$CaSO_4$ BONDED INVESTMENT FOR CASTING OF GOLD-BASED ALLOYS : STUDY OF THE THERMAL DECOMPOSITION

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ABSTRACT

Differential thermal analysis (DTA) and thermogravimetry (TG) have been used to study the thermal decomposition of calcium sulphate in the $CaSO_4$ bonded investment using also X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy + energy dispersive spectrometry (SEM+EDS) as ancillary techniques. The thermal decomposition of $CaSO_4$ generates sulphur dioxide, leading to gas porosity in the gold-based alloys and therefore, to defective jewellery products. The thermal decomposition has been studied as a function of the temperature and atmosphere (air, argon and argon-5 % H_2), in order to simulate as better as possible, different casting conditions of the jewellery industry. DTA-TG results have confirmed that the temperature of thermal decomposition of $CaSO_4$ bonded investment is lower with respect to the nearly pure $CaSO_4$ and is also influenced by the atmosphere. Unfortunately, it is very close to the casting temperature of some typical gold alloys. Furthermore, special attention has been given to the effect of the presence of ZnO, Cu_2O, CuO and Ag_2O on the $CaSO_4$ thermal decomposition and DTA-TG results show that the temperature of the decomposition is furtherly lowered in the presence of these latter oxides and when inert and reducing atmospheres are used.

KEY WORDS

Investment, Casting, Jewellery, Gold alloys, Gypsum thermal decomposition

INTRODUCTION

In the jewellery industry the quality of the casting products is remarkably influenced by the thermochemical properties of the investment materials as well as by the investing and casting processes [1-5]. The experimental works of Ott [1-5] have shown that the thermal decomposition of the calcium sulphate of the $CaSO_4$ bonded investment causes the troublesome gas porosity defect. This appears as round shiny pores, generally on the whole section and it is generated by the rapid heating and decomposition of the $CaSO_4$ by the molten gold alloy. Indeed, during the casting and solidification process, that rapidly takes place in a few seconds (4 - 6), $CaSO_4$ is heated to a temperature higher than 960°C, that is the lowest melting temperature of commercial gold alloys, and can reach 1200°C when casting Pd containing gold alloys.

In order to gain further insight, differential thermal analysis (DTA) and thermogravimetry (TG) have been performed on the calcium sulphate bonded investment that is by far the most commonly used investment and the best suited material for casting most carat gold alloys [1-6]. Furthermore, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS), have been used as ancillary techniques for obtaining microchemical and microstructural information. It is worth noting that XPS has been preferred because provides detailed information on the chemical composition and valence states of all the elements, except H and He, with an information depth of about 70-80 nm and a sampled area of about 1 mm. XPS is particularly suitable for this study as opposed to other surface analytical techniques, such as Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS), because material damage is generally avoided, the chemical states and fine bonding structure are much easier to disentangle and quantitation is straightforward.

The thermal characterisation has been 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, when casting gold alloys in air or in an inert atmosphere, a localised reductive atmosphere can be formed in the investment due to a reaction

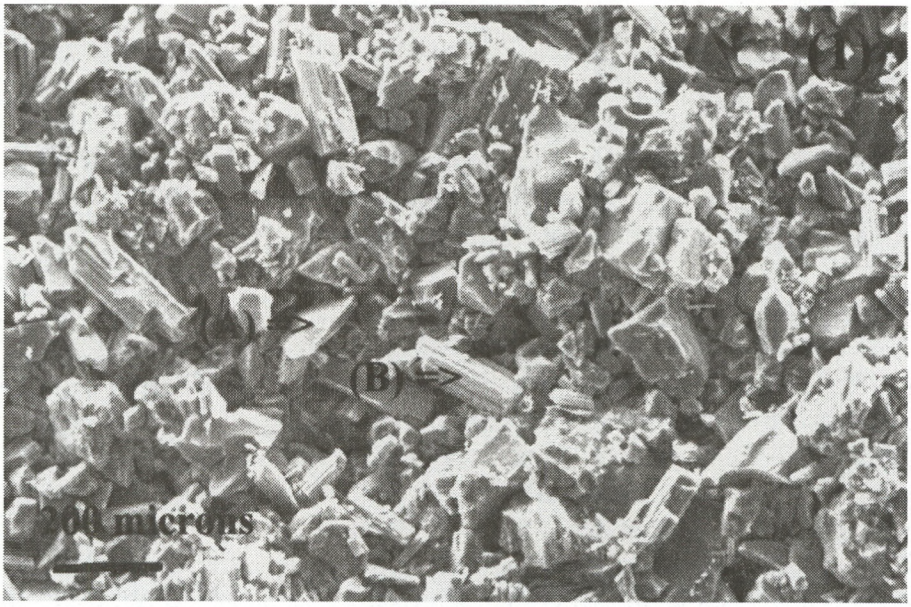
between air, entrapped in the porous investment, and residues of carbonised wax. This latter could be not entirely eliminated particularly in the case of dry dewaxing and burnout processes, thus forming carbon monoxide during the casting operation [2-6]. Furthermore, when melting or casting in air, the minor alloying elements such as silver, copper and zinc, can be oxidised, as shown by XPS. Consequently, the effect of adding of ZnO, Cu_2O, CuO or Ag_2O, on the thermal behaviour of the investment material has been investigated, also as a function of the atmosphere.

EXPERIMENTAL DETAILS

DTA-TG measurements were carried out in flowing air, argon and Ar-5% H_2 atmospheres 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 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. X-ray photoelectron spectroscopy was performed using an Escalab Mk II spectrometer. The investment powder has been commercially obtained and the investment was prepared according to the specifications of the producer. The addition of 9 wt% ZnO, Cu_2O, CuO or Ag_2O to the investment powder was made before the preparation of the investment slurry in order to facilitate the intimate contact between investment and the metal oxide.

RESULTS AND DISCUSSION

In figure 1, the microchemical structure and morphology of the powder $CaSO_4$ bonded investment is shown by a back scattered electrons (BSD) micrograph and EDS spectra. In figure 2, the microchemical structure and morphology of investment after the burnout cycle is shown. The images show that the investment is composed of well mixed $CaSO_4$ and silica particles, these latter being in the form of cristobalite and quartz as indicated by the XRD results of figure 3. It is worth noting that XRD results have shown that



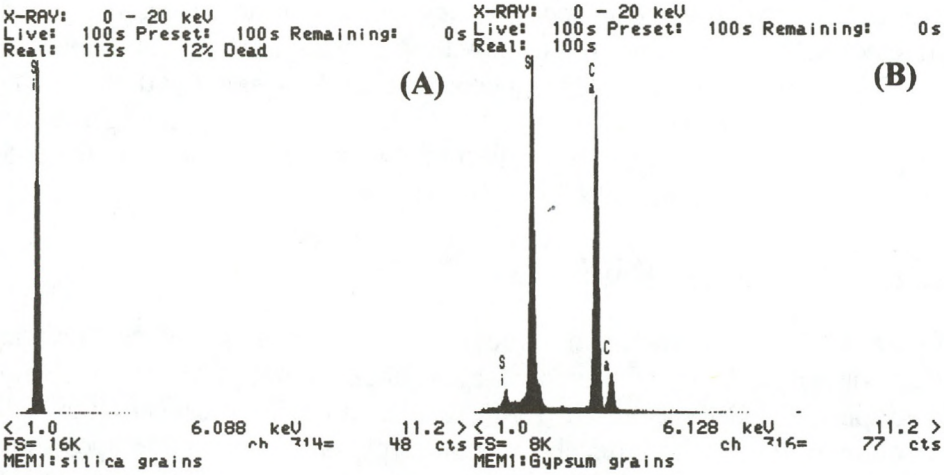


Figure 1. Particle morphology of the investment as shown by a back scattered electrons micrograph (BSD). The EDS spectra A and B allow to distinguish the silica and gypsum particles.

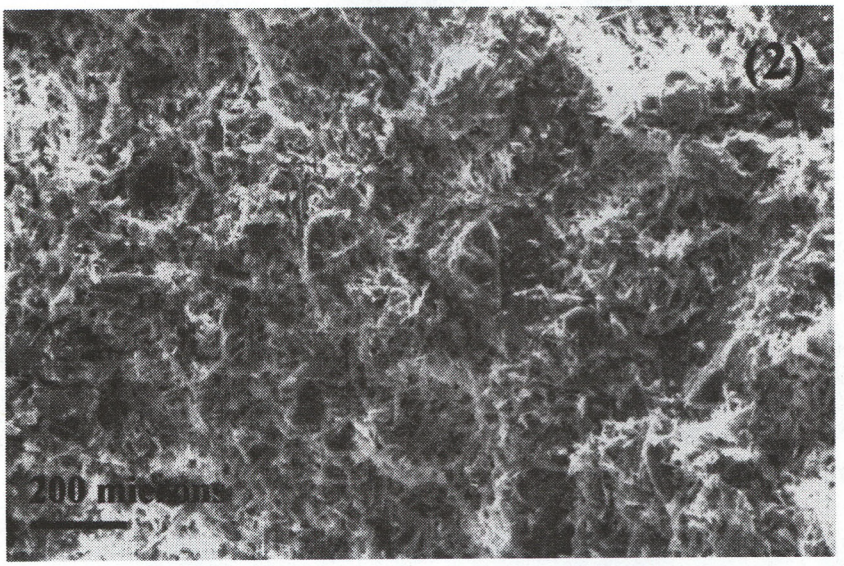


Figure 2. Morphology of the fracture surface of the investment after the burnout cycle as shown by a BSD image.

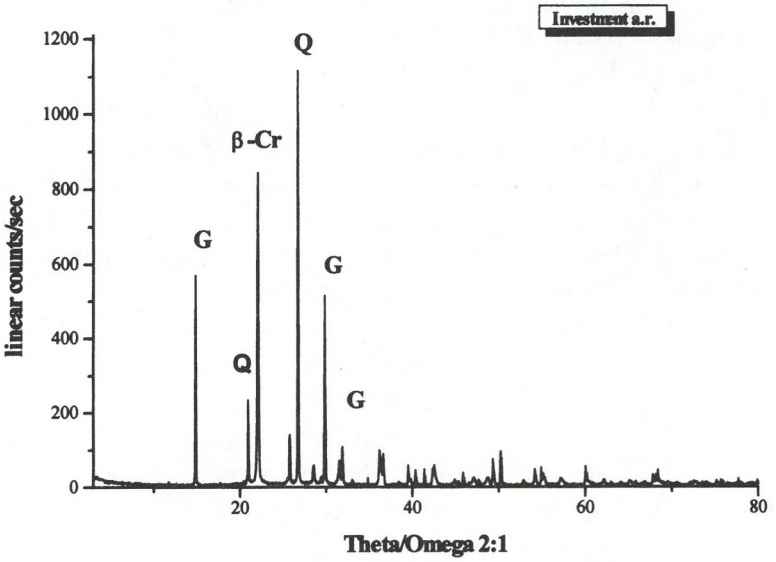


Figure 3. X-ray diffraction pattern for the $CaSO_4$ bonded investment.
Q = quartz; β-Cr = β-cristobalite; G = $CaSO_4$.

the cristobalite and quartz ratio, in the investment powder, is not constant at all for different commercially obtained materials, therefore, for this study we have always used the same commercial product.
The comparison between the TG curves in air for analytical grade $CaSO_4$ and $CaSO_4$ bonded investment is shown in figure 4. As already pointed out by Colussi and Longo [7,8] in order to differentiate the thermal behaviour of the $CaSO_4$-SiO_2 material, we have used TG analysis to measure the decomposition temperature, defined as the temperature at which the TG curve deviates from the straight line. Furthermore, TG allows to measure the extent of thermal decomposition in the range of temperatures commonly used for casting. As shown in figure 4, 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. The TG results of figure 4 indicate that the thermal decomposition of pure $CaSO_4$ begins at about 1240°C and is practically complete at 1450°C. At this temperature the weight loss of the specimen is about 42% and the formation of calcium oxide and sulphur anhydrides takes place according to the following reactions [8] :

$$CaSO_4 \Rightarrow CaO + SO_3$$

$$SO_3 \Rightarrow SO_2 + 1/2\ O_2$$

The TG curve for the $CaSO_4$ bonded investment shows the influence of silica on decomposition temperature and on the extent of thermal reaction. Indeed, the beginning of thermal decomposition is lowered at about 990°C and the reaction is practically complete at 1260°C. At this temperature the weight loss of the investment is 14.5 % and it shows that decomposition of the calcium sulphate is complete. 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_2 and $CaSO_4$. It is worth noting that such kind of interaction plays a relevant role also in many phenomena such as adhesion, corrosion and catalyst, and at a molecular level this interaction occurs between the active electron donor/acceptor sites.
In order to identify the different chemical steps of the thermal decomposition as a function of the temperature, the surface chemical nature of the products has been studied by means of XPS and X-ray induced Auger spectroscopy (XAES). For this characterisation the calcium sulphate-bonded silica investment was isothermally treated in the DTA-TG apparatus, at different

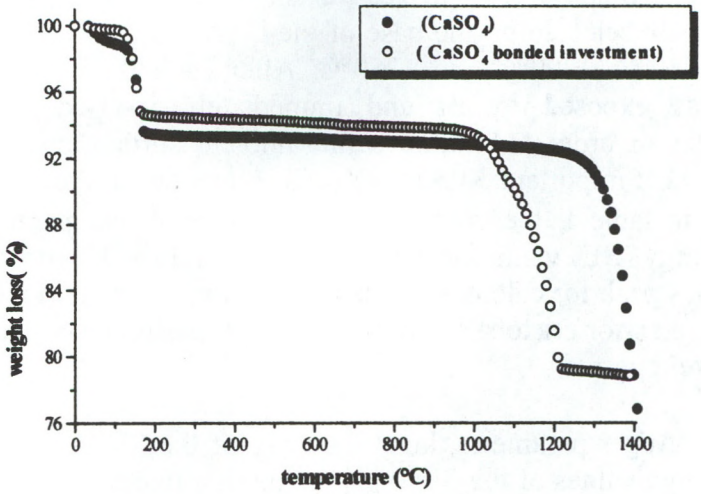


Figure 4. TG curves for analytical grade $CaSO_4$ (solid circle) and for $CaSO_4$ bonded investment (open circle). TG measurements were carried out in air at a heating rate of 10°C/min.

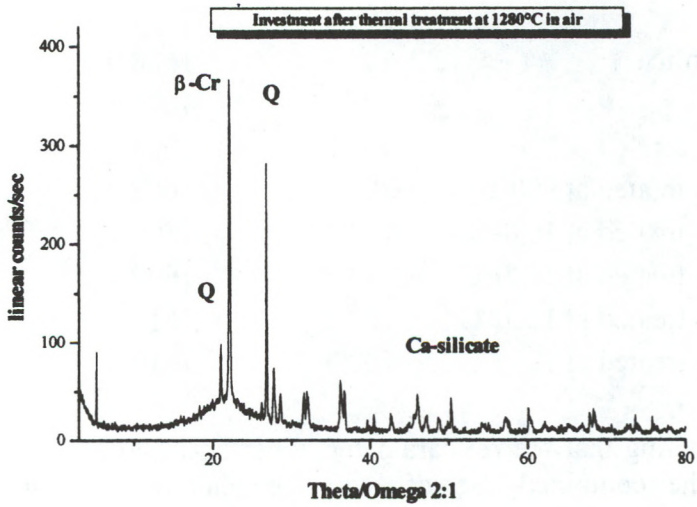


Figure 5. X-ray diffraction pattern for the $CaSO_4$ bonded investment treated in air at 1280°C. The pattern shows the presence of quartz (Q), β-cristobalite (β-Cr) and calcium silicate as well as of amorphous phases.

temperatures from 900°C up to 1250°C for 60 min. The temperature of the treatment were selected on the base of the DTA-TG curve and were 900°C, 1040°C, 1120°C, 1200°C and 1250°C. After each thermal treatment, the sample was exposed to air and immediately inserted into the XPS spectrometer in order to minimise the ambient surface contamination. In table I the most important XPS and XAES results for silicon are reported. In particular, in table I, the values of the so called Auger parameter α', the binding energy (BE) value for the Si 2p signal and the kinetic energy of the Si $KL_{2,3}$ $L_{2,3}$ peak for calcium sulphate bonded investment in the as received conditions (a.r), for cristobalite, quartz, amorphous silica and thermal treated samples, are reported.

Table I. α' Auger parameter, kinetic energy of the Si $KL_{2,3}$ $L_{2,3}$ peak and binding energy values of the Si 2p photoemission line for quartz, amorphous silica, cristobalite, calcium sulphate bonded investment in the as received conditions (a.r.) and after thermal treatments carried out at different temperature in air.

Sample	Si 2p (eV)	Si $KL_{2.3}$ $L_{2.3}$ (eV)	α' (eV)
quartz	103.4	1608.5	1711.9
amorphous silica	103.4	1608.0	1711.4
cristobalite	103.2	1608.6	1711.8
$CaSO_4$-SiO_2 a.r.	103.3	1608.5	1711.8
$CaSO_4$-SiO_2 treated at 900°C	103.0	1608.7	1711.7
$CaSO_4$-SiO_2 treated at 1040°C	102.7	1609.2	1711.9
$CaSO_4$-SiO_2 treated at 1120°C	102.9	1609.4	1712.3
$CaSO_4$-SiO_2 treated at 1200°C	102.2	1610.2	1712.4
$CaSO_4$-SiO_2 treated at 1250°C	102.3	1610.2	1712.5

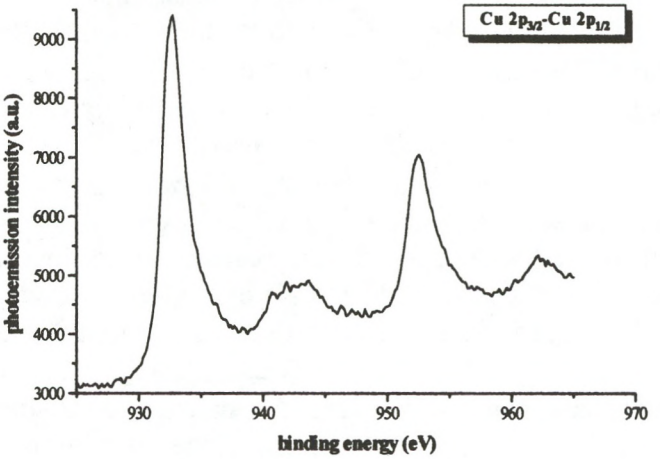
It is worth noting that the α' parameter, reported in table I, is obtained by means of the combined use of both the photoelectron and X-ray or Bremstrhlung induced Auger line according to:

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

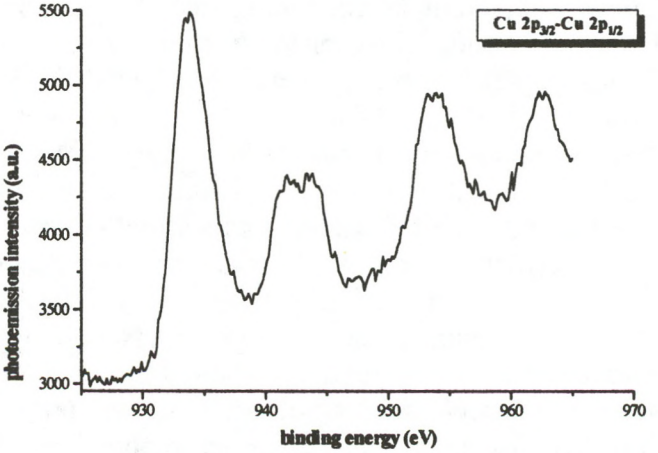
So conceived α' has the advantages of being independent of photon energy, of having always positive values and is independent of the charge referencing operation. Therefore, α' is found with higher accuracy than the determination of either photoemission line energy alone and allows a more detailed assignement of the chemical and physical structure of the surface phases. From the comparison between the α' Auger parameters for silicon in our samples and literature data, we deduce that the silicon phases of the thermal treated calcium sulphate-bonded silica investment change their chemical nature and at 1040°C calcium sulphate reacts with cristobalite or quartz forming calcium orthosilicate according to the following reaction :

$$2CaSO_4 + SiO_2 \Rightarrow Ca_2SiO_4 + 2\ SO_3$$

The secondary reaction between the calcium orthosilicate and the excess cristobalite or quartz takes place at higher temperature to yield probably calcium pyrosilicate and then, calcium metasilicate ($CaSiO_3$) at 1250°C as shown in figure 5, where the XRD pattern for an investment treated at 1280°C is reported. It is worth noting that the thermal decomposition of calcium sulphate bonded investment is slow at 1050 °C and 60 min are required for complete reaction, whereas at 1200°C the reaction is complete in a few minutes. These data are in good agreement with some of the results reported in literature, whereas also contradictory data are sometimes present [8]. Indeed, the studies on thermal decomposition of calcium sulphate indicate that many uncertainties still persist on the real mechanism of the process, in particular, for what concerns the decomposition starting temperature, the influence of impurities and of some parameters of the thermal treatment such as theheating rate, atmosphere, gas flow rate and the physical structure of the material. As pointed out by Colussi and Longo [8], variation or 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 commonly used temperature for casting, it is evident that the investment thermal decomposition of calcium sulphate is considerably accelerated by the presence of silica and unfortunately, occurs at a temperature very close to the casting temperature of the carat gold alloys. Furthermore, we should take into account that when melting or casting gold alloys, a slightly oxidising environment could be present, and therefore, a considerable amount of



spectrum (a)

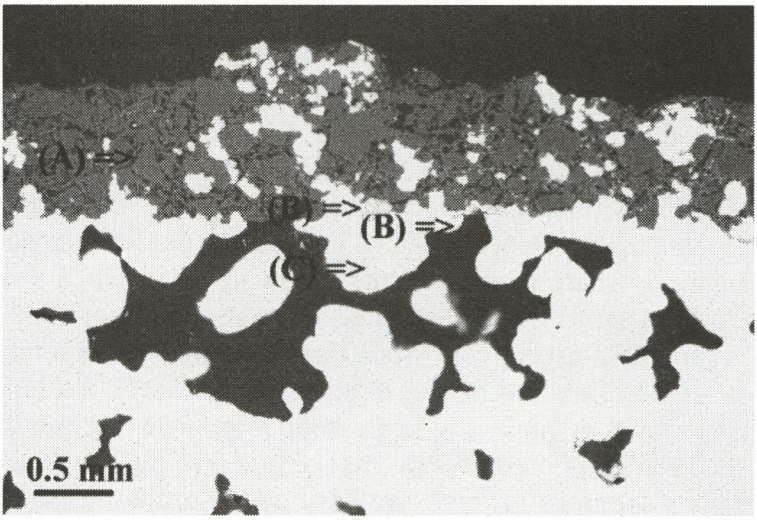


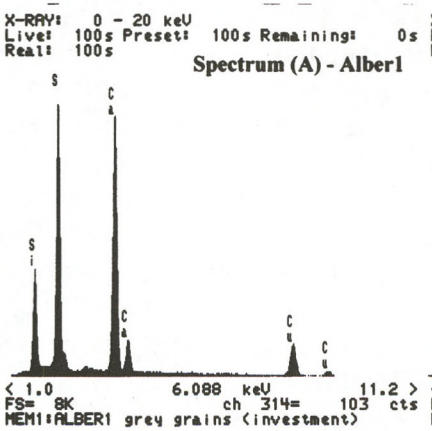
spectrum (b)

Figure 6. XPS Cu $2p_{3/2}$-Cu $2p_{1/2}$ 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 oxidation of copper with the formation of Cu (II) oxide species, spectrum (b) indicates also the presence of Cu (I) oxide and Cu°.

›xygen could react or be absorbed by the minor alloying elements, i.e. ›opper, silver and zinc [9]. This oxygen is not released as a gas, but separates ›s Cu_2O, ZnO and probably also as Ag_2O. Indeed, as copper and zinc are nore reactive than silver, they tend to act as deoxidants [10,11] and in ›articular, copper and oxygen form a copper-cuprous oxide eutectic with 3.5 ›er cent Cu_2O (melting point 1066°C) at the grain boundaries of the olidifying metal. The presence of Cu (I) and Cu (II) oxides on a gold alloy is hown in figure 6, where is reported the XPS $Cu2p_{3/2}$-$Cu2p_{1/2}$ spectra for a .2 Ag-12 Cu-1 Zn carat gold alloy treated in air at 960°C for 600 s and 15 s, pectrum (a) and (b), respectively. Spectrum (a) indicates the total oxidation ›f 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 a hinner oxide layer composed of also Cu (I) oxide on Cu^0.

With these considerations in mind, we have added to the investment 9 wt% ›f Cu_2O, CuO, ZnO or Ag_2O in order to study the effect of these compounds ›n the thermal decomposition of the calcium sulphate bonded silica nvestment. The occurrence of these oxide phases at the interface between he investment and the carat gold, when the porosity defect is present, has ›een observed in some cases, as shown in figure 7 and 8. In figure 7 and 8, ›ack scattered electrons (BSD) micrographs and EDS spectra for a cross ›ectioned contact surface between a 12,5 Cu (wt%)-12,5 Ag gold alloy and $CaSO_4$ bonded investment and a white gold alloy surface where the gas ›orosity defect is present, respectively, are reported. In figure 7, the EDS ›pectra for the small grey particles near the silica grains, the grey particles at he contact surface and the gold based alloy near this latter have been abelled spectrum A, B and C, respectively, and the chemical composition of hese latter phases is also reported. In particular, in this sample the presence ›f a copper oxide on the carat gold alloy and surrounding the silica and gypsum particles has been observed. It is worth noting that the quantitative chemical composition obtained from the EDS spectrum (A), reported in figure 7, shows that the Ca/S atomic ratio for the relics of gypsum particles is not close to unit, thus indicating a loss of sulphur due to the thermal decomposition of gypsum. The TG curves for the as received investment and for the investment with the addition of Cu_2O, CuO, ZnO or Ag_2O as a function of the atmosphere are reported in figures 9-11, for air, argon and Ar-





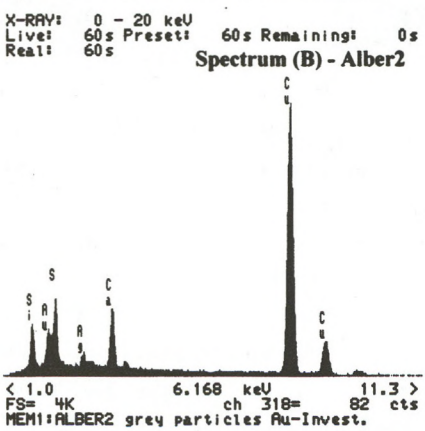
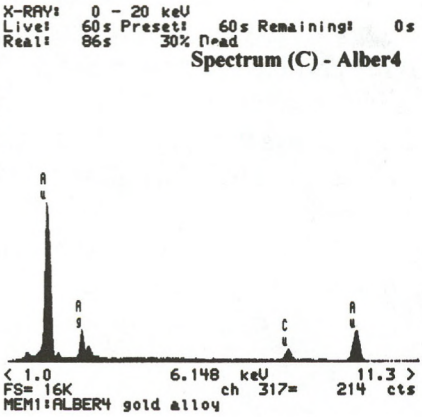
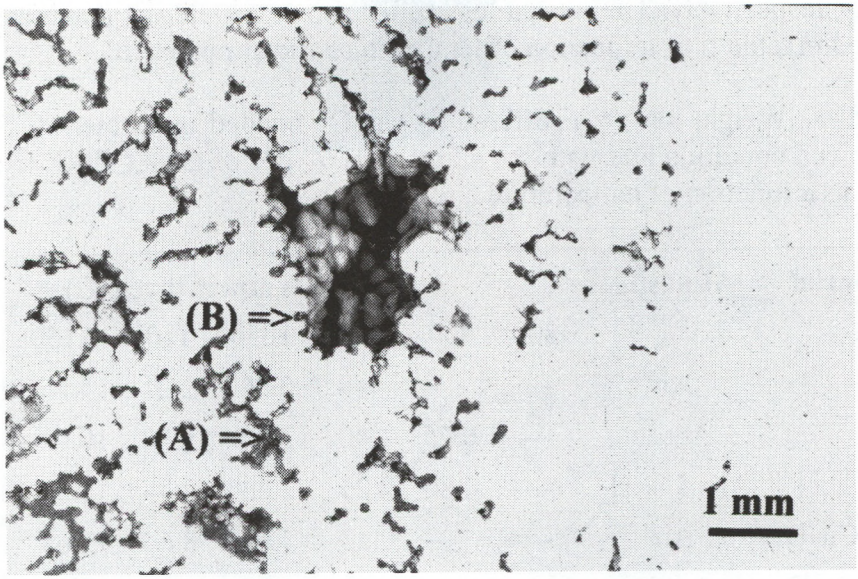


Figure 7. BSD micrograph and EDS spectra for a cross sectioned 12,5 Cu (wt%)-12,5 Ag gold alloy, where gas porosity defect is present. The composition of the phases A, B and C are following reported.



EDS	Cu	Ag	Au	Si	S	Ca
(A)	20.6	1.6	0.7	11.3	28.8	36.7
(B)	78.3	2.1	7.7	3.4	3.3	3.9
(C)	8.7	16.0	75.1	---	---	---



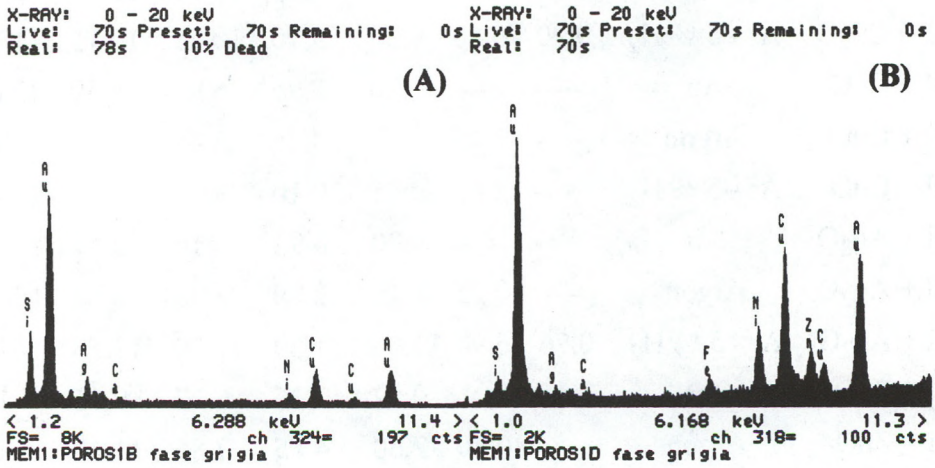


Figure 8. BSD micrograph and EDS spectra that show the microchemical structure of a white gold surface where a porosity defect is present. EDS spectra disclose the presence of investment relics and Cu species. Chemical composition of the phases A and B is following reported.

EDS	Si (wt%)	S	Ca	Cu	Zn	Ni	Au	Ag
A	7.9	---	0.4	6.1	0.4	2.2	76.1	6.4
B	0.8	---	0.8	17.5	3.4	6.8	68.3	2.4

5 % H_2, respectively. The weight loss suffered by the different materials are reported in table II as a function of temperature and atmosphere.

Table II. Weight loss (%) suffered by $CaSO_4$ bonded investment (CSI) in as received condition and with the addition of 9 wt% of Cu_2O, ZnO, CuO or Ag_2O, as a function of temperature and atmosphere.

Material	Atmosphere	Temperature (°C)						
		800	900	1000	1050	1100	1150	1250
CSI	Air	-----	-----	-----	0.56	2.21	4.25	14.55
CSI	Argon	-----	0.25	1.40	2.95	5.40	10.90	15.30
CSI	Ar - 5 % H_2	-----	4.80	12.25	12.64	12.94	13.57	13.94
CSI + Cu_2O	Air	-----	-----	0.43	3.07	8.60	12.65	13.88
CSI + Cu_2O	Argon	-----	2.10	4.85	6.75	10.60	14.85	15.90
CSI + Cu_2O	Ar - 5 % H_2	0.90	6.50	9.35	9.70	10.25	10.75	11.70
CSI + CuO	Air	-----	-----	0.38	2.95	6.90	8.39	13.66
CSI + CuO	Argon	-----	1.45	3.60	3.65	5.45	9.65	14.60
CSI + CuO	Ar - 5 % H_2	-----	2.80	10.15	10.10	9.85	10.10	11.40
CSI + Ag_2O	Air	-----	-----	0.20	0.92	2.16	3.47	14.00
CSI + Ag_2O	Argon	-----	0.25	1.15	2.00	3.90	6.65	15.55
CSI + Ag_2O	Ar - 5 % H_2	0.76	6.94	11.65	11.50	11.50	11.50	14.00
CSI + ZnO	Air	-----	-----	0.52	2.36	6.27	9.16	13.07
CSI + ZnO	Argon	-----	0.40	2.60	4.85	7.85	11.60	15.65
CSI + ZnO	Ar - 5 % H_2	2.50	10.50	15.24	16.50	17.90	19.55	20.10

These results show the influence of the atmosphere on the temperature of thermal decomposition of $CaSO_4$ and on the extent of the reaction at the casting temperatures of the most common gold-based alloys.

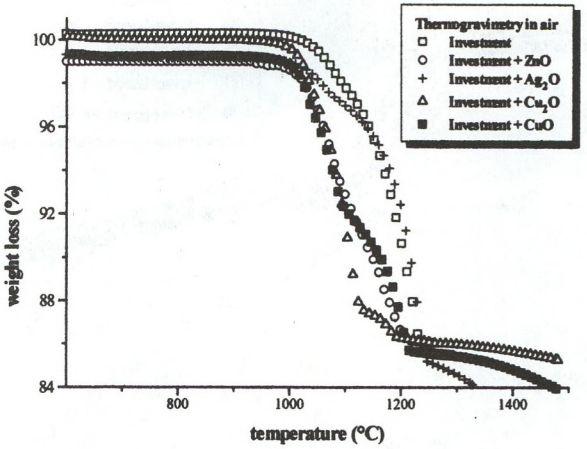


Figure 9. TG curves in air for calcium sulphate bonded investment (open square) and for the investment with the addition of Cu_2O (open triangle), ZnO (open circle), CuO (solid square) and Ag_2O (cross).

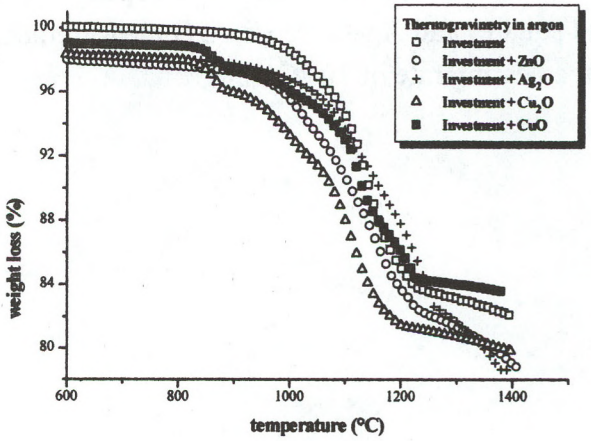


Figure 10. TG curves in argon for calcium sulphate bonded investment (open square) and for the investment with the addition of Cu_2O (open triangle), ZnO (open circle), CuO (solid square) and Ag_2O (cross).

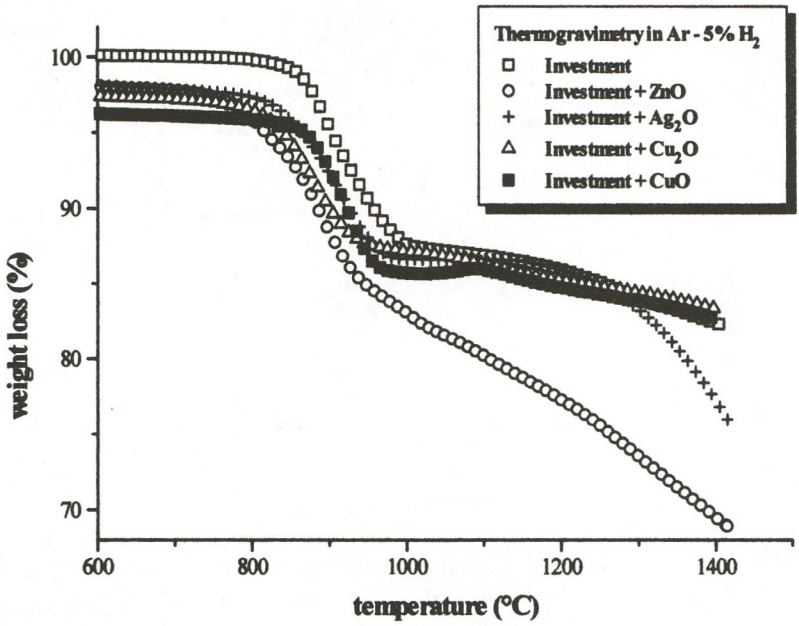


Figure 11. TG curves for calcium sulphate bonded investment (open square) and for the investment with the addition of Cu_2O (open triangle), ZnO (open circle), CuO (solid square) and Ag_2O (cross). TG measurements were carried out in Ar-5%H_2 at a heating rate of 10 °C/min.

particular, the decomposition temperature is lowered when an inert mosphere is used. A reducing atmosphere affects more drastically the ermal decomposition of calcium sulphate. Furthermore, these results dicate that the presence of Cu_2O, CuO and ZnO plays a relevant role on the :composition of gypsum. On the contrary Ag_2O does not greatly affect the ermal behaviour of the investment. Therefore, to avoid the decrease of the mperature of the gypsum thermal decomposition and the occurrence of the ıs porosity defect in gold jewellery products, a heavily oxidising or a ducing atmosphere as well as an over heating of the gold-alloy should be 'oided.

ONCLUSIONS

hermal and microchemical results have shown that the temperature of ermal decomposition of $CaSO_4$ bonded investment is lower with respect to e nearly pure $CaSO_4$ and unfortunately, it is very close to the casting mperature of some typical gold alloys. In addition, the decomposition mperature is furtherly lowered when inert or reducing atmospheres are used ; well as in the presence of the oxides of the alloying elements of the carat ›ld alloy. The results indicate that the worst condition for casting are a :ducing atmosphere and the presence of Cu_2O and ZnO as well as an over :ating of the gold alloy.

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