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MICROSCOPIC DETERMINATION OF CONTENT OF CHALCOCITE IN MIXTURES WITH GALENA AFTER THERMAL MODIFICATION OF THEIR SURFACES

Summary. Chalcocite heated in air at 470-600^{o}C tends to change its color from grey to red due to cuprite formation. Similar procedure applied to galena, which is grey in color, does not change much its color because pale grey lanarkite is formed. These facts, determined by the X-ray analyses and DTA method. The metods of chalcocite and galena heating were utilized to determine the content of chalcocite in synthetic mixtures with galena. The described method is quite accurate and the error in the chalcocite content was about ±5 per cent points.

MIKROSKOPOWE OKREŚLANIE ZAWARTOŚCI CHALKOZYNU W MIESZANINACH Z GALENĄ PO TERMICZNEJ MODYFIKACJI ICH POWIERZCHNI

Streszczenie. Ogrzewanie chalkozynu w powietrzu w temp. 470-660^{o} pozwala na zmianę jego koloru na czerwony z powodu tworzenia się czerwonego kuprytu. Podobna procedura zastosowana do galeny, która jest szara, nie zmienia jej koloru, gdyż na powierzchni galeny tworzy się jasno-szary lanarkit. Fakty te, określone za pomocą analizy rentgenowskiej oraz termicznej analizy różnicowej wykorzystano do określenia zawartości chalkozynu w modelowych mieszaninach z chalkozynem. Opisana metoda jest bardzo dokładna i pozwala na określenie procentowej zawartości chalkozynu w mieszaninach z galeną z dokładnością do ±5 punktów procentowych.

Introduction

Microscopic observations are important and helpful for both qualitative and quantitative analyses of mineral bulk materials and powdered samples (Bolewski 1988). The microscopic methods coupled with the chemical techniques are able to provide complete information about the investigated mineral system (Tokarski 1953). In some cases, however, the microscopic

method is not reliable and difficult to conduct. This may happen when opaque as well as similar in colour minerals are investigated. A solution to this problem can be a chemical modification of either the bulk or surface of the minerals present in the sample. In this work procedures of modification of surfaces of galena (PbS) and chalcocite (Cu_2S) have been developed to analyse mixtures of these two minerals produced in model flotation tests. Without the chemical modification the microscopic analysis of the galena - chalcocite mixtures was impossible partially due to the similar color, shape and lustre of both minerals and partially due to the limitations imposed by the optics of the microscope. In addition, the methods seem to be much easier, faster and more accurate than the procedure based on preparation of samples in epoxy resins and their polishing to produce smooth and flat surfaces.

Experimental

Materials

Galena from the Trzebionka Mine in Trzebinia (Poland), chalcocite from Lubin-Glogow Copper Deposit, and synthetic chalcocite (an intermediate product in the copper smelting process in Legnica, Poland) were used in the experiments. The minerals were crushed in an agate mortar and screened to get the 0.1 - 0.2 mm size fraction. Mineralogical identification of sulfides was carried out by the X-ray powder diffraction method (XRD) with Siemens D-500 diffractometer utilizing standards of the Joint Committee on Powder Diffraction (JCPD).

Equipment

The samples were analyzed with a MBS-9 stereo microscope. To modify the surface of sulfides the samples were roasted in a muffle furnace or in the furnace and subsequently in a Bunsen burner. Differential thermal analyses were made with Derivatograph Q-500D.

Methods

a) Roasting

For the best accuracy and reproducibility of the of planimetric analysis slightly different methods were used for mixtures consisting of synthetic chalcocite and galena in comparison to samples containing natural galena and natural chalcocite.

For the natural galena and synthetic chalcocite mixtures a ceramic crucible with a thin layer of the galena-chalcocite mixture was placed in a furnace preheated to 470°C. After 10 min. of heating in the furnace the sample was transferred to a test-tube and heated in the oxidizing part of the flame of Bunsen's burner until the sample turned red from the heat. It was important to shake the tube frequently to prevent partial melting and sintering of the particles. Next, the sample was cool down in the test-tube in the air. Then, the sample was washed with 25% aqueous solution of ammonia to remove excess amount of cuprite (which makes the particles sticking together) and finally subjected to the planimetric analysis.

It was found that this method was not well suitable for mixtures containing natural chalcocite and natural galena, therefore another procedure was worked out. In this method the sample was heated only in the furnace at 660°C for 2 min. (instead of heating it in the furnace at 470° and then in a test-tube). Then, the sample was cool down in the crucible in the air and washed with 25% aqueous solution of ammonia and subjected to the planimetric analysis.

b) Planimetric analysis

The content of chalcocite in the sample was determined after immersion a small sample containing about 500 particles in the Canada balm. To estimate the composition of sample the Tokarski planimetric method (Tokarski 1939, 1953, Bolewski 1986) was used. To prepare the sample less than 0.1 g of the material was immersed in a melted drop of the Canada balm placed on a microscopic slide. The drop was mixed well with the particles by stirring with a stainless steal needle. The sample on the microscopic slide was covered with a microscopic glass. Finally, the specimen was inserted under microscope and the population of red particles established by taking into account about 300 particles. The weight percentage of chalcocite in the mixtures with galena was calculated taking into account their densities.

Results and discussion

Roasting the galena-chalcocite mixtures at 470-600°C makes the analysis of the samples quite easy because the chalcocite particles become red while galena remains grey. To find out what reactions take place in the system during roasting fresh and heat-treated galena and chalcocite were subjected to the X-ray analysis. The X-ray results in the form of interplanar distances and the intensity of the peaks for untreated galena and for galena after roasting are shown in Table 1 while the results for chalcocite are given in Table 2.

It results from the X-ray analysis that heating the samples produces cuprite on the surface of chalcocite. Cuprite is red in colour (Bolewski, 1986) and therefore easy visible. Table 2 indicates that heating galena leads to the formation of a layer of lanarkite. Lanarkite, lead oxysulphate ($Pb_2O[SO_4]$), density - 6.92 g/cm^3, (Clark, 1993; CRC Handbook 1986-87) is grey to greenish white or pale yellow and often the layer of this mineral on the heated galena is thin making a distinction between the grey lanarkite and red cuprite very easy.

It is known from literature that different products including Cu_2O, CuO, $CuSO_4$, SO_2, O_2 can be formed from chalcocite during heating (Shultze, 1974). The DTA and TG curves obtained for both natural (Fig.1) and synthetic chalcocites in natural atmosphere (air) revealed that at about 450^o the TG curve increases due to the copper sulfate and some Cu_2O formation (Reimers and Hjelmstad, 1987). A further increase in the temperature leads to a decrease of the weight of the sample most likely due to the red Cu_2O formation (Shultze, 1974). The oxidation of the sample at temperatures greater than 500^{o}C makes them to gain weight apparently because of the CuO formation which is black. These facts also agree with the XDR data for chalcocite shown in Table 2 because no copper sulfate was detected for chalcocite samples roasted between 470 and 660^{o}C. Thus, the roasting temperature from 470^o to 660^o seems to be the most suitable for converting chalcocite to cuprite, and hence making the microscopic distinction between chalcocite and galena possible.

To find out the accuracy of the method leading to the change of the color of chalcocite three galena-chalcocite mixtures were roasted according to the described procedure and subsequently examined with the planimetric Tokarski method. The results of are shown in Tables 3-4. The estimation of the mineralogical composition was made taking into account densities: galena - 7.58 g/cm^3, natural chalcocite - 5.6 g/cm^3, synthetic chalcocite - 5.7 g/cm^3.

It results from Tables 3-4 that the accuracy of the method is quite good and that the error in the either galena or chalcocite content is ±5 per cent points.

Table 1

X-ray data for galena including interplanar distances (d) and intensity of the peaks (I)

Galena from Trzebionka		Galena from Nat Lead Co.*		Galena from Trzebionka afte heating		Galena from Nat Lead Co.*		Lanarkite (synthetic)**	
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
3.42	25	3.43	84	3.72	7				
3.28	4			3.24	18	3.34	84		
2.96	100	2.96	100	3.34	11			3.33	80
2.09	19	2.09	57	3.11	5			3.17	6
1.79	12	1.79	35	2.96	100	2.96	100	2.95	100
1.71	6	1.71	16	2.85	6			2.85	30
1.48	9	1.48	10	2.25	5			2.26	16
1.36	4	1.36	10	2.09	17	2.09	57		
1.33	7	1.33	17	1.89	4			1.90	8
1.21	4	1.21	10	1.79	16	1.79	35		
1.14	4	1.14	6	1.71	7	1.71	16		
				1.64	4			1.64	6
				1.48	19	1.48	10		
				1.36	9	1.36	10		
				1.32	16	1.33	17		
				1.28	3				
				1.21	6	1.21	10		

* -JCPD Standard No. 5-592

** - JCPD Standard No. 18-70

Table 2

XRD data for chalcocite including interplanar distances (d) and intensity of the peaks (I)

Chalcocite (synthetic)		Chalcocite (synthetic.)*		Chalcocite (synthetic) after heating		Chalcocite (synthetic)*		Cuprite (synthetic)**	
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
3.73	43	3.73	20	4.19	32				
3.59	41	3.59	16	3.73	33	3.73	20		
3.31	46	3.31	25	3.55	36	3.59	16		
3.26	45	3.27	25	3.44	37	3.41	6		
3.18	53	3.18	40	3.34	47	3.31	25		
3.16	47	3.15	30	3.27	37	3.27	25		
3.05	45	3.05	20	3.16	34	3.15	30		
2.95	61	2.94	45	3.04	34	3.05	20	3.02	9
2.85	48	2.87	16	2.83	36	2.87	16		
2.72	72	2.72	55	2.74	52	2.76	16		
2.66	46	2.66	25	2.66	34	2.66	25		
2.52	56	2.52	40	2.61	40	2.61	16		
2.47	66	2.47	45	2.52	44	2.52	40		
2.39	74	2.39	85	2.46	100			2.47	100
2.32	56	2.33	40	2.40	48	2.40	85		
2.23	45	2.24	25	2.30	46	2.33	40		
2.21	49	2.21	30	2.26	35	2.24	25		
2.11	40	2.12	12	2.21	36	2.21	30		
2.09	48	2.09	10	2.13	47			2.14	37
1.97	100	1.97	100	1.99	42	2.00	14		
1.95	56	1.95	30	1.97	44	1.98	100		
1.88	84	1.88	90	1.96	41	1.95	30		
1.79	44	1.79	14	1.87	43	1.88	90		
1.70	51	1.70	35	1.78	31	1.79	14		
1.52	39	1.53	25	1.70	38	1.70	35		
				1.51	41			1.51	27
				1.29	35			1.29	17

* JCPD Standard No. 23-961

** JCPD Standard No. 5-667

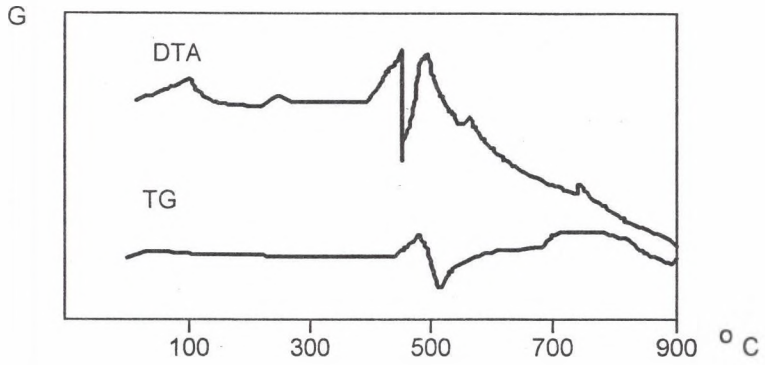

Fig. 1. Differential thermal analyses of natural chalcocite
Rys. 1. Różniczkowa analiza cieplna naturalnego chalkozynu

Table 3

A comparison of composition of galena-chalcocite mixtures determined by the planimetric method after roasting with that for the untreated mixture of know chalcocite content.
Data for mixtures containing natural chalcocite and natural galena

No	Composition of prepared mixtures (in weight percent)		Composition of roasted mixtures determined by planimetric method (in weight percent)	
1.	10 % Cu_2S	90 % PbS	13 % Cu_2S	87 % PbS
2.	50 % Cu_2S	50 % PbS	44 % Cu_2S	56 % PbS
3.	90 % Cu_2S	10 % PbS	93 % Cu_2S	7 % PbS

Conclusions

It results from this study that roasting galena-chalcocite mixtures at 470-660°C for a few minutes at limited access of air to the reaction vessel makes the sample ready for a quick and simple planimetric microscope analysis to determine the content of chalcocite in mixtures with galena and probably with other sulfides.

Table 4

A comparison of composition of galena-chalcocite mixtures determined by the planimetric method after roasting with that for the untreated mixture of know chalcocite content.
Data for mixtures containing synthetic chalcocite and natural galena

No	Composition of prepared mixtures (in weight per cent)		Composition of roasted mixtures determined by planimetric method (in weight per cent)	
1.	10 % Cu_2S	90 % PbS	11 % Cu_2S	89 % PbS
2.	50 % Cu_2S	50 % PbS	48 % Cu_2S	52 % PbS
3.	90 % Cu_2S	10 % PbS	95 % Cu_2S	5 % PbS

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Streszczanie

Ogrzewanie chalkozynu w powietrzu w temp. 470-660° C pozwala na zmianę jego koloru na czerwony z powodu tworzenia się czerwonego kuprytu. Podobna procedura zastosowana do galeny, która jest szara, nie zmienia jej koloru, gdyż na powierzchni galeny tworzy się jasnoszary lanarkit. Fakty te, oznaczone za pomocą analizy rentgenowskiej oraz termicznej analizy różnicowej wykorzystano do określenia zawartości chalkozynu w modelowych mieszaninach z chalkozynem. W celu określenia zawartości chalkozynu małe próbki (~0.1 g) były ogrzewane przez 2 do 10 minut w piecu muflowym w temp. 470-660°C, myte 25% wodnym roztworem amoniaku, suszone i poddawane analizie planimetrycznej. Metoda planimetryczna, znana jako metoda Tokarskiego, polegała na umieszczeniu prażonej próbki w kropli balsamu kanadyjskiego i określeniu za pomocą mikroskopu pracującego w świetle odbitym, procentu czerwonych ziarn, biorąc pod uwagę około 300 ziarn. Opisana metoda jest bardzo dokładna i pozwala na określenie procentowej zawartości chalkozynu w mieszaninach z galeną z dokładnością do ±5 punktów procentowych.