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Pyrolysis of synthetic copper telluride in an inert atmosphere

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ABSTRACT
The paper presents the study results of the thermal behavior of synthetic copper telluride in an inert atmosphere at pressures of 92 and 0.07 kPa under isothermal and non-isothermal vacuum-thermal conditions. The thermal analysis results showed that the synthesized copper telluride undergoes polymorphic transformations at 185.7, 259, 318, 350, 470, and 834.5 °C. These transformations were established by early studies and are characteristic of copper tellurides of stoichiometric and non-stoichiometric compositions. It was found that the reduction of the pressure in the system slightly increases the final value of mass loss of the synthetic sample. The X-ray phase analysis results of the residues obtained at constant and increasing temperatures at a pressure of 0.07 kPa showed the absence of the formation of new phases relative to the initial composition. A change in the quantitative ratio of the available phases was found in the direction of an increase in the amount of $Cu_{0.656}Te_{0.344}$ relative to the initial composition with an increase in the process temperature.

Keywords: pyrolysis, tellurium, copper, copper telluride, phase composition, thermal analysis

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Introduction

Due to the depletion of natural resources and, as a consequence, the involvement of poor and substandard raw materials in production, the issue of improving existing technologies for processing copper-containing raw materials remains relevant today [[1], [2], [3], [4], [5]]. At the same time, the final stage of most copper production around the world continues to be copper electrorefining.

A multicomponent product – copper electrolyte sludge containing chalcogenes in the form of their compounds with copper, silver, and gold is produced during the electrorefining of copper [[6], [7], [8]]. First of all, the sludge serves as a raw material to obtain noble metals, besides the products of its processing are selenium and tellurium. There is quite a wide range of methods of sludge processing associated with the complexity and diversity of chemical and phase compositions of sludge. Some of the proposed methods can be found in [[7], [8], [9], [10], [11], [12], [13], [14], [15], and [16]].

Schemes intended to obtain tellurium from copper-electrolyte sludge are a process combining hydro-, pyro-, and electrometallurgy methods [[13], [14], [17], [18]]. A valuable product in this scheme is copper telluride in addition to tellurium of different purity. Copper telluride contains phases of both stoichiometric (Cu_2Te) and non-stoichiometric compositions ($Cu_{2-x}Te$) and includes impurities of

other elements and compounds [[19], [20], [21], [22], [23]]. Some companies prefer to accumulate or sell copper telluride at relatively low prices rather than further separate tellurium and copper. This approach is associated with the presence of technological and technical difficulties due to multistage, significant consumption of reagents, formation of large volumes of wastewater containing heavy metals, etc. Therefore, the development of an economical and environmentally safe process for the extraction of Te and Cu from copper telluride is of great importance for the metallurgical industry.

In this regard, there has been a growing interest of scientists in the issue of the creation of new and improvement of existing technologies for processing copper telluride in recent years.

Traditionally, the tellurium-containing middling product is subjected to oxidative-alkaline leaching with the addition of NaOH at the first stage [[14], [17]]. As a result, tellurium is concentrated in the solution in the form of sodium tellurite (Na_2TeO_3), and copper – in the residue. The solution is further sent for electrolysis, and the copper-containing residue is sent for copper extraction. Liang Xu et al. [22] compared the classical leaching method at atmospheric pressure with their proposed autoclave leaching. The best performance was achieved with autoclave leaching: more than 95 % of tellurium was transferred into solution. The residue contained exclusively crystalline phase Cu_2O that allows it to be returned to copper production. Neutralization of the tellurium-containing solution with sulfuric acid is proposed to precipitate tellurium in the TeO_2 form. The resulting tellurium-containing residue contains 95 % of TeO_2. When H_2O_2 was used in a two-stage oxidative-alkaline leaching process [24], the degree of tellurium recovery was 93 %. The total through the recovery of tellurium was almost 90 %, and the content of TeO_2 in the obtained residue was 96 %. The authors also suggest that the tellurium-containing residue should be sent to the electrolytic production of elemental tellurium.

The most preferable methods well combined with schemes intended to obtain the pure element, are pyrometallurgical ones. According to the dependences of tellurium vapor pressure over solid Cu_2Te specified in studies [[25] and [26]], decomposition of the compound into copper and tellurium is possible only at above 2704 °C [27]. As a consequence, pyrometallurgical methods have not found both application in practice and the development of research in this area.

An effective way to reduce process temperature is to perform the process at low pressure. Besides, the use of a vacuum contributes to the improvement of the personnel's working conditions because the process is performed in hermetically sealed and compact equipment. However, theoretically, the production of tellurium by decomposition of Cu_2Te in real conditions of the vacuum-thermal method is also not possible, due to the low dissociation pressure of liquid copper telluride at the rate of 0.7 kPa at 1780 °C. Nevertheless, we have established the fact of extraction of tellurium from industrial copper telluride in an inert atmosphere (argon) during the development of a pyrometallurgical method of tellurium extraction at low pressure in oxide form [28]. In this regard, it is of interest to study the pyrolysis of copper telluride in an inert atmosphere to determine the presence or absence of the formation of less stable phases during vacuum-thermal processing.

The state diagram of the tellurium-copper system is given in [29] and is characterized by the presence of three compounds of stoichiometric composition: Cu_2Te, Cu_4Te_3, and CuTe. Further studies of the system summarized in [30] showed that the Cu_2Te phase has several polymorphic modifications: A-Cu_2Te, B-Cu_2Te, C-Cu_2Te, D-Cu_2Te, and E-Cu_2Te; whose formation depends on the synthesis temperature of the compound. The presence of peritectoid and eutectoid reactions at below 317 °C resulted in the formation of phases stable at elevated temperatures ($Cu_{13+x}Te_7$, $Cu_{9\pm x}Te_5$, and Cu_9Te_5), as well as phases existing at room temperature as monophase or in alloy with other phases ($Cu_{13+x}Te_7$, $Cu_{9\pm x}Te_5$, Cu_7Te_4, and $Cu_{3-x}Te_2$). In this case, the compound Cu_2Te is the only congruently melting one in the system. Its melting temperature is generally accepted to be 1125 °C.

The analysis of available information has shown that the matter of structural changes in copper telluride close to the composition Cu_2Te at atmospheric pressure up to temperatures of 500-600 °C is well enough studied. At the same time, there is no data on the behavior of telluride at higher temperatures and low pressure.

This paper presents the results of our laboratory study of the thermal behavior of synthetic copper telluride in an inert atmosphere at pressures of 92 and 0.07 kPa under isothermal and non-isothermal vacuum-thermal conditions.

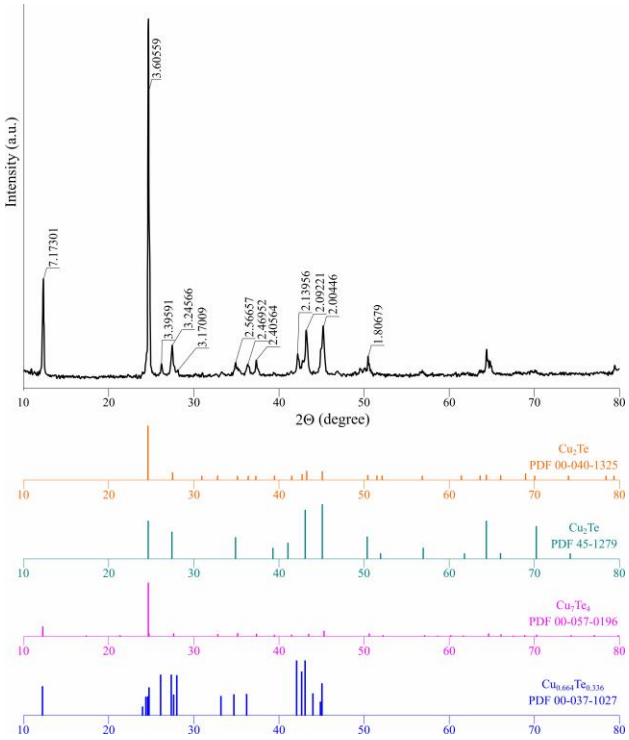


Figure 1 – Phase composition of synthetic copper telluride

Experimental part

Material Synthesis.

Synthetic copper telluride obtained by direct fusion of the initial components in an evacuated quartz ampoule was used in this paper.

Synthesis and production of copper telluride were performed in RT 50/250/ 13 tubular electric furnaces (Nabertherm, Germany) with a B-180 controller. The vacuum system consisting of a 2NVR-5DM UHL4 vacuum rotary vane pump (Vacuummash, Russia) and McLeod manometer was used for ampoules evacuation. Argon (as an inert gas) was used to wash the ampoules. The material of the ampoules was quartz glass.

The initial components for synthetic copper telluride production were electrolyte copper shavings (99.99 %) and elemental tellurium powder (99.98 %) taken in the amounts of 49.92 wt. % of Cu and 50.08 wt. % of Te which corresponds to the stoichiometric composition of the compound Cu_7Te: 66.667 at. % of Cu and 33. 333 at. % of Te. The synthesis temperature was 1200 °C. The heating rate of the suspension to the required temperature was 2 °C/min. The synthesis time was 6 hours. Slow cooling of the obtained alloys in the furnace was performed after the expiration of the specified holding time.

X-ray phase analysis with Bruker D8 Advance diffractometer with Cu-Kα radiation was used to identify the phase composition. The obtained X-ray diffractograms were analyzed using the ICDD PDF-2 (relies on 2020) and literature data [[31], [32]].

The object of the study.

The phase composition of the averaged sample of the obtained copper telluride is shown in Figure 1. The synthesized material is mainly represented by a mixture of copper tellurides with stoichiometric (Cu_2Te) and non-stoichiometric ($Cu_{2-x}Te$) compositions. The phase of Cu_7Te_4 (or $Cu_{1.75}Te$) is the base of the alloy. Besides, there is a phase $Cu_{0.664}Te_{0.336}$ (or $Cu_{1.91}Te$) in the alloy. The heterogeneity of composition can be explained by the fact that the production of homogeneous samples having reproducible stoichiometric composition is complicated since the generally accepted melting point of the compound (1125 °C) exceeds the boiling point of Te (990 °C) [33]. A slight shift and differences in the intensity and shape of the peaks are possible due to the different grain sizes of milled samples, defects in the crystal structure, and the joint presence of several polymorphic modifications of copper telluride [34].

Pyrolysis of the copper telluride.

The experimental part intended to study copper telluride pyrolysis was performed with the use of vacuum units with horizontal and vertical reactor arrangements.

The horizontal unit (Figure 2) consists of a Nabertherm electric furnace with a B-180 controller, a 2NV3-5DM UHL4 vacuum pump, and a quartz reaction vessel where a boat with a suspension of a given mass was placed. A split porcelain condenser required to collect the condensing material was placed on the boat. Chromel-alumel thermocouple (DTPK021-1.2/0.7 thermoelectric converter) with a single-channel TRM1 microprocessor meter-regulator was used to control the temperature in the reaction zone. The pressure was measured with a McLeod manometer with an accuracy of ±10 Pa and an M110 aneroid barometer with an accuracy of ±0.13 kPa.

The methodology of the experiment was as follows. An alundum boat with a copper telluride sample of a given mass was placed in the reactor. The system was sealed and flushed with argon several times. The required pressure in the system was created using a vacuum pump and controlled by a barometer and manometer. When the pressure in the reactor reached the desired value, the retort

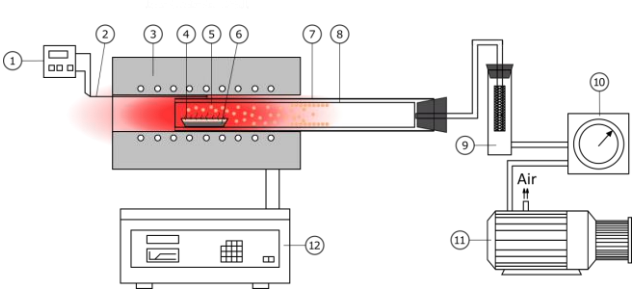
with the sample was transferred into an electric furnace heated to the required temperature so that the sample was in the isothermal zone of the furnace. The reactor was removed from the furnace and cooled under vacuum after the end of the process. The system was then disassembled. The boat with the residue was weighed. The residue was further pulverized and sent for quantitative and qualitative analyses. The extraction degree was calculated from the quantitative analysis based on the difference in tellurium content in the initial sample and the vacuuming residue. The sample was weighted before and after the experiment on PA214C analytical scales (Ohaus-Pioneer) with an accuracy of ±0.1 mg.

The material composition was studied by X-ray fluorescence analysis using an Axios "PANalytical" wave dispersive combined spectrometer.

X-ray phase analysis on a Bruker D8 Advance diffractometer with Cu-Kα emission, and ICDD PDF-2 bar graph reference database (2020) was used to identify the phase composition.

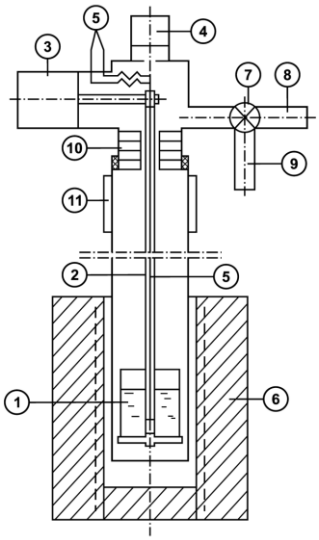
A horizontal unit (Figure 3) was used to determine the mechanism of mass loss during the heating of copper telluride under non-isothermal conditions at a pressure of 0.07 kPa. The apparatus was a retort made of two parts: the lower one was made of alloy steel, placed in the RT 50/250/13 electric furnace, and the upper one was made of heat-resistant glass. A crucible with a sample of copper telluride was mounted on a hollow suspension inside the steel retort. The junction of a platinum and platinum-rhodium thermocouple was placed inside the suspension at the level of the crucible with suspension. The suspension was supported on the scales of the mass loss measurement system placed in the upper part of the retort. The retort parts were articulated by a rubber seal placed outside the high-temperature zone. The lower and upper parts of the retort were separated by screens to reduce heat flow from the high-temperature zone. The upper part of the retort contained the pressure measurement system, channels for gas evacuation and argon filling, and thermocouple end outlets. The mass, pressure, and temperature measurement systems had signal outputs to a multi-point potentiometer that recorded measurements on a chart tape.

A sample of the alloy was placed in a quartz crucible and then mounted on a suspension with a disconnected retort outside the heating zone to experiment. Then the lower part of the retort was



1 – temperature controller in the reaction zone; 2 – control thermocouple; 3 – electric furnace; 4 – boat; 5 – isothermal zone; 6 – suspension; 7 – reactor; 8 – split condenser; 9 – filter; 10 – barometer and manometer; 11 – vacuum pump; 12 – furnace controller

Figure 2 – Scheme of the unit intended to study the pyrolysis process of copper telluride



1 – crucible; 2 – suspension; 3 – weight measurement system; 4 – pressure measurement system; 5 – thermocouple; 6 – electric furnace; 7 – flow valve; 8 – gas evacuation channel; 9 – inert gas supply channel; 10 – screen; 11 – caisson

Figure 3 – Scheme of the unit intended to study the pyrolysis process of copper telluride

articulated with the upper one. Gases were evacuated from the retort by a vacuum pump and filled with argon during studies in an inert atmosphere. Then the lower part of the retort was placed in the isothermal zone of the electric furnace, and the furnace heating was switched on. The mass loss of the material sample and the change in its temperature, as well as the change in pressure in the system, were recorded during the heating process of the furnace synchronously. A leak valve was used to keep the pressure in the system constant. The retort was removed from the furnace at the end of the

process. The curve of mass change over time was used to determine the degree of mass loss of the material at certain time intervals.

A thermal analysis was performed with the use of an STA 449 F3 Jupiter synchronous thermal analysis instrument to find phase and structural transformations occurring in synthetic copper telluride during heating in an inert atmosphere at a pressure of 92 kPa. The furnace space was evacuated before heating, (evacuated volume level ~ 92 %) and then purged with inert gas for 5 minutes. The heating of the sample was performed at a rate of 5 °C/min in an atmosphere of highly purified argon. The total volume of incoming argon was kept within the range of 100-110 ml/min. The results were processed with the use of NETZSCH Proteus software.

Results and Discussion

Several researchers, for example [[35], [36], [37], [38], [39], [40], [41], and [42]], studied the structural changes in copper telluride of various compositions up to temperatures of 500-600 °C. Thus Stevels [35] showed by a combination of thermal and X-ray phase analyses that the compound of Cu_2Te (or $Cu_{2-x}Te$, where $0 \le x \le 0.2$) underwent 4 polymorphic transformations at 190, 260, 310, and 475 °C. It was noted that the compound Cu_7Te_4 (or $Cu_{1.75}Te$) had the following transformation temperatures: 255, 305, and 340 °C. In the paper [36], found by thermal analysis that the compound $Cu_{2-x}Te$ (where $0 < x < 0.16$) underwent structural changes at 172, 305-320, 360, and 425-560 °C. Similar temperatures of polymorphic transformations were obtained for the compound $Cu_{2-x}Te$ (where $x < 0.05$) [37] and for the compound containing 35.2 at. % of Te [38]. At the same time, [39] states that the combination of endothermic effects with maximum development at 180, 305, 345, and 465 °C shows the presence of the compound $Cu_{2-x}Te$ with a homogeneity range of 33.3-34.2 at. % Te, which corresponds to the compound Cu_2Te.

Figure 4 shows the results of the thermal analysis of copper telluride in an argon atmosphere at a pressure of 92 kPa. As it can be seen the DTA curve showed several endothermic effects of varying intensity during heating of the synthesized material at a rate of 7 °C/min. Their extremes occurred at the following temperatures: 185.7, 259.5, 318, 350, 470, 507.8, 834.5, and 948.5 °C. An additional endothermic effect with an extremum was recorded on the dDTA curve at 459.5 °C.

For clarity, the temperatures of phase transitions from various sources, including our study, are summarized in Table 1. It should be noted that the differences in the temperatures of polymorphic transformations are related to the amount of tellurium in the compound, as well as differences in the methods used to obtain the data. The presence of transformation in the interval 255-275 °C, according to [37], indicates the presence of the rhombohedral phase of telluride in the initial compound.

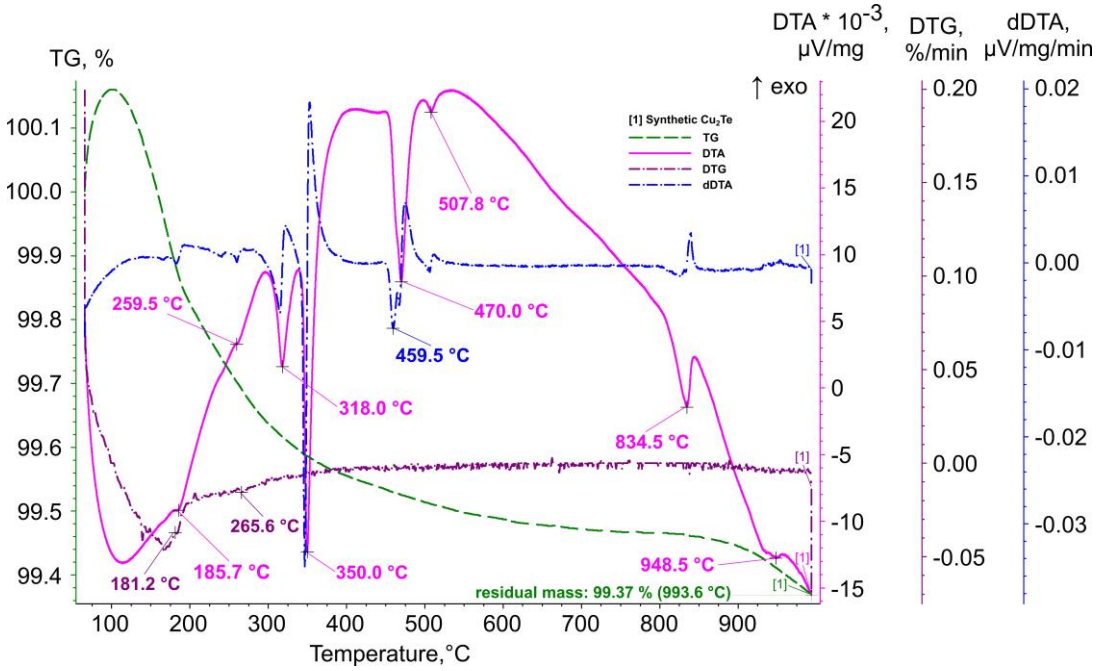


Figure 4 – Thermogram of synthetic copper telluride at atmospheric pressure

Table 1 – Temperatures of polymorphic transformations in Cu_2Te

Source	Temperatures of polymorphic transformations in Cu2Te					
[35]	190	260	310		475	
		255	305	340		
[36]	172		305-320	360	425-560	
[37]	175	275	320	365		575
[38]	190		310	360	460	550
[39]	180		305	345	465	
[42]	160	258	317	360		568
our research	185.7	259	318	350	470	

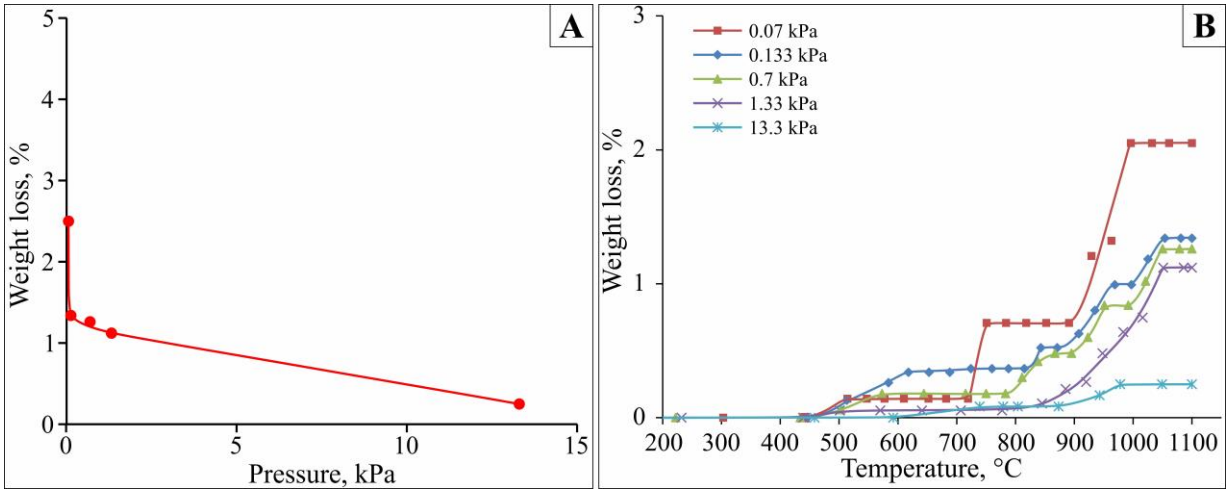


Figure 5 – Dependence of mass loss on pressure (a) and temperature (b)

As can be seen, the data obtained by us are in good agreement with the known values of the temperatures of polymorphic transformations. So, the combination of effects at 185.7, 259, 318, and 470 °C refer to the compound Cu_2Te (or $Cu_{2-x}Te$, where $0 \le x \le 0.2$). At the same time, the presence of an endothermic effect at 350 °C is explained by the presence of non-stoichiometric telluride $Cu_{1.75}Te$. The peak on the dDTA curve at 459 °C probably refers to the melting of unreacted elemental tellurium (450 °C). The endothermic effect with maximum development at 507.8 °C probably reflects the decomposition of copper telluride [40]. the polymorphic transformation ε→ζ mentioned by Hansen in [41] is at 834.5 °C.

The residue obtained after thermal analysis is a molten material, although the generally accepted melting point of Cu_2Te is 1125 °C [13]. Therefore, the effect at 948.5°C can be attributed to the melting of copper telluride with subsequent evaporation of tellurium from it. This conclusion is also supported by information [42] about a lower melting temperature (875-1111 °C).

A slight increase in mass loss was observed (Figure 5a) when the pressure was lowered to 0.07 kPa. The curves of copper telluride mass loss (Figure 5b) at continuous temperature increase up to 1100 °C and low pressure (0.07-13.3 kPa) are characterized by two stages. At the same time, the condensation of tellurium in the cold zone of the reactor can also be visually divided into two stages. The first of them refers to process temperatures of about 500 °C and is characterized by a light grayscale (at a pressure of 0.07-0.7 kPa). The second stage occurs in the range of 700-800 °C and is accompanied by a sharp increase in the amount of condensate in the deposition zone and a change of its color to black. At a pressure of 13.3 kPa, condensation of tellurium is noted at higher temperatures. The vacuumization residue is a sintered material with elemental copper on the surface.

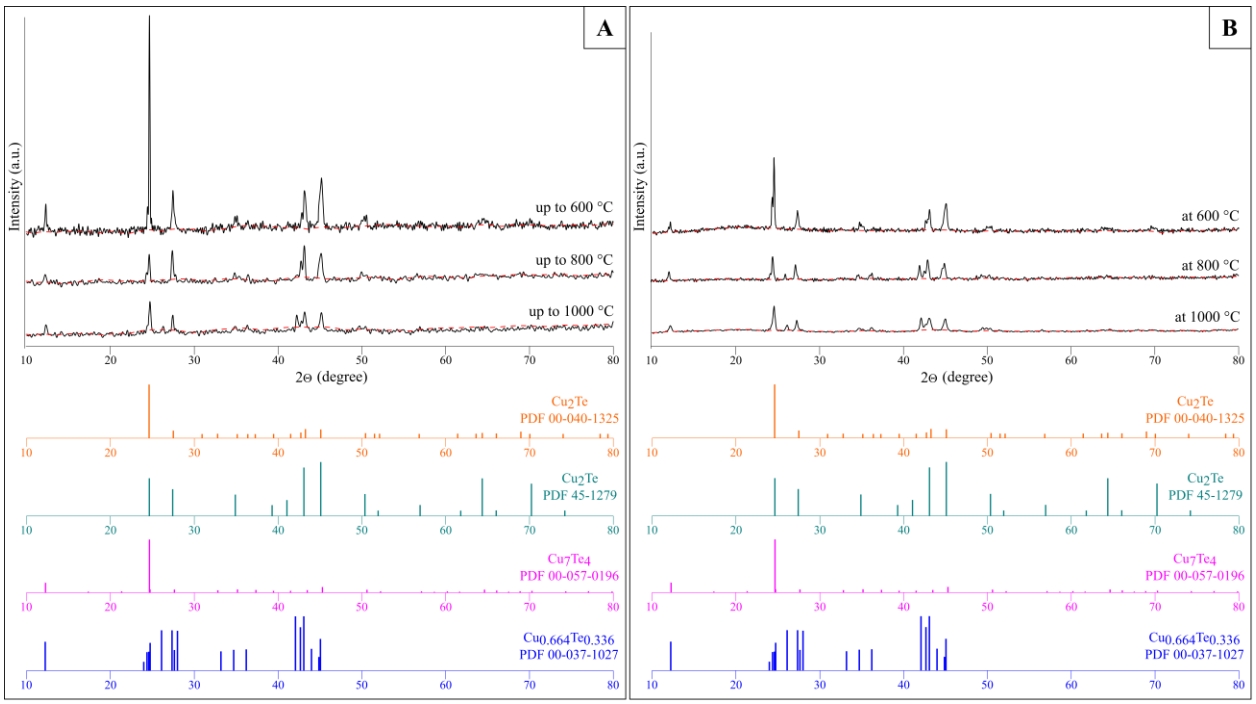


Figure 6 – X-ray radiographs of residues obtained at constant (a) and increasing (b) temperature

Samples intended to analyze possible phase transitions in copper telluride during its heating in vacuum were obtained at a pressure of 0.07 kPa under conditions of constant (600, 800 and 1000 °C) and increasing temperatures (up to 600, 800 and 1000 °C). The X-ray phase analysis results (Figure 6) of the obtained residues showed the absence of formation of new phases relative to the initial composition. At the same time, there are changes in the quantitative ratio of the existing phases in the direction of increase in the amount of $Cu_{0.656}Te_{0.344}$ with increase in the process temperature. It should be noted that the specified phase is predominant with the content up to 86 % in process conditions with heating of samples.

A partial amorphization of the obtained samples, expressed by the presence of an amorphous halo, was also established using X-ray phase analysis. The presence of the latter in the X-ray diffraction patterns is probably related to the partially disordered structure of the material due to polymorphic transitions.

Conclusions

Thus, a laboratory study was performed to investigate the thermal behavior of synthetic copper telluride in an inert atmosphere at pressures of 92 and 0.07 kPa under isothermal and non-isothermal vacuum-thermal conditions.

The results of the thermal analysis showed that the synthesized copper telluride at 185.7, 259, 318, 350, 470, and 834.5 °C undergoes polymorphic transformations established by earlier studies and characteristic for copper tellurides with stoichiometric and non-stoichiometric compositions.

The nonlinear character of the curve of mass loss dependence on temperature was established during the determination of the mechanism of mass loss during the heating of copper telluride in non-isothermal conditions at low pressure. In this case, lowering the pressure in the system insignificantly increases the final value of mass loss of the synthetic sample.

The results of X-ray phase analysis of residues obtained at constant (600, 800, and 1000 °C) and increasing temperatures (up to 600, 800, and 1000 °C) at a pressure of 0.07 kPa showed the absence of formation of new phases relative to the initial composition. Changes in the quantitative ratio of the existing phases towards an increase in the amount of $Cu_{0.656}Te_{0.344}$ were established at the increasing process temperature. Partial amorphization of the obtained samples was also established. It is probably connected with a partially disordered structure of the material due to polymorphic transitions.

The obtained data are theoretical.

Conflicts of interest. The corresponding author declares that there is no conflict of interest.

CRediT author statement. **A. Nitsenko**: Conceptualization, Writing-Original Draft, Methodology, Formal analysis. **X. Linnik**: Writing – review & editing, Investigation. **V. Volodin:** Conceptualization, Methodology. **F. Tuleutay:** Investigation. **N. Bakhytuly:** XRD Investigation.

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Синтетикалық мыс теллуридінің инертті атмосферадағы пиролизі

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Мақала келді: *23 шілде 2024*
Сараптамадан өтті: *16 қыркүйек 2024*
Қабылданды: *26 қыркүйек 2024*

ТҮЙІНДЕМЕ

Жұмыста изотермиялық және изотермиялық емес вакуум-термиялық үрдіс жағдайында инертті атмосферада 92 және 0,07 кПа қысымда синтетикалық мыс теллуридінің жылулық әрекетін зерттеу нәтижелері берілген. Термиялық талдау нәтижелері синтезделген мыс теллуриді 185,7, 259, 318, 350, 470 және 834,5 °С температураларында ерте зерттеулерде анықталғандай стехиометриялық және стехиометриялық емес құрамдағы мыс теллуридіне тән полиморфты өзгерістерге ұшырайтынын көрсетті. Жүйедегі қысымды төмендету синтетикалық үлгінің массалық жоғалуының соңғы мәнін сәл жоғарылататыны анықталды. 0,07 кПа қысымда тұрақты және көтерілетін температурада алынған қалдықтарды рентгендік фазалық талдау нәтижелері бастапқы құрамға қатысты жаңа фазалардың түзілмейтінін көрсетті. Үрдістің температурасының жоғарылауымен бастапқы құрамға қатысты $Cu_{0,656}Te_{0,344}$ мөлшерінің ұлғаюына қарай қолда бар фазалардың сандық қатынасының өзгеруі анықталды.

Түйін сөздер: пиролиз, теллур, мыс, мыс теллуриді, фазалық құрамы, термиялық талдау.

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Пиролиз синтетического теллурида меди в инертной атмосфере

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АННОТАЦИЯ

В работе приведены результаты изучения термического поведения синтетического теллурида меди в инертной атмосфере при давлении 92 и 0,07 кПа в условиях изотермического и неизотермического вакуум-термического процесса. Результаты проведенного термического анализа показали, что синтезированный теллурид меди при температурах 185,7, 259, 318, 350, 470 и 834,5 °С претерпевает полиморфные превращения, установленные ранними исследованиями и характерные для теллуридов меди стехиометрического и нестехиометрического составов. Установлено, что понижение давления в системе незначительно повышает конечное значение потери массы синтетического образца. Результаты рентгенофазового анализа остатков, полученных при постоянной и повышающейся температурах при давлении 0,07 кПа, показали отсутствие образования новых фаз относительно исходного состава. С повышением температуры процесса установлено изменение в количественном соотношении имеющихся фаз в сторону увеличения количества $Cu_{0,656}Te_{0,344}$ относительно исходного состава.

Ключевые слова: пиролиз, теллур, медь, теллурид меди, фазовый состав, термический анализ.

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