

## **CORRELATION BETWEEN THE SURFACE ACID-BASE NATURE OF SOLID METAL OXIDES AND TEMPERATURE OF CaSO<sub>4</sub> DECOMPOSITION**

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### **Abstract**

By means of the combined use of scanning electron microscopy+energy dispersive spectrometry (SEM+EDS), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), differential thermal analysis (DTA) and thermogravimetry (TG), the thermal decomposition of gypsum and gypsum bonded investment used for casting jewellery products has been studied in order to gain a further insight into the origin of the gas porosity in gold-based alloys produced via lost wax casting. The occurrence of the defect is related to the thermal decomposition of CaSO<sub>4</sub> that constitutes with silica the investment material and the decomposition of which takes place at a temperature very close to the casting temperature of some typical gold alloys. The decrease of the thermal decomposition temperature of gypsum is induced by the presence of silica and is related to the surface acid-base interaction between SiO<sub>2</sub> and CaSO<sub>4</sub>. On the base of these results, the solid state thermal decomposition of calcium sulphate in the presence of other metal oxides characterised by different acid-base nature has been investigated and a correlation between the surface acid-base properties measured as isoelectric point of the solid surface (IEPS) and via XPS analysis and the temperature of CaSO<sub>4</sub> thermal decomposition is observed.

**Keywords:** CaSO<sub>4</sub> thermal decomposition, gas porosity in jewellery production, lost wax investment casting, surface acid-base properties of metal oxides

### **Introduction**

One of the most frequent defects present on the surface of the gold-based jewellery products is 'gas porosity' [1–4]. The nature of this defect was described in a previous work [1] where also its origin has been related to the rapid heating of the gypsum of the investment by the molten gold alloy. Indeed, during the casting and solidification process, the investment is very rapidly heated, from the casting temperature of about 600, to a temperature higher than 980°C, that is the lowest melting temperature of commercial yellow gold alloys, and can reach 1200°C when casting Pd containing white gold alloys.

In order to gain a further insight into the thermochemical behaviour of gypsum bonded investment, differential thermal analysis (DTA), thermogravimetry (TG),

X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) have been used. Furthermore, because the decrease of the thermal decomposition temperature of gypsum has been attributed to the presence of silica and related to a surface acid-base interaction, the solid state thermal decomposition of calcium sulphate in the presence of metal oxides characterised by different acid-base nature has been investigated.

## Experimental

DTA-TG measurements were carried out in air from room temperature to 1400°C using an automated thermal analyser (Stanton Redcroft STA-781).

The XPS study was carried out on an Escalab Mk II spectrometer using AlK<sub>1,2</sub> radiation as excitation source ( $h\nu=1486.6$  eV). The electron hemispherical analyser was operated in fixed analyser transmission mode (FAT) by selecting a constant pass energy of 20 eV. Under these conditions, the full width at half maximum (FWHM) of argon ion cleaned Ag 3d<sub>3/2</sub> line was 1.0 eV. Binding energies (BEs) were referenced to the Fermi level of the analyser and confidence in the linearity of BE scale was based upon setting the position of Au 4f<sub>7/2</sub>, Cu L<sub>3</sub>M<sub>45</sub>M<sub>45</sub> and Cu 2p<sub>3/2</sub> peaks at 84.0, 567.8 and 932.5 eV, respectively. Corrections for the energy shift, due to the steady state charging effect, were accomplished by assuming the C 1 s line, resulting from the adsorbed hydrocarbons, as lying at 285.0 eV. Reproducibility in the results was  $\pm 0.15$  eV.

XRD patterns were recorded directly on the powders by multiple scanning using an automated Seifert XRD-3000 diffractometer. The identification of the species was carried out by using a Seifert XDAL 3000 Software Index I.

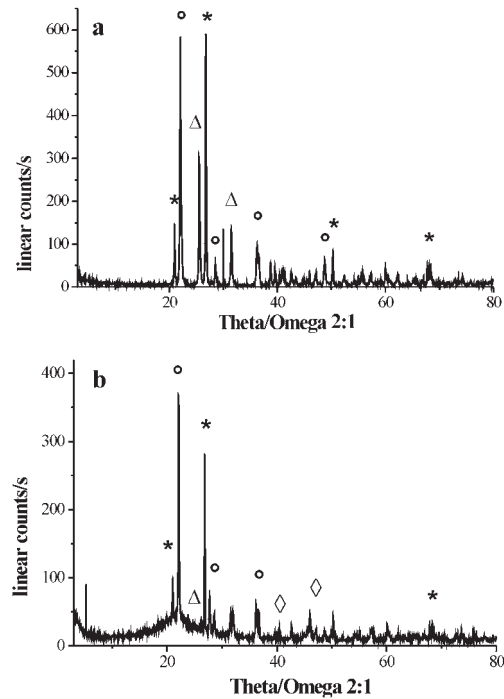
SEM and EDS characterisation was carried out by using a Cambridge 360 scanning electron microscope equipped with an EDS apparatus and a LaB<sub>6</sub> filament.

The investment powder was commercially obtained and the investment was prepared according to the specifications of the producer.

## Results and discussions

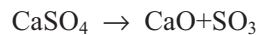
The microchemical structure and morphology of the powder CaSO<sub>4</sub> bonded investment has been studied via the combined use of SEM+EDS and XRD. The results have shown that the investment is composed of well mixed CaSO<sub>4</sub> and silica particles, these latter being in the form of cristobalite and quartz as indicated by XRD results reported in Fig. 1.

The comparison between the TG curves in air for analytical grade CaSO<sub>4</sub> and CaSO<sub>4</sub> bonded investment is shown in Fig. 2. DTA-TG results evidence different chemical and physical steps suffered by the CaSO<sub>4</sub> and CaSO<sub>4</sub> bonded investment during the thermal treatment. During the removing water step, the materials undergoes a two-stage dehydration with peak temperatures of 104 and 246°C. The small endothermic peak occurring at 332°C is due to unstable forms of cristobalite transformation that induces a consequent volume change. The small exothermic peak occur-



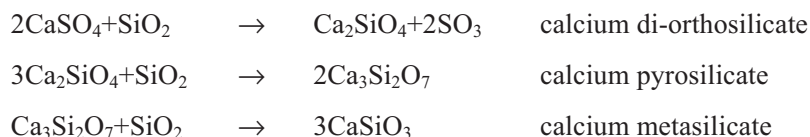
**Fig. 1** XRD patterns for the as received investment and for the investment after a thermal treatment carried out in air at 1280°C. The presence of quartz,  $\beta$ -cristobalite, anhydrite and calcium silicate is evidenced by the following symbols: \*, o,  $\Delta$  and  $\diamond$ , respectively

ring at 466°C has been attributed to a  $\gamma$ -CaSO<sub>4</sub>→ $\beta$ -CaSO<sub>4</sub> phase transition and at 607°C the  $\alpha$ -quartz to  $\beta$ -quartz transformation takes place with the well known expansion phenomenon. With increasing temperature, the TG curve for pure calcium sulphate shows only a very little deviation in the temperature range of casting of the most common carat gold alloys and that the thermal decomposition of pure CaSO<sub>4</sub> begins at about 1240 and is practically complete at 1450°C. At this temperature the mass loss of the specimen is about 42% and the formation of calcium oxide and sulphur anhydrides takes place according to the following reactions [5–7]:



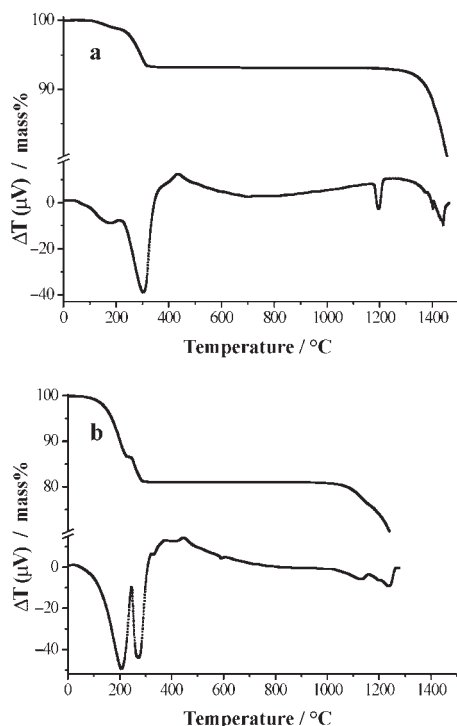
On the contrary, the TG curve for the CaSO<sub>4</sub> bonded investment shows the influence of silica on decomposition temperature and on the extent of thermal reaction. Indeed, at about 990–1000°C, the gypsum bonded investment exhibits endothermic dissociation. The reaction mechanism has been previously proposed [7] and it is based on the occurrence of the calcium sulphate thermal decomposition at 990–1000°C and then, only at 1040°C the reaction between cristobalite or quartz occurs thus forming

calcium orthosilicate ( $\text{Ca}_2\text{SiO}_4$ ). The secondary reaction between the calcium orthosilicate and the excess cristobalite or quartz takes place at higher temperature ( $1130^\circ\text{C}$ ) to yield probably calcium pyrosilicate and finally, calcium metasilicate ( $\text{CaSiO}_3$ ) is formed at  $1250^\circ\text{C}$  according to the following reactions:



Furthermore, we note that the presence of different endothermic peaks in the temperature range from 1000 and  $1250^\circ\text{C}$  combined with the mass loss suffered by the gypsum could be also related with the formation of polysilicates that could affect the dissociation of  $\text{CaSO}_4$ . It is worth noting that the XRD pattern, reported in Fig. 2, for the  $\text{CaSO}_4$  bonded investment after a thermal treatment at  $1280^\circ\text{C}$  discloses the presence of quartz,  $\beta$ -cristobalite and a small amount of calcium metasilicate ( $\text{CaSiO}_3$ ) as well as amorphous phases.

With these considerations in mind, XPS and X-ray induced Auger electron spectroscopy (XAES) has been used for determining the surface chemical reactions that



**Fig. 2** DTA-TG curves for analytical grade anhydrite (curve A) and for calcium sulphate (75 mass%)-bonded silica investment (curve B). The measurements have been carried out in air at a heating rate of  $10^\circ\text{C min}^{-1}$

take place as a function of temperature and chemical nature of the resulting products. In particular, calcium sulphate-bonded silica investment was isothermally treated at different temperatures from 900 up to 1250°C for 60 min. The temperature of the treatment was selected on the basis of the DTA-TG curve and was 900, 1040, 1120, 1200 and 1250°C. After each thermal treatment, the sample was exposed to the air and immediately inserted into the SAXPS spectrometer and after this characterisation into the SEM microscope, in order to minimise the ambient surface contamination.

In Table 1, the  $\alpha'$  Auger parameters and the binding energy (BE) values for the calcium sulphate-bonded silica investment in the as received conditions and after the thermal treatment are reported. It is worth noting that  $\alpha'$  Auger parameter [9, 10] is obtained by means of the combined use of both the photoelectron and X-ray induced or Bremsstrahlung Auger line according to:

$$\alpha' = KE_{(\text{Auger peak})} - KE_{(\text{photoelectron peak})} + h\nu$$

So conceived  $\alpha'$  has the advantages of being independent of photon energy, of always having positive values and is independent of the charge referencing operation. Therefore,  $\alpha'$  is found with higher accuracy than the determination of either photoemission line energy alone.

**Table 1**  $\alpha'$  Auger parameter, kinetic energy ( $KE$ ) of Si  $KL_{2,3}L_{2,3}$  peak and binding energy (BE) values of the Si 2p photoemission peak for  $CaSO_4$ -bonded silica investment in the as received conditions (a.r.) and for the thermal treated sample at different temperature in air

Sample	Si 2p <sub>3/2</sub>	Si KL <sub>2,3</sub> L <sub>2,3</sub>	$\alpha'$
CaSO <sub>4</sub> -SiO <sub>2</sub> a.r.	103.0	1608.7	1711.7
900°C	103.0	1608.7	1711.7
1040°C	102.7	1609.2	1711.9
1120°C	102.9	1609.4	1711.3
1200°C	102.2	1610.2	1712.4
1250°C	102.3	1610.2	1712.5

From the comparison between  $\alpha'$  Auger parameters for silicon in our samples and literature data [8, 9], we deduce that the silicon phases of the thermal treated calcium sulphate-bonded silica investment change their chemical nature as a function of temperature and calcium sulphate reacts with cristobalite and quartz according to the previously proposed reactions giving rise to the formation of calcium metasilicate as a final product.

We stress that the decomposition temperature of  $CaSO_4$  is lowered at about 990°C when silica is present and we suggest that this effect could be related to the surface acid-base interaction between  $CaSO_4$  and  $SiO_2$  being this latter characterised by a surface acid nature. Furthermore, previously reported studies have revealed a different thermal behaviour of calcium sulphate as a function of the presence of metal oxides that in some cases accelerate the decomposition and reduce the temperature at which the reaction occurs [1, 5].

Previously, we put forward the hypothesis [1] that this influence could be related to the surface acid-base interaction between  $\text{CaSO}_4$ , silica and metal oxides, interaction, the role of which have already been recognised in other surface phenomena such as adhesion, corrosion and catalysis. In order to verify if exists a more general correlation between the calcium sulphate decomposition and surface properties of metal oxides in terms of acid-base interaction, the study of the gypsum thermal decomposition has been extended considering the effect played by the presence of oxides characterised by different surface acid-base character.

According to Parks and Kurbatov *et al.* [10, 11] the acid-base properties of an oxide surface depend on some properties of the cation such as valence, co-ordination and radius of the cation. Indeed, oxidation leads to an increase in acidic properties as well as the increase of crystal perfection increases the acidic properties. The ability of a surface metal oxide for electron donor-acceptor interactions with other species can be described in the Lewis definition, while the ability for  $\text{H}^+$  and  $\text{OH}^-$  exchanges is considered in the Brönsted definition. These two definitions are close of correlation and thus the reactive acid-base sites in the Lewis and Brönsted definitions can transform to each other in aqueous solutions.

In order to verify the existence of a correlation between the surface acid-base character of a ceramic metal oxide and the temperature of calcium sulphate thermal decomposition, we have selected some metal oxides characterised by different isoelectric point of solid surfaces (IEPS). The term isoelectric point reflects the chemical composition and structure of the surface metal oxide and is variously used to present the pH value at which the surface charge is zero. The existence of a IEPS results from the amphoteric character of a metal oxide, thus being able to react either as an acid or as a base and in particular, the value of IEPS characterises the acid-base properties of a metal oxide surface: it is equal to the pH of the aqueous solution in contact with the surface for which the surface is electrically neutral. It is worth noting that IEPS has already proved to be an important parameter for the prediction of metal-to-polymer adhesion [12–14] when Brönsted acid-base interaction is involved. Indeed, IEPS val-

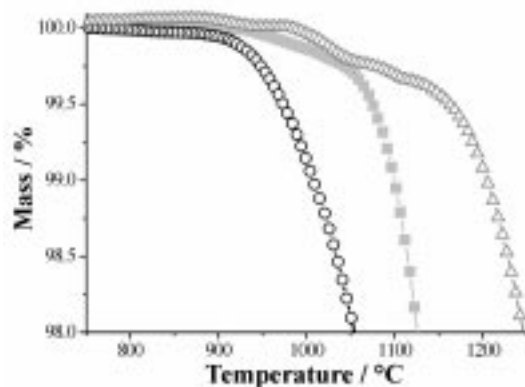


Fig. 3 TG curves for  $\text{CaSO}_4$  with the addition of  $\text{SnO}_2$ ,  $\text{CuO}$  or  $\text{Al}_2\text{O}_3$  (o,  $\Delta$  and  $\blacksquare$ , respectively)

ues are used to predict trends in a simplified approach of adhesion energies of polar polymers on oxide surfaces [12–14] and the relative stabilities of organic coatings containing different functional groups on metal oxide surfaces [14]. Many methods have been used to estimate the IEPS and an extensive collection of these methods and IEPS values has been reported as a reference list in the paper of Parks [10].

On the base of the information reported in reference [10], 10 anhydrous metal oxides characterised by largely different values of isoelectric point of solid surfaces (IEPS) have been selected and added to pure calcium sulphate in order to measure the temperature of  $\text{CaSO}_4$  thermal decomposition. Some selected TG curves for  $\text{CaSO}_4$  with the addition of metal oxides are reported in Fig. 3 as an example of the different thermal behaviour that  $\text{CaSO}_4$  exhibits with the variation of the added metal oxide.

In Table 2, the thermal decomposition temperature of  $\text{CaSO}_4$  with the addition of the 10 anhydrous metal oxides are listed together with the values of IEPS and the measurements of the surface acid-base nature obtained via XPS as proposed by Delamar [12]. These data disclose the existence of a roughly linear correlation and seem to predict that the temperature of  $\text{CaSO}_4$  thermal decomposition should vary linearly with IEPS, increasing as IEPS increases and therefore, increasing as the basic character of the metal oxide increases [12].

**Table 2** Values of the isoelectric point of solid surfaces (IEPS), DO+DM values (see text) of 10 metal oxides and temperature of  $\text{CaSO}_4$  thermal decomposition (TTD) with the addition of the same metal oxides

	TiO <sub>2</sub>	SnO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	NiO	Y <sub>2</sub> O <sub>3</sub>	CuO	MgO	ZnO
IEPS	4.7	5.5	6.7	6.6	6.8	10.3	9	9.3	12.4	9
DO+DM	4.5	3.4	4.1	3.5	3.3	2.1	1.2	1.8	1.2	0.7
TTD	890	900	940	950	950	960	980	990	1000	1030

Furthermore, the data reported in Table 2 evidence that another correlation exists between the temperature of the  $\text{CaSO}_4$  thermal decomposition and the overall acid-base behaviour of an oxide surface that results from the competition between the acidic character of the cation and the basicity of oxygen [12]. This surface feature is measured via XPS and expressed as (DO+DM). In particular, this latter term is obtained from the sum of two values, DO and DM, the first one is calculated from the XPS O1s BE according to the equation  $\text{DO}=(\text{O1s BE}-530)$  and describes the basicity of oxygen while DM is calculated from the XPS peaks of the metal as  $\text{DM}=(\text{cation BE}-\text{metal BE})$  and describes the acidity of the metallic cation considering the chemical shift experienced by core electrons when going from the metal to the cation.

In Fig. 4, the correlation between (DO+DM) and temperature of thermal decomposition of  $\text{CaSO}_4$  is shown with the correlation between this latter and IEPS values. The existence of a linear correlation is roughly verified and seems to predict that the temperature of  $\text{CaSO}_4$  thermal decomposition should vary linearly with the surface acid-base nature of metal oxides, increasing as (DO+DM) increases and therefore, increasing as the base character of the metal oxide increases [12–14].

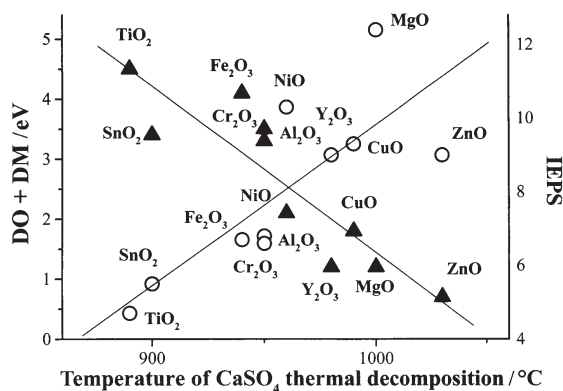


Fig. 4 Relationship between the temperature of CaSO<sub>4</sub> thermal decomposition with the addition of metal oxides characterised by different surface acid-base properties of these metal oxides expressed as (DO+DM) and as IEPS (see text)

Such a simple correlation cannot apply accurately because the high temperature solid state interactions between metal oxide surfaces and calcium sulphate or another decomposable chemical compounds are undoubtedly more complex than the simple description presented in this paper. However, the experimental approach of this work and the results previously reported have shown that the variation of the surface acid-base character of an oxide can be correlated to the variation of the temperature of CaSO<sub>4</sub> thermal decomposition.

## Conclusions

By means of the combined use of SEM+EDS, XPS, XRD and DTA-TG, the thermal decomposition of gypsum and gypsum bonded investment used for casting jewellery products has been studied.

The thermal reaction is related to the presence of silica and it is due to the surface acid-base interaction between SiO<sub>2</sub> and CaSO<sub>4</sub>.

The solid state thermal decomposition of calcium sulphate in the presence of other ceramic oxides has evidenced a correlation between the temperature of CaSO<sub>4</sub> thermal decomposition and the surface acid-base properties of these latter compounds, measured as isoelectric point of the solid surface (IEPS) and via XPS analysis.

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