COMPOSITE ENAMELED STEEL ELEMENTS FOR AIR PREHEATERS AND GAS–GAS HEATERS: AN INTEGRATED APPROACH FROM SHEET FORMING AND ENAMELLING TO BASKET ASSEMBLY

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Composite Enameled Steel Elements for Air Preheaters and Gas-gas Heaters: an Integrated Approach from Sheet Forming and Enamelling to Basket Assembly

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1. Introduction

Effects of the pollutant substances made from the combustion, in particular in the power plants, brought to the worsening of the directives and laws of environmental conservation. To respect this norms is necessary to reduce strongly emissions of NO_x and SO_x; for those mentioned, old power plants provided with plants for desolforation of fumes. To the purpose, Fig. 1.1-A, issued fumes are subjected to "wet" neutralization with calcium hydroxide. In this way purified gas, poor of sulphur and cold (having the temperature of 50°C) is formed and must be heated to at least 80°C to avoid the drop in temperature under dew point and therefore increase of the corrosion of chimney.

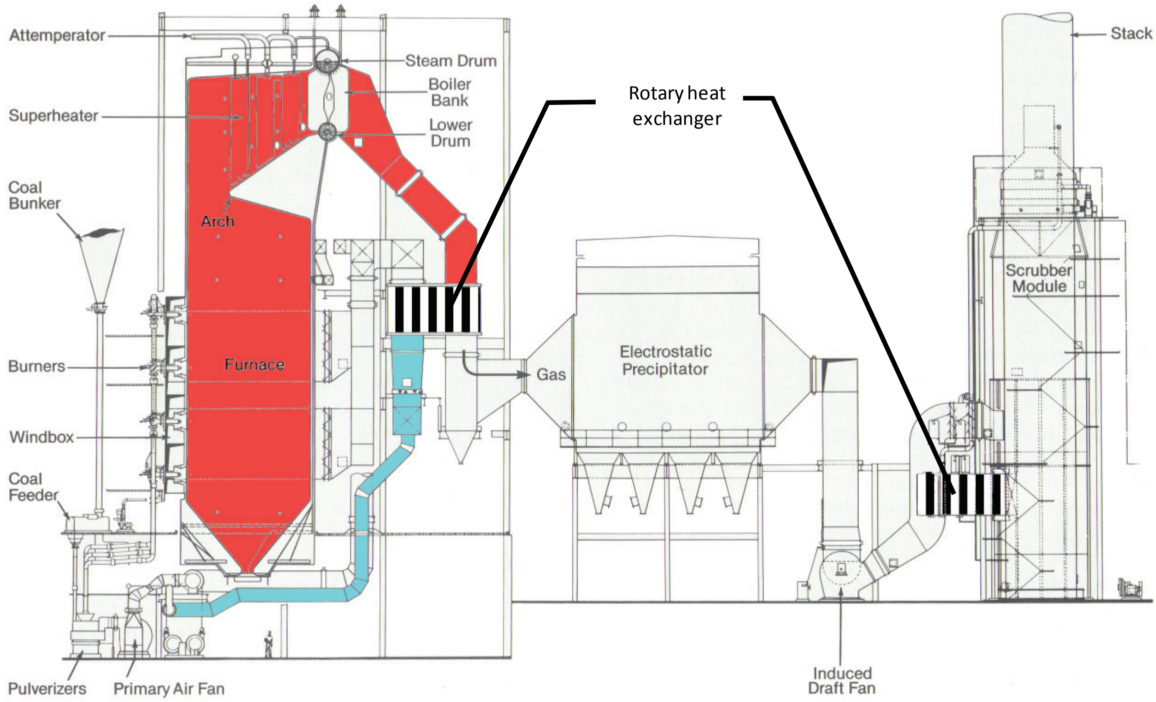

Fig. 1.1-A Scheme of the typical plant for the control of SO_x
(from Babcok&Wilcox, STEAM, its generation and use, 1992)

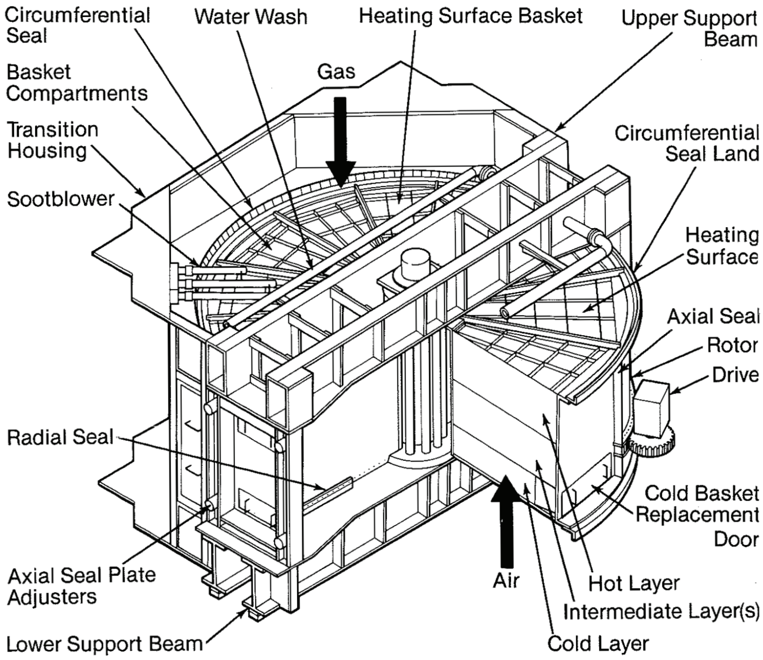

Fig. 1.1-B Schematical drawings of the pre-heater gas-gas (GGH) of rotative type (from Babcok&Wilcox, STEAM, its generation and use, 1992)

Customarily for fumes heating, are assumed heat exchangers (Gas-Gas Heater, GGH) of which realization requires the use of the materials of the corrosion resistance, regarding the fumes aggressivity and in particular, of those cold and humid coming from out and out desolforation plant. Anyway the environmental conditions, where preheater makes its functions, aren't certainly similar to those conventional GGH of which the necessity of preparing suitable protection systems becomes essential to guarantee suitable duration of related components to the phenomenon.

In particular, regarding the protection of heating elements from corrosive processes, the composite materials obtained during the combination of *steel.- porcelain enamel* - were revealed as one of the most appropriate solutions. Nonetheless this composite material has revealed an excellent compatibility also what pertain to thermal efficiency.

FIG. 2-A shows some examples of sheets morphology that come covered with porcelain enamel and that one time assembled in appropriate baskets, Fig. 2-B, are inserted in the rotative exchangers. Thus baskets filled with sheets permit to obtain media exchange surfaces of about 30.000 m^2.

Under the technical profile it is enameling submited to the corrosive attacks with long duration that have few in common with the traditional enameling (for ex. for the home appliances).

For this reason the enameling of GGH represents today a compromise between the maximum mechanical and chemical resistance and thermal conductibility. Given this premises, types and characteristics of appropriate frits are well defined. The quality of available enameling products is however influenced also by the choice of sheet and intermediate processing (pretreatments of sheets, formula of grinding, process of application and the cooking). In consequence of the multiplicity of the parameters, that play their different role in enameling, there is a system, extremely complex, characterized by numerous interactions of which optimization is searched quasi for each application. This is valid especially for mono coating highly resistant to the corrosion, where typical defects of enameling such as dimples, pin holes, sagging, copper heads that can lead up to important worsening in particular regarding chemical resistance.

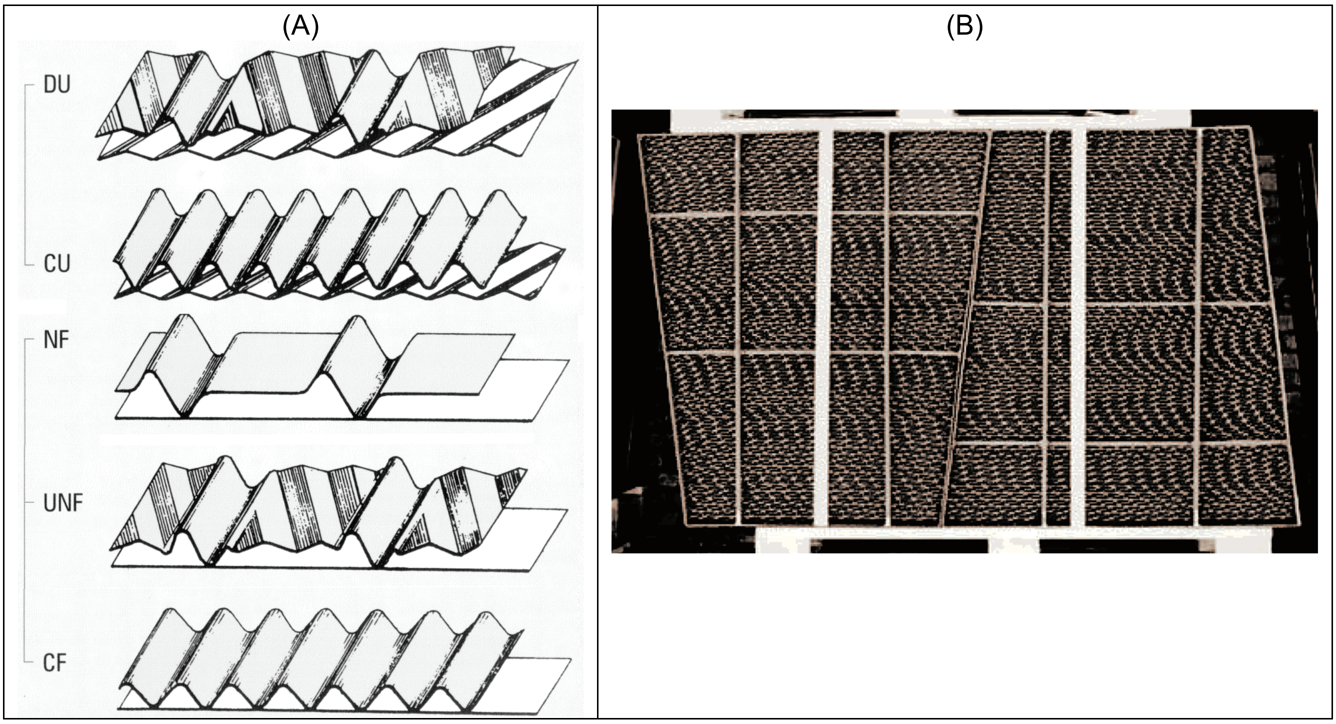

Fig.2 (A) some examples of sheets profiles ready to be covered with porcelain enamel, (B) example of two baskets filled with enameled sheets and ready for the shipment

The present day an effort of exchanging elements for preheaters and for GGH made in composite material is a common practice and gives its continues strategic relevance to be the object of researches sometimes to imTest efficiency and quality.

How put in evidence in this work [1] enameling of good quality and which presents at least one of already mentioned defects can compromise in significant way function of power plants for production of electricity involving consequently economical damages.

Research lines which are today more in development phase regarding both materials with which is made porcelain enamel, that productive processes for obtaining exchange elements.

In this work are presented the methods and results of systematic research relative to the preparation of the exchanging elements for the rotative exchangers GGH and in particular is highlighted the importance of the unit vision in their preparation: starting from the process of mechanical forming of exchanging elements to the enameling and their assembly of baskets. This work beyond to offer the unit vision of the process of basket production for rotative exchangers elaborates also the linked aspects of the development of a new enamel for electrostatic application that can represent a valuable alternative to the conventional liquid enameling for exchanging elements.

2. Definition of the planning methodology of forming tools

Following steps have been adopted to define the systematic design methodology of exchanging elements forming tools:

- study of the numerical formulation appropriate for the treatment of the cold deformation of thin sheets
- definition of the software for the functional verification of profiles

Formulation assumed for the study of process of cold forming of sheets is based on finite element method. In particular for the simulation of tools were used bi- and tri-dimensional elements of isoparametric type that admit in one case four degrees of freedom (two translations and two rotations) and in the other six degrees of freedom (three translations and three rotations) for each node. While regarding modulation of sheets were implemented mono- and bi-dimensional elements that admit elasto-lastical model for material behavior. For the numerical solution of this deformation process two separate approaches have been adopted: one approach based on implicit solution algorithm and the other based on the explicit one. The reasons that suggested the usage of both formulations is to take into account the cinematic effects that happens during the forming process.

In Fig. 2.1 is reported an example of a solution of the elements sheet forming process.

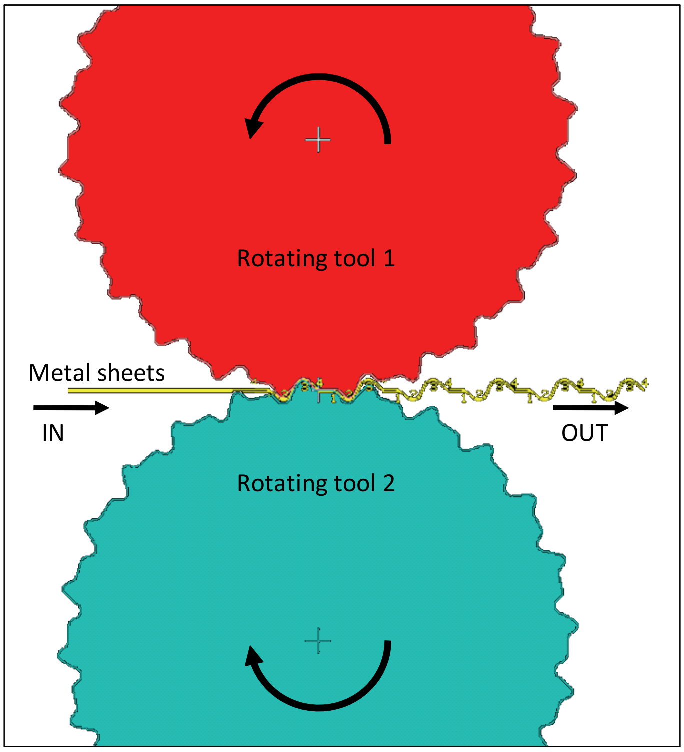

Fig. 2.1 imagine of the sheet forming process simulation

The tool design process begin with the geometrical study of desired profile (supplied by buyer). The second step regards the design of the CAD geometrical model of the first geometry of relative attempt to the tools profiles. The third step consists in the numerical simulation of the forming process having at disposal the principal mechanical characteristics of the sheet material (curve complete stress-strain: elastic and plastic behavior). Some of obtained results through the simulation process are shown in Fig. 2.2, and in particular the points of contact between the sheet and tools and the reactions of contact between the tools and same sheet are highlighted.

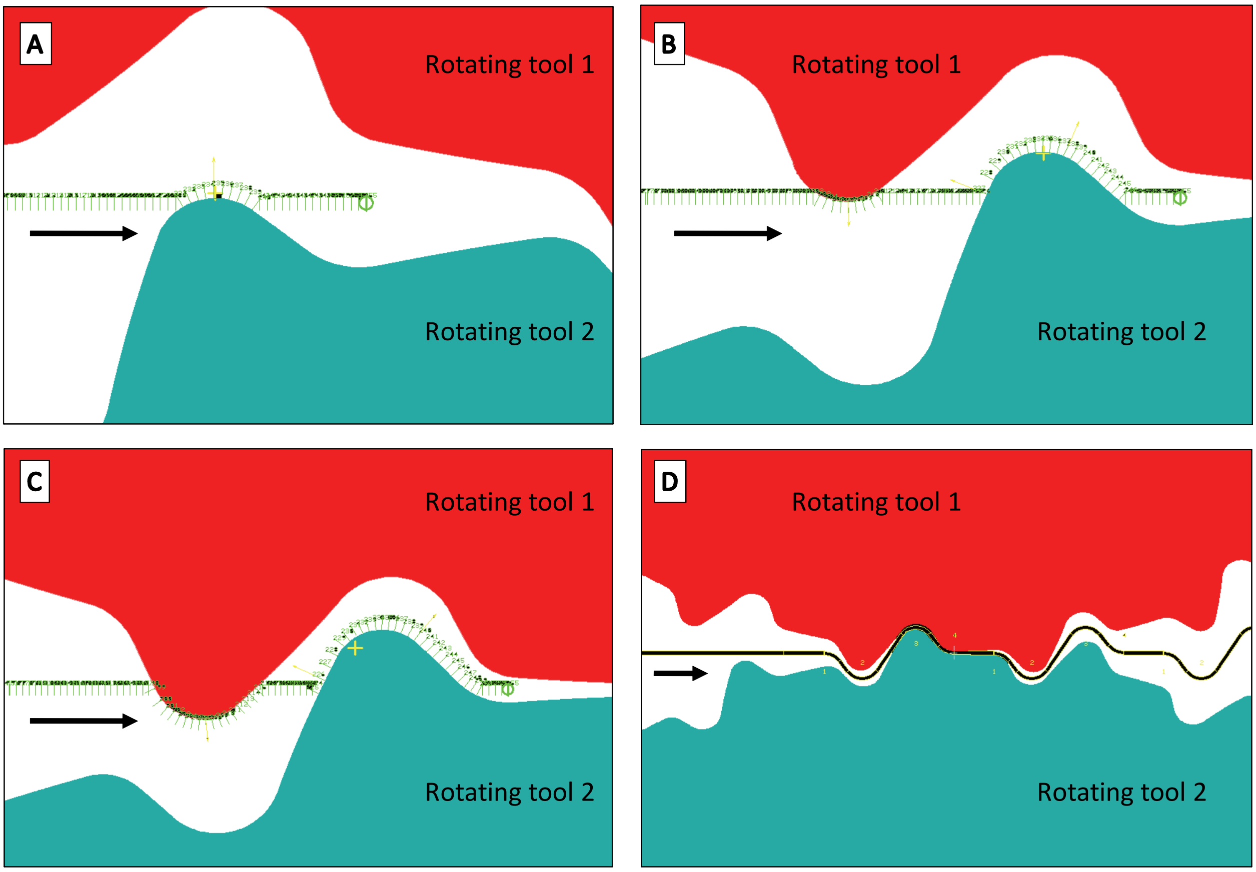

Fig. 2.2 results of the process of deformation relative to four subsequent time instants (A, B,C, D)

On the base of results obtained through the numerical simulation the profiles of tools are optimized using a performance function that combine both morphological quality of final profile and maximum contact pressures on the same tools. After tools re-design, further numerical simulations are performed in order to identify stress distribution in tools. Known maximum levels of stress that act in the tools their detailed design is performed identifying construction material and defining the manufacturing cycle.

3. New process of parallel lines synchronous for the cold forming of sheets

The new sheets cold forming process was realized on the base of a SMALTIFLEX patent. In particular the process optimize the forming cycle of sheets predisposing execution of the processing according to a parallel scheme. In fact for the realization of exchanging elements in general pairs of sheet of different morphology are considered: one sheet characterized by the curved accentuated profile and the other characterized by the profile weakly curved or n certain cases plate. New process of parallel lines synchronous implements forming tools that are projected how mentioned in §2. Respect to known processes for the elements sheets formation that are characterized by a simultaneous cutting phase of the couple of sheets, in the new one the cutting phase is done on each single sheet of the couple. The reason for which particular attention has been taken in studying and in realizing the new configuration for the elements manufacturing, is linked the necessity to guarantee high quality of borders, critical area regarding the resistance of enameling relative to the corrosive process. In fact, how it was previously demonstrated [2] a good morphological quality of borders of the enameled sheet can arrived to reduce the risk of corrosive process of about 90%.

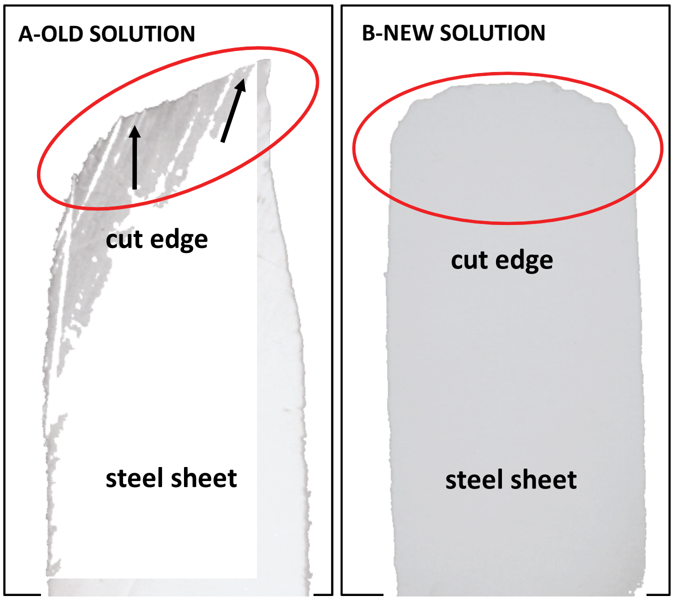

Fig. 3.1 relative picture of the cut area (A) old solution of cut edge and (B) new solution – singular cut of sheets

The final result of the new process of forming of exchanging elements results to be a couple of sheets characterized by cut of borders having superior finishing (major planarity of the cut sheets and better quality of borders of sheets, Fig. 3.1) and major compatibility with subsequent process of enameling relative to this day proposed in industrial practice.

4. New porcelain enamels applicable through the electrostatic technology

The research inherent porcelain enamel that was developed had as purpose to reach the formulation of new frits that can be applicable on the sheets through electrostatic technology.

The practice more common for enameling of exchanging elements is to this day based on the application of enamels according to the technology of wet-spray. New frits were developed to be applicated through the electrostatic-dry-spraying technology. Requested efficiency to new porcelain coatings are as follows:

- high resistance to the acid corrosion[1]
- low value of bollosity percentage[2]
- high adherence to the substrate
- good mechanical behavior[3]

The study of the enameling was developed according to a comparative scheme, in particular three porcelain enamels have been considered: two products through frits already homologated by SMALTIFLEX for application in exchanging elements (SM005 ed SM006) and the enamel made through new frits (SM013). In particular enamel SM006 was provided by the other producer of frits, while the enamel SM005 was obtained starting by the frits of same producer but in phase of grinding in the SMALTIFLEX laboratory, were added some metallic oxides in order to modify chemical and mechanical performances.

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[1] Acid corrosion was studied considering how prescribed in specifications of supply major constructors or users of exchangers of GGH type. Relative verifies of behavior of new enamels of acid setting was verified according to the norm ***EN 14483:2004***

[2] How pertain to the percentual bollosity was made reference how prescribed in specifications of supply of major constructors or users of exchangers of GGH type.

[3] Regarding the tricological and mechanical behavior of enameled exchanging elements

New frits, developed by COLOROBBIA-ITALIA, were initially characterized from point of view of their thermal behavior. In particular for new frits were conducted experimental tests finalized to the determination of the linear thermal expansion (α), of the relative analyses to the characteristic temperatures for the physical state of enamel (fusibility analysis) and the determination of the viscosity curve of enamel vary of the temperature.

4.1 *Analysis of the enamel thermal property*

Regarding the determination of the coefficient of thermal expansion relative to new enamel was determinate preparing geometrical prismatical bars noted through the same melted enamel. The preparation of the bars on which was conducted the rays analysis (X-Ray-Difraction, XRD) in order to verify the quality of the crystal-glassy structure of the enamel with which were realized. This control is necessary to guarantee an applicability of the results obtained also of porcelain coating of sheet.

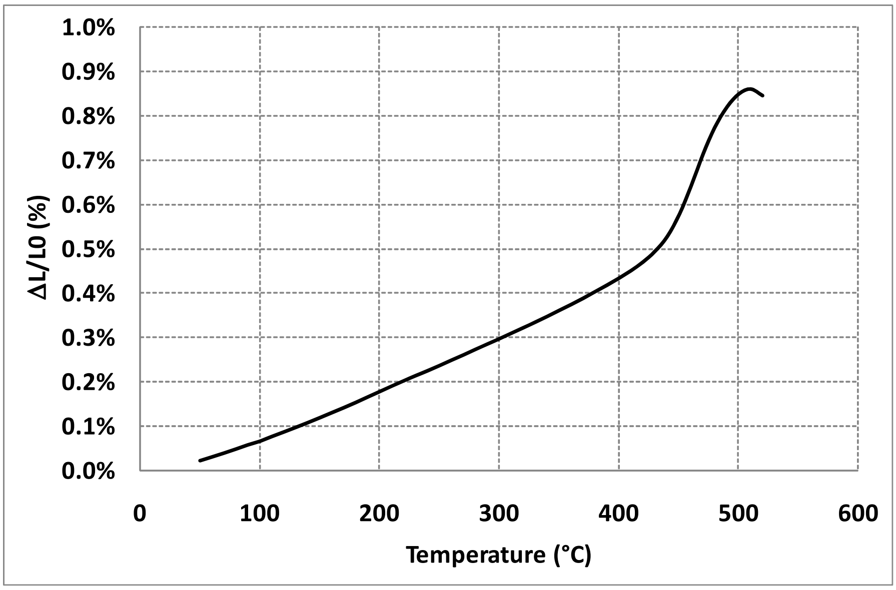

Fig. 4.1 process of the percentual expansion ($\Delta L/L_0$) in function of temperature

Coefficients of thermal expansion were determined through dilatometer with heating of electrical resistance. In Fig. 4.1 the graph of curve with the characteristic of expansion percentage of versus the temperature is reported. In the range of temperature of work scheduled for the enameled elements, coinciding with behavioral tract nearly linear like in Fig. 4, and in this tract the coefficient of thermal medium expansion results equal to 1.177 10^{-5} °C^{-1}. In the chart 1 are related values of coefficients of thermal expansions relative to three considered enamels.

Table 1 valori relativi al coefficiente di dilatazione termica

ID	Application technology	Coefficient of thermal expansion (α) $\times 10^{-5}$ °C^{-1}
SM005	Liquid	1.091
SM006	Liquid	1.205
SM013	Dust	1.177

The dates of coefficient of thermal expansion relative to enamels SM005 and SM006 were supplied in case of enamel SM005 by the producer of the same enamel SM006 were determinate in analogical way what was made for new enamel SM006. It was observed that a different coefficients α for three enamels influence in significant way both the mechanical that chemical behavior of porcelain coatings of sheets. In fact, how is noted the previous studies, even small variations of coefficient of thermal expansion determinate in composite system porcelain sheet-coating the different state of residue stress (of compression in coating and of tensile in metalic sublayer). These residual stress permit generally, and by certain limits, to obtain the best mechanical performances[4] and at the same time can reduce chemical resistance of coating [5].

The second thermal analysis that was conducted regards fusibility of enamel. In Fig. 4.2 are related five pictures relative to three physical states of major interest that assumes the enamel to vary the temperature.

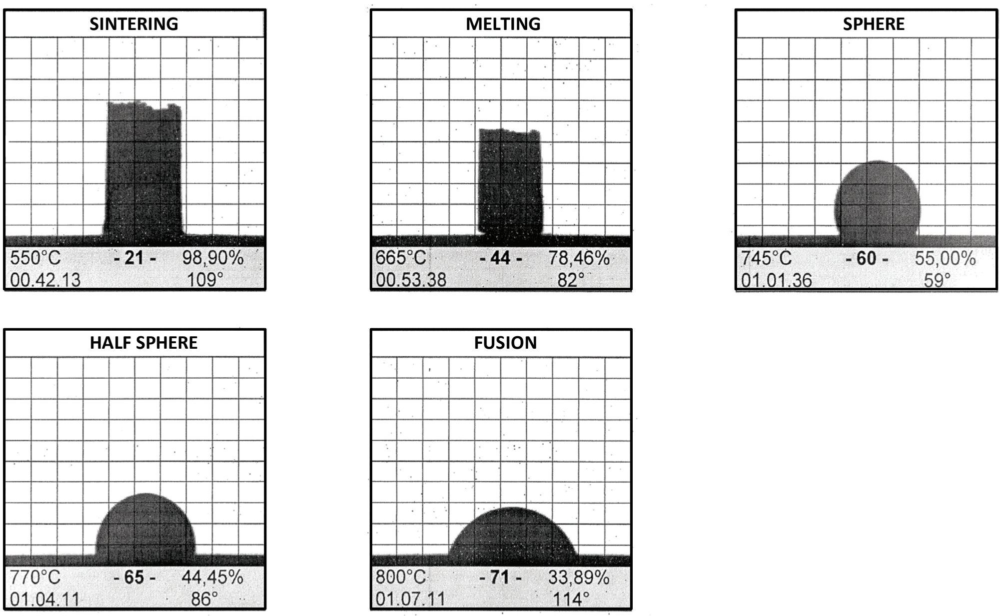

Fig. 4.2 photo of the enamel tablet state with the different temperatures

By the conducted analysis with the heating microscope appears in particular that fusion of the enamel begin with 800°C and this temperature will be put on like reference for the following relative analysis of viscosity.

The third characteristic of new enamel that was studied is viscosity in temperature function. In graph in Fig. 4.3 is related the process concerning logarithm in base ten of the viscosity of new enamel.

[4] It was indeed demonstrated that the residual tensions permit of delay the formation of the first fracture in covering both in conditions of membrane that bending charge. It's important to make precise that in the case of excessive values of residual tensions of compression in covering can cause its fracture for buckling, and this phenomenon results to be particularly critical in case of coverings giving low adherence to substrate.

[5] It has to be noted in fact that the process of the chemical corrosion of covering reduces thickness of the same covering and this global level causes progressive distension of the residual tensions in metal. Being that mentioned residual tensions of traction those are reduced against sheet contraction. Contraction of the sheet brings to growth of residual tensions in residual coverings and this can cause its detachment for buckling associated to a propagation instable to cliques. The cliques that are formed are deep in major of cases and can bring to the penetration of the acid solution since a direct contact with substrate causing corrosion. The behavior here described can result critical in case of components like exchanging elements since working in environment with strong acid aggressivity, can be verified the case of exponential state in time of the same covering and so their final break.

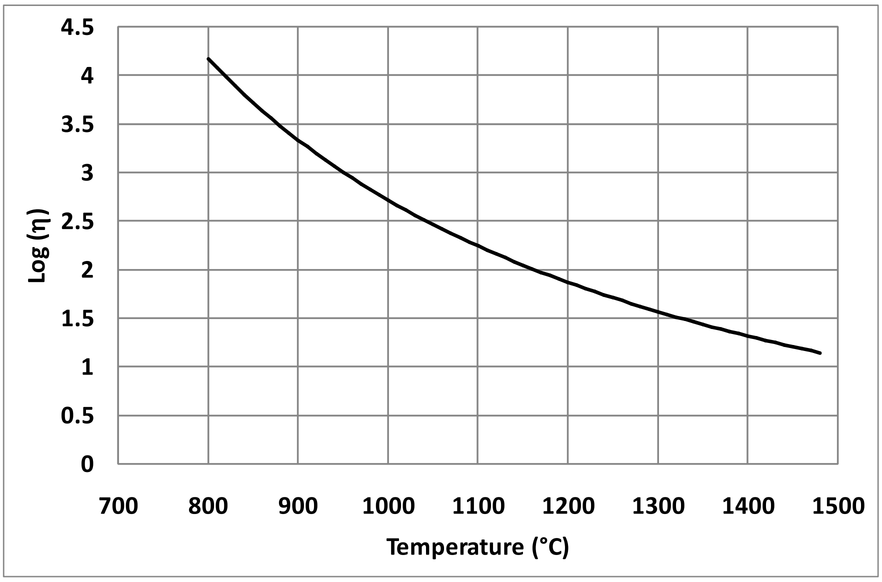

Fig. 4.3 process of the logarithm of viscosity of temperature function

4.2 *Morphological-functional characterizing of porcelain coating*

We define the morphological-functional characteristics as following parameters: ***blistering percentage***, enamel density and its ***hardness***. The characterizing of porcelain enamels relative to this three characteristics results to be fundamental both regarding quality of enameling (according to the most important norms in this field) that chemical-mechanic-tribological efficiency and functionality of enamel: mechanical resistance to deformation, resistance to abrasion and resistance to chemical aggression.

4.2.1 The preparation of covered test through the enamels in test was conducted according to the standard procedures of the society SMALTIFLEX. In particular in case of applicated liquid enamels was made a sheet pre-treatment (degreasing, acid attack, deposition of metallical nickel and neutralization) after which followed application of enamel, dehydration and the cooking in the oven with temperature of 870°C for 6' and 30''. In the case of powder enamel wasn't made a sheet pre-treatment but the enamel was applicated in direct way on the samples and cooked in oven with the temperature of 870°C for 6' and 30''.

4.2.2 Micrographic test were conducted on the transversal sections of samples and were finalized to the quantitative analysis of empty present in section of coating (***blistering percentage***). The micrographical test of the transversal sections, in Fig. 4.4, shows the microstructure of the composite made by the coating and by substrate. It is noted in all sections the characteristic area of interface between coating. In case of coatings obtained through the use of liquid enamels in the area of interface coating-substrate is possible to note the presence of fine "filaments" (dendriti) that start from metal base and extend themselves in profound way in area of interface. In case of coating obtained through new powder enamel applicated is observed an area of interface coating-substrate corrugated that guarantee an excellent adhesion from mechanical point of view. The analyzed coatings present moreover blister structure, passing from numerous concentration of small bubbles in proximity of interface, to an inferior presence of the bubbles but with major dimensions.

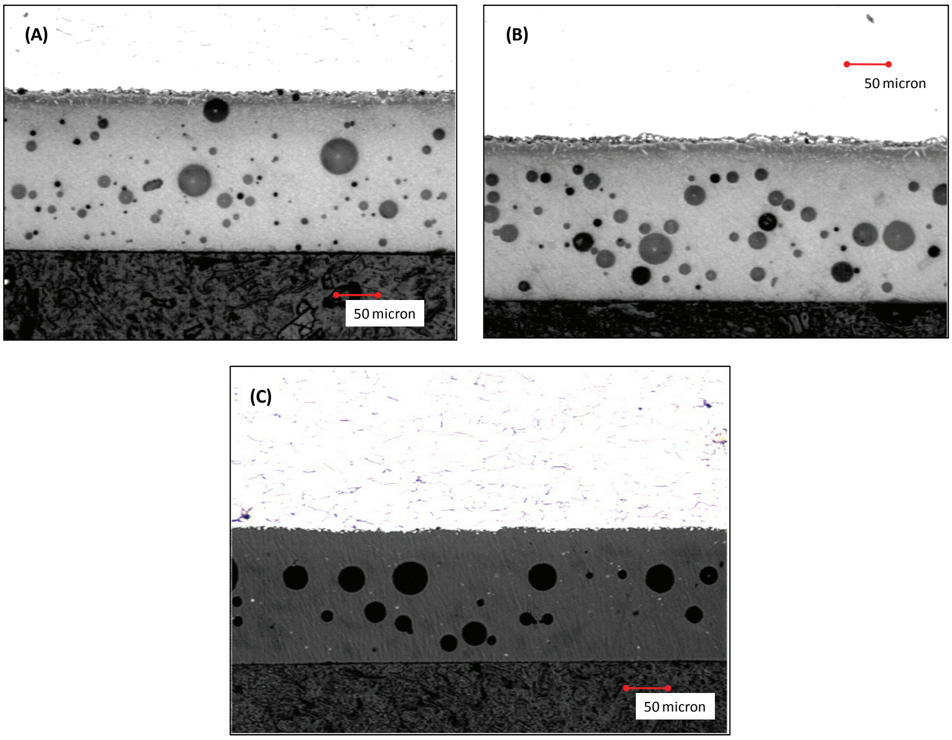

Fig. 4.4 examples of micrographs relative to the enamels (A) SM005, (B) SM006, (C) SM013

Through the quantitative analysis of the micrographs was possible determinate for each type of coating, percentual blistering, their diameter and their circularity. In schedule 2 are summarized values obtained on statistic base for all three types of analyzed enamels.

Table 2 Density % of bubbles, Diameter of bubbles and their Circularity

		% Bubbles		Diametre [μm]		Circolarity	
ID	Tecnology	M.V.	S.D.	M.V.	Dev.St.	Media	Dev.St.
SM005	Liquid	11	9	11.89	0.88	0.95	0.04
SM006	Liquid	12	7	10.04	0.47	0.97	0.02
SM013	Dust	10	4	9.51	0.49	0.96	0.03

4.2.3 Density of coating as determinate through the in direct measure based on the survey of the weight of coating and the measure of its volume. To follow the density measure were used samples of rectangular geometry. The weight of coating was obtained like as the difference between the weight of the covered sample and the bar not yet covered. The volume of coating was calculated through the variation calculus of the rise of static water-blame, Fig. 3, when in this were immersed one covered sample and one non covered. The containment of the static water-blame for the volume measure, has following dimensions: length 290 mm, width 57 mm and thickness 4.5 mm. Dates obtained for the density of coatings are collected in schedule 2. From analysis of dates results that density of the liquid enamels is major that in the powder enamel density and this is due to the fact that in those of liquid density are added clays that make densification function (suspensionally).

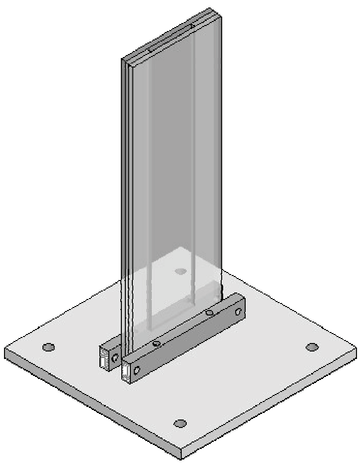

Fig. 4.5 Volume meter

Table 2 Density of the glassy coating

		Density [kg/m^3]	
ID	Tecnology	M.V.	S.D.
SM002	Liquid	2570	160
SM003	Liquid	2470	153
SM013	Powder	2280	118

4.2.4 Micro hardness of coating was determinate through microhardness (Vickers), applying charge P = 300g, for the time t = 5 s.

For the determination of the micro hardness Vikers were conducted experimental Tests both on massives of porcelain enamel that on enamel already appicated on sheets. In particular the Vikers measures on the applicated coatings on sheets were conducted extracting from the sheets the same samples that were subsequently inlobated in the way to expose covered surface. For each type of coating both on massive enamel slab and on coatings applied on the sheet were made multiple indentations in order to gave an appropriate statistic rapresentation of results.

The relative dates of micro hardness of coatings are related in schedule 3.

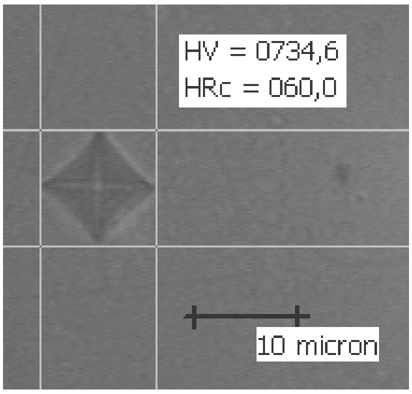

Fig. 4.6 example of measure HV

Table 3 Micro hardness of coatings

		Microhardness (HV)	
ID	Tecnology	M.V.	S.D.
SM005	Liquid	735	14
SM006	Liquid	711	8
SM013	Powder	681	10

It is observed that micro hardness of the liquid enamels result to be major of those micro hardness of powder enamel and in particular enamel SM005 is on average the most dense and the most hard.

4.3 *The study of mechanical behavior of the enameled sheets* had following objectives:

(I) estimate of module o Young and of coefficient of Poisson of coatings,
(ii) estimate of residual stress that act on coatings;

(iii) estimate of values of the first crisis (First Crack Failure, FCF in terms of stress and curves) of coatings both in conditions of bending stress membrane stress;
(iv) valuation of the adhesion grade of substrate coating.

To obtain these information were developed following Test typologies:
- bending Tests on four point and tensile Tests;
- relative measures concerning relative deflections to the substrate coating system induced by the difference between coefficients of thermal expansion;
- impact Tests.

Study of the mechanical behavior of the covered sheets through the porcelain enamel was competed through the numerical analysis based on the method of the finished elements. The scope of this analysis is to show detailed process of the stress in system substrate-coating in different configurations of the test and to highlight effect of the residual stress. For the enameling of all used samples for Tests described here below were followed procedures already described in §4.2.1

4.3.1 Four point bending test were conducted in conformity to the norm ASTM D6272-02 [11] and the scheme of the test is related in Fig. 4.7 Appliance is made from one trestle structure, of which essential elements are as follows:

- mobile traverse which is returned supportive the system made from the charge cell and cindrical inner span; distance between *inner span*s was set equal to 25 mm;
- set traverse which is supportive device of ----------, -------------- have (*outer span*) of 65 mm.

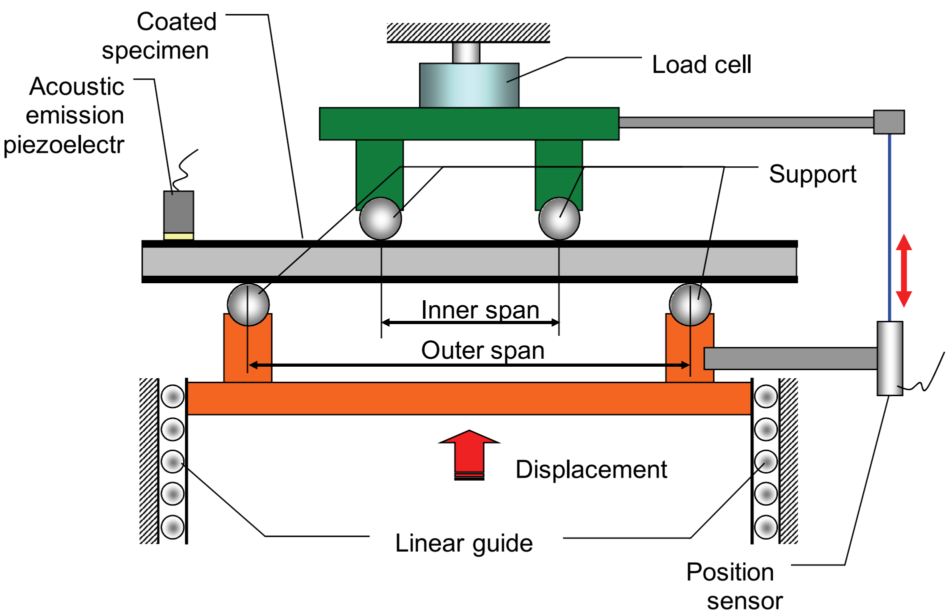

Fig. 4.7 Scheme of used device for the four point bending test.

For the four point bending test were prepared rectangular geometry samples, 40 mm x 100 mm, starting from the sheets of decarburated steel with thickness of 1.0 mm. The thickness of porcelain coating for the samples was choose variable in range of 0,15 ÷ 0.30 mm and for each sample was measured in systematical way on all the useful surface.

Tensile test were conducted in conformity to the norm UNI EN 10002 and were realized samples of clessidral geometry, Fig. 4.8, using always steel sheet of very low carbon contain and with thickness of 1 m. Sheets having the geometry in Fig. 4.8 were covered through the porcelain enamel in one central tract in order to be able to grab the sample without damage same coating.

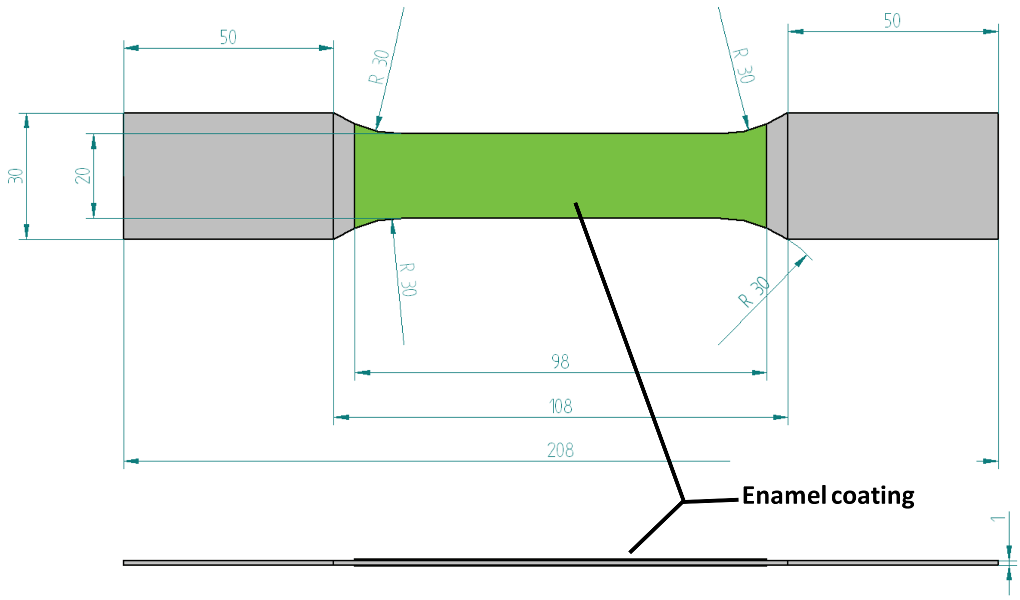

Fig. 4.8 geometry of sample for the tensile Test

Some samples for the tensile test were provided of extensimeter having directions of measure respectively longitudinal and transversal relative to principal direction of sample.

To be able to study in detailed way the behavior of the coating fracture, both the bending test that of tensile test were monitorated through appropriated transducers to obtain **acoustic emissions** (AE) released from the material during the same test.

In present work the acoustic emissions were obtained through the appliance PAC-DISP and used piezoelectric transducers model PAC-R15. The analysis of the acoustic signals that were assumed is of parametrical type considering following sizes Fig. 4.9:

- maximum wideness (dB);
- duration of the event (μsec);
- number of counts for event;
- associated energy to the acoustic event;

where associated energy to each event is determined through the integration of signal on existential domain of the same event (duration of event).

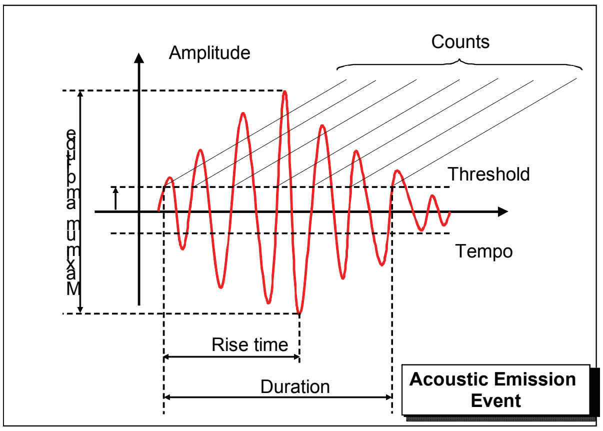

Fig. 4.9 esempio di evento acustico

In the field of the present research, monitoring of EA permit to individuate for the porcelain coatings FCF (first significant fracture). In particular during experimentation, to be able to individuate FCF, was made use of the energy from acoustic events since it condensates all useful information. So deformation value (displacement δ of the mobile transverse) in correspondence of which is reveled the first acoustic event of significant energy is made correspond the first significant fracture (δ_{FCF}).

All experimental Tests were conducted in control of displacement. In the case of four point bending test the speed of the mobile traverse was imposed to a value equal to 0.03 mm/sec, while in the case of tensile the speed was imposed equal to 0.008 mm/sec.

For monitoring of the acoustic emissions was imposed a minimum wideness equal to 40dB (are excluded events with values of max. inferior wideness to 40dB) and signal preamplification was imposed to 40dB. Pertain to **bending test**, example of diagram loaded displacement is related in graphs in Fig. 4.10. beyond the structural answer of displacement.

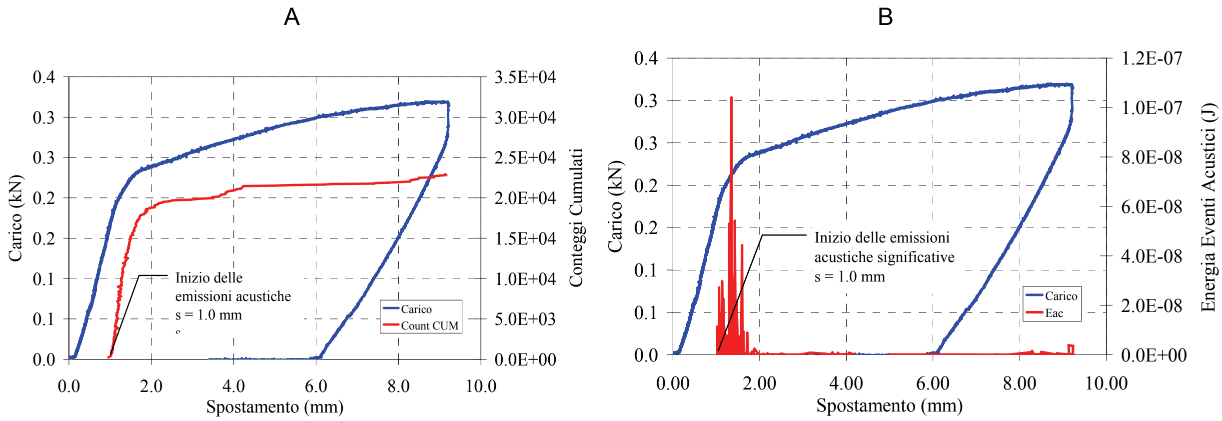

Fig. 4.10 bending test – charge process, hoarded counts (A) and of associated energy to each acoustic event (B) in displacement function

How is observed in both diagrams, exists the period of Tests during which the imposed deformation to composite doesn't result to provoke coating significant fractures. The displacement field by which don't have significant acoustic emissions(in the case in Fig. 18, this field is highly limited from the value s = 1.0 mm) is the Free Failure Zone (FFZ). That is immediately deductible from graphs in Fig. 4.11. In fact arising of acoustic emissions determines almost immediate variation in characteristic trend of the charge-displacement curve: from the figure 6 results evident that after FFZ the charge-displacement curve inclination begins to decrease. In fact arising of the first significant coating fractures , that are obtained through the EA, determinate reduction of the resistant section of the composite and this is revealed by the reduction of the inclination of charge-displacement curve.

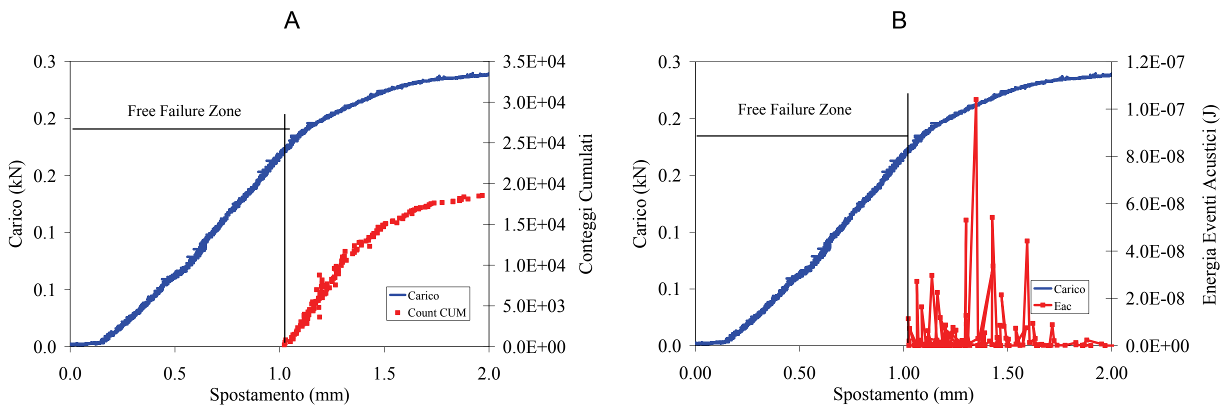

Fig. 4.11 bending test- Particulars of the curves hoarded counts (A) and acoustic energy (B) with particular evidence to Free Failure Zone (FFZ)

Similarly how was seen for bending Test, is possible to obtain the diagrams conjoined charge-displacement and relative information to acoustic parameters in function of displacement also for the bending test. In figure 7 are supplied two examples relatively to the tensile Tests.

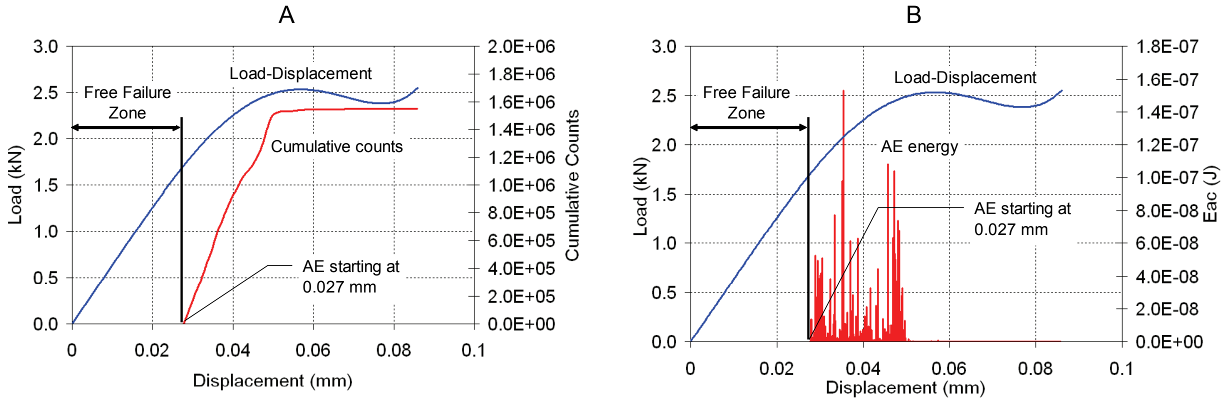

Fig. 4.11 bending test – charge process, of hoarded counts (A) and the acoustic energy (B) in function of displacement; in evidence the FCF and the FFZ.

4.3.2 Measure of residual stress results like the other fundamental step for the mechanical behavior comprehension of the enameled sheets. In fact how was already mentioned during the cooling process of the enamel on sheet because of the different elasticity and coefficient of thermal expansion[6] grow out of residual stress. In particular in a room temperature the enamel results to be in the compression state (stress compression) while steel is submitted to the tensile stress (stress tensile). The study and estimation of the residual stress are conducted both through the experimental approach that numerical aproach.

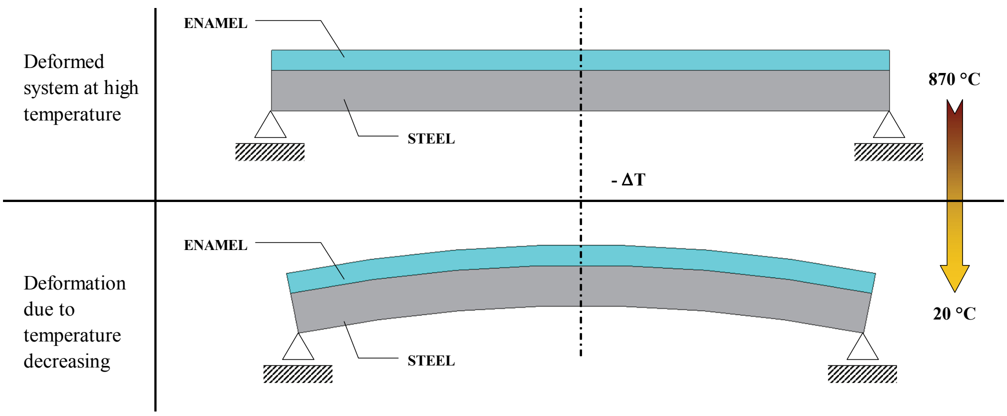

Fig. 4.12 relative scheme to the geometrical configuration of the system coating-substrate during cooking by 870° and room temperature

From experimental point of view was used the method of the cantilever beam [Normative] (cantilever beam test). Although residual stress depend in intrinsic way not only by the elastic and thermal property of two materials but also by the geometry assumed by the factor, in this first phase

[6] As numerical reference was assumed as coefficient of thermal dilatation of steel the following value $\alpha_{steel} = 1.3\times10^{-5}\ °C^{-1}$.

of the study was taken in consideration a simple and compatible geometry with the chosen norm. In particular were predisposed sheets of rectangular geometry having width 40 mm and length of 250 mm and thickness of 1mm. The sheets one time predisposed for the enameling were covered only on one of two principal faces. After cooking in the oven, by the temperature of 870° C for the time equal to 6' e 30'', was obtained the natural samples bending because of their non symmetrical configuration in the thickness, Fig. 4.12. The sheet was blocked how is shown in Fig. 4.13 and through the scanner laser was determinate the indicator h. The used length of block is of 30 mm while measure field L was assumed equal to 100 m.

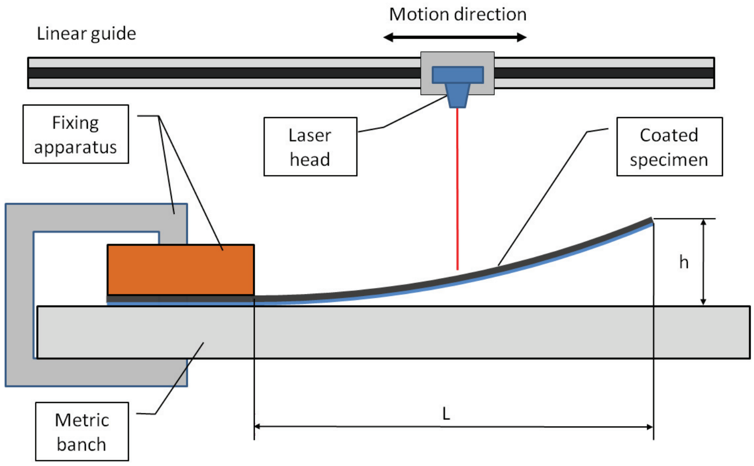

Fig. 4.13 appliance for the deflection measure of enameled sample regarding metrical plane

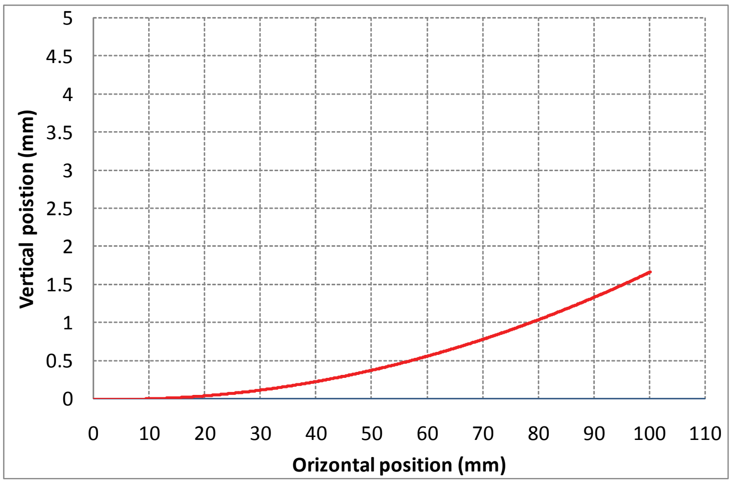

Fig. 4.14 result of the laser measure in terms of position of lecture and vertical quote

In the graph in Fig. 4.14 is related an example of the laser scanning concerning enameled sample with the enamel SM005.

4.3.3 To complete the study of the mechanical property of the enamels were conducted also some **numerical analysis**. As objective of these analysis is to study the process of the stresss and of the deformations in specimen. These analyses have permitted to estimate in realistic way the real state of stress that act on samples after the mechanical charge application. The model for analysis of bending test was realized considering whole geometry of sample, Fig. 4.15, and it wasn't utilized its natural symmetry in order to append bonds in the best way. The supports are made in the way to reproduce the condition of the experimental test.

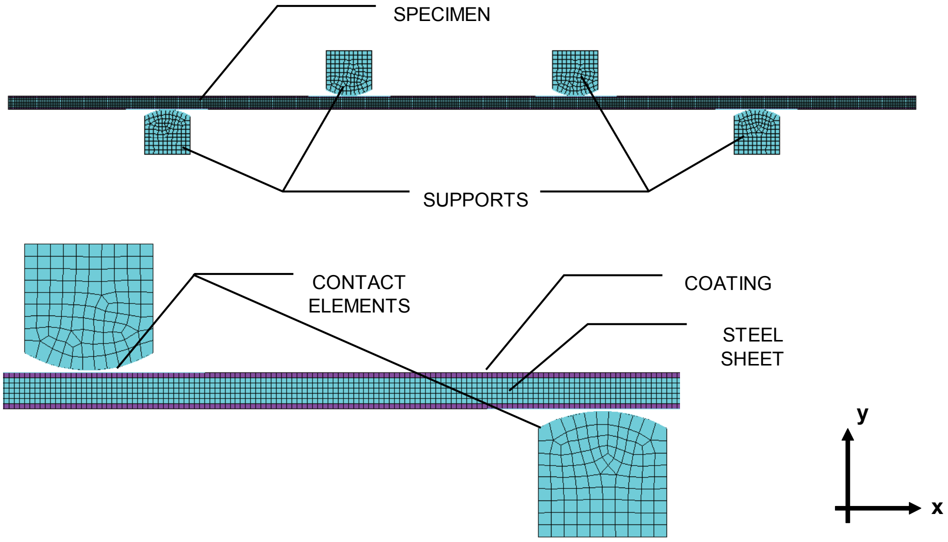

Fig. 4.15 geometry and meshing of the model for the bending test

Given the particular geometry of the used samples for the bending test, was chosen numerical modelation in the principal plane x-y and for the used elements (elements of parabolic type was assumed the plane-strain formulation. In the Fig. 4.16 were related some concerning the geometry and the meshing of the used sample to simulate numerically the tensile test.

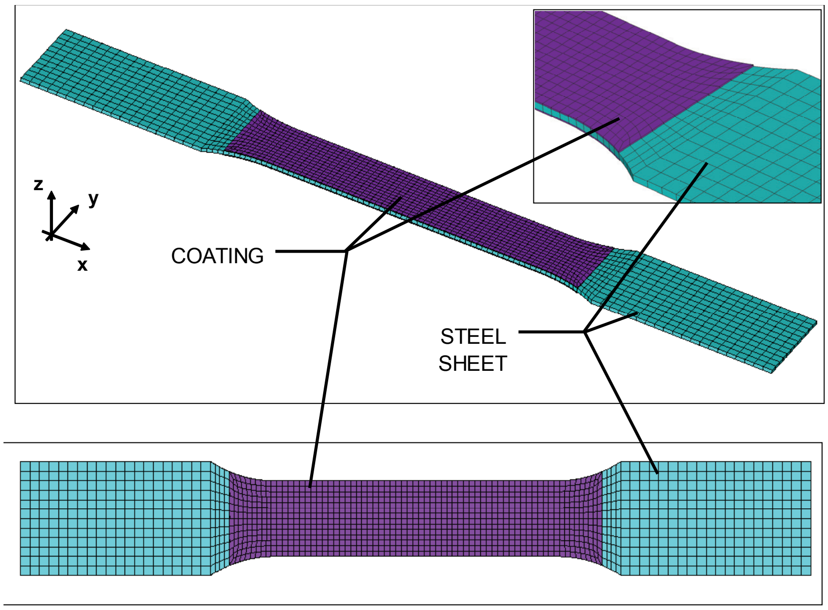

Fig. 4.16 numerical model for the analysis of tensile test

The numerical model for the tensile test is three-dimensional since the particular clessidra geometry requires some solutions for the correct representation of the geometry and of the boundary conditions.

4.3.4 Impact test was conducted following a standard practice for the enameled components. In Fig. 4.17 is related the scheme of the used device to make impact test.

In particular for this test was used an impact device having weight equal to 2 kg and having extremity that enter in contact with hemispheric geometry sample with diameter of 20 mm. The distance of the adopted for the test, H, is of 1 m and the weight was guided in its race through appropriate punch guide. In order to guarantee good stability of the sample, during the test were Testd squared samples having parts long 100 mm. The samples for this type of test were enameled on both main faces.

Further to the impact test the samples were submitted to an analysis to optical microscope and to SEM (Scanning Electron Microscopies).

4.3.5 Results of the mechanical Tests are then related and analyzed. Regarding the value of Young module were conducted two analysis: the first based on the bending test and the other based on the tensile Tests. In particular, following already described procedures in other works [3,4] was possible to reach values of Young Modulus (E) related in table 4. As regards the coefficient of Poisson the count was developed on the base of deformations of strain gauge measurement applicated on the tensile samples. In chart 5 are related experimental results obtained for the Poisson coefficients (ν)

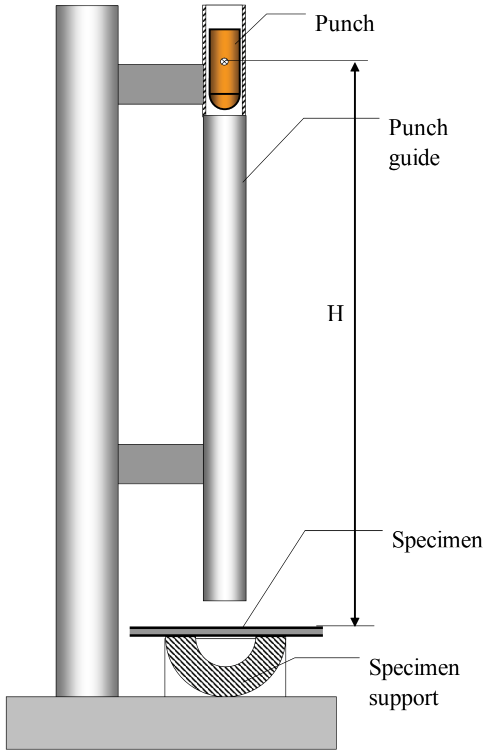

Fig. 4.17 schema della prova di impatto per l'aderenza dello smalto

Table 4 Young Modulus (E) values

		E [MPa]		ν	
ID	Tecnologia	M.V.	S.D.	M.V.	S.D.
SM005	Liquido	6.7 E+4	0.1 E+4	0.28	0.05
SM006	Liquido	6.4 E+4	0.3 E+4	0.26	0.07
SM013	Polvere	6.8 E+4	0.3 E+4	0.25	0.04

It is noticed that, relative to obtained medium values, new dust enamel results to be slightly harder (the smallest coefficient of Poisson). Prior to get an analysis of the conditions of the first fracture (First Crack Failure, FCF) we relate results and analysis relative to residual stresss. In fact all information get from residual stresss result fundamental for the valuation of the stress of the first fracture both in bending conditions that of those of tensile. The internal stresss of enamel-substrate system (or residual stresss of thermal nature, thermal residual stresses) were inferred through the laser scanning relative to the deflections of the enameled samples only on one principal face (§ 4.3.2). In particular the maximum values of the stresss that act on the coating were estimated through the Stoney formula. Stoney formula, to the origins introduced to estimate tensile stresss that act on some polymeric coating classes, can be applicated also on this class of glassy coating how already demonstrated in presence [5]. Stoney formula, (1) consists of two terms that derived taking into account balance of the forces and of moments that act on the system substrate-coating by virtue of difference between coefficients of linear thermal dilatation of materials that constitute them [6-8]. The mathematic form of Stoney formula related as follows:

$$\sigma_{c,max} = \frac{h E_s t^3}{3L^2 c(t+c)(1-\nu_s)} + \frac{h E_c (t+c)}{L^2 (1-\nu_c)} \tag{1}$$

where2:

- E_s, ν_s and t are respectively Young module, the Poisson coefficient and thickness of substrate;
- E_c, n_c and c are respectively Young module, the Poisson coefficient and thickness of coating;
- L is the maximum distance from joint where passes the deflection measure relative to metrical plan (Fig. 4.8);
- h is the deflection of the sample from metrical plan (Fig. 4.13).

Using the (1), it was possible to estimate the values of residual stresses as reported in table 5.

Table 5 values of the residual medium stresss maximum obtained for the experimental and numerical via

		$\sigma_{x,experimental}$ [MPa]		$\sigma_{x,numerical}$ [MPa]	
ID	Tecnologia	Valore Medio	Dev.St.	Valore Medio	Dev.St.
SM005	Liquido	78	8	82	5
SM006	Liquido	50	7	52	4
SM013	Polvere	70	8	69	4

Using relative dates of coefficient of linear dilatation, chart 1, and those relative to the elastic property of enamels, chart 4, were conducted also the numerical analysis relative to the residual stresss. The geometry of the sample for the numerical analysis is that relative to the scheme in Fig. 4.13. With regard to numerical model construction is observed that to be able to compare the results given from the simulations with those experimental one must be allow for the real thickness of the sample the object of the experimental research. The characteristics of the metal substrate that were used are as follows: E_s= 180 E+4 MPa, E_t= 0.1 E+3, σ_{yp}= 200 MPa, ν =0.3, a = 1.3 E-5 °C^{-1}. The charge condition that is set to the numerical model is the temperature reduction from 870°C to 20°C. In Fig. 4.18 is related relative example to the numerical solutions obtained for three typologies of the enamel and considering the thickness of the coating equal to 200µm.

The values relative to the residual stresss calculated per numerical via related in the chart 5 make reference, for each enamel, to the obtained results considering the respective distributions of thickness. From the confrontation between the obtained experimental results and those obtained through the numerical simulations can be observed substantial agreement . It is observed moreover that the residual stresss that act on enamel SM013 result to be those of major entity. This fact can be explained not only on base of value of coefficient of thermal dilatation but also on base of elastical characteristics of this material. Finally it is important to point out that this type of approach has permitted to obtained the following results

- estimate, for this particular geometrical configuration, the residual stresss that act on enamels in exam;
- defining and verify a numerical procedure that permit to obtained reliable dates for the valuation of the same residual stresss

To complete the analysis of the mechanical comportment of the enameled sheets were analyzed the conditions of the first fracture (First Crack Failure, FCF). The accepted criterions to identify experimentally the condition of FCF is linked to the monitorage with the acoustic emissions: is considered how the displacement of FCF that in correspondence of which passes the first significant

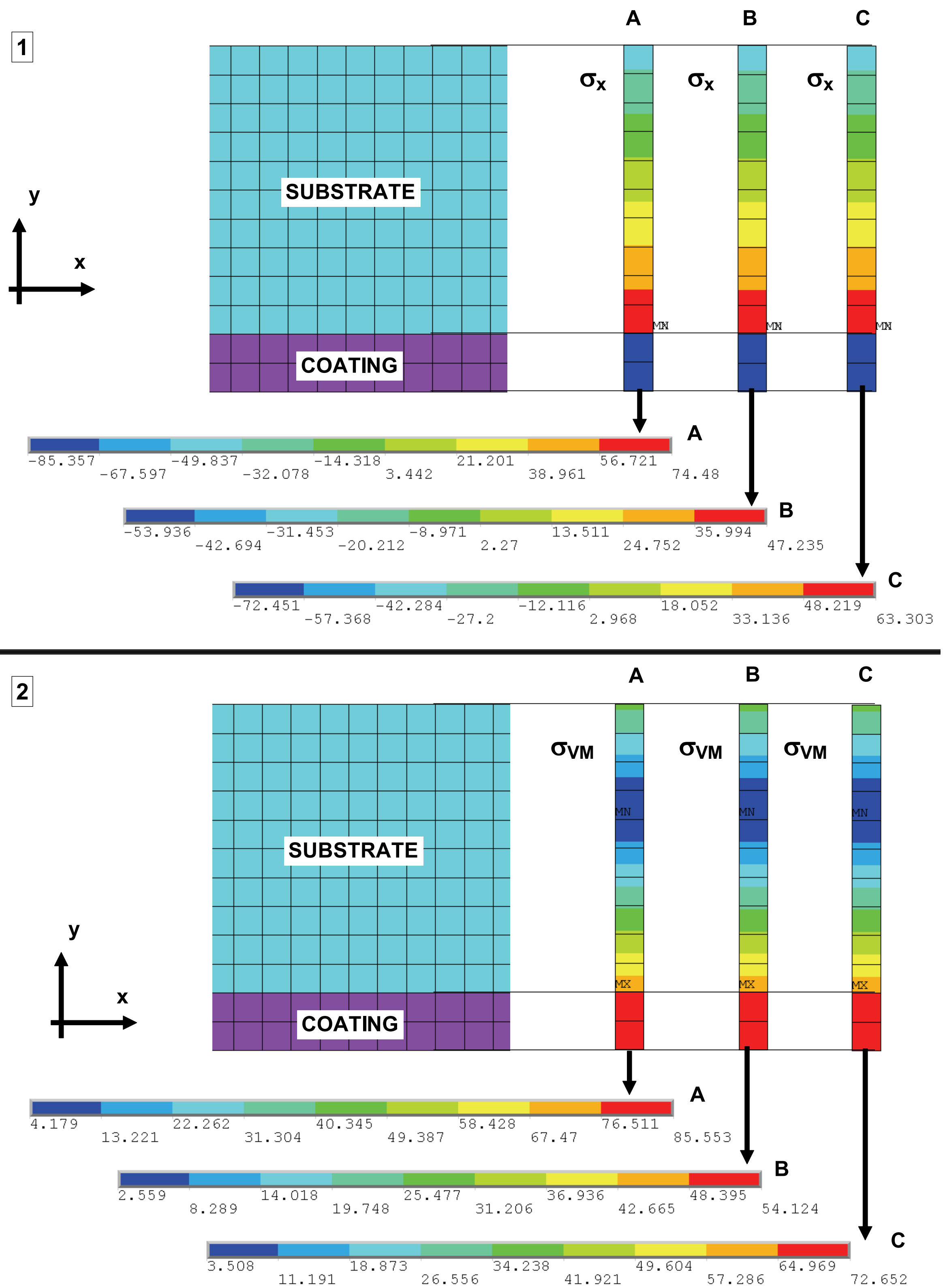

Fig. 4.18 andamento delle stressi residue in direzione x [(1); σ_x] ed equivalenti secondo il criterio di Von Mises [(2); σ_{VM}] nel caso di (A) SM005, (B) SM006, (C) SM013

acoustic event. On base how was mentioned in §4.3.1 the first significant acoustic event is that which set the zone free from damages both considering hoarded counts, Fig. 4.10, that the distribution of the energy of acoustic events, Fig. 4.11. To be able to confront relative values to the displacements of FCF (dFCF) for a different samples, is introduced adimensonal parameter defined as follows:

$$FCF_{displ} = \delta_{FCF} / t \quad (2)$$

Where t is the maximum value of the coating thickness for each sample subjected to bending or tensile. How can be inferred from the given definition FCFdispl is the parameter that hasn't direct correlation with the other known sizes for the study of the fracture mechanics. However FCFdispl permits to consider simultaneously the fact that the given value of the displacement set to the sample (both in bending that in tensile) the coating in theory the most critical has undergone a damage. In the chart 6 are obtained relative values to FCFdispl for three types of studied enamel.

The numerical results to the stresss that act on coating, related in charts 6 and 7, were obtained from the test of numerical simulation according how was already mentioned in §4.3.3. In particular in the numerical simulations was obtained count of the thickness distributions of coating and of the distribution of the displacement that have generated the condition of FCF as well as the relative residual stresss due to the productive process. It is observed that the stresss that were taken into reference are the first (s1) and the third (s3) principal stress maximum that act on coating.

Table 6 values relative to the first fracture for the bending test

		Experimental		Numerical			
		FCF_{displ}		σ_1 [MPa]		σ_3 [MPa]	
ID	Tecnologia	M.V.	S.D.	M.V.	S.D.	M.V.	S.D.
SM005	Liquido	1.24	0.26	115	12	-50	4
SM006	Liquido	1.48	0.35	125	15	-24	6
SM013	Polvere	1.62	0.28	150	11	-29	4

From the numerical analysis, relative to the bending test, appears that the action direction of the first and the third principal stresss coincides respectively with the direction of the x axes, principal axis of the sample, and of z axes, transversal axes to principal axes and pertaining to the principal plane of the sample. From the experimental test is moreover appeared that the first fracture is shown according to orthogonal lines to principal axes of the sample and therefore rest upon the orthogonal plane to the exes according which act the first principal stresss (it is noted in particular that the values of this stress are also positive). From numerical and experimental information can be obtained as the primary cause of the first fracture the fulfillment of the maximum value of the first principal stress.

Table 7 values relative to the first fracture for tensile test

		Experimental		Numerical			
		FCF_{displ}		σ_1 [MPa]		σ_3 [MPa]	
ID	Tecnologia	Valore Medio	Dev.St.	Valore Medio	Dev.St.	Valore Medio	Dev.St.
SM005	Liquido	0.08	0.03	85	6	-5	2
SM006	Liquido	0.09	0.03	78	7	-7	3
SM013	Polvere	0.15	0.02	102	6	-8	3

In case of the tensile test the first principal stress has parallel direction to x axis, principal axis of the sample, while the third principal stress has parallel direction to y axis, axis that rest upon the plane of sample and is orthogonal to principal axis. From the mechanical point of view similarly how is seen for the bending test, in the case of tensile test is that the dominant stress to study the origin to the first fracture is the first principal stress.

It is also possible to notice that the stress that cause the first fracture in case of the bending test are, for all porcelain enamels, superior to that which are in the tensile test. This fact can be explained noting how in the case of bending the first principal maximum stress, that is caused of the first fracture, doesn't act in constant way on all the section. To the contrary in the case of the tensile test the stress on the section of coating has constant process. Assuming as the reference value the critical stress obtained for the tensile test, is that in case of the bending test the part of section that has superior stress to the value is always shorter than one.

4.3.6 The impact test to verify the degree of adherence of the coating to substrate were conducted considering three productive periods during one year.

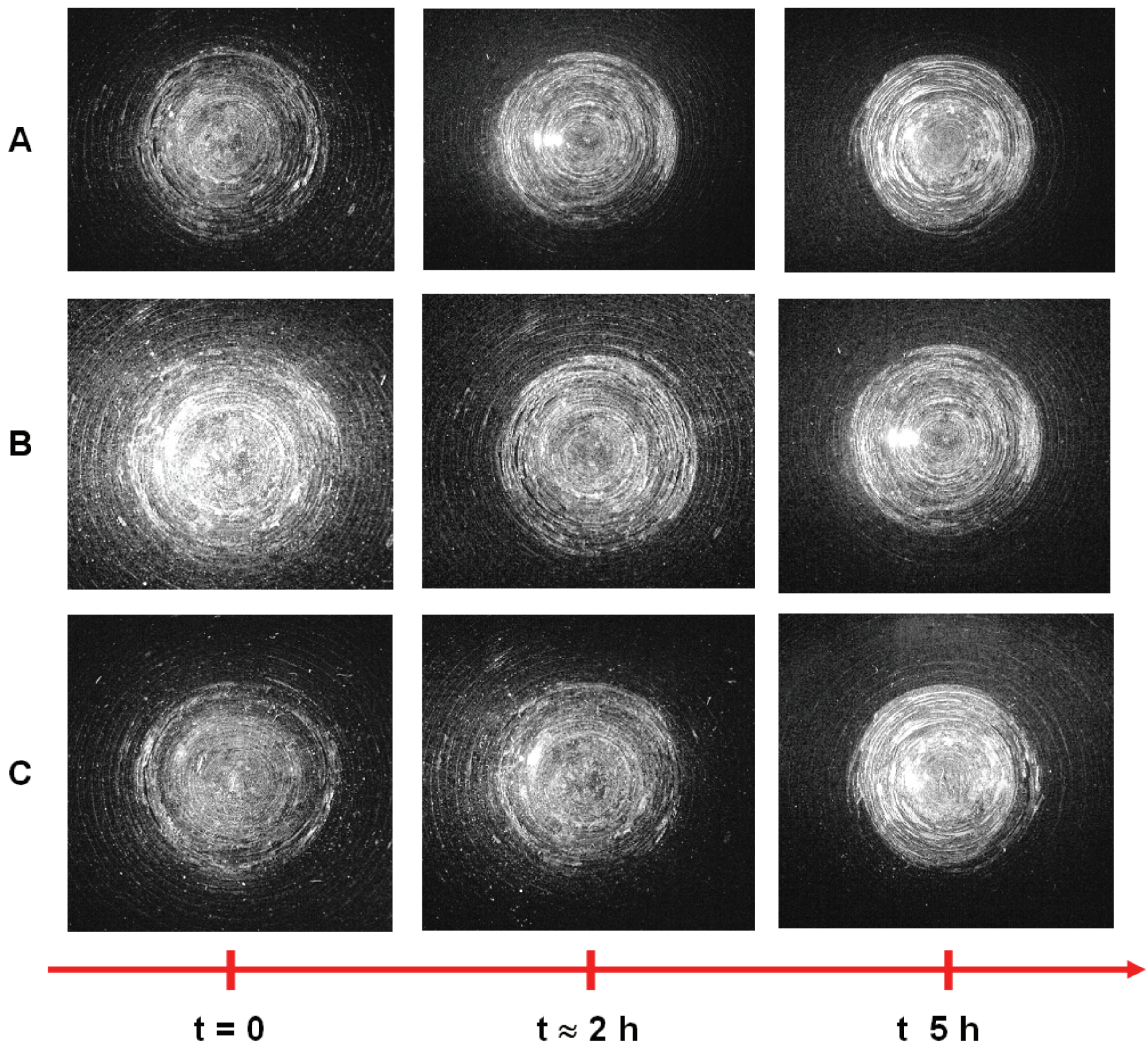

Fig. 4.19 foto relative all'area danneggiata dall'impatto per lo smalto (A) SM005, (B) SM006 e (C) SM013

For each productive period were predisposed 20 samples of the square form, having side of 100 mm, enameled on both sides. For each typology of the enamel and for each sample after impact were made photographical detections of impacted area.

After the impact, the observations relative to an impacted area were made prolong in time: in time of 0, immediately after the impact, after 2 hours and after 5 hours. The scope of making the photographic detections distributed in time was finalized to time verify in time of enamel stability in nearness of impact area. In Fig. 4.19-A,-B,-C are related three examples of relative pictures to impact zone retrieved in three instants of set time. How can be noted from the photos for nearly all types of enamels the coating in damaged area undergoes the progressive worsening in time. However for all the enamels the degree of adherence can be considered excellent.

4.4 The test of **acid corrosion resistance** of considered enamels were made in conformity to the standard EN14483:2004 and using one reaction room of which scheme is related in Fig. 4.20. Tool's bottom is the sample to be submitted to Test. The reactor were filled for three quarters, with one watery solution of sulphuric acid to 30% (v/v). The solution for the acid attack was brought into boiling by the temperature of T=105°C for 6 hours. The essential phases of test are as follows:

- preliminary measure of the thickness (mm), of the rugorosità (mm) and of weight (g) of sample;
- positioning of sample and replenishment of reactor;
- boiling for 6 hours;
- extraction of sample;
- evaluation of loss in percentual weight, of increase of the rugosità and of the thickness reduction.

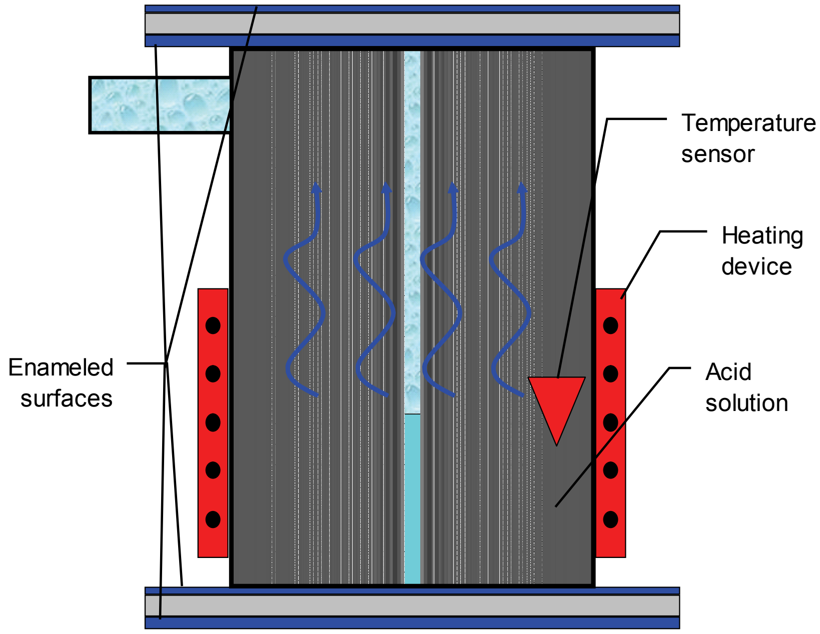

Fig. 4.20 schema della camera di reazione per le prove di corrosione acida

In Fig. 4.21 are related three imagines relative to three samples covered through the analyzedenamels and that have undergone a corrosion cycle.

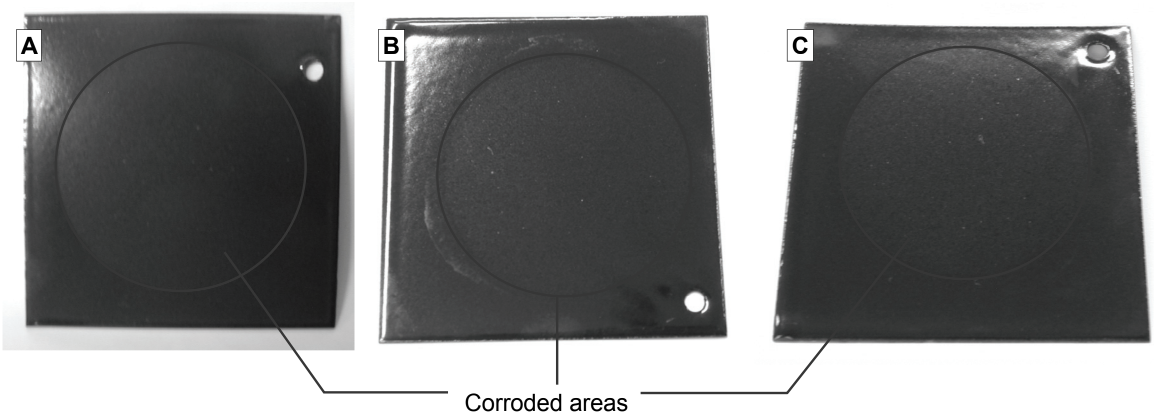

Fig. 4.21 foto relative a tre provini rivestiti mediante gli smalti (A) SM005, (B) SM006, e (C) SM013 che hanno subito corrosione acida

In the table 8 are summarized values relative to the weight variations, of rugosità and thickness for three analyzed enamels.

Table 8 characteristic dates of the enamel efficiency in respect to the acid corrosion process

	Tecnologia	Roughness percentage variation	Thickness percentage variation	Weigth loss (g/m^2)	
				M.V.	S.D.
SM005	Liquid	10%	1%	0.40	0.05
SM006	Liquid	5%	1%	0.63	0.04
SM013	Powder	6%	2%	0.65	0.04

How is observed from the summarized results in chart 8 the comportment relative to acid attack of new dust enamel results to be comparable with that exhibited form other dust enamels traditionally used for exchanging elements.

5. Numerical analysis and analysis of the experimental verify of enameled exchanging elements

Regarding mechanical characteristics of coatings were conducted of numerical and experimental analysis finalized to evaluate the comportment of the enameled exchanging elements. In particular the condition of mechanical solicitation that was taken into consideration is that which is obtained during the assembly of exchanging elements in the baskets, Fig. 5.1. In fact in order to stabilize exchanging elements in the baskets, that is verified during their use in plant, it's necessary to make their pressure. The pressure passes imposing to a cover sheet a vertical displacement that therefore causes "constipation" of elements in basket. The closure phase of the basket and therefore of pressure of elements result to be particularly critical as the coating could become seriously damaged: in coating can be induce (according the mechanisms of (according mechanisms of "crack onset" and/ or "crack propagation") or, in some cases, can arrive to cause the detachment of the whole parts of coating ("coat spalling"). All these phenomena of damaging of coating show substrate to an possible corrosive process during exercise in the exchanger that can cause their distraction within short time. The degree of pressure depends of entity of the displacement D that is imposed to the cover sheet, Fig. 5.1-A.

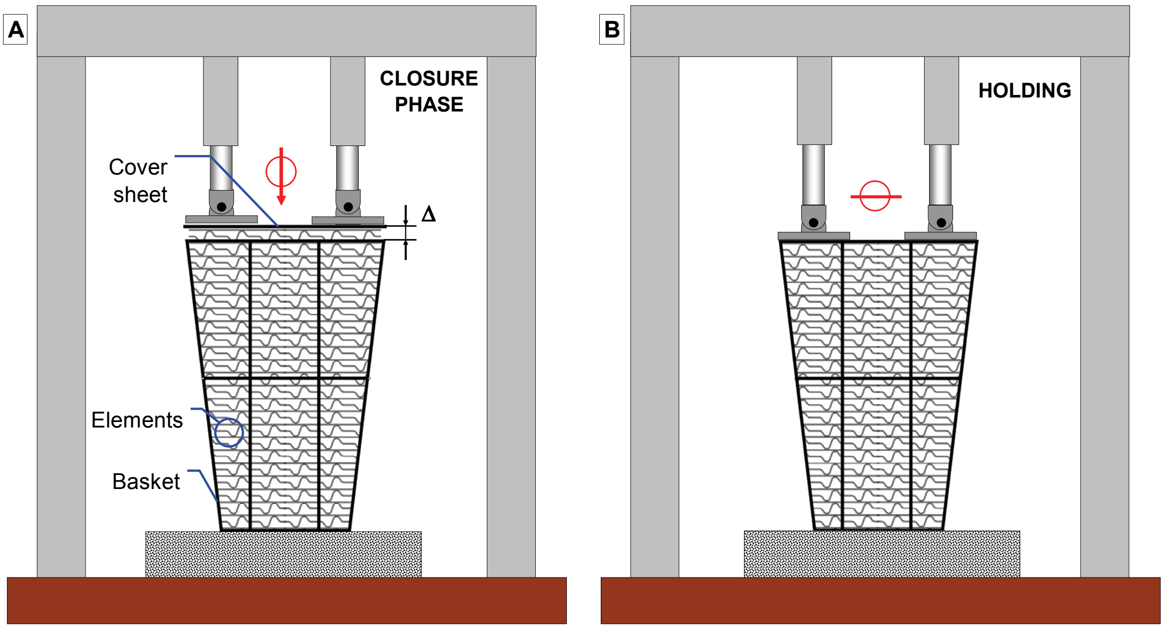

Fig. 5.1 scheme of the appliance of the basket closure containing exchanging elements, displacement D that is imposed to the cover sheet serves to stabilize exchanging elements. (A) initial condition before the closure phase, (B) final condition after the holding that is maintained till the complete closure of basket

The structural answer of the elements in the basket depends in general by following factors:
- geometry of elements;
- number of couple of sheets present in basket ;
- configuration of the elements assembly (reciprocal position of the elements and of point of reciprocal contact);
- typology of used material.

The study and the methodology of analysis that was implemented were finalized to identify, on base of mentioned factors, right value of variable D to impose in progress of the closure of baskets containing emameled elements in order not to damage them. For the development of the study are imposed two approaches:

1. one preliminary numerical analysis based on the modelation of the characterized element that constitute assemblage of the exchanging elements
2. one serie of the experimental laboratory analysis, monitorated through the acoustic emissions, that reproduce simulated numerical condition.

5.1 To be able to conduct the first analysis of numerical type it was necessary to individuate and modelate one characteristic part relative to assemblage of exchanging elements.

In the pictures in Fig. 5.2 are highlighted the characteristic zone of the assemblage of the exchanging elements and the numerical model that was realized on base of this option. In particular the selection of the characteristic zone of assemblage was made considering conditions of charge that is created during the closure of basket. In fact application of displacement D on cover sheet causes vertical displacement that is divided in each element contained in basket in proportional way to proper compliance. As the undulated elements, from structural point of view, are certainly stiffer if compared to the flat sheet, they were chosen to isolate one part of assemblage that contains two undulated elements that interact with a flat one. Moreover the number of waves that were considered equal to tree in order to construct the model in which central zone (Fig. 5.2 particulars 2 e 3) doesn't be effected of eventual border effects. In this way the information in stress terms that can be extracted from this zone (Fig. 5.2 particulars 2 and 3) can well represent the system comportment.

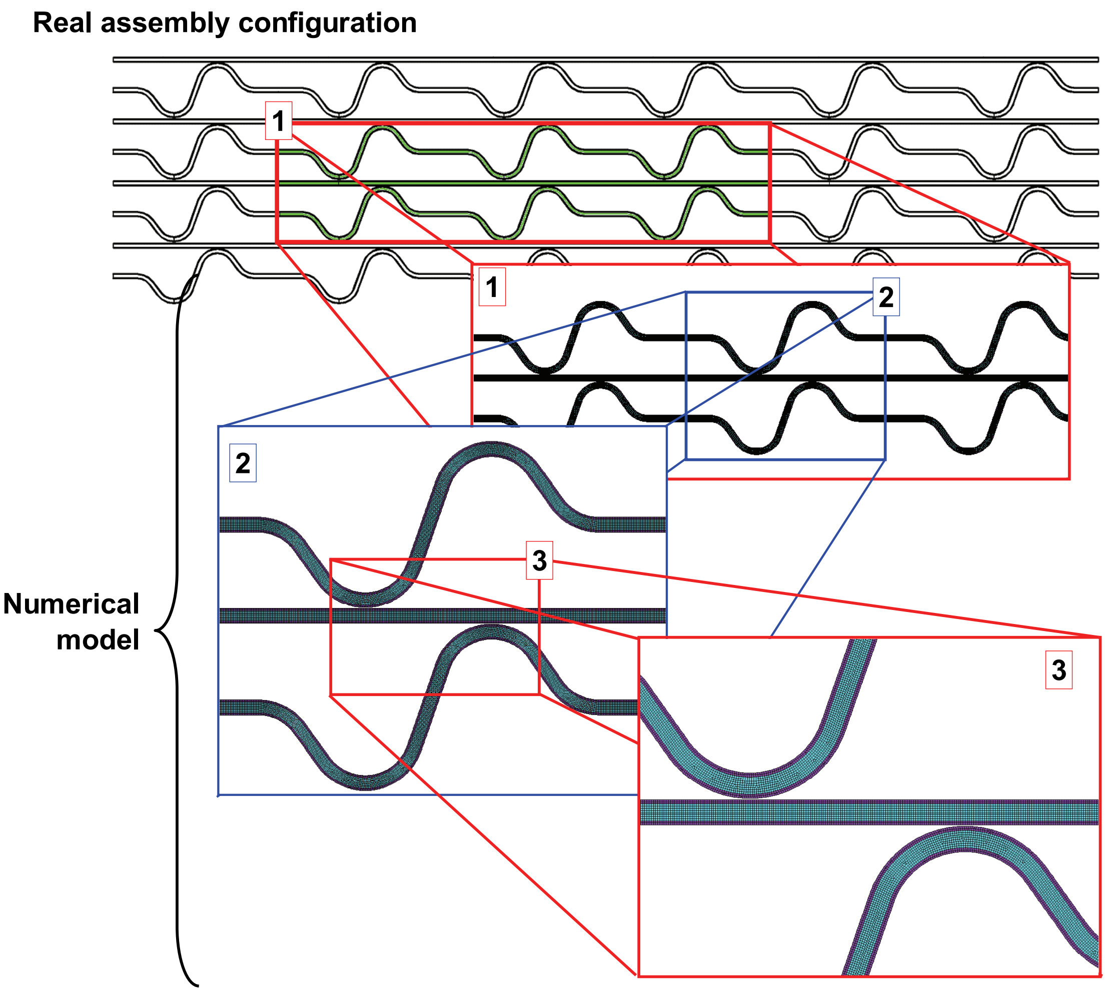

Fig. 5.2 individuazione della parte caratteristica dell'assemblaggio (1) e generazione del modello numerico (dettagli ingranditi 2 e 3)

In order to represent in realistic way the behavior of enameled elements numerical models were created. In these models thickness of sheet is equal to 0.8 mm, while the thickness of coating was chosen accordingly to experimental data. In the pictures in Fig. 5.3 is shown a numerical model in which the coating thickness is equal to 0.2 mm. The first numerical analysis that was performed regards residual stresses.

To analyze the residual stresses, and subsequently the stresses in case of mechanical charge, were considered the principal stresses. In fact in base how was already seen during the characterizing of the samples requested to bending and traction, principal stresses are good point from which start to define the real working conditions of the elements.

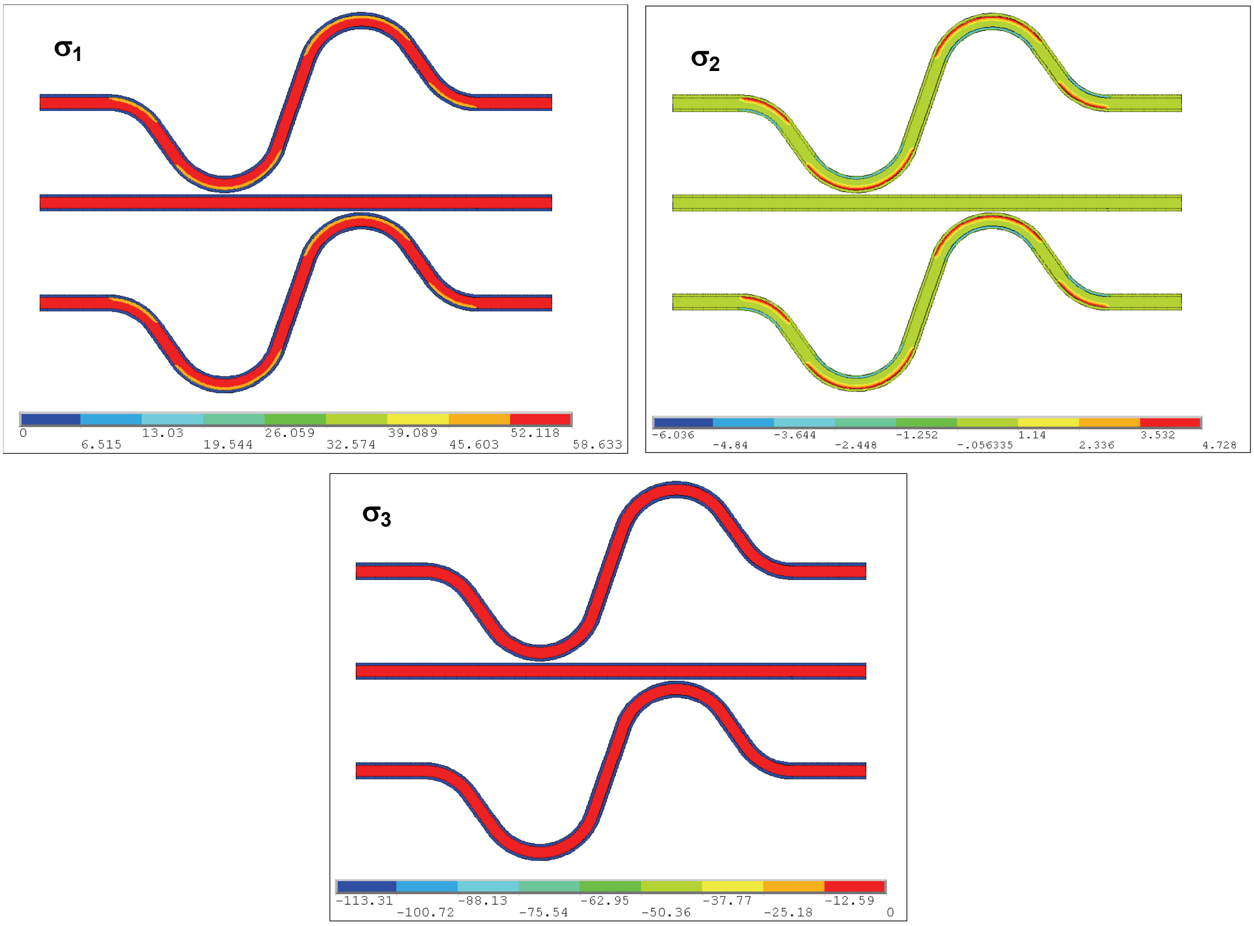

Fig. 5.3 process of principal thermal stresses (s1, s2, s3) for sheets covered with SM013

The load condition that has been considered for the numerical simulation is the displacement of the external part of the waved sheets. Results obtained from numerical simulation have been used to define the maximum allowable displacement that can be safely imposed to compresses the elements, otherwise it was possible to estimate the maximum displacement that can be applied to the elements without having the FCF condition in the enamel coating.

In particolare sono stati ottenuti i risultati riportati in tabella 9.

Table 9 results relative to the maximum admissible displacements deducted from the numerical Tests

	Technology	Maximum admissible Displacement (mm)
SM005	Liquid	0.09
SM006	Liquid	0.08
SM013	Powder	0.12

5.2 The laboratory analysis on exchanging elements were conducted equipping the machine of the servohydraulic Test INSTRON, provided of the charge cell of 100kN, through the pressure plates. These fungono from the elements of pressure. In Fig. 5. is related a photo relative to device of Test and to a Test. The Tests were conducted in control of charge imposing the velocity of advancing of mobile plate of 0.005 mm/sec. The selection of this velocity was made in reason of maximum imposed races and inferred from numerical Tests.

The Tests were monitorated through the acoustic emissions in order to be able to individuate the condition of the first fracture and to imTest the damaging. In particular were used two trasductors piezoelettrical model PAC-R15 and was imposed acquisition span of signals equal to 40dB. The preamplification was selected equal to 40dB. The transductors were collocated on the superior plate guaranteeing coupling of ceramic piezoelettrical with the metallical base through the syntetic fat not grafitical.

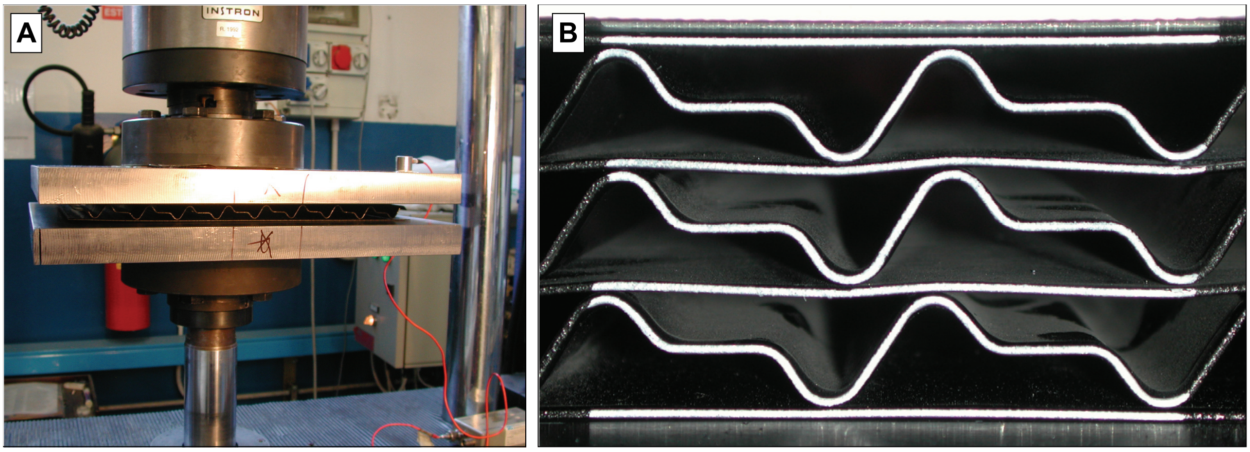

Fig. 5.3 (A) photo relative to Test tool and (B) photo of the package of sheets after the compression test (enameled sheets through SM013).

Tests in laboratory were conducted imposing preliminarily vertical displacements equal to those inferred from the numerical Tests. It could be revealed that in the case of enamel SM006 was obtained the origin of defects before having completed the race of the pressure plate. In particular ware observed fracture events to the 0.06 mm ÷ 0.01 mm span. The analysis of defects details created on the enameled surface was conduced through the job of passing liquids. Form the exam of zones that have undergone damage and highlighting through the passing liquids was observed that fractures were all of superficial type and consisted in the lost of the superficial part of covering. This fact is explainable on base of different entity of residual stresses.

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