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Thermal and microchemical characterisations of $CaSO_4$–SiO_2 investment materials for casting jewellery alloys

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Abstract

Differential thermal analysis (DTA) and thermogravimetry (TG), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) were used to study the thermal decomposition of calcium sulphate in the $CaSO_4$ (25 wt%)-bonded silica investment which is the commonly used material for casting jewellery gold-based alloys. The thermal decomposition of $CaSO_4$ generates sulphur dioxide, leads to gas porosity in the molten gold-based alloys and therefore, defective jewellery products. This latter reaction was studied as a function of the temperature and atmosphere (air, argon and argon-5% hydrogen), in order to simulate, as for as possible, different casting conditions used by the jewellery industry. Furthermore, special attention was given to the effect of the presence of ZnO, Cu_2O, CuO and Ag_2O on the thermal decomposition of $CaSO_4$. DTG-TG results confirmed that the temperature of the thermal decomposition of $CaSO_4$ bonded with silica was lower with respect to the nearly pure $CaSO_4$. Unfortunately, it was very close to the casting temperature of some typical gold alloys. In addition, the temperature of the decomposition was further lowered when inert and reducing atmospheres are used, as well as in the presence of ZnO, Cu_2O, CuO and Ag_2O. © 1998 Elsevier Science B.V.

Keywords: Investment; Casting; Jewellery; Gold alloys; Gypsum thermal decomposition

1. Introduction

The quality of the casting products in the jewellery industry is remarkably influenced by the thermochemical properties of the investment materials as well as by the investing and casting processes. The experimental works of Ott [1–5] have shown that the thermal decomposition of the calcium sulphate of the $CaSO_4$ (25 wt%)-bonded silica investment (hereafter CSI) causes the troublesome gas porosity defect. This appears as round shiny pores near to the surface and is generated by the rapid heating of the $CaSO_4$ by the molten gold alloy whose temperature is at least 60–80°C higher than the melting temperature. Indeed, during the casting and solidification process, that rapidly takes place (4–6 s), the $CaSO_4$ is heated to a temperature higher than 960°C, that is the lowest melting temperature of commercial gold alloys, and can reach 1200°C for the casting of Pd-gold alloys.

In order to gain further insight, differential thermal analysis (DTA) and thermogravimetry (TG) were performed on the calcium sulphate (25 wt%)-bonded silica investment that is by far the most commonly

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used and best suited material for casting most jewellery gold-based alloys [1–6]. Furthermore, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS), were used as ancillary techniques for obtaining microchemical and microstructural information. The thermal characterisation was performed under oxidising, inert and reducing atmospheres, flowing air, argon and argon-5% H_2, respectively, in order to simulate different casting conditions used by the jewellery industry. Indeed, during the casting of gold alloys, in air or in an inert atmosphere, the formation of a local reductive atmosphere in the investment could be possible due to a reaction between air, entrapped in the porous investment, and residues of carbonized wax. Indeed, this latter could not be entirely eliminated by dewaxing and burnout processes before casting, thus forming carbon monoxide during the casting [2–6]. Furthermore, during the melting or casting in air, the minor elements of the gold-based alloys, such as silver, copper and zinc, can be oxidised, as shown by X-ray photoelectron spectroscopy (XPS), the effect of the presence of ZnO, Cu_2O, CuO and Ag_2O on the thermal behavior of the investment material was also investigated as a function of the atmosphere.

2. Experimental details

DTA-TG measurements were carried out in air, argon and Ar-5% H_2 from room temperature to 1400°C using an automated Stanton Redcroft STA-781 thermal analyser at a heating rate of 10°C/min and a gas flow rate of 50 ml/min. X-ray diffraction patterns were recorded by multiple scanning on a 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. X-ray photoelectron spectroscopy was performed using an Escalab Mk II spectrometer.

The investment powder was commercially obtained from Rio Grande (USA) and the investment was prepared according to the specifications of the producer. The addition of 9 wt.% of ZnO, Cu_2O, CuO and Ag_2O to the investment powder was made before the preparation of the investment slurry in order to facilitate the intimate contact between the investment material and the metal oxide.

3. Results and discussion

In Fig. 1, CSI, is shown by back scattered electrons micrographs and X-ray elemental maps of Si, Ca and S. These images show that the investment material was composed of well mixed $CaSO_4$ and silica particles, that XRD results (not reported) are indicated in the form of cristobalite and quartz.

In Fig. 2, the comparison between the TG curves in air for analytical grade anhydrous $CaSO_4$ and CSI is reported. As already pointed out by Colussi and Longo [7,8], for the present study, in order to differentiate the thermal behaviour of the $CaSO_4$–SiO_2 materials, we have used thermogravimetry that allows the decomposition temperature to be measured, defined as the temperature at which the TG curve deviates from the straight line. Furthermore, TG allows the measurement of the extent of the thermal decomposition in the range of temperatures commonly used for casting. As shown in Fig. 2, the TG curve for pure calcium sulphate shows only a little deviation in the temperature range of casting of the most common gold alloys (reported in Table 1). In Table 1, the chemical composition and the melting temperatures of a wide range of yellow and white gold alloys to be considered as typical examples, are shown. The TG results of Fig. 2 indicate that the beginning of the thermal decomposition of pure $CaSO_4$ occurred at about 1240°C and is practically complete by 1450°C.

At this temperature the weight lost by the specimen was about 42% and gives rise to the formation of calcium oxide and sulphur anhydrides according to the following reactions [8]:

$$CaSO_4 \Rightarrow CaO + SO_3$$

$$SO_3 \Rightarrow SO_2 + \tfrac{1}{2}O_2$$

The TG curves for the calcium sulphate-bonded silica investment show the influence of silica on the decomposition temperature and on the extent of the thermal reaction. Indeed, the beginning of the thermal decomposition is lowered at about 990°C and is practically complete at 1260°C. At this temperature,

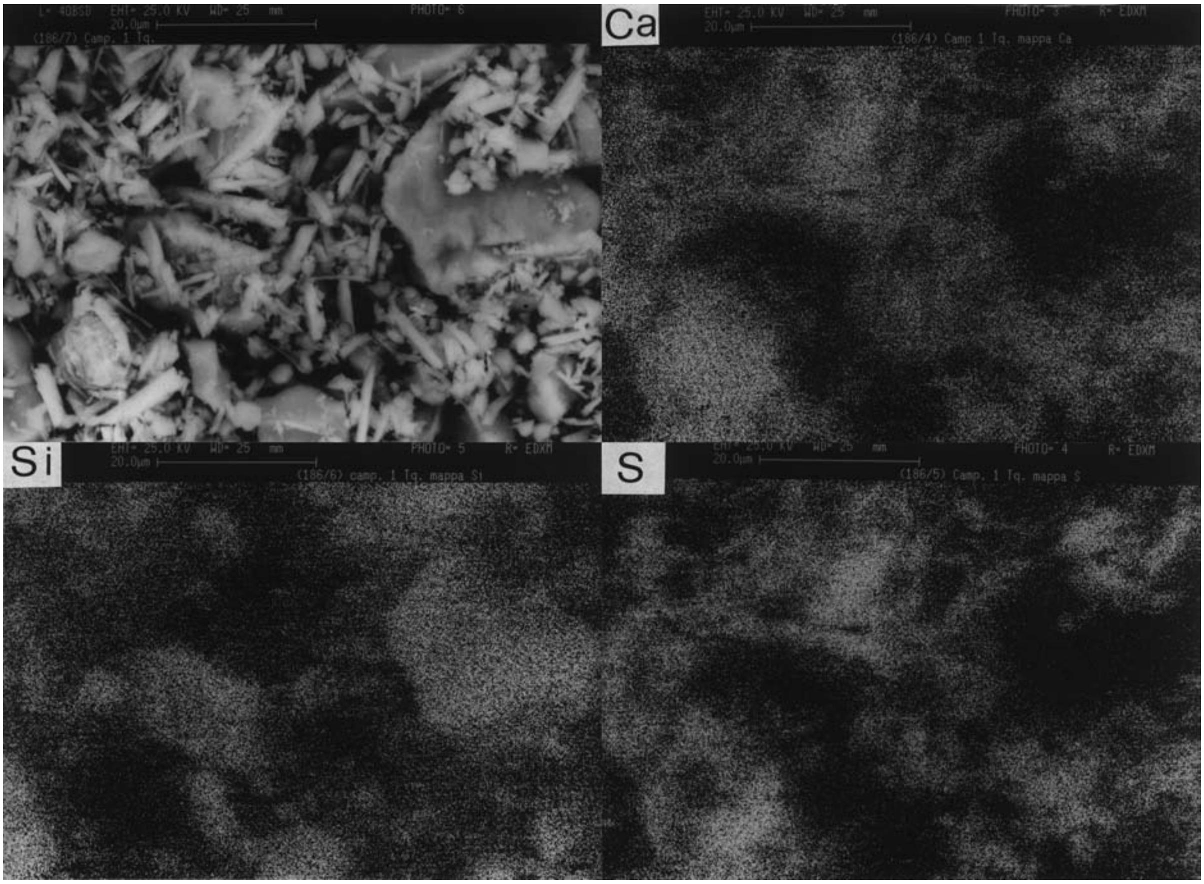

Fig. 1. Back scattered electrons micrograph and X-ray elemental maps of silicon, calcium and sulphur for calcium sulphate (75 wt%)-bonded silica investment.

Table 1
Chemical composition, solidus and liquidus temperature of some gold alloys[a]

Carat	Fineness	Fine gold (%)	Alloy (%)	Solidus and liquidus temperature (°C)
24	999.9	99.99	0.00	1064–1064
22	917.0	91.7	5.5 Ag-2.8 Cu	995–1020
22	917.0	91.7	3.2 Ag-5.1 Cu	964–982
18	750	75.0	12.5 Ag-12.5 Cu	885–895
18	750	75.0	16 Ag-9 Cu	895–920
18	750	75.0	9 Ag- 16 Cu	880–885
18	750	75.0	4.5 Ag-20.5 Cu	890–895
18	750	75.0	12.5 Ag-10 Pd-10 CuNiZn	1095–1150

[a] The alloys chosen are typical examples and their chemical composition are basic composition, indeed, commercial alloys may contain other minor elements.

the weight lost by the investment is 14.5%, thus demonstrating a complete decomposition of the calcium sulphate. These latter data are in good agreement with some of the results reported in literature where contradictory data are also present sometimes. [8].

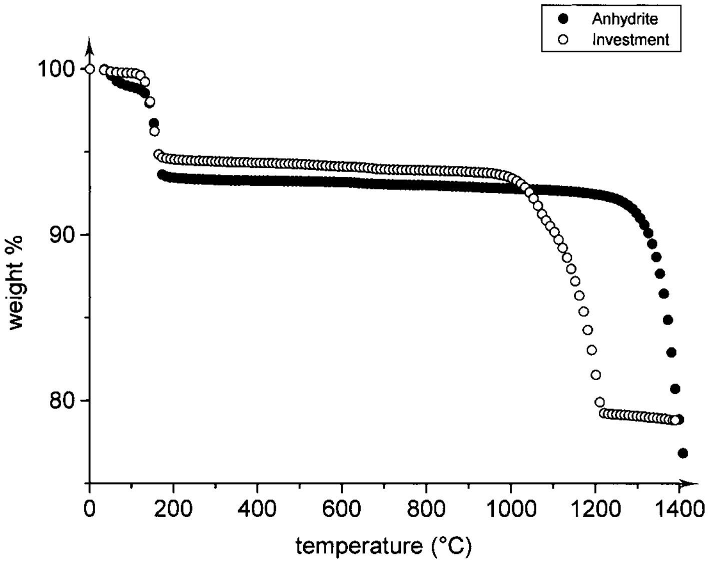

Fig. 2. TG curves for analytical grade anhydrite (solid circle) and for calcium sulphate (25 wt%)-bonded silica investment (open circle). TG measurements were carried out in air at a heating rate of 10°C/min.

Indeed, the studies on thermal decomposition of calcium sulphate indicate that many uncertainties still persist on the real behaviour of the process: in particular, the starting decomposition temperature, the influence of impurities and of some parameters of the thermal treatment such as heating rate, atmosphere, gas flow rate and the physical structure of the material. As pointed out by Colussi and Longo [8] variation and the inaccurate control of these parameters are undoubtedly responsible for the many discrepancies reported in literature.

From a comparison between the above discussed results and the casting temperature reported in Table 1, it is evident that the thermal decomposition of the calcium sulphate of the investment is considerably accelerated by the presence of silica and unfortunately it is very close to the casting temperature of the gold-based alloys used for producing jewels.

Furthermore, we have to take into account that during the melting or the casting of the gold alloys, a slight oxidising environment could be present, and therefore, a considerable amount of oxygen can be dissolved in the minor elements of the alloy, i.e. copper, silver and zinc [9].

This oxygen is not released as a gas, but separates as Cu_2O, ZnO and probably also as Ag_2O. Indeed, as copper and zinc are more reactive than silver, they tend to act as antioxidants [10,11] and in particular, copper and oxygen from a copper–cuprous oxide eutectic with 3.5% Cu_2O (melting point 1066°C) at the grain boundaries of the solidifying metal. For example, in Fig. 3, the XPS Cu $2p_{3/2-1/2}$ spectra for a 12 Ag-12 Cu-1 Zn gold-based alloy treated in air at 960°C for 600 s and 15 s, spectrum (a) and (b), respectively, are shown. Spectrum (a) indicates the oxidation of copper with the formation of a several nm thick Cu II oxide layer [12]. Spectrum (b) shows a more moderate oxidation with the presence of thinner oxide layer composed of also Cu I oxide on Cu^0.

With these considerations in mind, we have added to the investment 9 wt.% of Cu_2O, CuO, ZnO and Ag_2O in order to study the effect of these latter compounds on the thermal decomposition of the calcium sulphate bonded silica investment. It is worth noting that, as shown in Fig. 4, at the interface between a 92.5 wt.% Ag-7.5 Cu alloy and investment, subjected to a thermal treatment in air at 1130°C, a large amount of copper was observed surrounding the silica and gypsum particles, thus indicating the probable formation of copper oxides at the interface between the melt and the investment.

The TG curves for the as received investment and this latter with the addition of Cu_2O, CuO, ZnO and Ag_2O as a function of the atmosphere are reported in

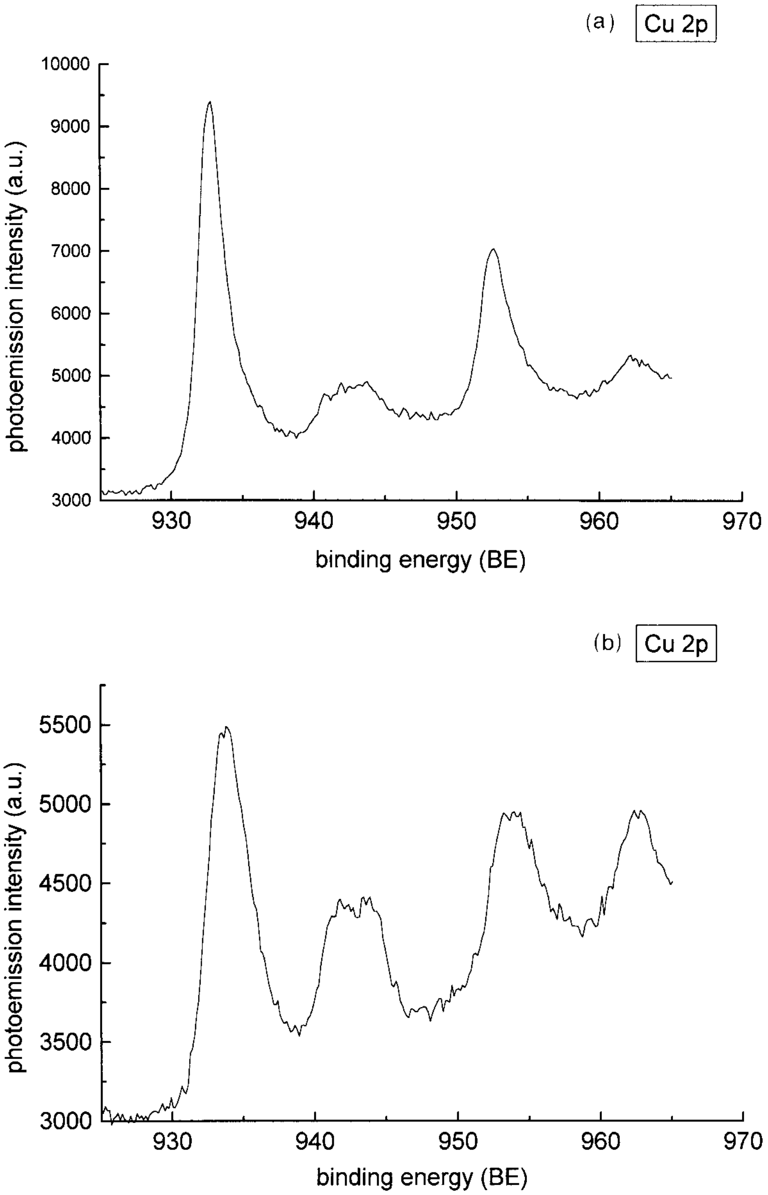

Fig. 3. XPS Cu $2p_{3/2-1/2}$ spectra for a 12 Ag-12 Cu-1 Zn gold-based alloy treated at 960°C for 600 s and 15 s, spectrum (a) and (b), respectively. Spectrum (a) indicates the total passivation of copper with the formation of Cu II oxide species, spectrum (b) indicate the presence of also Cu I oxide and Cu°.

Figs. 5–7, in air, argon and Ar-5% H_2, respectively. The weight losses suffered by these latter materials are reported in Table 2 as a function of temperature and atmosphere. These results show the influence of the atmosphere on the temperature of the thermal decomposition of $CaSO_4$ and on the extent of the reaction at the casting temperature of the most common gold-based alloys. In particular, the temperature of the decomposition is lowered when an inert atmosphere is used and a reductive atmosphere affects drastically the severe thermal decomposition of calcium sulphate. Furthermore, these results indicate that the presence of

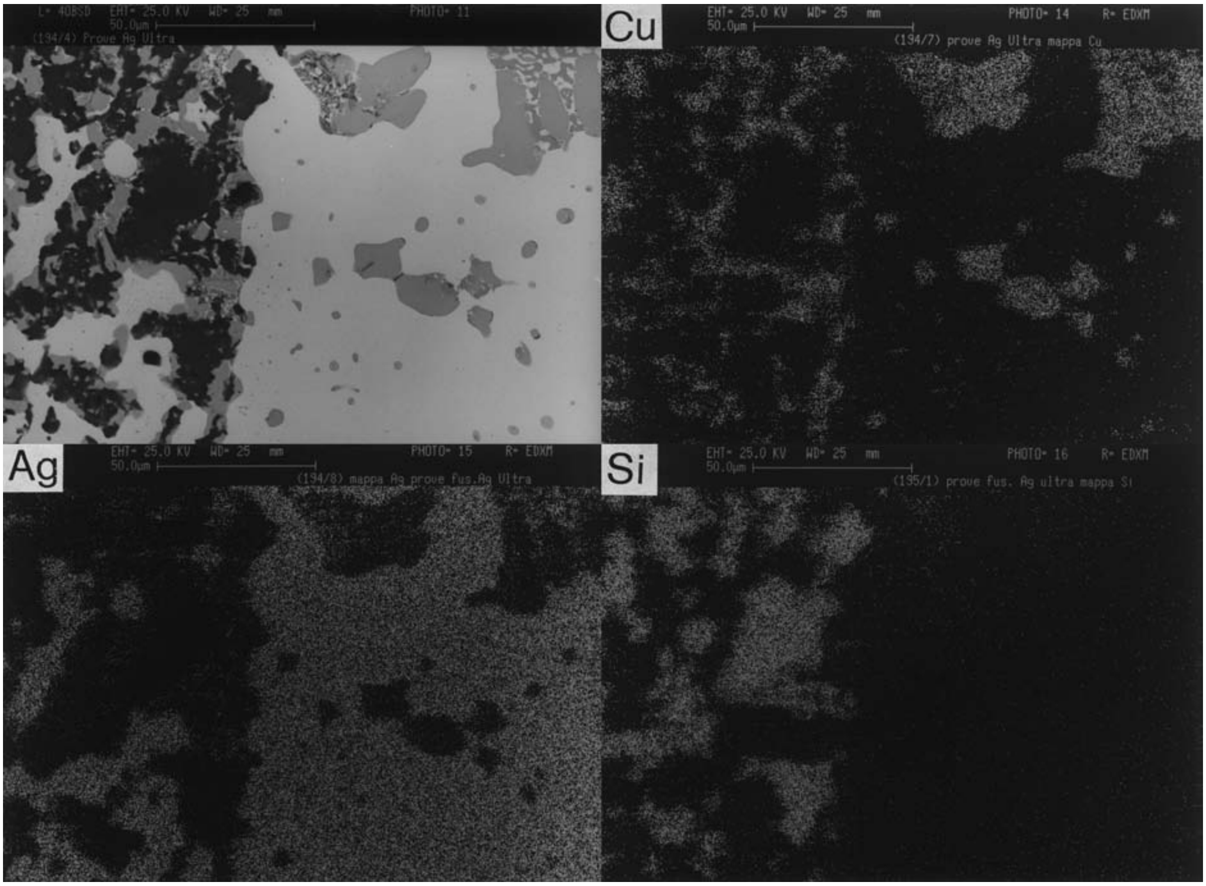

Fig. 4. Back scattered electrons micrograph and X-ray elemental maps of silicon, copper and silver of the direct contact surface between a 7.5 (wt%) Cu-Ag alloy and gypsum investment (1130°C, air).

Cu_2O, CuO and ZnO plays a relevent role on the decomposition of gypsum. On the contrary Ag_2O did not greatly affect the thermal behaviour or the investment. Therefore, to avoid the occurrence of the gas porosity defect in jewellery products during the casting of the gold-based alloys, a heavily oxidizing or a reducing atmospheres have to be avoided as well as over heating of the gold-alloy.

4. Conclusions

Thermal and microchemical results have shown that the temperature of the thermal decomposition of $CaSO_4$ bonded with silica is lower with respect to the nearly pure $CaSO_4$ and unfortunately, it is very close to the casting temperature of some typical gold alloys. In addition, the temperature of the decomposition is further lowered when inert or reducing atmospheres are used as well as in the presence of the oxide of the minor or alloying elements of the gold-based alloy. The results indicate that the worst conditions for the casting is a reductive atmosphere and the presence of Cu_2O and ZnO as well as an overheating of the gold alloy.

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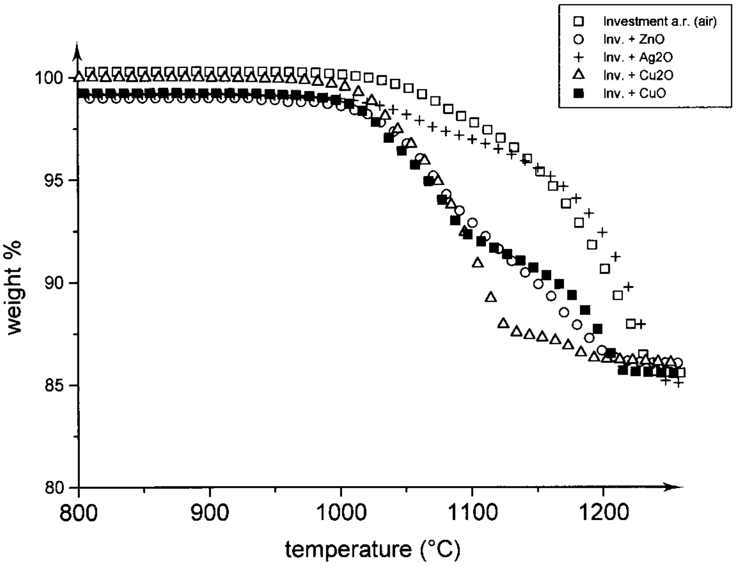

Fig. 5. TG curves for calcium sulphate (25 wt%)-bonded silica investment (open square) and for the investment with the addition of Cu_2O (open triangle), ZnO (open circle), CuO (solid square) and Ag_2O (plus). TG measurements were carried out in air at a heating rate of 10°C/min.

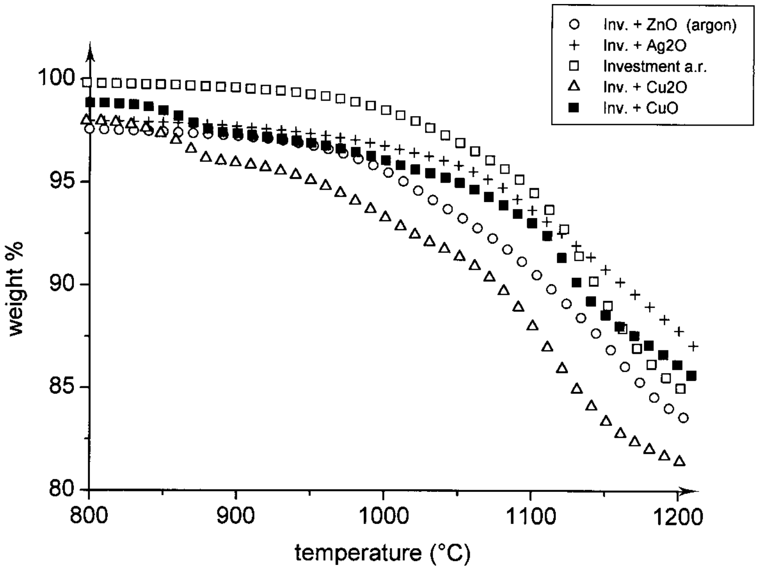

Fig. 6. TG curves for calcium sulphate (25 wt.%)-bonded silica investment (open square) and for the investment with the addition of Cu_2O (open triangle), ZnO (open circle), CuO (solid square) and Ag_2O (plus). TG measurements were carried out in argon at a heating rate of 10°C/min.

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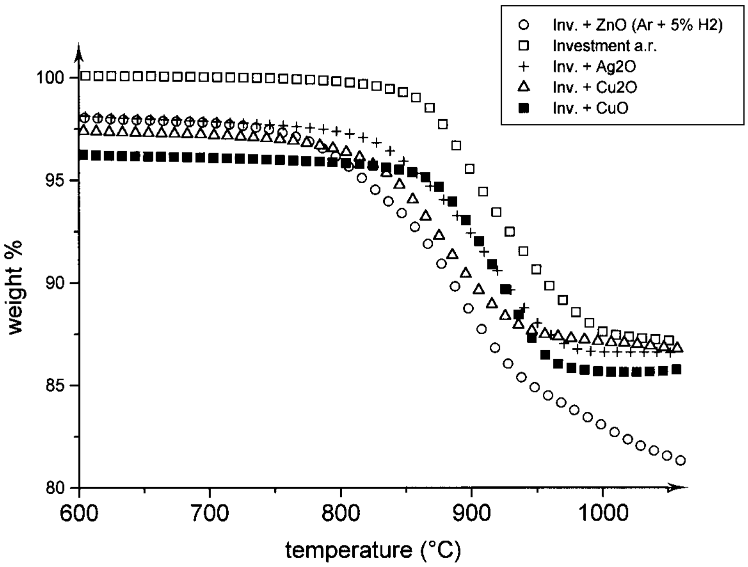

Fig. 7. TG curves for calcium sulphate (25 wt.%)-bonded silica investment (open square) and for the investment with the addition of Cu_2O (open triangle), ZnO (open circle), CuO (solid square) and Ag_2O (plus). TG measurements were carried out in air-5%H_2 at a heating rate of 10°C/min.

Table 2
Weight losses (%) suffered by $CaSO_4$ bonded silica investment (CSI) and this latter with the addition of 9 wt.% of Cu_2O, ZnO, CuO and Ag_2O, as a function of temperature and atmosphere

Material	Temperature (°C)							Atmosphere
	800	900	1000	1050	1100	1150	1250	
CSI	–	–	–	0.56	2.216	4.25	14.55	Air
CSI	–	0.25	1.40	2.95	5.40	10.90	15.30	Argon
CSI	–	4.80	12.25	12.64	12.94	13.57	13.94	Argon-5% H_2
CSI	–	–	0.43	3.07	8.60	12.65	13.88	Air
CSI+Cu_2O	–	2.10	4.85	6.75	10.60	14.85	15.90	Argon
CSI+Cu_2O	0.90	6.50	9.35	9.70	10.25	10.75	11.70	Argon-5% H_2
CSI+CuO	–	–	0.38	2.95	6.90	8.39	13.66	Air
CSI+CuO	–	1.45	3.60	3.65	5.45	9.65	14.60	Argon
CSI+CuO	–	2.80	10.15	10.10	9.85	10.10	11.40	Argon-5% H_2
CSI+Ag_2O	–	–	0.20	0.92	2.16	3.47	14.00	Air
CSI+Ag_2O	–	0.25	1.15	2.00	3.90	6.65	15.55	Argon
CSI+Ag_2O	0.76	6.94	11.65	11.50	11.50	11.50	14.00	Argon-5% H_2
CSI+ZnO	–	–	0.52	2.36	6.27	6.16	13.07	Air
CSI+ZnO	–	0.40	2.60	4.85	7.85	11.60	15.65	Argon
CSI+ZnO	2.50	10.50	15.24	16.50	17.90	19.55	20.10	Argon-5% H_2

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