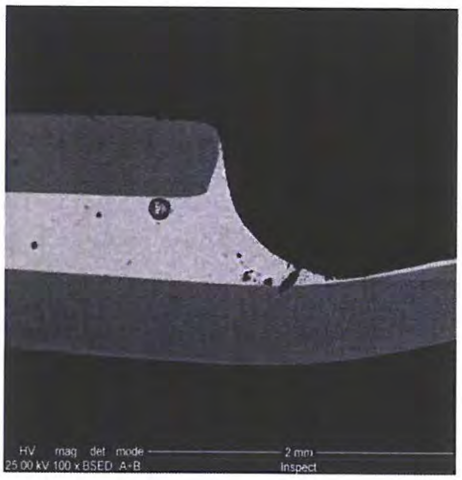


Figure 5.25. Macroscopic image of the overlapped brazed joint.
100X.

Visual examination highlighted pore like discontinues and some flux adherence, accompanied by remaining deformation of the base materials, but did not highlight imperfections such as filling lack, empty spaces, etc.; with a bigger size than 0.5 mm, which validates the process from a visual control point of view.

Examining samples by maro-structural section analysis has shown a good adherence of the addition materials to the base ones and small connection angles between them.

Characterizing the heterogeneous joint

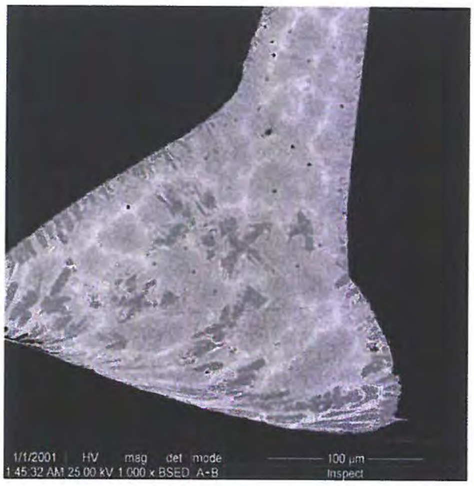


Figure 5.26. Root zone for the corner joint 1000X.

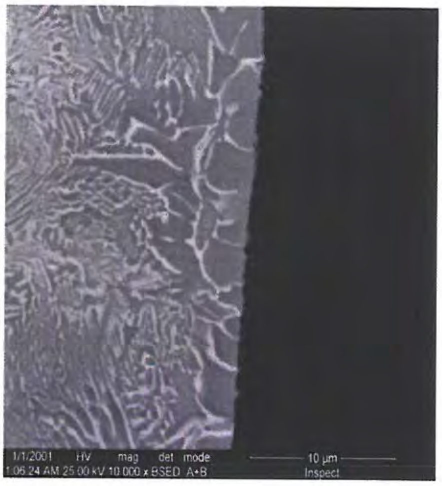


Figure 5.27. Transition zone between brazing material (alloy AgCuZnSn) and base material (stainless steel 18.8) 10000X.

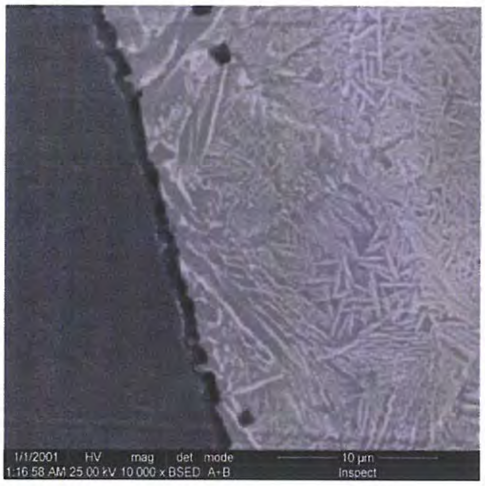


Figure 5.28. Detail in the interface between base material and deposited material. Good adherence and small pores. Addition materials with needle-like microstructure 10000X.

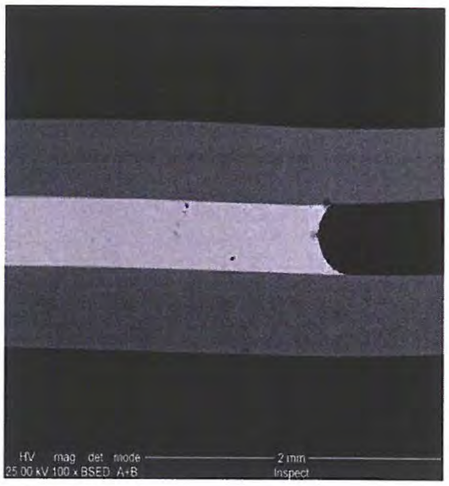


Figure 5.29 Macroscopic image of the brazed joint by overlapping. The addition material exiting zone 100X.

Structural analysis of specific corner and overlapped joint zones did not show defects like precipitation, microfissures or corrosion. The aderancy between addition materials and base materials is good.

Diffusion process analyse

The mettalographic analysis of the transition zones during the experiments, previously detailed, have highlighted diffusion phenomena. Taking into account the physical-chemical characteristics of stainless steel, researching diffusion processes can be considered representative to appreciate the new diffusion capacity of the new generation, chemically active brazing materials.

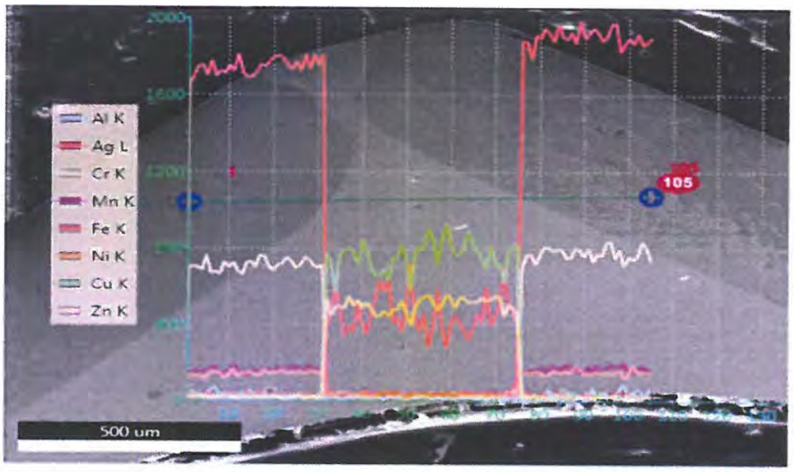


Figure 5.33. Point analysys of the chemical composition in the case of corner brazed joints between componets from austenitic stainless steel ussing Cu-Ag-Zn alloy.

Figure 5.34. Detection points of local chemical composition, Zone A (400x). 1) MB; 2-4) ZIT; 5) interfaces with melted addition material.

Analyzing the above mentioned data highlights copper, zinc and silvers diffusion phenomenon's, found in the brazing materials, in the heat affected zones of the base materials combined with minor effects of element transfer from the coat.

Theoretical personal contributions

- ✓ phenomenological assessment of brazing processes between homogeneous and heterogeneous joints, metallurgical speaking;
- ✓ synthesis of research identified widely in the delivery and use of materials for brazing;
- ✓ assessing issues in current use of filler material;
- ✓ analysis of specific legal norms on industrial use, namely the impact on safety and health operators, including environmental impacts;
- ✓ highlighting significant guidance towards the development of materials for brazing;
- ✓ drafting method of systemic approach to fabricating brazed structure processes;
- ✓ conducting a research on the diffusion process of the main constituents of chemically active brazing materials in stainless steels;
- ✓ elaboration on the principles of conservation laws of matter, method of prediction and formulation of product design and elemental chemical composition of deposits by mass participation in the total product of the alloying systems;
- ✓ development of methods for quick check the degree of mixing powders of mass coating composition and homogeneity freshly extruded rods;
- ✓ development endowment concept for coated brazing rods with the alloying system appropriate to the aim pursued;
- ✓ a concept of guidance system with high protection elastic buckling of nude rods;
- ✓ a concept of components rolling guidance with distinct properties and possibilities for adjusting the down force of soft silver alloy rods by adjusting the gap between mechanical constituents.

Practical personal contributions

- ➢ experimenting with two manufacturing processes used powder form of the alloys with increased physical-chemical and technological proprieties of the coated brazing rods;
- ➢ developing a data base of the chemically active alloys that contains 16 optimized product recipes and technologic manufacturing process parameters by three distinct melting procedures;
- ➢ evolving a homogenization method, dosage and organizing manufacturing lines of pre-alloys with pre-established proprieties;
- ➢ developing a data base with optimised recipes of fluxes used to accomplish through melting copper alloys;
- ➢ designing and developing six new and innovative powder materials, with pre-established proprieties and a mechanic alloy with immediate applicability in the production of new generation brazing materials;
- ➢ developing a data base with structural proprieties and hardness ones of alloys of high interest for developing coated rods for efficient brazing from a technical and economical point of view;
- ➢ developing a flexible manufacturing method for brazing materials with direct application and reasonable costs;
- ➢ developing a new research direction and accomplishing deposits, consisting of two layers, obtained through a single melting, validated by simultaneous experiments of the heating-cooling behaviour of the brazing alloys and the coat;

- ➢ developing a new generation of coated rods for brazing with high yield and enhanced proprieties by equipping the coat with metallic adjutant systems and/or process catalyst, exemplified by three representative marks: VIAg25SnSiPR, VIAg30SnR, VIAg40SnR;
- ➢ developing a new manufacturing process for coated rods for brazing, characterised by the fact that homogenisation and extrusion on the rod is done at T= 50-60°C;
- ➢ applying a new practice identification method through color and deposition mark of coated rods for brazing, characterised by introducing in the oxidizer-pickle coat oxides that are easy to eliminate in slag and some particles that remain in the deposits;
- ➢ appling a method to determine chemical composition of the deposited metal with the new generation rods for brazing;
- ➢ developing the technical sheets for products VIAg25SnSiPR, VIAg30SnR, VIAg40SnR;
- ➢ designing the manufacturing procedure so it assures quality, for rods VIAg25SnSiPR, VIAg30SnR, VIAg40SnR;
- ➢ designing and applying four brazing technologies, with high yield, all according to SR EN 13134:2002[SR 13134, 2002];
- ➢ developing manufacturing and qualifying procedures to assure quality for four industrial applications of brazed structures, implementing into production the new rods, validating results and establishing reasonable costs at three beneficiaries:
  - a) developing and characterising joints type steel pipe in copper pipe;
  - b) developing and characterising joints in deep joint o the reinforcement made from wolfram carbides in the low steel alloyed with chromium support from the component of the asphalt stripping mill teeth;
  - c) developing and characterising joints type steel pipe in tin pipe;
  - d) developing and characterising homogenous joints from stainless steel;

Research future direction and result capitalization

Results capitalization was made by experimenting and qualifying four brazing procedures and implementing them with reasonable costs at three beneficiaries during contract PN-II-PT-PCCA-2011-3.2-0918 - “Advanced materials and technologies designed to manufacture asphalt stripping mill knifes: – MATFREZ”.

The patented solutions have been presented at 5 invention conferences (EUROINVENT, PROINVENT) and won medals as a sign of valour.

Knowledge accumulated will be valued by research to:

- extend the efficient manufacturing principle of brazing materials for a large range of coated rods;
- implementing the principle of equipping the oxidizer flux with chemically/metallurgical active systems in the production of tubular rods for brazing;
- extending the concept of homogenous metallic powder mixture with oxidizer fluxes to develop calibrated doses under the form of pastilles, with usage at mechanized brazing in ovens at series production;
- expanding chemically active precursors to develop new research themes with point applications.

SELECTIVE BIBLIOGRAPHY

[ASTM E967, 2014] ASTM E967-08(2014) Standard test method for temperature calibration of differential scanning calorimeters and differential thermal analyzers.

[EABS, 2014] European Association for Brazing and Soldering, http://www.brazingandsoldering.org/ (accesat la data de 07.09.2014).

[Brevet, 2012a] RO 125835/2012 – *Vergea pentru brazare din aliaj de argint, cu înveliş dezoxidant* - Binchiciu, H., Voiculescu, Ionelia., ş.a.

[Brevet, 2012b] RO 125284/2012 - *Inductor pentru Imbinarea prin Brazare, Lipire sau Sudare a Tuburilor si Profilurilor Metalice* - Nicoară, M. Raduţă, A., Şerban, V.

[Constantinescu, 2008] Constantinescu, V. N. - *Dinamica fluidelor vîscoase în regim turbulent*, Editura Academiei Române, Bucureşti, 2008, ISBN 978-973-27-1694-6.

[Cojocaru, 2014] Cojocaru, M.O., Ghiban, N. - *Tratat de ştiinţa şi ingineria materialelor metalice, Vol.6, Proiectare-Calitatea produselor-Materiale speciale-Inginerie economică metalurgică*, Editura AGIR, Bucureşti, 2014, ISBN 978-973-720-533-9.

[EU, 2012] Commission Regulation (EU) No 835/2012 of 18 September 2012 amending Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) as regards Annex XVII (Cadmium).

[Matthey, 2001] Matthey, J. - *Metal Joining, Argo-braze for brazing of stainless steel, joint for wet environments*, 2001, UK; http://www.jm-metaljoining.com/pdfs

[MATFREZ, 2012] MATFREZ - *Materiale şi tehnologii performante destinate realizării cuţitelor de freză pentru asfalt* - Contract PCCA 188, 2012.

[Milosavljevic, 2014] Milosavljevic, A., Kostov, A. – *Ecological lead-free solders Sn-In-X (X=Ag, Cu)*, Publisher: Mining and Metallurgy Institute Bor, Serbia, 2014, ISBN 978-86-7827-045-1.

[Pascu, 2002] Pascu, D. R., Iacob, M., Buşilă, M. – *ATLAS Metalografic pentru îmbinări sudate*, Editura Eurostampa, Timişoara, 2002, ISBN 973-687-071-5.

[Schwartz, 2003] Schwartz, M. - *Brazing*, Second Edition, The Materials Information Society, ASM International, Materials Park, Ohio 44073-0002, 2003, ISBN 0-87170-784-5.

[Şaban, 2009] Saban, R., Dumitrescu, C., Petrescu, M. - *Tratat de ştiinţa şi ingineria materialelor metalice-Vol.3, Metale, aliaje, materiale speciale, materiale compozite*, Editura AGIR, Bucureşti, 2009, ISBN 978-973-720-261-1.

[Truşculescu, 2009] Truşculescu M. – *Materialotehnica,, vol.IV, Metale şi aliaje neferoase,* Editura Politehnica, Timişoara, 2009, ISBN 973-625-091-1,978-973-625-852-7.

[Voiculescu, 2016] I. Voiculescu, Ionelia., Geantă, V., ş.a – *New alloys from the Cu-P-Si system eased for brazing*, VIIth International Metallurgical Congress, Ohrid, Macedonia, 2016.