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DSC CHARACTERIZATION OF INDUCED STRESSES DURING TRADITIONAL CERAMICS FORMING PROCESS

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Abstract

The recovery of metals is the process of softening without crystallization in the mechanical stressed pieces and is well characterized by DSC measurements at temperatures < 600°C. The present investigation was undertaken to detect similar effects also in traditional ceramics. Several ceramic samples, coming from different productions, were thermally analyzed by DSC and the presence, in the most stressed samples, of an exothermic peak at about 350°C, was detected, confirming the presence of recovery in the ceramics too. However, owing to the complex structures of these materials, at present no mathematical model could be introduced.

Keywords: ceramics, DSC, induced stresses, mathematical model

Introduction

The forming processes of traditional ceramics are based on few well known techniques, above all pressing, cold-drawing and casting. These processes are important to attain high quality standard levels, essentially by strict controls of parameters as the grain size, the water content and, for pressing, the pressure applied by the plant machines, while in casting it is important to keep constant the viscosity of the slurries.

No studies are reported on mechanical stresses induced by forming and drying. These effects are due to mechanical working: a thermal treatment can cause the softening of stresses, with a mechanism similar to the recovery effect for metals.

Recently, several reports have appeared on the recovery in the metals [1, 2]: progress are due to the wide use of the DSC techniques at low temperatures, that permit to discover the energy release in the materials after thermal and mechanical stresses. The energy values involved in these processes are indicated in some studies to be about 20 J mol^{-1} (this is the energy amount released by Al [3]).

The models applied to justify these effects take in account the dislocations arrangement during annealing [4], and are based on the simple lattices of the metals: in this way, the relations between microstructure and atomic rearrangement after heat

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treatments can be described in a simplified way, since are not taken in account the lattice defects and the dislocations progress.

In addition, the metals present more simple structures, as respect to ceramics; it is therefore possible to use the analysis methods used for metals but not to introduce their models.

A simple model on recovery in the ceramics

For ceramics, it is possible to suggest some simple hypotheses that depend on the different forming process.

Cold-drawing

The materials produced by this process are usually roof tiles, bricks and tiles, starting from a plastic mixture with about 12% of water. The mechanical effect of the process on the greens can be shown in the Fig. 1.

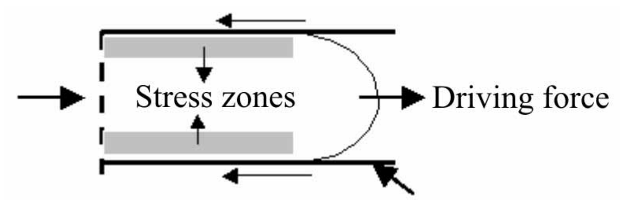

Fig. 1 Mechanical effect of cold drawing

In the course of this process, a mechanical strain is induced on the surface layers by attrition. The quantity of absorbed energy will be a function of the mixture plasticity and is conncected to the used clay-types minerals.

As for metals worked by cold-drawing, a thermal treatment (annealing) recover the balance of the system by means of energy release.

Pressing

The tile production is usually carried on by pressing the spray-dried powders which contain about 6% water. The attrition of the powders with the mould walls is illustrated in the Fig. 2.

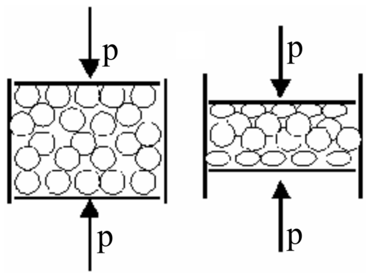

Fig. 2 Attrition effect of spray-dried powders on the mould

Table 1 List of samples

Sample no.	Type	Production	Position
1a	Plate	Tognana [tableware]	Edge
1b	Plate	Tognana [tableware]	Up
1c	Plate	Tognana [tableware]	Down
1d	Plate	Tognana [tableware]	Bulk
2a	Plate	Tognana [tableware]	Edge
2b	Plate	Tognana [tableware]	Up
2c	Plate	Tognana [tableware]	Down
2d	Plate	Tognana [tableware]	Bulk
3a	Cup	Tognana [tableware]	Edge
3b	Cup	Tognana [tableware]	Up
3c	Cup	Tognana [tableware]	Down
3d	Cup	Tognana [tableware]	Bulk
4a	Roof tile	Germany	Surface
4b	Roof tile	Germany	Bulk
5a	Roof tile	Norco [roofs]	Surface
5b	Roof tile	Norco [roofs]	Bulk
6a	Roof tile	Norco [roofs]	Bulk (up)
6b	Roof tile	Norco [roofs]	Surface (up)
6c	Roof tile	Norco [roofs]	Surface (down)
6a	Cold drawing	Meta [spray-dried]	Up
6b	Cold drawing	Meta [spray-dried]	Down
6c	Cold drawing	Meta [spray-dried]	Bulk
7a	Cold drawing	Meta [spray-dried]	Up
7b	Cold drawing	Meta [spray-dried]	Down
8a	Cold drawing	Meta [spray-dried]	Up
8b	Cold drawing	Meta [spray-dried]	Centre
9a	Cold drawing	Meta [spray-dried]	Up
9b	Cold drawing	Meta [spray-dried]	Centre
10a	Cold drawing	Meta [spray-dried]	Up
10b	Cold drawing	Meta [spray-dried]	Centre
11a	Cold drawing	Meta [spray-dried]	Up
11b	Cold drawing	Meta [spray-dried]	Centre
12a	White brick	Spain	Up
12b	White brick	Spain	Cemtre
13a	Red brick	Spain	Up
13b	Red brick	Spain	Centre

In this case it is possibile, too, to suggest a strain in the outer layers that could be released after annealing.

In order to verify the possibility of recovery effects on the industrial ceramics, low temperature DSC data were then carried on industrial products.

Experimental

A lot of ceramics pieces, obtained from several products, was considered and samples coming from different positions in the bulk and in the edges of the products were subjected to the below described tests. InTable 1 are reported the used samples and their sources.

The specimens were examined by a DSC Setaram attachment with Al crucibles in the thermal interval 30–500°C, using a scanning speed of 5°C min^{-1}.

Results and discussion

The results obtained are summarized in Table 2, together with the energies released during the tests and the temperatures where some thermal effects were detected. Some of the thermal diagrams are reported in the Figs 3a–b and 4a–b.

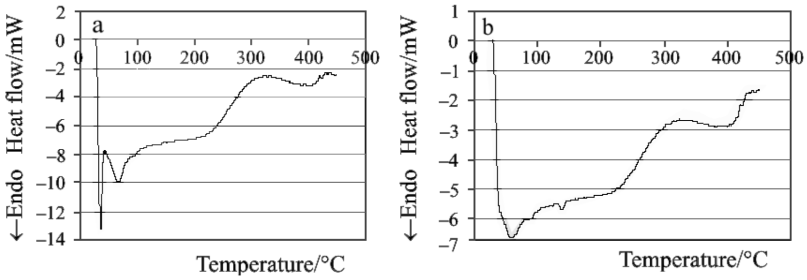

Fig. 3a–b DSC plot of border and of the bottom layer of plates

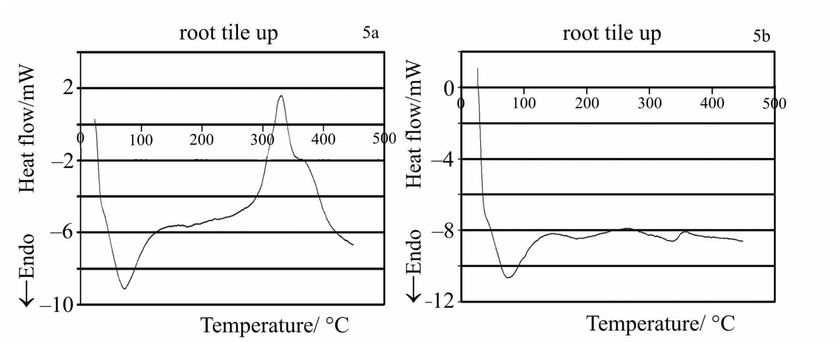

Fig. 4a DSC plots of a roof tile (5a, 5b)

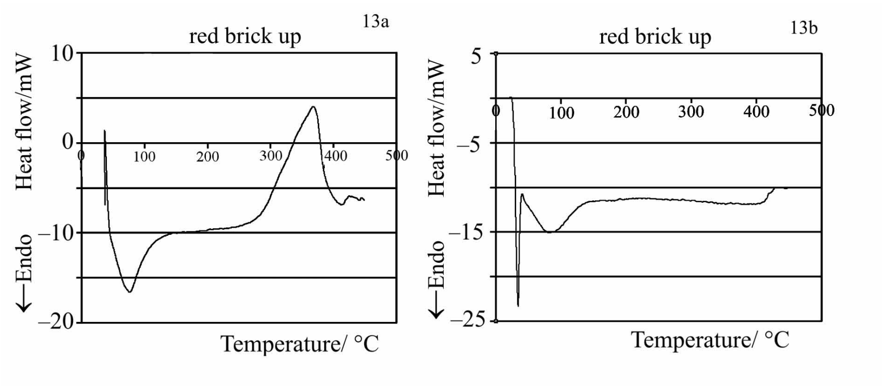

Fig. 4b DSC plots of a red brick (13a, 13b)

It is possible to detect, in some diagrams, the presence of a low-temperature endothermic effects, referred to the hydration water release, and a second effect that happens at about 300°C: these effects cannot be ascribed to chemical reactions occurring during the heating and appears only in the samples obtained from strongly worked places, while are not present in the specimens coming from the bulk of the ceramics (not subjected to strong mechanical forces). It is reasonable to suggest that these effects could be ascribed to the mechanical energy release.

Table 2 Temperature and stress energy released

Sample no.	Type and position	T/°C	E/J g^{-1}
1a	Plate edge	305	12.01
1b	Plate up	305	8.20
1c	Plate bottom	302	9.65
1d	Plate bulk	–	–
2a	Plate edge	305	33.93
2b	Plate up	305	18.35
2c	Plate bottom	302	29.29
2d	Plate bulk	315	9.46
3a	Cup edge	336	5.28
3b	Cup up	303	4.64
3c	Cup bottom	303	5.73
3d	Cup bulk	–	–
4a	Roof surface	350	53.5
4b	Roof bulk	–	–
5a	Roof surface	335	113.5
5b	Roof bulk	–	–

Table 2 Continued

Sample no.	Type and position	T/°C	E/J g^{-1}
6a	Roof bulk - up	313	0.42
6b	Roof surface - up	331	61.25
6c	Roof surface - down	334	111.98
6a	Cold drawing - up	423	0.46
6b	Cold drawing - bottom	423	0.38
6c	Cold drawing - centre	429	0.19
7a	Cold drawing - up	–	–
7b	Cold drawing - bottom	–	–
8a	Cold drawing - up	–	–
8b	Cold drawing - centre	–	–
9a	Cold drawing - up	–	–
9b	Cold drawing - centre	–	–
10a	Cold drawing - up	–	–
10b	Cold drawing - centre	–	–
11a	Cold drawing - up	–	–
11b	Cold drawing - centre	–	–
12a	White brick up	–	–
12b	White brick bulk	–	–
13a	Red brick up	367	185.15
13b	Red brick bulk	–	–

To verify this hypothesis, products coming from different types of ceramics were taken into account (Table 3). The DSC results (Table 2) show strong energy releases for the colored products, while white ceramics products exhibited by far lower exothermic effects.

Table 3 Details of tested samples

Color	Process type	Product
Red	Cold drawing	Roof tile
		Tile
		Brick
White	Cold drawing	Tile
		Tableware
White	Pressing	Tableware

The analyses of the energy values showed that white or clear ceramic products yielded energy values of the same order as respect to the metals [3], while the red products gave greater and greater energy values.

Conclusions

The investigations performed by DSC on ceramic samples coming from different productions showed, in the specimens obtained from parts that were subjected to strong mechanical stresses, the presence of an exothermic peak at about 350°C. This effect, that does not appear in the samples coming from the bulk of the pieces (not stressed), was referred to the release of mechanical stresses collected during forming processes.

The energy values associated to these peaks were calculated and found similar to the ones obtained from recovery in the metals.

The perfomed tests have evidenced that DSC methods at low temperatures is a correct method to reveal the stress collected during mechanical forming works.

However, at this point it is not possible to introduce a model to explain such a mechanism, owing to the complexity of the crystal systems of ceramics and to the difference of the processing systems.

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