Lead extraction from waste funnel cathode-ray tubes glasses by reaction with silicon carbide and titanium nitride

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ABSTRACT

As a possibility to clean waste CRT glass, treatment of lead-containing glass with a reducing agent, SiC or TiN, leads to a porous material containing metallic lead, Pb(0), located on the surface of the pore, and unreduced lead, Pb(II). The influences of reducing agent content, of the time, and at last of the temperature on lead reduction were analysed. Our investigations have pointed out significant differences as a function of the used reducing agent. CRT glass heat treated with SiC lead to less Pb(0), compared to TiN as shown by X-ray diffraction, and differential scanning calorimetry (DSC). It has been also evidenced that lead reduction occurs on randomized zones inside the sample leading to macroscopic lead beads inside glassy samples. XPS and XAS measurements were also carried out to investigate the local structure of lead and have evidenced a change of role of lead inside the glassy framework in function of the used conditions.

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1. Introduction

Since the end of the 90s, the re-use of waste electrical and electronic equipment (WEEE) also called e-waste, generated over the world is of great interest [1–7]. Considering that electrical and electronic equipment (EEE) is hazardous containing components and that the amount of WEEE has grown rapidly, the occidental governments have edited directives concerning their waste management and their re-use to ensure an environmental safety [8–10]. For example in the European Union (EU) WEEE represent about 7.5 million tons each year [11]. As a consequence, the computer monitors and TV sets containing cathode-ray tubes (CRTs) represent about 80% of the total electronic waste [12]. At the beginning of the decade it was estimated that 300,000 tons of e-waste ended up in landfill [13] and CRTs represent about one-third of electronics waste tonnage in the United States [14]. Considering that current CRT technology will become obsolete and replaced by thin-film transistor liquid display (TFT-LCD), a huge number of TV sets and computer monitors will be potentially disposed in landfill. CRTs are made of different glasses: the front part, usually known as the panel which is a barium–strontium containing glass, the hidden parts inside the monitor, called funnel glass and the neck glass which are lead-rich silicate glass which envelopes the electron gun [15]. The amount of lead present in glasses used in cathode-ray tube could lead to an important social problem [12,15]. Some studies have demonstrated that the lead containing CRT glasses must be considered as hazardous waste, because of the well-known health effects of lead. Landfilling of CRT glasses, strictly restricted in the EU, could or should be solved by (i) recycling new CRTs glasses with the waste one (called closed loop system) [5,16]; (ii) manufacturing other outlets with CRT waste glasses (called open-loop system) [12,17–25]. However these solutions will be efficient if the leachability of heavy metal does not exceed the threshold limits; (iii) encapsulating lead [26]; or at least (iv) decontaminating the lead [27] or heavy metals [28,29] containing glasses. Development of techniques for the extraction of heavy metal ions from glass is also important in disposing waste glass used in electronic applications since these devices contain hazardous heavy metal elements, such as lead. These applications are the most revelling ones and more details on re-use of CRTs are given by Herat [7]. Previous studies were carried out in our laboratory [15,30–35] with investigations of the recycling of PbO-containing waste CRT glasses. Foam glass appeared to be a promising solution to re-use waste CRT glasses. The reduction of lead (+II) to metallic lead occurs to be a result of the reaction between SiC (or TiN) and the lead oxide contained in the glass, generating CO_2 (or N_2) within the framework [17,31–33] producing a porous cellular structure. It has been

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Table 1
Reducing agent contents, temperature and time used to determine the lead content in the samples for the various conditions (fixed parameters are underlined).

	Reducing agent content (wt.%)		Temperature of reaction (°C)	Time of reaction (min)
	SiC	TiN		
Effect of the reducing agent	1 → 17		850	60
Effect of the temperature	5		700 → 1000	60
Effect of the time of reaction	5		850	10 → 180

demonstrated that metallic lead located on the surface of the pore, was obtained in different proportions depending on the elaboration parameters. In extreme conditions, i.e. high reducing agent content, high temperature and long time of reaction, it has been possible to extract lead from the initial glass. This work aimed to investi-gate the influence of reducing agent content (1–17 wt.%), time of reaction (10–180 min) and temperature of reaction (700–1000 °C) on the lead extraction. The effects of elaboration parameters on the lead reduction process are also described. The local structure around unreduced lead has been studied by spectroscopic tech-
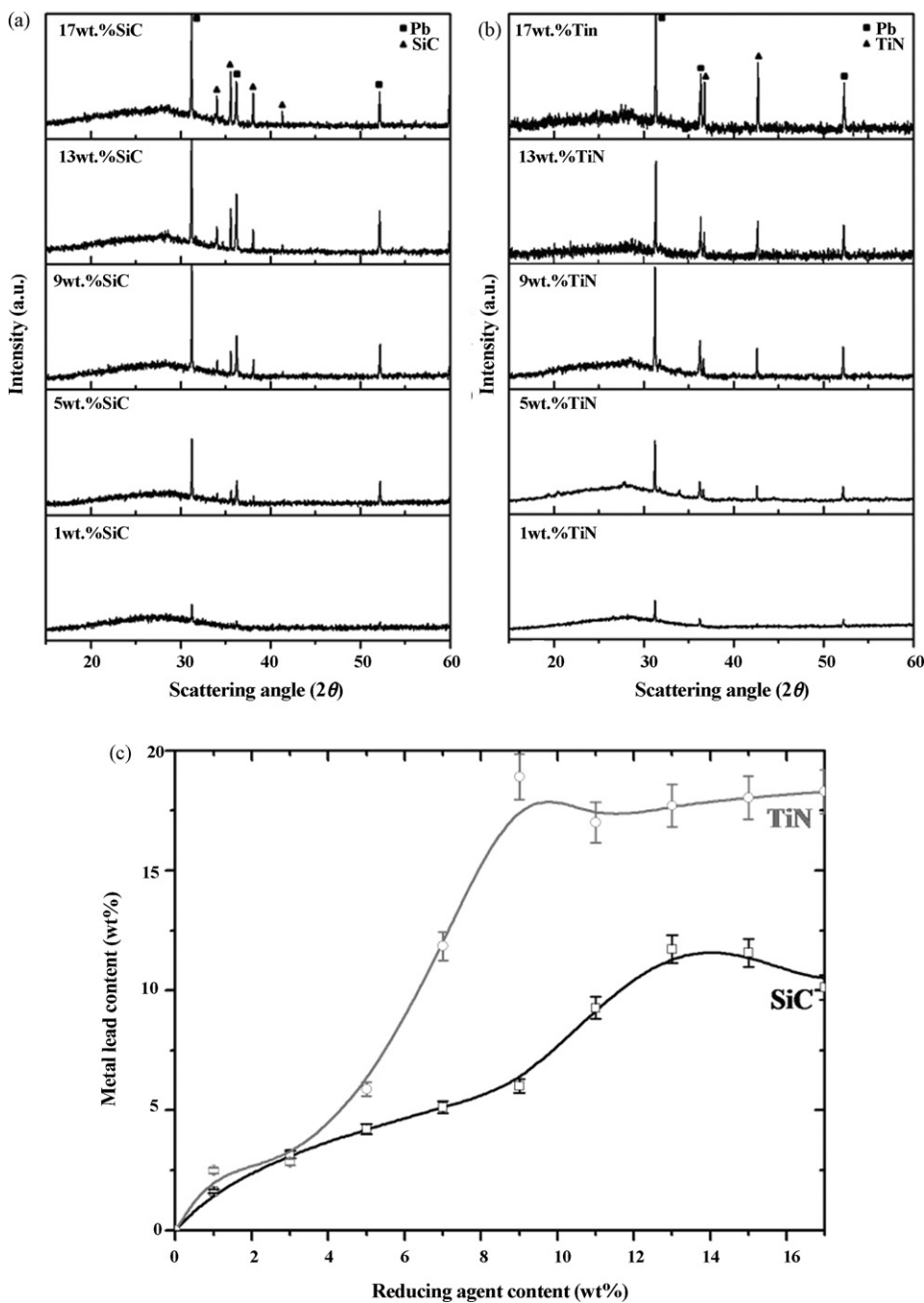
Fig. 1. XRD patterns obtained as a function of the reducing agent content for samples elaborated with SiC (a) and TiN (b). Reduced lead content evolution (c) obtained by DSC for various SiC and TiN contents (in wt.% of the initial lead (+II)).

Fig. 2. XRD patterns obtained as a function of the temperature for samples elaborated with SiC (a) and TiN (b). Reduced lead content evolution (c) obtained by DSC for various SiC and TiN contents (in wt.% of the initial lead (+II)).
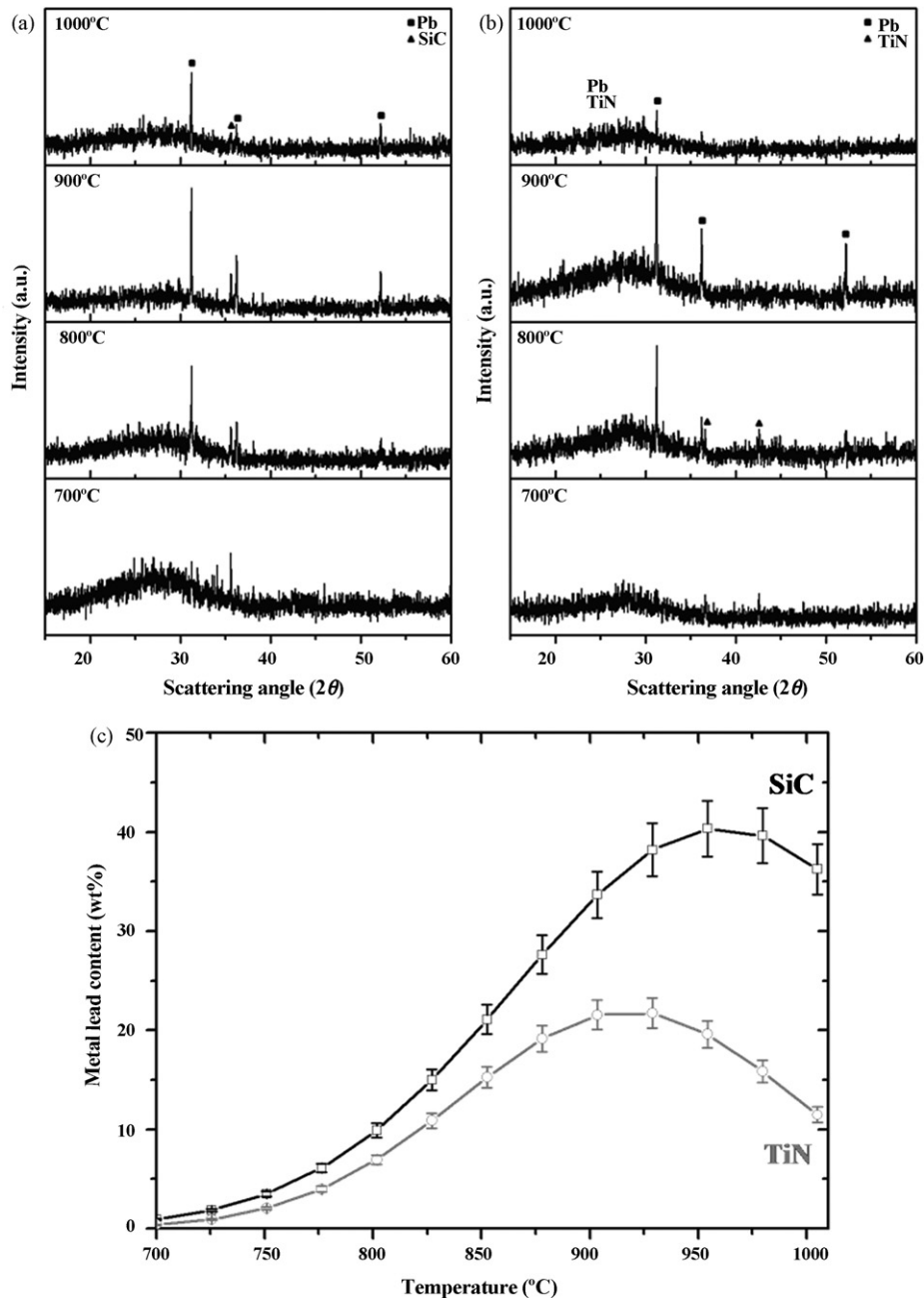
niques in previous paper and will be used to discuss the results obtained here.

2. Materials and methods

2.1. Preparation of the samples

Waste funnel glass powder and reducing agent both in powder forms (SiC Aldrich 99.9% and TiN Alfa Aesar 99.8%), were mixed with a binder and then pressed at room temperature under 5 tons to get pellets with 40 mm of diameter and thickness of 6–8 mm. The average particle sizes of the different powders used were smaller than 63 μm. All the pellets were treated in an electric furnace under air atmosphere in the heating conditions summarized in Table 1. In

the whole conditions, the samples were removed from the furnace and allowed to reach room temperature in 'free fall'.

2.2. Lead reduction reactions

Based on the previous works [31], the reaction processes of interest for the two reducing agents can be described with the following equations:

$$2PbO(s) + 2TiN(s) + O_2(g) \leftrightarrow 2Pb(s) + 2TiO_2(s) + N_2(g)$$

$$2PbO(s) + SiC(s) + O_2(g) \leftrightarrow 2Pb(s) + SiO_2(s) + CO_2(g)$$

where TiO_2 and SiO_2 are in a vitreous phase [32].

2.3. Lead content determination

X-ray diffraction patterns were determined for samples with various quantities of the reagent grade SiC or TiN using a PANalytical X'PERT diffractometer. Each sample was grinded to a fine powder (50 μm) and was introduced into a sealed silica capillary tube of 0.3 mm diameter. The X-ray diffraction (XRD) patterns of the whole samples were collected for 2θ from 10° to 60° using CuK_α radiation (λ = 1.5604 Å).

The variation of the lead content in the samples was measured using the areas of the differential scanning calorimetry (DSC) peaks corresponding to the lead melting point (327 °C). The measurements were carried out on a dynamic heat-flux differential scanning calorimeter (NETZSCH DSC 200) in a sealed aluminium crucible using a heating rate of 5 °C/min from 20 to 400 °C.

3. Results and discussion

3.1. Effect of the reducing agent content

The influence of the reducing agent on the lead content was studied at constant temperature (850 °C) with a reaction time of 60 min. X-ray diffraction patterns obtained for 1–17 wt.% of reducing agent are shown in Fig. 1(a) and (b). Sharp diffraction peaks due to the crystallization of the lead are seen, in addition to a broad diffraction peak revealing the conservation of an amorphous character. All the crystalline peaks are identified to belong to Pb (PCPDF 04-0686) and residual reducing agent SiC (PCPDF 49-1428, Fig. 1(a)) or TiN (PCPDF 08-0418, Fig. 1(b)) phases. In addition, it is seen that the fraction of Pb(0) phase increases significantly (revealed by the height of the diffraction peaks) with increase the initial content of SiC or TiN.

The quantitative estimation of the reduced lead content was carried out by DSC and presented in Fig. 1(c). The variation of the lead (0) content as a function of reducing agent content in case of samples reduced with SiC was found to be linear up to 9 wt.%, whereas the variation with TiN was found to be exponential (Fig. 1(c)). Thus with 9 wt.% TiN using, it would appear that 20 wt.% of the lead initially present in the glass is reduced to the lead metal form after heat treatment, for only 12 wt.% with SiC using.

3.2. Effect of the temperature

The effect of temperature was investigated using a fixed SiC or TiN reducing agent content of 5 wt.% and a synthesis time of 60 min. The corresponding X-ray diffraction patterns, shown in Fig. 2(a) and (b), indicate, as mentioned before, the presence of both non-crystalline phase, metallic lead, and residual reducing agent. Fig. 2(c) shows the results of the DSC measurements of the lead quantity as a function of the temperature. For both SiC and TiN, the trends are quite similar. The two curves present a maximum of reduced lead at 950 and 925 °C for SiC and TiN, respectively. At higher temperatures, the reduced lead quantity found by DSC decreases with the temperature. This significant decrease is the result of the coalescence of lead granules, as observed by microscopy, inside the material (Fig. 3). On the effect of the high temperature, macroscopic granules of lead have coalesced inside the pellet (see the arrows on the picture in Fig. 3) to give an inhomogeneous material with lead rich zone and poor lead zone. The powder used for the XRD and DSC analysis, came from the zone lacking of lead (0) in the sample. The higher is the temperature of reaction, the largest are lead granules and then the lowest is the lead (II) content inside the glassy frameworks. Hence, the probability to use for the DSC measurements poor lead containing zone increases, explaining the shape of the two curves in Fig. 2(c). We can
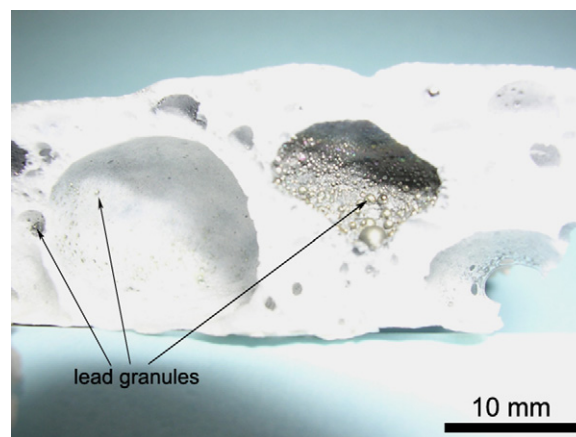

Fig. 3. Photograph of the lead granules obtained by coalescence inside the material at high temperature.

therefore assume that more than 20 and 40 wt.%, could be obtained with increasing the temperature, for TiN and SiC, respectively. Based on these results, increasing both the temperature and the reducing agent content, could lead to 'phase separated samples': a pure lead metallic phase and a more or less poor lead silicate glass phase.

3.3. Effect of the time of reaction

The effect of the reaction time on the lead content was investigated at 850 °C with 5 wt.% content of SiC and TiN reducing agent. Once again, the corresponding X-ray diffraction patterns indicate, the presence of non-crystalline phase, metallic lead and remaining reducing agent. The lead content increases with increasing the reaction time and reaches to a maximum at 20 wt.% for both, SiC and TiN using (Fig. 4(c)). Such behaviour is similar whatever the nature of the reducing agent.

The metallic lead amounts obtained by the investigated process are lower than those obtained through pyrovacuum process by Chen et al. [27] using carbon. As is well known, carbon is one of the best reducing agent used in the metallurgy for steal synthesis. Considering this point, it gives a response on the lower lead quantities obtained in our case. Analysing the aforementioned results, the reduced lead content could be more important increasing temperature and/or reducing agent content. Nevertheless, as the reaction occurs in air atmosphere, oxygen pressure will be a limitative parameter for the lead reduction.

3.4. Evolution of the local structure around lead

The local environment of the unreduced lead was then investigated using X-ray photoelectron spectroscopy (XPS) [33,36] and X-ray absorption spectroscopy (XAS) [37]. In our previous work [33] XPS spectra obtained for sample with 5 wt.% of TiN treated at 850 °C compared to $PbSiO_3$, respectively. XPS spectra of four Pb 4f XPS peaks were observed: two symmetric XPS peaks due to Pb $4f_{7/2}$ and Pb $4f_{5/2}$. The XPS results confirm the presence of two types of lead in the foam glass:

- Pb^{2+} ions with binding energies of Pb $4f_{7/2}$ (143.6 eV) and Pb $4f_{5/2}$ (138.6 eV), respectively corresponding to those of $PbSiO_3$ and
- Pb^0 metallic lead with binding energies Pb $4f_{7/2}$ (141.5 eV) and Pb $4f_{5/2}$ (136.6 eV).

As is well known, $PbSiO_3$ consists of infinite metasilicate chains interconnected by Pb^{2+} ions. The lead oxide is a glass modifier in CRT glasses, so its introduction results in the depolymerization of the

silica network [36]. Nevertheless, the relative position of the main transition (Pb 4f) for lead (II) is not significantly influenced by the variation of the reducing agent content [33]. The three dimensional framework of SiO_4 tetrahedra is maintained as lead oxide is present at low concentrations (20–22 wt.% corresponding to 2–3 mol.%) that vary slightly from one sample to another. The results show that the spectra obtained for a higher temperature of reaction are the same as those obtained for different reducing agent content. Lead (0) and (II) binding energies corresponding to Pb $4f_{7/2}$ and Pb $4f_{5/2}$ have been found at similar values showing that lead (II) remains present in the same environment. Nevertheless, the relative area of the peaks corresponding to lead metal increases, while the relative area of the Pb 4f peaks corresponding to lead in a $PbSiO_3$ environment decreases (Fig. 5).

In some previous works, the influence of the hydrogen reduction on the structure of lead silicate glasses was studied by EXAFS [38,39]. It has been demonstrated that the coordination number of unreduced lead decreases without change in Pb–O bond length which remains equal to 2.23 Å. In our case EXAFS has been also used and it allowed us to measure the influence of the reducing agent content. Lead–oxygen coordination number was determined using EXAFS amplitude which is proportional to a product of the coordination number (N) and the amplitude reduction factor S_0^2 which has been fixed to 0.75 [40]. Fig. 6 summarizes the evolution of the coordination number as a function of the reducing agent content. In the both cases lead coordination number decreases increasing the reducing agent content. Nevertheless the decrease is more pronounced in case of TiN than SiC. Lead–oxygen coordination number
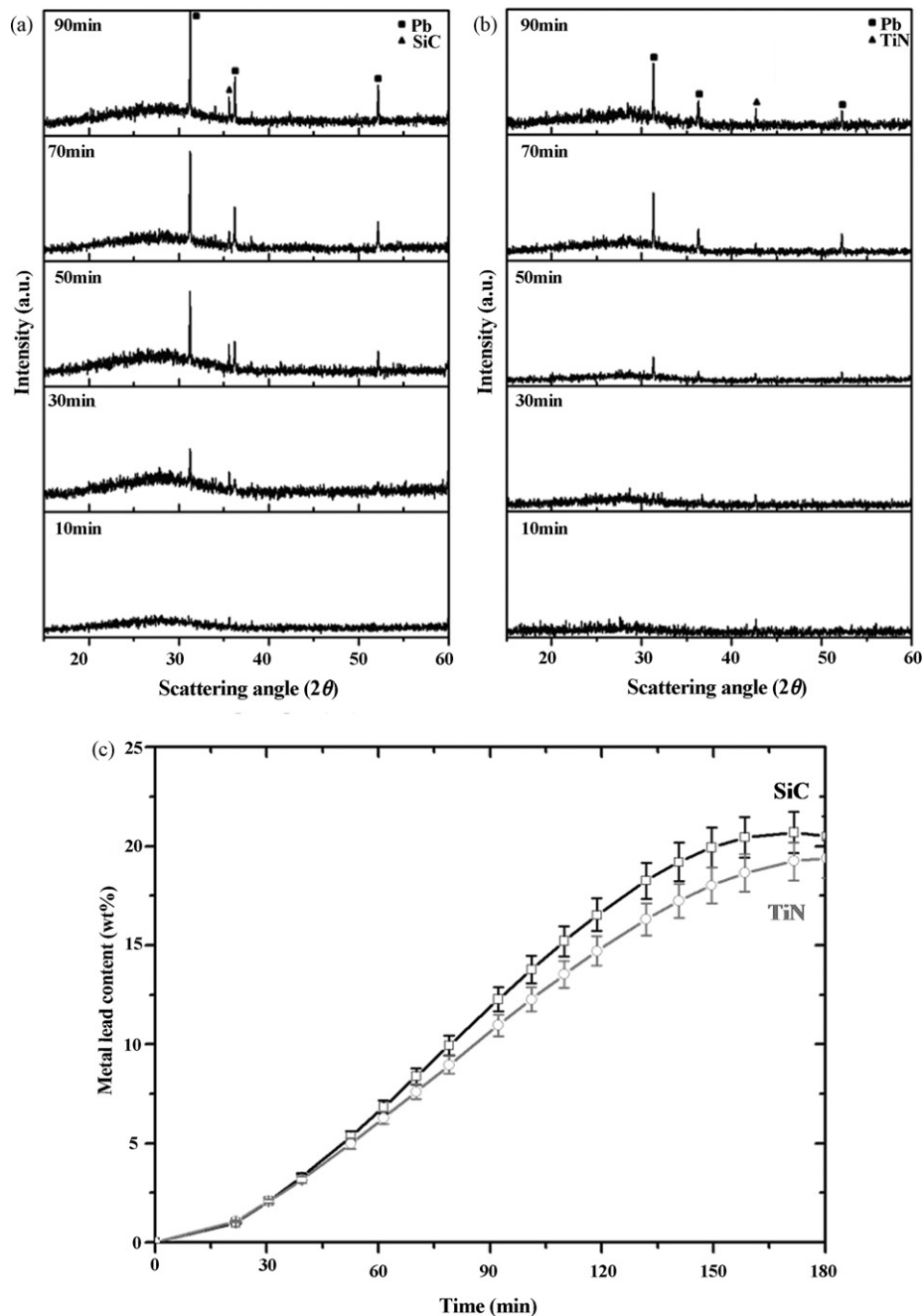

Fig. 4. XRD patterns obtained as a function of the time of reaction for samples elaborated with SiC (a) and TiN (b). Reduced lead content evolution (c) obtained by DSC for various SiC and TiN contents (in wt.% of the initial lead (+II)).
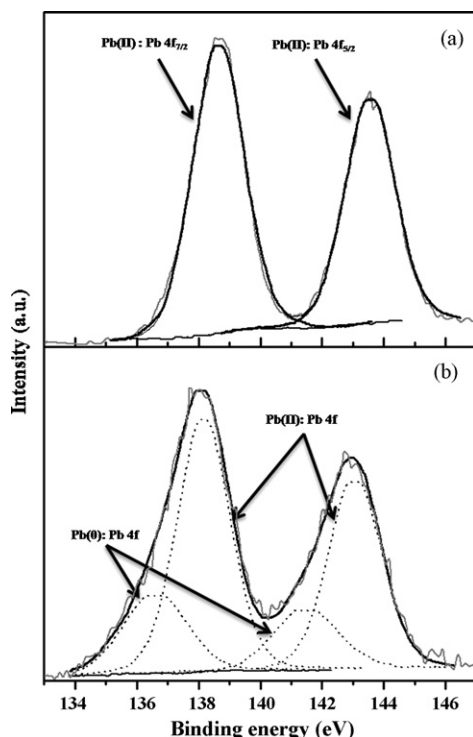
Fig. 5. Pb 4f core level spectra of the foam glasses (a) and PbSiO$_3$ glass (b).
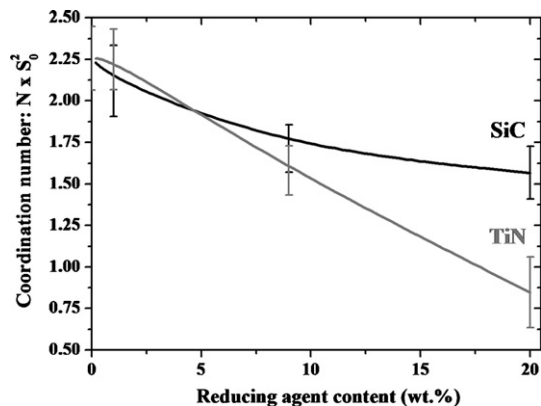

Fig. 6. Evolution of the average coordination of Pb–O as a function of the reducing agent content.

dramatically falls from 3 to 1 for TiN instead of 3 to 2 in case of SiC [37]. In both cases the Pb–O bond length remains around (2.23 Å); which is the same distance found in initial funnel glass [41]. These results are then consistent with results previously reported [38,39] and show the change of role of lead inside the glass under the influence of the reduction.

4. Conclusions

The influence of the lead metal content on the parameters as a function of reducing agent content, time and temperature on the foam glass synthesis has been studied using lead-containing waste CRT glasses (funnel) and two reducing agents, SiC and TiN. The treatment of glasses in adapted conditions leads to more and more friable and porous materials containing more Pb(0) granules and less unreduced Pb(II).

In this study, it has been shown that lead metal content is function of the experimental parameters. In fact, the higher the

experimental conditions (reducing agent content, temperature and time) the higher the lead metal content. As it has been demonstrated by XRD, DSC and XAS, TiN treatment of CRT glasses gives less reduction of Pb(II) to Pb(0) than SiC treatment. As a result it could be possible to extract nearly whole the lead contained in the funnel glass (initial content 20–22 wt.% of lead oxide) in extreme condition of temperature, time of reaction and/or reducing agent content.

Function of the reducing agent content, 12 and 20 wt.% of total lead reduced (in foam glass synthesized 60 min at 850 °C) to metal form can be extracted with 9 wt.% SiC and 9 wt.% TiN used, respectively. Function of the temperature, 40 and 20 wt.% of total lead reduced (in foam glass synthesized 60 min at 950 °C) to metal form can be extracted with 5 wt.% SiC and 5 wt.% TiN used, respectively. And finally, function of time of reaction, 20 wt.% of total lead reduced (in foam glass synthesized 180 min at 850 °C) to metal form can be extracted with both 5 wt.% SiC and 5 wt.% TiN used.

The chemical process has been studied by various spectroscopic methods. No variation of Pb–O bond length was found with XAS. In contrast the reduction process induces a dramatic decrease of number of coordination of lead–oxygen leading to a change in role of the unreduced lead in the glassy frameworks. This process allows both to obtain foam glass (a promising insulator material with thermal, electric or phonic insulator properties) and also to obtain a glass with low lead content. Nevertheless if SiC and TiN reducing agents could be used to extract lead from funnel CRT glass this process could be limited by its cost.

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