Thermal study and mechanism of Ag_2S oxidation in air

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Abstract The results of thermal study and mechanism of the oxidation process of synthetic Ag_2S in air are presented in this article based on the comparative analysis of DTA and XRD results, as well as by constructed phase stability diagrams (PSD) for the Ag–S–O system.

Keywords Ag_2S · Thermal analysis · Reaction mechanism · Phase stability diagrams

Introduction

Sulfide of silver, Ag_2S, is a dense black solid constitutes the tarnish that forms over time on silverware and other silver objects [1]. It was used as a photosensitizer in classic photography and its high temperature forms are electrical conductors [1]. Recently, some new electrochemical characteristics, as well as application modalities of Ag_2S at nano-level, have been presented in literature [2–6].

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Concerning the crystallography, three crystal forms of Ag_2S are known [7]: monoclinic crystal form, stable at room temperature and at the temperatures below 173 °C, body centered crystal form, stable above 173 °C, and face centered crystal form, stable at higher temperatures, above 571 °C. A summary of the phase equilibria of Ag–S system is given by Sharma and Chang [8, 9], which results of the assessment are presented in Fig. 1.

Comparing to well referred crystallographic and phase equilibria data on Ag–S system, literature information on the Ag_2S oxidation process is sparse and incomplete [10–13]. Therefore, the contribution to the better knowledge of thermal study and mechanism of Ag_2S oxidation in air is given in this article.

Experimental

Synthetic Ag_2S of 99.99% purity, produced by MERCK, was used as the sample material.

Differential thermal analysis (DTA), as well as X-ray diffraction (XRD) analysis, were used for the experimental investigation in this article.

The DTA-TG-DTG measurements were carried out on the Derivatograph (MOM Budapest) apparatus under following conditions: air atmosphere, heating rate 10°/min up to a maximum 1,000 °C, and alumina as the reference material.

The XRD analysis was done on investigated samples by apparatus PHILIPS, model PW-1710, with curved graphite monochromator and scintillating counter, at a voltage of 40 kV and electric current of 30 mA. The intensities of diffracted CuKα radiation $\lambda = 1.54178$Å were measured at room temperatures in the intervals $0.02°2\theta$ and time of 0.5 s, within the range of $4–65°2\theta$.

Fig. 1 Phase diagram of the
Ag–S system [9]
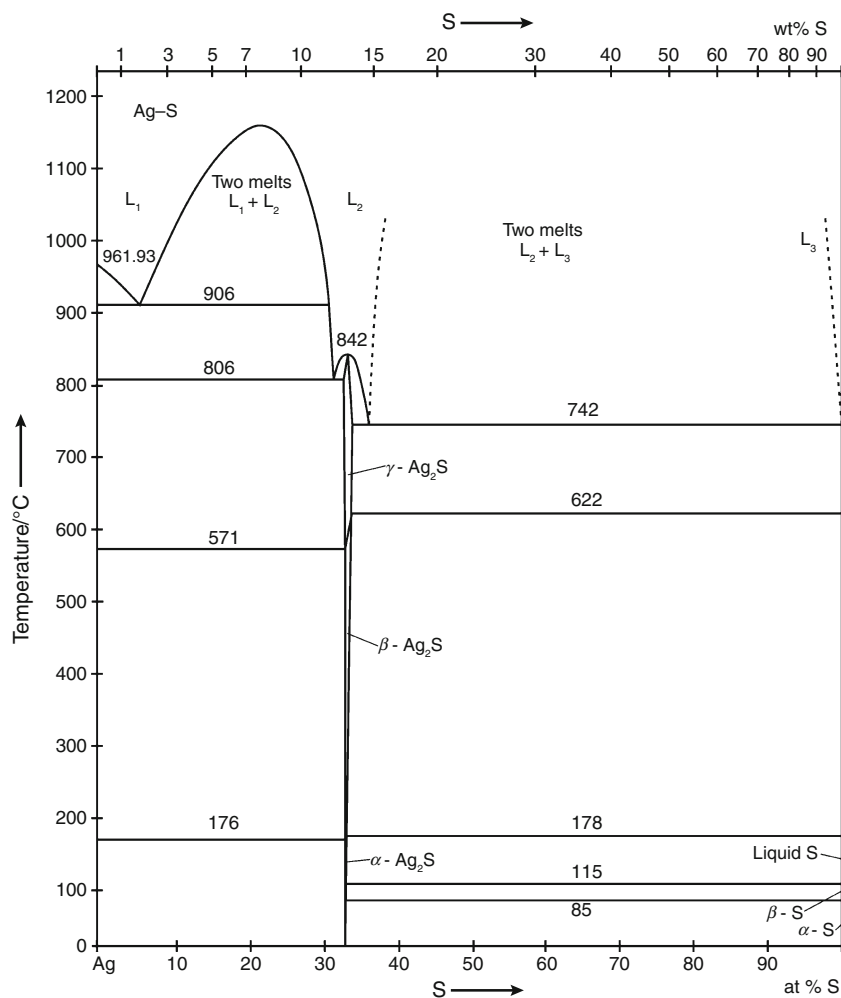
Results and discussion

The results of differential thermal analysis (DTA) of the
Ag_2S oxidation process includes measurements done for
the samples oxidized in air at the temperatures up to
700 °C and 1,000 °C. DTA curve for the sample oxidized
up to 1,000 °C is given in Fig. 2.

Four peaks can be noticed in DTA curve presented in
Fig. 2, occurring at: first, endothermic—starting at about
165 °C and achieving maximum at 175 °C; second, exo-
thermic—starting at about 510 °C and achieving maximum
at 550 °C; third, endothermic—starting at about 720 °C
and achieving maximum at 730 °C; and fourth, endother-
mic—starting at about 845 °C and achieving maximum at
860 °C. Beginning at the temperatures over 550 °C, mass
loss of total 4.4% at 700 °C and 12.8% at 1,000 °C was
obtained in thermograms, where the last percentage cor-
responds to the almost stoichiometric loss of sulfur in
starting Ag_2S sample, equal to 12.9%.

The results of X-ray diffraction (XRD) analysis of the
starting material—Ag_2S, as well as of the residuals
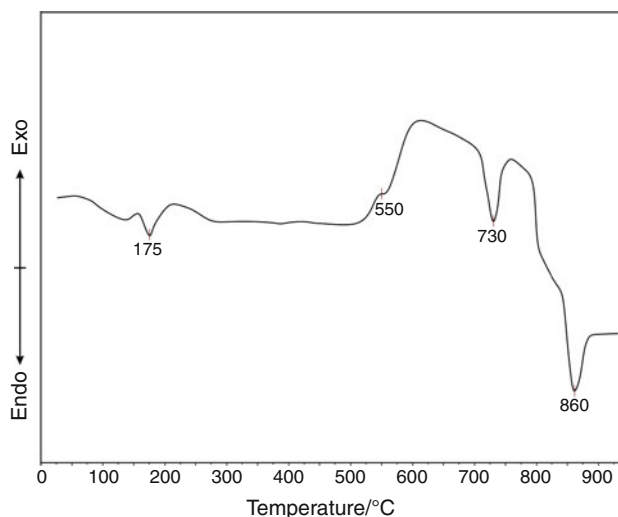

Fig. 2 DTA curve for the Ag_2S oxidation process in air up to
1,000 °C

obtained after oxidation of the samples in air up to the
temperatures of 700 °C and 1,000 °C, are presented in
Fig. 3.

XRD analysis showed following phase composition: (a) starting sample—Ag_2S and amorphous matter, with low expressed crystallinity; (b) residual after oxidation of the sample up to temperature of 700 °C—decreased content of Ag_2S, elemental silver and amorphous matter, with very low expressed crystallinity; and (c) residual after oxidation of the sample up to temperature of 1,000 °C—elemental silver and amorphous matter, with more expressed crystallinity.

In order to aprove such thermal behavior of Ag_2S during oxidation process, thermodynamic analysis was also done using phase stability diagrams (PSD) construction for the system Ag–S–O, which are given in Fig. 4 for two investigated temperatures 700 and 1,000 °C.

As can be seen, phase equilibria obtained in constructed PSD diagrams indicates to direct oxidation of Ag_2S to elemental silver, according to simple reaction:

$$Ag_2S + O_2(g) = 2Ag + SO_2(g). \qquad (1)$$
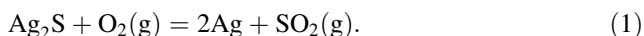
The oxidation of Ag_2S to Ag_2O is not favored thermodynamically, as shown in the Ag–O phase diagram (Fig. 5) that above 180 °C only elemental silver is stable. This statement was also confirmed experimentally in this article by XRD analysis.
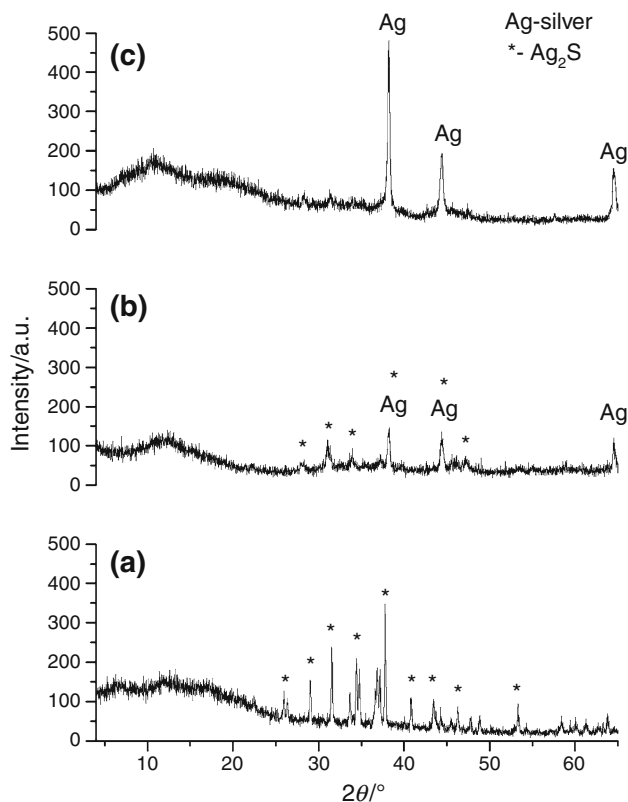

Fig. 3 XRD results for the starting material Ag_2S (a) and the residuals obtained after oxidation process in air at 700 °C (b) and at 1,000 °C (c)
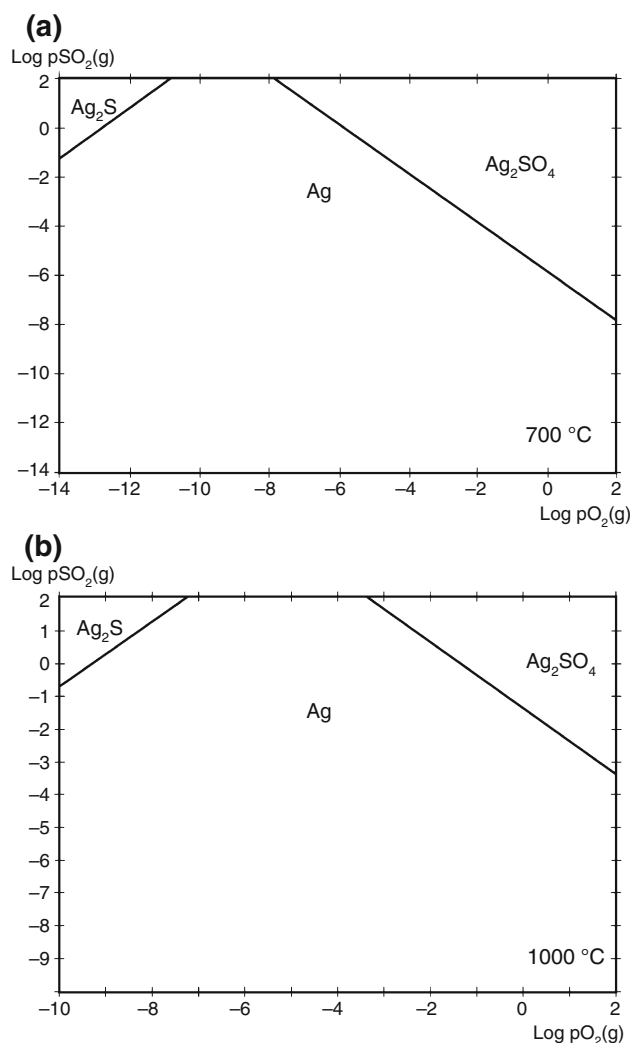

Fig. 4 PSD diagrams constructed for the Ag–S–O system at 700 °C (a) and at 1,000 °C (b)

According to presented and explained results of investigation, and considering phase diagram of Ag–S system (Fig. 1), mechanism of investigated process can be completed. The first peak in DTA curve (Fig. 2), for which there are no mass loss in thermograms, correspond to the phase transformation of monoclinic to body centered crystal form of Ag_2S. The second peak is related to the start of Ag_2S oxidation to silver, according to reaction (1), and is followed by the adequate mass loss obtained at the thermogram. Accompanying effect can also be connected to transformation of body centered to face centered cubic crystal form of Ag_2S at mentioned temperature. The third peak represents partial melting of residual amount of Ag_2S, while the fourth peak corresponds to final Ag_2S congruent melting temperature [8, 9].

Such obtained results present a contribution to the better knowledge of oxidation processes of non-ferrous metal
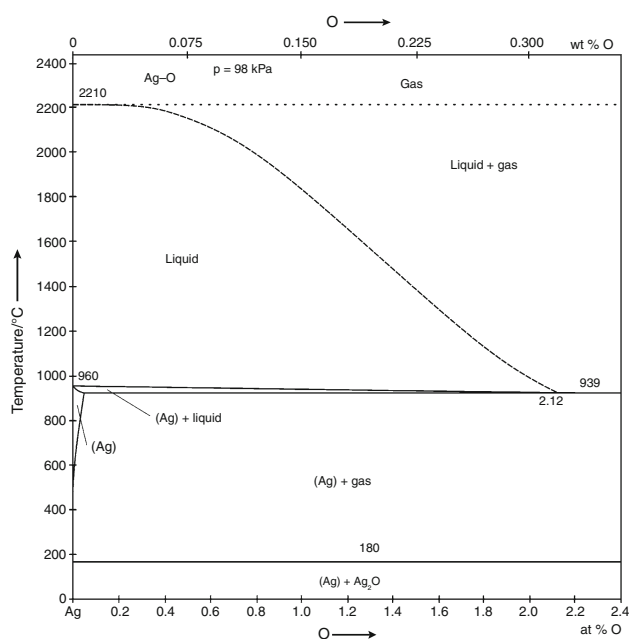
Fig. 5 Phase diagram of the Ag–O system [9]

sulfides, which are available in literature [14–18], but still not completely.

Conclusions

The results of thermal study and mechanism determination of synthetic Ag_2S oxidation in air, using DTA and XRD analysis and PSD diagrams construction, are presented in this article.

The investigations showed that oxidation of Ag_2S went directly to elemental silver, according to the reaction (1): $Ag_2S + O_2(g) = 2Ag + SO_2(g)$, which occurred over 510 °C.

The Ag_2S oxidation process is followed by several phase transformations of Ag_2S—first, starting at about 165 °C and related to monoclinic—body centered crystal form transformation; second, partially overlapping with the oxidation process occurring over 510 °C, related to transformation of body centered to face centered cubic crystal form; third, starting at about 720 °C and related to partial melting of residual Ag_2S amount; and fourth, starting at about 845 °C, corresponding to Ag_2S congruent melting.

Proposed mechanism was confirmed experimentally and thermodynamically.

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