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تحضير القصدير باستعمال الطريقة الرطبة

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الخلاصة

درس وحضر فلز القصدير من محلول كلوريد القصدير باستعمال الطريقة الرطبة بوجود مسحوق الألمنيوم عامل مختزل يبدأ التحضير من خلال خطوة الاختزال ، إذ تتبع عملية توافر العامل المختزل بخطوة الصهر في درجات حرارية تصاعدية باستخدام فرن كهربائي قابل للبرمجة . في خطوة الاختزال درس تأثير الحامضية ، وقت إضافة مسحوق الألمنيوم وتأثير زيادة العامل المختزل في تحول كلوريد القصدير إلى فلز القصدير .
أما في خطوة الصهر فان ثلاثة عوامل تمت دراستها وهي معدل التسخين ، ودرجة الحرارة ، ووقت الاستبقاء الحراري.
ولغرض تشخيص المنتج فقد استخدمت أجهزة تحليل مختلفة :-

- حيود الأشعة السينية لغرض التثبت من توافر عنصر القصدير بعد خطوة الاختزال في المادة المتكتلة ، وكذلك توافر اوكسيد القصدير بعد خطوة الصهر في المخلفات .
- قياس الامتصاص الذري لتحديد كمية القصدير في المادة المحضرة المتكتلة بعد الاختزال .
- استعملت (DSC) لغرض التشخيص .
- المسح الالكتروني لغرض دراسة تأثير متغيرات خطوة الصهر في التركيب البلوري للقصدير المتكون .

إن درجة الحرارة هي المتغير الوحيد من بين المتغيرات الثلاثة التي تمت دراستها والذي أبدى تأثيرا ملحوظا في إنتاجية عنصر القصدير كما ان دراسة التركيب البلوري للقصدير المنتج أكدت تأثير درجة الحرارة الكبير في شكل وحجم البناء التركيبى للقصدير المنتج .

الكلمات المفتاحية: قصدير ، كلوريد القصدير ، مسحوق الألمنيوم ، الأشعة السينية

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Preparation of Tin Using Wet Method

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Abstract

The preparation of tin metal from stannous chloride solution by wet method in the presence of aluminum powder as a reducing agent is studied. The preparation is commenced through a reduction step in the presence of reducing agent followed by smelting step at elevated temperature in a programmable electrical furnace. In the reduction step, preliminary experiments are conducted to study the effect of initial acidity, time of addition of the aluminum powder and excess amount of reducing agent on the conversion of stannous to tin metal. Three different parameters are studied through smelting step, these are : heating rate, temperature and residence time.

To characterize the product, different instrumental analyses are used:

- X-ray diffraction to check the existence of tin after reduction step in the agglomerates and the existence of tin oxide after smelting step and in the remaining slag.
- Atomic absorption to determine the quantity of tin in the agglomerates after reduction step.
- Diffraction scanning calorimetry (DSC) for identification.
- Electron scanning to study the effect of smelting step variables on the crystal structure of the prepared tin.

Reasonably between the three studied variables, only temperature shows a significant influence on the productivity of tin. Studying the crystal structure of the produced tin confirms the enormous effect of temperature on the shape and size of grain structure.

Key words: Tin ,Stannous chloride , Aluminum powder

Introduction

The tin element comprises 0.0006 % of the earth's crust. The extraction of this element at least 5000 years old and it can be expected by now that it has reached an advanced state of evolution [1]. Tin is obtained from cassiterite, which is a tin oxide SnO_2 [2]. Cassiterite is smelted to metal by reduction with carbon most commonly in a reverberatory furnace. Temperatures in excess of 1200 °C are required. The difficulty is that cassiterite is hardly ever produced entirely free from other minerals many of these are reduced to metal at the same time forming alloys with the tin. It is therefore necessary to refine the tin to make it commercially useful. Fire refining involves various procedures on the molten metal. Iron is removed by passing steam through the molten metal; arsenic and antimony are removed by addition of aluminum alloy and copper is removed with sulfur. Very pure tin was obtained by electrolysis [3].

Tin is used in various industrial applications as cast and wrought form and tinplate, i.e. low carbon steel sheet or strip rolled to 0.15- 0.25 mm thick and thinly coated with pure tin [4]. Tin is also used as a reducing agent in chemical processes and in the production of other compounds such as stannic oxide and organo-tin compounds. Tin is used in coat copper wire and soldering material. Alloys of tin are used to make dental materials (silver-tin-mercury), nuclear reactor components (tinzirconium), aircraft components (tin-titanium), bronze (copper-tin) and brass. Tin is the principal component of pewter. Inorganic tin compounds are used in the glass industry to add strength to glass. Inorganic tin compounds also serve as the base for the formulation of colors, as catalysts, and in perfumes and soaps [5].

One of the suggested programs is to study the preparation of tin metal from its ore or its salts as prior needs for further recommendation to start a new technology for purifying tin from waste. To meet this requirement, the present was conducted study under concern was directed to aim the feasibility and applicability of predicting new technology and studying the conditions of its stages that might incorporate for further implementation into large-scale units.

To incorporate the currency of the study, the experimental work is suggested to monitor the production of tin metal (not less than 99% purity) through two stages: the reduction stage in the presence of a reducing agent and the smelting stage. Different parameters were investigated for their influences on the conversion of tin metal from its salt and furtherly in purifying the agglomerated tin through smelting stage.

In this study , wet method for production of 99 % purity of tin metal from its salt was mainly aimed to use stannous chloride ($SnCl_2$), which could be found from electrolysis waste of electronic printed circuit board factory or from scrap. In the first stage , a reducing agent (aluminum) was suggested for its ability to reduce the stannous chloride and precipitating tin in agglomerate form that incorporates different impurities. Unlike the pyro-metallurgy method where the smelting stage needs four furnaces with temperatures range from 1000 to 1200 °C, this method would require lower temperature (350 °C). Eventually this approach would open new horizon in the purification of other metals.

Tin is amphoteric and reacts with both acids and bases; it is relatively resistant to nearly neutral solutions. The overvoltage of hydrogen on a tin surface is high (0.75 V), so that attack by acids and bases is fairly slow unless an oxidizing agent is present to act as a depolarizer. Distilled water has no effect on tin, which is in fact the preferred medium for preparing and storing this water [6].

Stannous oxide is a predominantly basic oxide reacting with acids to produce stannous salts, which are strong reducing agents With strong alkalis, stannites are formed; these are known only as solution and on concentrating , dissociate to stannates and spongy metallic tin:

$$2NaHSnO_2 \leftrightarrow Na_2SnO_3 + Sn + H_2O \qquad (1)$$

Stannous chloride formed from metal or stannous oxide and hydrochloric acid is soluble in water, alcohol and acetone. The aqueous solution is a strong reducing agent which precipitates $SnOCI_2$ if exposed to air and Sn(OH)CI in dilute air-free solution. Gaseous $SnCI_2$ reacts with oxygen according to following equations:

$$SnCI_2 + \frac{1}{2}O_2 \leftrightarrow SnOCI_2 \qquad (2)$$

$$2SnCI_2 + O_2 \leftrightarrow SnO_2 + SnCI_4 \qquad (3)$$

The usual crystalline hydrate salt has $2H_2O$ [1].

In general, wet processes are costly and they offer no prospect of success commercially, although in exceptional cases-say in the preparation of tin compounds, or in preparing tin or its compounds for chemical investigations, wet processes may be used. Moulin and Dole in 1873 [7] allowed gaseous hydrogen chloride to act on the etchings until the iron was attacked. The products were washed out with water and precipitated from the solution by zinc. Lung in 1884 described the preparation of tin chloride by treating tinned plate with chlorine gas . The stannic chloride collected as fuming liquid. Labotte in 1884 used a mixture of chlorine and air at 100 °C [8].

The wet methods for recovery of tin from scraps of tinned plate had been proposed, and also for preparing tin salts from the cuttings of tin-plated sheet and from the waste of dye-works . In 1906, Svedberg [8] obtained colloidal solution of tin in organic solvents by suspending tin-foil in the solvent and using electrodes of iron or aluminum with a potential difference of 110 V. Bradford [8] (1866) digested the granulated metal with nitric acid, washed the hydrated oxide with diluted hydrochloric acid and water and reduced the dried oxide by heating it with sugar-charcoal or the hydrated oxide can be dissolved in concentrated hydrochloric acid. The solution then was diluted with water and treated with diluted sulfuric acid. The washed product is dried, mixed with sugar-charcoal and ammonium carbonate, and heated in a porcelain crucible to redness. Cohen and Goldsch (1904) [9] removed any oxide dissolved in the metal by heating the tin in a stream of hydrogen.

Krajewski, (1988) [9] described a process for recovering tin from oxide or oxide/sulfide low-grade starting materials and concentrates containing little or relatively low concentrations of tin, by mixing with KOH and decomposing at high temperatures. The decomposed substance is then leached with water, and metallic tin is separated out electrolytically in one or more stages. The electrolyte with reduced tin content is concentrated by evaporation ; impurities being removed and dehydrated. The potassium hydroxide solution recovered is re-used for decomposition.

Ino and Takyuki (1998) [10] studied the method of treating sludge precipitated in process of tin electroplating. By adjusting the filtrate to pH 7.5 to 10, the precipitate with the principal component of tin hydroxide is deposited to recover the tin components contained in the sludge. Furthermore, the recovered tin is refined into the metal tin for recycling and used as the electrode for plating .

Recently , Kawamura and Katsuhito (2000) [11] improved the recovery of tin from sludge formed during a halogen-type electrolytic tin plating b alkalifying the filtrate obtained in the first separation step to deposit tin-containing sludge, re-dissolving the tin-containing sludge in an alkaline solution and electrolytic reduction of the alkaline solution. High purity metallic tin is recovered from sludge at a high yield .

Scott (1997) [12] indicated that the recovery of copper, lead and tin from scrap printed circuit boards (PCBs) has been achieved using a combination of leaching and electrodeposition. For recovery of tin, he added hydrochloric acid to convert tin to metastannic acid (H_2SnCI_6) . Preliminary current-potential linear sweep voltammetry confirmed tin deposit from a solution of 0.01 M H_2SnCI_6 + 1.5 M HCI . The tin deposit obtained was adherent to the stainless steel cathode at lower current densities. At the higher current density, the morphology of the deposit appeared spongy due mainly to hydrogen evolution, which occurred when the tin concentration fall and current densities were greater than the limiting current density. Overall current efficiencies for tin deposition were high and typically greater than 95 %.

Experimental Work

Chemicals

The following chemicals were used for the preparation of tin metal :

1- Stannous chloride, $SnCl_2.H_2O$ of 95 % purity, (BDH) .
2- Aluminum powder of 88.7 % purity and 53 µm particle size.
3- Industrial stannous chloride of 95 % purity.

Experimental Apparatus

The experimental work for preparation of tin metal through reduction and smelting steps incorporates many instruments, these are as follows:

- Magnetic stirrer - hot plate, Type gallenkamp, England.
- Reaction container made of Pyrex glass of 2 liters capacity, Germany.
- Cooling coils of Pyrex glass type, of 30mm I. D. and total length of 80 mm while the outside diameter is 7 mm.
- Mercury thermometer ranging from 0°C to 150 °C, England.
- Chiller system Type HAAKE GH, 001- 4551, Germany .
- pH meter, Type METRO HM, 686 TIT- Processor, Swiss.
- Drying cabinet for drying tin agglomerates after reduction step at working temperature of 100 °C. This is lasted for 2 hours. The drying cabinet of Type VOUTOMTIC 50, Bicasa, Italy.
- Furnace for smelting the agglomerates ,Type Naberthenn, Model L08/14,Germany.
- Sieve shaker of Type RETSCH, Germany and sieve of 150 µm aperture size was used to separate the metal tin from the slag material. The period of sieving is lasted for 2 hours.
- Electronic Balance, Type Shimadzu , LIBROR AEU-210, of four digits accuracy, Japan.
- Flame atomic absorption spectrophotometer used for the determination of tin after reduction step and for determination of impurities. in the remaining slag, Shimadzu, model AA- 670 , Japan .
- X-ray spectrophotometer used to identify the purity of the produced tin and the constituents of the agglomerates.

- Electron microscope used for imaging the crystal structure of tin metal after smelting stage, Olympus PMG3,TOYO, Japan.
- Diffraction Scanning Calorimetry (DSC) of Themohake, model 6100, Japan, used to identify the existence of tin in the agglomerates and to check the purity of tin metal after smelting step, Measurements are conducted under nitrogen atmosphere, heating rate= 10 °C /minute.

Experimental Procedure:

Preliminary Experiments:

Through these experiments, pH of the aqueous solution, time for introducing aluminum powder and the excess ratio of aluminum are examined at reaction temperature of 45 °C, using 10 % concentration of stannous chloride and lasting the time of reduction up to 3.5 hour. Fifteen experiments were conducted. These experiments are conducted at following ranges:

1- pH value of aqueous solution is ranged between 0.5 to 1.38. This is controlled by the addition of 1.6M of HC1 to the mixture of the reaction.
2- Time for addition of aluminum powder is ranged between instantaneous addition to 75 minutes.
3- Excess ratio of aluminum powder is ranged between 0 to 100 %.

Results and Discussion

pH of Solution:

Table (1) illustrates the effect of pH on the conversion of stannous chloride to tin metal (tin agglomerate incorporate different impurities). Data indicate that higher acidity (lower pH value) decreases the production of tin. This was attributed to two reasons lower solubility of stannous chloride in the aqueous solution and higher hydrogen over potential that decreases the possibility of reducing stannous chloride to tin since the presence of acid encourages the $SnCl_2$ to dissociate otherwise the reaction will be very slow .

Initial Time of Introducing of Aluminum:

Table (2) shows the effect of time of introducing the reducing agent (aluminum powder with amounts equivalent to Sn concentration in solution) to the reaction mixture on reduction of stannous chloride. The time of introducing was varified between spontaneous addition and 60 min. The amount of produced tin in the agglomerates increases with longer time of addition, this was monitored up to 30 minutes then no influences on the quantity of tin was noticed. The lower reduction of stannous chloride at spontaneous addition of the reducing catalyst (aluminum powder) was attributed [to the generation of excessive temperature that lowers the reaction rate and also to hydrogen evolution that shifts to reactions other than reduction of stannous ions] encourages oxidation of the reducing agent] on surface of solution .

Excess Ratio :

Table (3) shows the effect of excess ratio of the reducing agent (aluminum powder) on the amount of the produced tin in the formed agglomerates. The working condition was in the range between no excess and 100 %. The increase in the percentage of aluminum powder causes an increase in the amount of tin in the agglomerates. It was found that best result happens at excess ratio of 90 % beyond that no influence was observed.

Smelting Stage Experiments:

Studying temperature effect of smelting step on the structure of produced tin, clarify dramatically its effect as can be seen in images shown in Figs (1) to (7). In this step , the temperature was raised beyond melting temperature of tin 231.8 °C to achieve best separation from unreacted aluminum with higher purity and productivity.

Fig. (1) shows sample of tin produced in run number 13, when heating rate, temperature and residence time (i.e., time after attaining the designed temperature) were equal to 8.5 °C/min, 232 °C and 1 h , respectively, Herein, the structure contains small approximately flat layers packed tightly together with a high degree of alignment.

Fig (2) shows image of sample of tin that produced in run number 7 , when heating rate, temperature and residence time were equal to 12 °C /min, 288 °C and 0.42 h , respectively, Herein heating begun to produce the disordered grain structure material, besides higher productivity of tin was noticed.

Fig. (3) shows sample image that produced in run number (5) when heating rate, temperature and residence time were equal to 4.75 °C/min, 288 °C and 1.58 h , respectively. As noticed, large crystals of high random packed structure began to form. This structure was made up of curved and faceted layer planes. Seemingly herein the crystal growth was dependent on the growth that results from the movement of whole layers of large fragments rather than individual atom. In this picture, orientations of the individual structural units were oriented randomly and cross-links were sufficiently strong to impede back movement into a more parallel arrangement Besides, even the temperature was same as that shown in Fig (2), the difference in residence time and heating rate had slightly affected tin productivity because higher residence time and low rate of heating guaranties the necessities of crystal existence and increases the productivity of tin.

Fig. (4) illustrates run number (11) when heating rate, temperature and residence time were equal to 8.5 °C/min, 366 °C and 2 h respectively. Tin crystals formed were shown to be in good conditions, with no sign of fiber structure. Herein, the transformation into such crystalline structure indicates the dependence of crystallite growth on the orientation of the individual structural units. Comparison between images in Fig (2) and Fig (4) incorporated with their productivity, clarifies that the existence of fiber structure indicates lower extracting of tin from the agglomerates.

Fig. (5) illustrates run number (12) when the heating rate, temperature and residence time were equal to 2 °C/min, 366 °C and 1 h , respectively. Tin crystals formed were shown to be in good conditions with no sign of fiber structure. Herein, the rate of heating and residence time results in slight increase in size of the crystals.

Fig. (6) shows run number (4) when the heating rate, temperature and residence time were equal to 12 °C/min, 443 °C and 0.42 h , respectively. Tin crystals were in good conditions but an indication of tin oxide was noticed that indicates the influence of temperature as depicted from lower productivity of tin in comparison to the previous two figures.

Fig. (7) shows run number (2) when the heating rate, temperature and residence time were equal to 4.75 °C/min, 443 °C and 1.58 h , respectively. It shows that excessive heating results in higher percentage of tin oxide in the final product hence lower productivity. Also , longer residence time results in pronounced effect on crystal growth. Further the influence of rate of cooling on the crystalline structure showed a significant role in giving the two allotropic forms of tin. Sudden cooling or quenching of melted tin results in changing the ordinary metallic tin into less dense gray (α) tin as clearly noticed in Figs (8) to (10). In Fig. (8), cooling was conducted naturally, which shows the transformation of half of the product from the metallic nature of tin into non-metallic tin in both appearance and properties. The influence of rapid cooling as shown in Fig (9), shows larger than 50% of the resulting tin was in non-metallic type of tin. While, Fig (10) shows the effect of rapid cooling (quenching) where no tin crystals were noticed (i.e., no existence of white tin).

In general, insignificant effect of heating rate on the productivity was determined . Although, it seems that a small decrease in productivity was determined with higher heating rate due to lesser time to extract higher amount of tin or lesser time for the crystalline growth to attain, this comparison was advocated from Figs (4) and (5).

Whereas, temperature has the highest influence on tin productivity, higher than its melting point at which largest dispersion of tin crystals in the agglomerates would occur. Thus, increasing the temperature of smelting higher than melting point increases the kinetic energy for facilitating agglomeration and crystalline growth of tin. Once more, Figs (5) and (6) assure the expectance of crystalline structure that correspond to higher productivity. However, increasing the temperature above 388 °C results in decreasing the productivity due to partial oxidation of tin.

Eventually, the effect of residence time on tin productivity shows the insignificance of time on the productivity of tin. Nevertheless, minor increase in productivity was determined with increasing time.

Thermal analysis was performed on a sample taken after smelting steps. Fig (11) shows a sample of the remaining slag after smelting step where no evidence was noticed over 300 °C for the existence of tin. At the same time Fig (12) shows a sample of the separated tin from the remaining slag where clear evidence was noticed at 232 °C, which assures the high purity of the produced tin.

Conclusions

The following conclusions can be pointed out from the present study :

1-In the reduction step , it was found that the three variables had significant influences on reduction of stannous ions in the presence of the reducing agent .

2- Higher conversion to tin metal was incorporated in the reduction step with higher temperature , concentration and time at lower levels of these variables afterwards , lower conversions were consisted with higher values of temperature , concentration and time .

3-Higher productivity of tin in the smelting step was matched with lower rate of heating and higher temperature and residence time Although temperature of smelting has the significant attributable to the productivity of tin in comparison to the other studied variables .

4-Optimum conditions were predicted and found equal to : in the reduction stage to temperature of 53 °C , concentration stannous chloride of 8.5 wt . % and reduction time of 4.7 h . The optimum conditions of the smelting stage were equal to rate of heating of 2 °C / min , temperature of 388 °C and residence time of 2 h .

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Table (1): Effect of pH on the Production of Tin .

Experiment No.	1	2	3	4	5
HCI Added (ml)	25	17.9	10.8	3.70	0.00
pH of Salt Solution	0.5	0.75	1.0	1.25	1.38
Tin Produced (g)	3.35	8.38	13.49	18.60	21.26
Productivity	0.134	0.34	0.54	0.74	0.85

Table (2): Effect of the addition time of Aluminum Powder on the Production of Tin.

Experiment No.	1	2	3	4	5
Time (min.)	0	15	30	45	60
Tin Produced (g)	10.32	17.67	21.15	21.26	21.27
Productivity	0.41	0.71	0.85	0.85	0.85

Table (3) :Effect of the Excess ratio of Aluminum Powdor on the Production of Tin.

Experiment No.	1	2	3	4	5
Excess ratio *	0	25	50	75	100
Weight of Al Added(g)	3.787	4.734	5.68	6.627	7.574
Tin Produced (g)	7.82	12.12	16.42	19.62	21.3
Productivity	0.31	0.48	0.66	0.78	0.85

* starting weight of $SnCl_2$ = 39.9 g/L

Fig. (1): Effect of smelting conditions on crystal structure of tin, when heating rate, temperature and residence time are equal to 8.5 °C/min, 232 °C and 1 h , respectively.

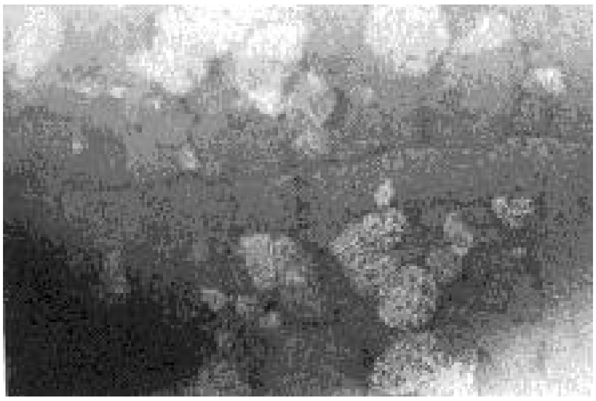

Fig. (2): Effect of smelting conditions on crystal structure of tin, when heating rate, temperature and residence time are equal to 12 °C/min 288 °C and 0.42 h , respectively .

Fig. (3): Effect of smelting conditions on crystal structure of tin, when heating rate, temperature and residence time are equal to 4.75 °C/min, 288 °C and 1.58 h , respectively.

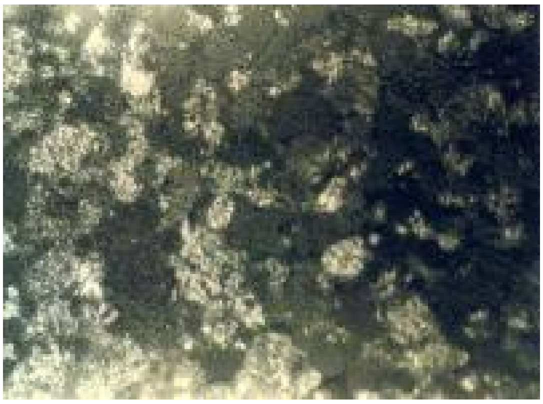

Fig. (4): Effect of smelting conditions on crystal structure of tin, when heating rate, temperature and residence time are equal to 8.5 °C/min , 366 °C and 2 h , respectively.

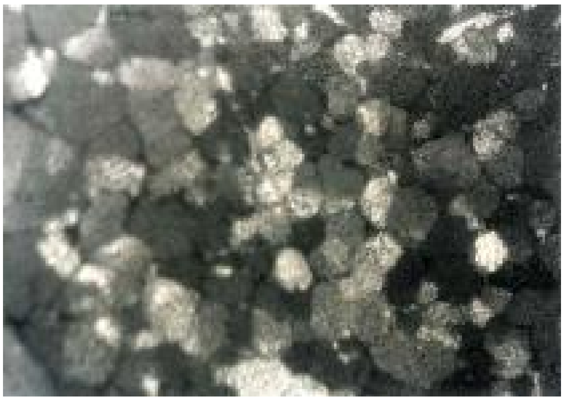

Fig. (5): Effect of smelting conditions on crystal structure of tin , when heating rate, temperature and residence time are equal to 2 °C /min, 366 °C and 1 h , respectively.

Fig. (6): Effect of smelting conditions on crystal structure of tin, when heating rate, temperature and residence time are equal to 12 °C /min, 443 °C and 0.42 h , respectively.

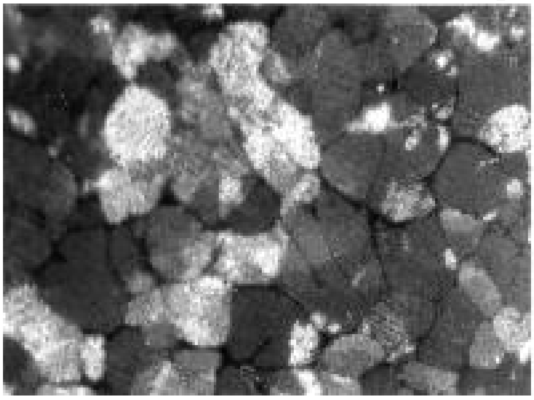

Fig. (7): Effect of smelting conditions on crystal structure of tin, when heating rate, temperature and residence time are equal to 4.75 °C /min, 443 °C and 1.58 h , respectively .

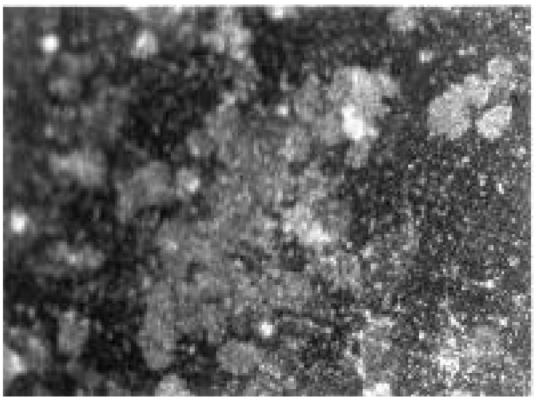

Fig. (8): Effect of cooling rate on the metallic type of tin crystal, natural cooling.

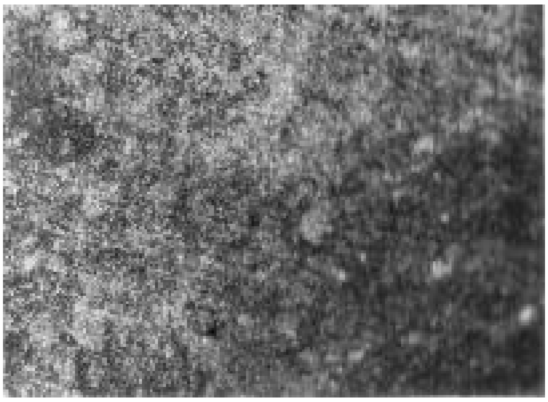

Fig. (9): Effect of rapid cooling shows that 50% of tin was in non-metallic form.

Fig. (10): Effect of quenching on the non-metallic form that satisfied no existence of white tin.

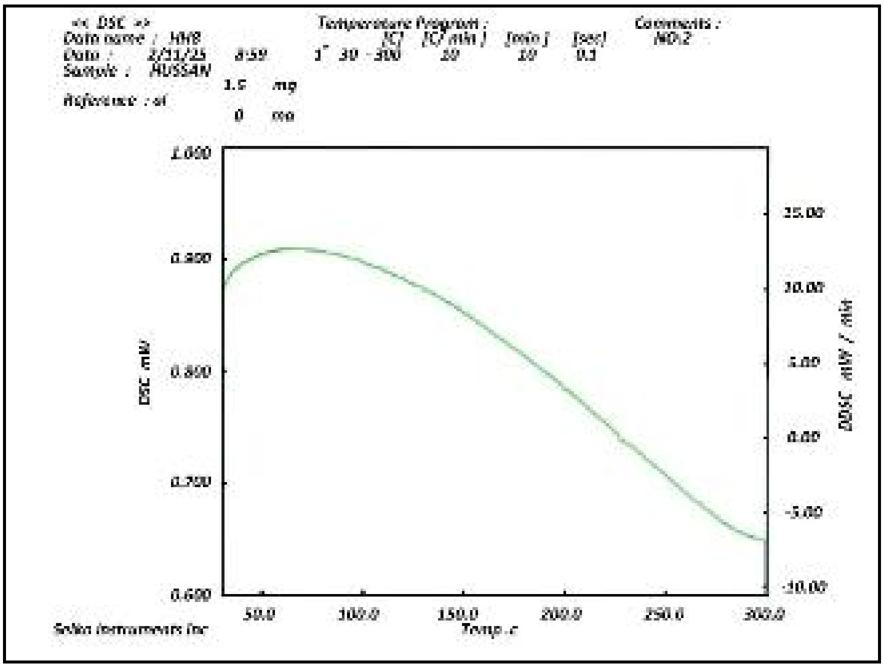

Fig. (11): Thermal analysis for remaining slag confirms no existence of tin.

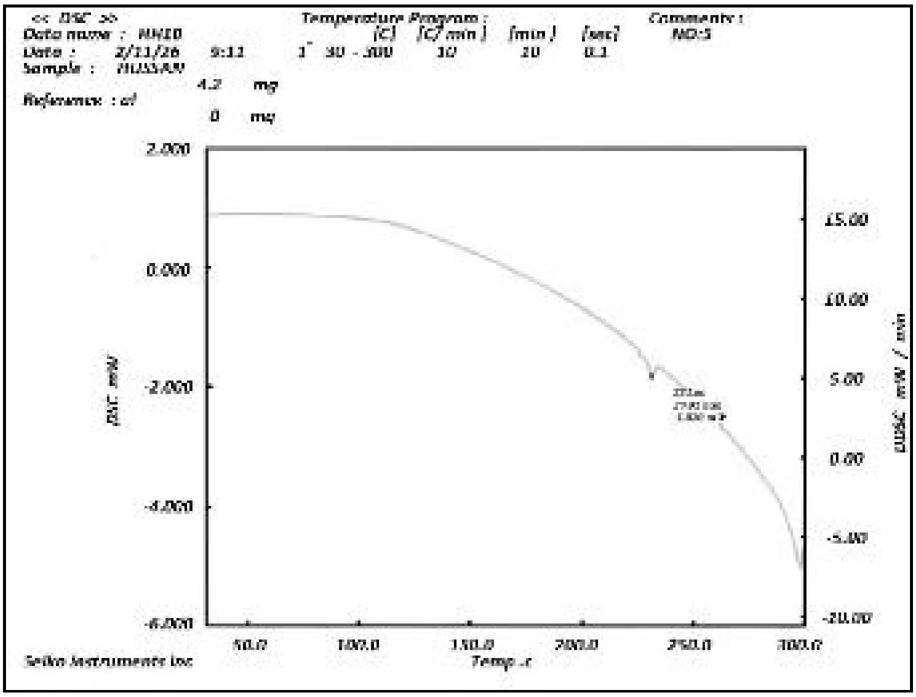

Fig. (12): Thermal analysis for the separated tin from the remaining slag .