Thermochimica Acta, 20 (19[illegible]-86

THERMOANALYTIC STUDIES BY THE DEVELOPMENT OF CERAMIC MULTILAYER CAPACITORS*

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ABSTRACT

During the last five years monolithic ceramic capacitors have enjoyed increasingly widespread application[1]. This paper presents one specific method of making ceramic multilayers.

A very important step is the burnout of the organic binder. The degradation kinetics of several polymers was analysed by differential thermal analysis, thermogravimetry and IR spectroscopy.

INTRODUCTION

Thermoanalytic studies[2] of the thermal degradation of polymeric materials are important to explain the behavior of polymers exposed to high temperature. This paper describes the application of Differential Thermal and Thermogravimetric Analysis for the selection of polymers by the development of Multilayer Ceramic Capacitors (Fig. 1).

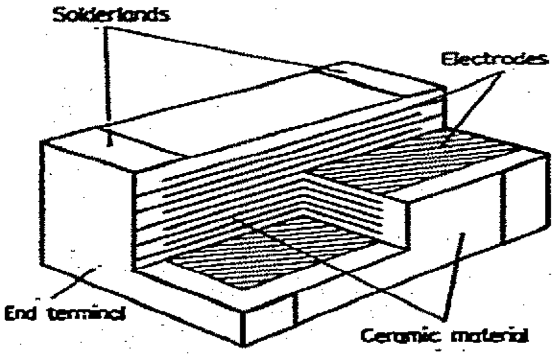

Fig. 1. Multi-layer ceramic chip capacitor.

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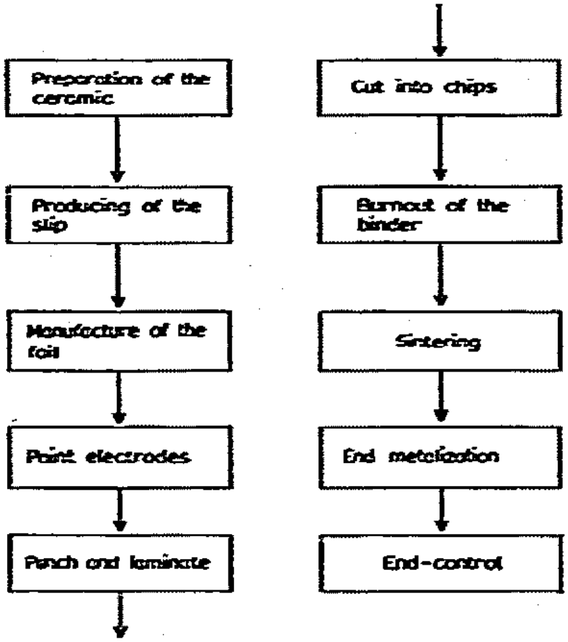
* Presented at the 2nd Symposium of the German Society for Thermal Analysis, held at the University of Konstanz, from 5–6 July, 1976.

EXPERIMENTAL

The multilayer capacitor consists of many thin layers of ceramic with precious metal electrodes separating the thin layers. The electrodes exit on alternate ends of the capacitor so that a paralleling of the individual plates is achieved. The electrodes are printed on green (unfired) ceramic tape and the capacitor is assembled before firing. The result is a highly compact capacitor.

The final capacity of a multilayer ceramic capacitor is controlled by varying the area of the electrodes, the thickness of the ceramic layers, the number of layers and the dielectric constant of the ceramic.

The process of manufacturing multilayer ceramic capacitors is described by the following flow chart.



Several methods are used to produce thin sheets, but the doctor blading process is by far the most popular and is considered to be the best all-round method (Fig. 2). This process basically consists of suspending finely distributed ceramic powder in a liquid system comprising solvents, plasticizers, and binders to form a slurry that is cast onto a moving carrier surface. The slurry passes below the knife edge of a blade that levels the slurry into a layer of controlled thickness and width as the carrier surface moves along a supporting table. When the solvents evaporate, the fine, solid particles coalesce into a relatively dense, flexible sheet.

The doctor-blade process as a method for forming ceramics is usually applied because of its advantage in providing relatively thin, large area shapes of uniform high density. There are often other concomitant objectives with a given ceramic composition or application. For instance, electronic properties, surface finish, grain

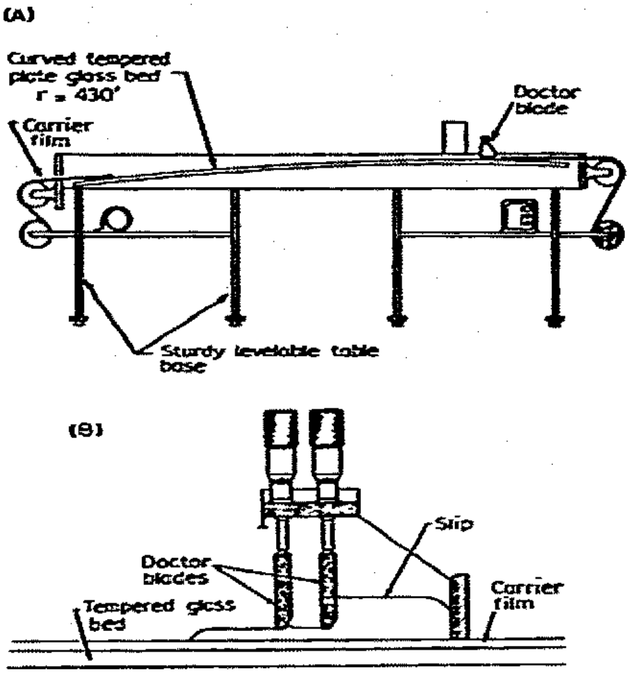


Fig. 2. (A) Precision tape casting machine. (B) Doctor blade process.

size, fired density and strength, and minimizing heat treatment may be essential requirements too. In addition, high green density in the as-cast tape reduces firing shrinkage which in turn reduces warpage and supports dimensional control. All of these items have become recognized as being strongly dependent upon the characteristics of the starting ceramic powder[3].

A fundamental step in the production of multilayer capacitors is the burnout of the organic binder from the green chips.

The thermal degradation of various polymeric materials was studied by DTA, TG and IR-spectroscopy.

RESULTS

Figure 3 shows the thermogravimetric curves of three polymers—polyvinylacetates, polyamides and polyvinylalcohols—at a heating rate of 0.1 °C min^{-1}.

The fast thermal decomposition of polyvinylacetate makes it unsuitable as an organic binder. For the production of multilayer capacitors a slowly thermosetting polymer is needed. Polyamides and polyalcohols fill this demand. Moreover, the binder has to be removed completely at relatively low temperatures to prevent a reduction of the dielectric—$BaTiO_3$, TiO_2—during the sintering by hydrocarbons and carbon residues.

We explain the thermal degradation of polyvinyl alcohols[4] as follows (Figs. 4 and 5). By the thermal decomposition of polyvinylalcohol in air there is an equal

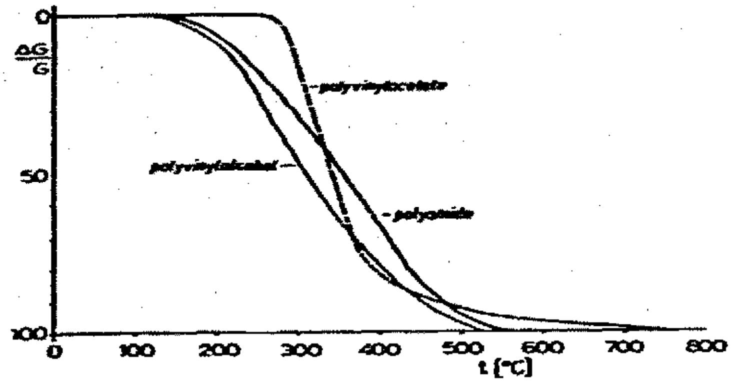


Fig. 3. Thermal degradation of polymers.

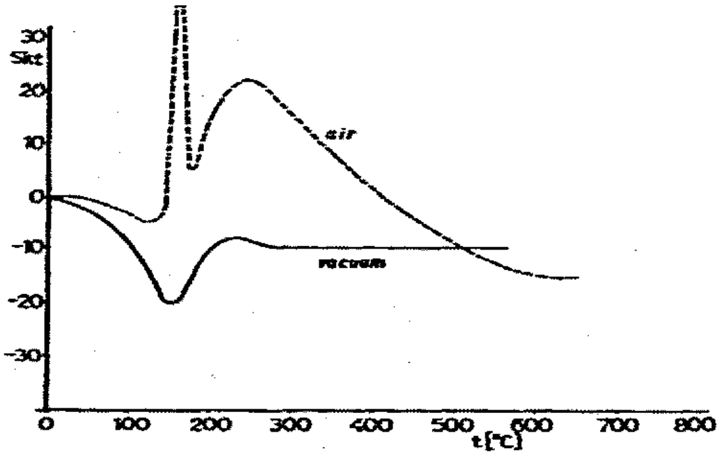


Fig. 4. DTA of polyvinylalcohol.

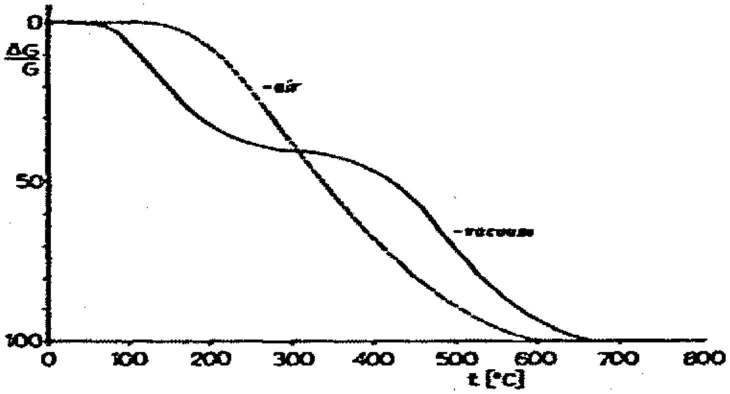


Fig. 5. TG of polyvinylalcohol.

decomposition stage over a broad temperature interval. TG-curves in vacuum (1 Torr) show, that the decomposition takes place in two separate reactions.

During the thermal decomposition of polyvinylalcohol in vacuum the first endothermic reaction lies between 100 and 260°C, the initial stage represents the liberation of water from hydroxyl and hydrogen groups of C-atoms on the polymer chain. Only about 75% of the theoretical amount of water is liberated. The result is a colored residue containing isolated hydroxyl groups and carbon–carbon double bonds.

It was also found that the second main decomposition stage involves two different processes. Thus, between 260 and 390°C, the main products liberated were identified by IR measurements as consisting of the low molecular weight aldehydes: formaldehyde, acetaldehyde and acrolein.

Between 390 and 490°C a yellow oil was liberated which contained unsaturated hydrocarbons. Above 490°C a dark residue remained, which represented about 10% of the original sample weight.

Above 300°C, the DTA curves do not indicate any further reactions. This was attributed to the great sample shrinkage which occurred and affected the DTA measurements at the higher temperature.

The mechanism of the decomposition in air is very complex, the interpretation is difficult. The first step, which is indicated by an endothermic peak, is the liberation of water, accompanied by the formation of double bonds. Immediately above 160°C two exothermic DTA-peaks appear when oxygen is present. We explain the first exothermic reaction as an addition of oxygen to the carbon double bonds, combined with the connection of the polyvinylalcohol chains. The loss in weight proceeds less rapidly, this indicates also the addition of oxygen. We suppose that the second exothermic reaction is attributed to a polymerisation reaction. This reaction is superposed by oxidative decomposition.

At about 300–400°C (in which aldehydes are produced) the loss in weight becomes greater than the addition of oxygen. Above 400°C the weight loss is less over a certain temperature range in the presence of oxygen than it is in vacuum.

Figures 6 and 7 show how important a continuous, thermal decomposition of the organic binding agent is for the production of multilayer-capacitors. Figure 6

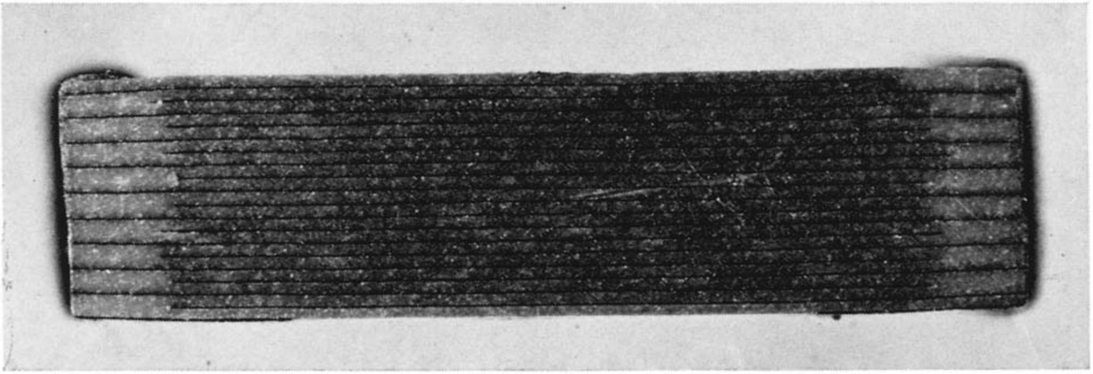


Fig. 6. Multi-layer chip.

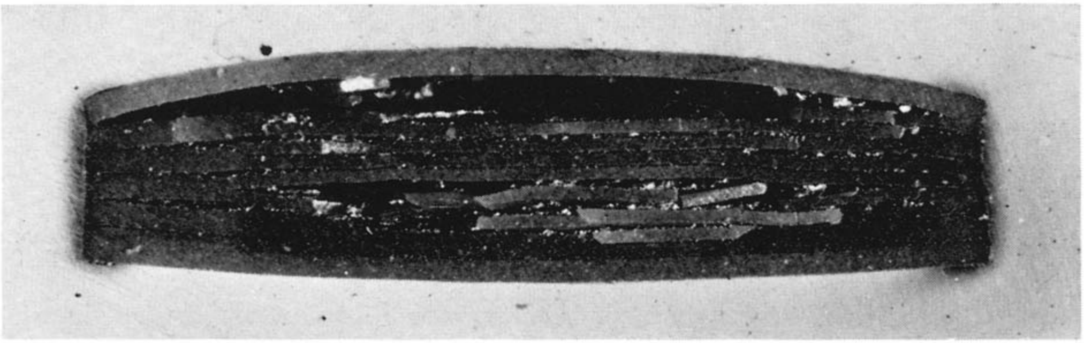


Fig. 7. Multi-layer chip with bubbles.

presents a multilayer chip, where the binder was burned out very slowly. Figure 7 shows that by rapid burnout of the binder gas bubbles occur, which destroy the multilayer structure completely.

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