

INVESTIGATION OF THE OXIDATION OF NICCOLITE BY THERMAL ANALYSIS

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ABSTRACT

The interaction of the mineral niccolite with oxygen was studied by using differential thermal analysis (DTA) and thermogravimetry (TG). The course of the oxidation was critically dependent on niccolite particle size and on oxygen partial pressure. It appeared to be governed by the formation and disruption of protective product layers on the surface of the particles. The disruption of the product layers was due to their reaction with volatilized arsenic from the thermal dissociation of nickel arsenides.

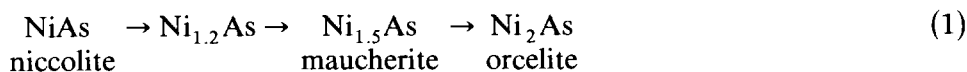
The thermal dissociation behaviour of niccolite was also examined by thermal analysis. It was found to be gradual and could be predicted from the Ni–As phase diagram.

INTRODUCTION

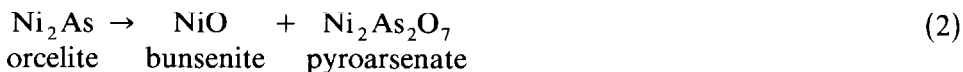
Niccolite (NiAs) occurs widely as a minor constituent in Canadian base metal sulphide ores, particularly in Ni–Co–Ag deposits [1,2], and in some uranium ores [3]. During pyrometallurgical processing of niccolite-bearing concentrates, arsenic volatilizes and may be emitted with the flue gases creating a potential environmental hazard [4,5]. A better understanding of the oxidation of niccolite would be of value in developing control strategies which can reduce arsenic emissions.

A number of investigators have examined nickel arsenide oxidation but there is disagreement about the intermediate phases and the final products. Asensio and Sabatier [6] produced characteristic differential thermal analysis (DTA) curves for niccolite in air and reported that the oxidation of niccolite occurred in steps between 450 and 700°C giving a final product of bunsenite (NiO).

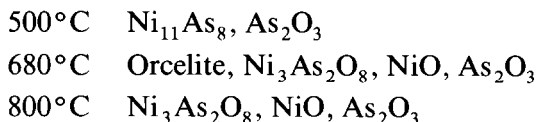
Caillère et al. [7,8] studied the reactions in air of the Ni–As minerals, niccolite, maucherite and orcelite, using DTA and thermogravimetry (TG). They concluded that oxidation occurred in two segments. The first segment was defined by a weight loss due to partial release of arsenic yielding a sequence of nickel arsenides progressively enriched in metal:



The second segment was defined by a weight gain due to fixation of oxygen to form a mixture of oxide and arsenate:



Maurel [9,10] investigated the oxidation of niccolite in air using DTA. A three-step process was observed and the products associated with each step were identified by X-ray diffraction (XRD) and chemical analyses as:



One source of discrepancy among these authors is the uncertainty about Ni-As species. For example: some early investigators [2,11] reported that the formula for maucherite was Ni_3As_2 , while another [12] determined it to be $\text{Ni}_{11}\text{As}_8$; and Maurel [10] referred to the arsenic-poor phase following $\text{Ni}_{11}\text{As}_8$ as orcelite without giving its composition which has been stated as Ni_2As by Caillère et al. [7,8]. Such confusion about intermediate species has since been resolved by Heyding and Calvert [13] and by Yund [1] who examined the equilibrium phase diagram of the Ni-As binary system. In both phase diagram studies it was concluded that: niccolite has a variable composition which can be represented by $\text{Ni}_{1\pm x}\text{As}$; maucherite is a stoichiometric compound with a formula of $\text{Ni}_{11}\text{As}_8$; a phase with the composition Ni_2As may exist only below 250°C and is very similar to the mineral called orcelite; and there is a phase of variable composition represented by $\text{Ni}_{5-x}\text{As}_2$.

In the present work, the oxidation of niccolite was studied in order to resolve the discrepancies concerning the oxidation route and the final products. The thermal dissociation of niccolite in an inert atmosphere and the effects of niccolite particle size and of oxygen partial pressure on the oxidation process were examined. DTA was the main technique employed in this investigation. Concurrent TG/DTA was used to provide complementary information whenever the interpretation of results was inconclusive. X-ray diffraction and spectrochemical analyses were used in the identification of the starting materials and the reaction products.

EXPERIMENTAL

Materials

Two types of niccolite were used in this study: a synthetic material with particle sizes of 74–90 μm (–170 + 200 mesh) and a mineral sample from the Great Slave Lake area, North West Territories, Canada. The niccolite

ore was ground on a lap wheel to remove surface oxides, and then crushed and sized into fractions of 74–105 μm (–150 + 200 mesh), 45–53 μm (–270 + 325 mesh), and < 38 μm (–400 mesh). The identity of both materials was confirmed by XRD analysis to be niccolite and the content of impurities was determined by semi-quantitative spectrochemical analysis to be less than 1%.

Differential thermal analysis

A schematic of the DTA equipment is shown in Fig. 1. The apparatus consisted of a vertically suspended Kanthal-wound tube furnace with controlled heating rates, a stabilized DC microvolt amplifier for the differential-thermocouple signal, and a two-pen Leeds and Northrup Speedomax strip-chart recorder. Pt–Pt 13% Rh thermocouples were used to measure the sample and reference temperatures. An average heating rate of 6–7°C min⁻¹ was employed throughout the present study.

Platinum pans, each with a shallow indentation in the bottom to house the thermojunction, were used to hold the sample and reference materials

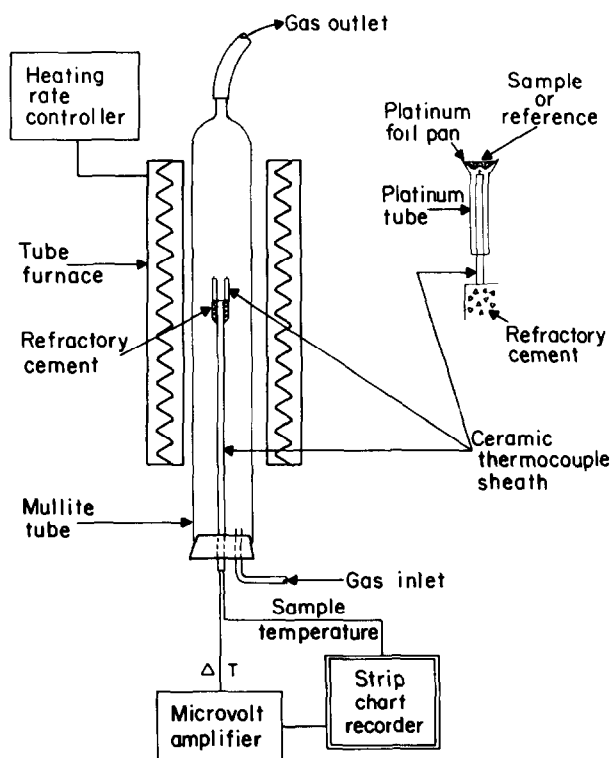


Fig. 1. Assembly for differential thermal analysis.

during oxidation experiments (Fig. 1). Silica crucibles and supports were used, however, for tests in inert atmosphere since platinum is attacked by arsenic in the absence of oxygen.

A series of experiments was carried out to determine the optimum quantity of niccolite to be used in the DTA tests. Sample weights of 0.01 and 0.02 g were found suitable to produce reasonable-sized peaks (recorder sensitivity of 10 μV per inch) with the platinum pan and the silica crucible, respectively. Calcined alumina ($\alpha\text{-Al}_2\text{O}_3$) was employed as the reference material. A layer of alumina (~ 0.003 g) on the bottom of the platinum pan was employed as a heat sink for the highly exothermic reactions. This was not necessary in the case of the silica crucible because of its higher thermal mass.

Oxygen, nitrogen and air were dried by passage through magnesium perchlorate. A total gas flow rate of 100 ml min^{-1} was maintained in all experiments. The initial oxidation tests were carried out in undiluted oxygen. Subsequent tests were carried out in air (21% O_2), and in mixtures of oxygen and nitrogen (50% O_2), and air and nitrogen (5% O_2). The thermal dissociation of niccolite was examined in nitrogen.

Concurrent TG/DTA

Concurrent TG/DTA, performed with a modified DuPont 951 TGA-1090 thermal analysis system [14], was used to identify various reactions on the basis of weight changes as well as thermal effects. Tests were done under flowing argon, air and oxygen and at heating rates of 10 and 20°C min^{-1} . The gases were pre-dried by passage through calcium chloride. The argon (Linde 99.995%) was deoxygenated by passage over copper turnings at 500°C. High sensitivity was ensured by using a thin layer of sample in the silica sample containers.

RESULTS AND DISCUSSION

Thermal dissociation—inert atmosphere

Arsenides generally have high vapour pressures at elevated temperatures [15]. If the partial pressure of arsenic above niccolite is sufficiently high for appreciable dissociation to occur, dissociation can be a critical step during the oxidation process. An understanding of the thermal dissociation behaviour of niccolite is, therefore, useful in determining the factors affecting its oxidation behaviour.

Dissociation of NiAs

DTA diagrams of natural niccolite in a platinum pan and under a flowing nitrogen atmosphere exhibited a slight endothermic drift which started at $\sim 450^\circ\text{C}$. A sudden baseline shift at $\sim 620^\circ\text{C}$ was, however, found to be due to sample pan failure. XRD analysis of the products showed the presence of niccolite and maucherite and, in one case, sperrylite (PtAs_2). These results indicate that niccolite dissociated to maucherite plus arsenic. The arsenic evolved as As_4 vapour [16,17] and reacted with the platinum pan (forming PtAs_2) leading to the pan's disintegration.

Further evidence of dissociation was obtained by heating natural niccolite samples in silica crucibles under a dynamic inert atmosphere up to $700\text{--}750^\circ\text{C}$. XRD analysis of the products revealed again the presence of a mixture of maucherite and niccolite or, in some cases, maucherite alone. Hewitt [2] observed the dissociation of niccolite to maucherite and a vapour in evacuated, sealed tubes at temperatures greater than 450°C . These results suggest that, under inert conditions, thermal dissociation of niccolite may occur according to the following scheme:



In a dynamic system, such as the one used in this investigation, the extent of dissociation is not necessarily determined by the equilibrium of reaction (3). The continuous purging of the gaseous reaction product, arsenic, lowers its partial pressure above the system and hence shifts the equilibrium of the reaction to the right. Thus, even when the equilibrium vapour pressure of As_4 is much less than one atmosphere, dissociation can occur to a significant extent. Evidence of dissociation was observed at temperatures as low as 370°C during TG/DTA tests.

A typical concurrent TG/DTA diagram of synthetic niccolite under argon is shown in Fig. 2. The TG curve exhibits a gradual weight loss starting at $\sim 370^\circ\text{C}$. A white condensate, which was identified by XRD as arsenolite (As_2O_3), was observed on the walls of the gas exit tube. The formation of arsenolite was observed during every test, even when the apparatus had been purged with argon for several hours prior to heating. It may be that the last traces of oxygen were difficult to remove and they subsequently reacted with the evolved arsenic to form arsenolite (As_4O_6) which condensed on the cooler portions of the apparatus. Assuming that the observed weight loss was mainly due to the vaporization of dissociated arsenic, the amount of arsenic remaining in the condensed system at a particular temperature was calculated and the composition of the condensed dissociation product was determined by using the Ni-As phase diagram shown in Fig. 3. This procedure gives an estimate only since the experimental system was not necessarily in equilibrium.

The weight-loss line from Fig. 2 was transposed onto the phase diagram in Fig. 3. The resulting curve indicates that dissociation takes place and

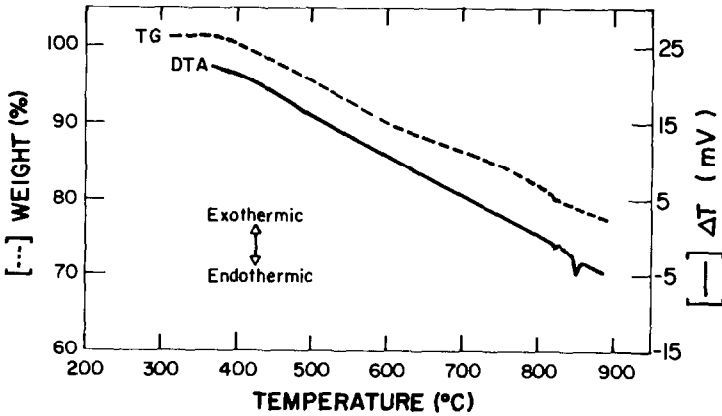


Fig. 2. TG/DTA diagram for synthetic niccolite in argon.

arsenic vaporizes leaving maucherite and niccolite as condensed phases. This is consistent with XRD analysis of samples which attained a weight loss of less than 15% when heated in an inert atmosphere to 750°C. XRD analysis

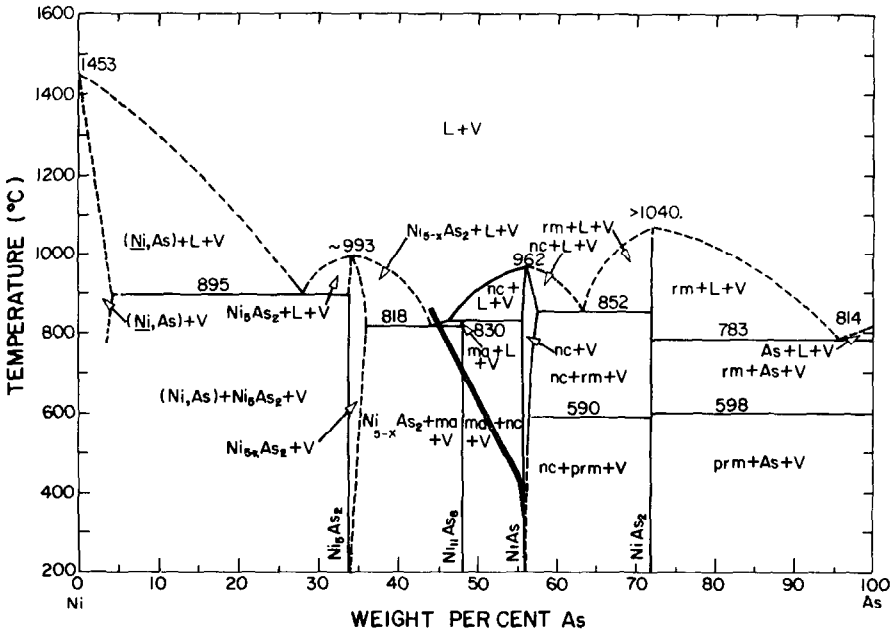


Fig. 3. $T-X$ diagram of the “condensed” system Ni-As [1]. Dashed lines represent earlier work or relations which were not accurately determined. The weight-loss line for the thermal dissociation of niccolite (from Fig. 2) is represented by the thick line. Abbreviations: ma = maucherite; nc = niccolite; rm = rammelsbergite; prm = parammelsbergite; L = liquid; V = vapour.

of a sample which attained a weight loss of 15.5% revealed the presence of maucherite only. The theoretical weight loss associated with reaction (3) is 15.3%.

As shown in Fig. 3, the weight loss continued beyond the maucherite composition indicating further dissociation according to the following equation:



The dissociation of natural niccolite was also examined by TG and the weight loss was found to start about 40°C higher than that for the synthetic material. Furthermore, the rate of weight loss was found to be lower. This may be due to the presence of a layer of oxide at the surface of the mineral particles; an oxide layer would hinder the escape of arsenic vapour and hence delay, as well as reduce the rate of, dissociation of the mineral. Other results indicated that the dissociation of the mineral is not affected by the sample particle size within the range 45–105 μm.

Melting phenomena

Examination of the phase diagram (Fig. 3) indicates that a liquid phase will form when the sample temperature is raised above 800°C. Depending on the sample composition, the three likely melting phenomena are: Ni_{5-x}As₂/Ni₁₁As₈ eutectic formation at 818 ± 5°C; incongruent melting of Ni₁₁As₈ at 830 ± 5°C; and complete melting at a liquidus above 818°C.

Evidence of melting transitions is found in the DTA diagram of Fig. 2. There are two small, reproduceable, endothermic peaks at ~ 820°C and ~ 850°C. Melting was confirmed when the cooled products were examined and found to be smooth, rounded, non-porous spheres of metallic appearance. XRD analysis of the metallic product (maximum temperature 950°C, weight loss 21.2%) showed a mixture of Ni₅As₂ and Ni₁₁As₈ which is the expected room temperature composition (44.3 wt% As) after the recorded weight loss.

It should be noted that for every test where melting occurred, a trace amount of green powder was also present in the sample container. It is postulated that a trace amount of oxygen was available during heating (as evidenced by the arsenolite formation), that a trace amount of niccolite was therefore oxidized, and that the oxidation product transformed at high temperatures into a bright green arsenate.

Oxidation

In spite of disagreement among the various earlier investigators, there is concurrence that the oxidation of niccolite is complex with intermediate stages between the arsenide and the final products. This stepwise oxidation is illustrated in Fig. 4 (concurrent TG/DTA) which reveals four exothermic

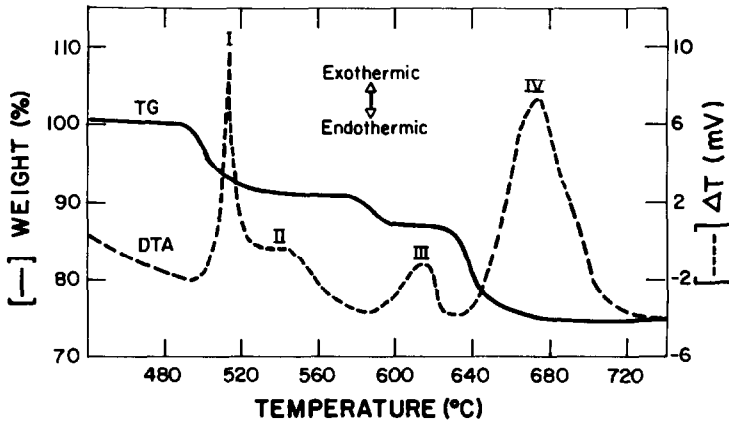


Fig. 4. TG/DTA diagram for natural niccolite (45–53 μm) in pure oxygen.

peaks and three weight-change steps associated with the oxidation of natural niccolite (45–53 μm) in pure oxygen. The shift towards higher temperature of the DTA diagram relative to the TG diagram may be related to the use,

TABLE 1

Identity of solid products of the stepwise oxidation of niccolite

Particle size (μm)	T_{max} ($^{\circ}\text{C}$)	No. of DTA peaks	Identification by XRD	Colour
74–105	522	1	$\text{Ni}_{11}\text{As}_8 + \text{NiAs}$	brown
74–105	585	2	$\text{Ni}_{11}\text{As}_8$	brown
74–105	627	3	$\text{Ni}_{11}\text{As}_8$	brown
74–105	755	4	$\text{NiO} + \text{unidentified}$	brown
45– 53	519	1	$\text{NiAs} + \text{Ni}_{11}\text{As}_8$	brown
45– 53	575	2	$\text{Ni}_{11}\text{As}_8$	brown
45– 53	615	3	$\text{Ni}_{11}\text{As}_8 + \text{trace NiAs}$	brown
45– 53	780	4	$\text{NiO} + \text{unidentified}$	brown
< 38	512	1	NiAs	brown
< 38	572	2	$\text{NiAs} + \text{Ni}_{11}\text{As}_8$	brown
< 38 ^a	635	3 ^b	$\text{Al}_2\text{O}_3 + \text{Ni}_{11}\text{As}_8 + \text{trace Ni}_5\text{As}_2$	grey
< 38	630	3 ^c	powder: $\text{NiO} + 3:1$ core: $\text{Ni}_5\text{As}_2 + \text{NiO}$	green brown
< 38	715	4 ^c	$\text{NiO} + \text{unidentified}$	green
< 38 ^a	740	4	$\text{Al}_2\text{O}_3 + \text{NiO} + \text{unidentified}$	grey

^a Diluted with Al_2O_3 .

^b Fourth peak initiated.

^c Runaway reaction at third peak.

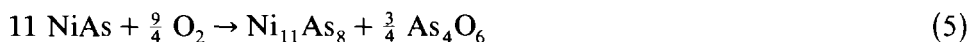
^d 3 : 1 = xanthiosite ($3\text{NiO} \cdot \text{As}_2\text{O}_5$).

as a sample container, of a quartz crucible for the DTA sample and a quartz pan for the TG sample. In order to identify the intermediate phases and the final products, the experiments were stopped at the end of each DTA peak and the samples were examined by XRD. The results are presented in Table 1.

Interpretation of TG / DTA diagrams

The thermal activities which appear on the DTA diagram and the corresponding weight changes on the TG diagram of Fig. 4 may be explained as follows.

Peak I. The oxidation of niccolite in pure oxygen started around 490°C and resulted in a substantial exothermic peak and a weight loss of 9%. XRD results (Table 1) indicated that the reaction product associated with peak I is Ni₁₁As₈ and hence the reaction, at this stage, may be represented by the following equation:



It is possible that reaction (5) occurs via a two-step mechanism which consists of an endothermic thermal dissociation of NiAs (reaction (3)) and a highly exothermic reaction between As₄ and O₂ to form As₄O₆ vapour. These overlapping steps would result in an exothermic DTA peak accompanied by a weight loss due to the evolution of arsenic. The recorded weight loss of 9% indicated that reaction (5) does not reach completion (theoretical weight loss is 15.3%).

Peak II. The second stage of oxidation was found to overlap with the first stage producing an irregular shoulder around 540°C. Upon closer examination of the later part of the weight loss associated with peak I, a change in the rate of weight loss can be seen on the TG diagram. The second stage may be caused by some surface oxidation of maucherite with the formation of an impervious oxide product layer which separates the arsenic product from the oxygen atmosphere, preventing further reaction. However, the XRD results (limit of detection is 4–5%) identified the product of the second stage as Ni₁₁As₈ only (Table 1) which indicated that any oxide surface layer is relatively thin.

Peak III. The third stage of oxidation began around 590°C as indicated by the weight loss and the exothermic peak on the diagram in Fig. 4. The weight loss and associated exothermic effect may be initiated by the rupturing of the impervious product layer (formed in the second stage) due to reaction of the layer with trapped arsenic. A fresh mineral surface would then be exposed to oxygen and reaction (5) would resume. XRD results, as shown in Table 1, identified the product of this stage as maucherite. These results are similar to those for the second stage.

It should be noted that in one DTA test, heating was stopped after the second peak and the differential temperature was monitored during cooling

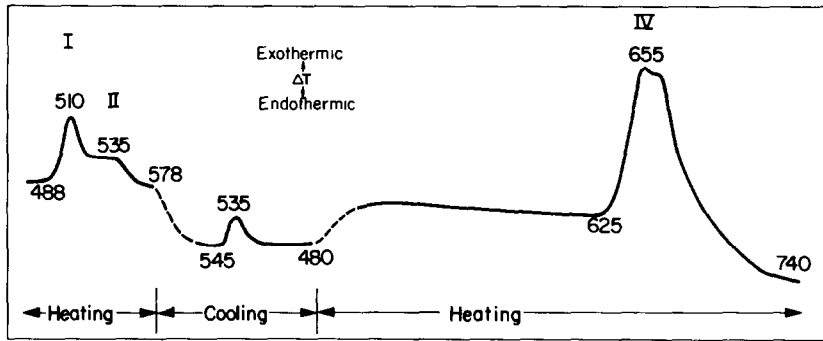


Fig. 5. DTA diagram for natural niccolite (45–53 μm) heat-cycled in pure oxygen.

to $\sim 475^\circ\text{C}$ and during subsequent reheating. The DTA diagram is shown in Fig. 5. On cooling, an exothermic peak appeared at $\sim 535^\circ\text{C}$ and on reheating, peak III at 600°C was absent. These results indicate that during cooling, the impervious layer on the surface of the particles is disrupted and reaction (5) reaches completion. This disruption may be caused by spalling or cracking of the impervious layer due to shrinkage during cooling.

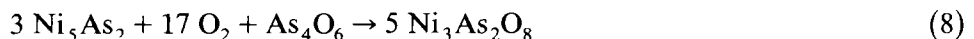
Peak IV. The final stage of oxidation started around 635°C and resulted in a weight loss and a broad DTA peak with noticeable shoulders indicating overlapping reactions.

A DTA test was interrupted just after the initiation of the fourth peak. The products were identified by XRD as $\text{Ni}_{11}\text{As}_8$ and a trace of Ni_5As_2 (Table 1). This result indicates that the first reaction to occur is the oxidation of maucherite as follows:



Reaction (6) may occur via a two-step mechanism which consists of the dissociation of maucherite to form Ni_5As_2 plus arsenic vapour (reaction (4)), and the oxidation of the latter.

Evidence of additional reactions comes from one DTA test which resulted in a runaway reaction at the third peak (Table 1). The product consisted of a sintered brown core covered with green powder. The core was identified by XRD as Ni_5As_2 plus NiO and the powder as NiO plus $\text{Ni}_3\text{As}_2\text{O}_8$ (xanthosite). These results indicate further oxidation of the Ni_5As_2 to form NiO and nickel arsenate. The reactions may take place as follows:



The weight loss associated with peak IV was 12%. The theoretical weight loss is 28.8% if the only product is NiO , which suggests that reaction (8), the weight-gaining formation of arsenate, is a major contributor to the reaction sequence.

DTA tests which were terminated around 750°C resulted in a brown product which was identified by XRD as a mixture of NiO and an unidentified material (Table 1). The unidentified product is most likely an arsenate from the NiO/As₂O₅ double oxide system. Taylor and Heyding [18] synthesized compounds having nickel oxide to arsenic pentoxide ratios of 1:1, 2:1, 3:1 and 6:1. They found that prolonged heating (up to 9 days) was required to produce good powder diffraction patterns.

Whenever a runaway reaction occurred or whenever a sample was heated to more than 800°C, the product was either brown and green or entirely green. The products were identified by XRD as mixtures of NiO and one or more of the following: 3:1 arsenate, 6:1 arsenate, unidentified product. These results indicate that higher temperatures promote the formation of brightly coloured arsenates. During some TG/DTA tests which were terminated at 900°C, a gradual weight gain was observed above 700°C. This result suggests that weight-gaining arsenate formation continued after peak IV.

The effect of particle size on oxidation

From the DTA diagrams in Fig. 6, it is obvious that the sizes of the exothermic peaks are dependent on the particle size of the niccolite sample.

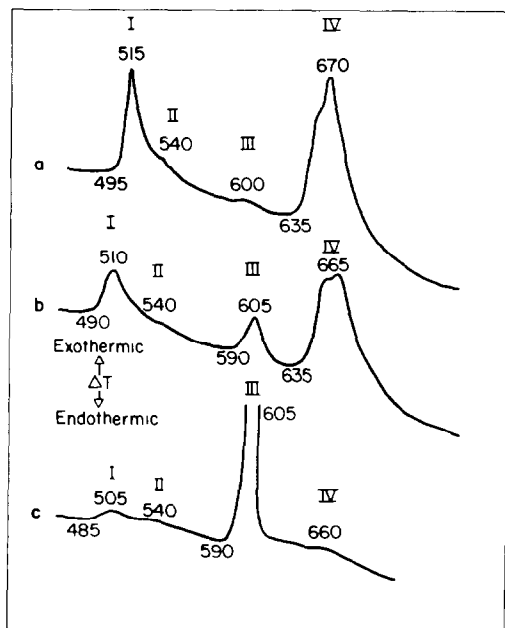


Fig. 6. DTA diagrams for different particle sizes of natural niccolite in pure oxygen: (a) 74–105 μm ; (b) 45–53 μm ; (c) < 38 μm .

For peak I, the exothermic activity decreased with a decrease in particle size. It is suggested that this phenomenon might be related to the interparticle channel size (the finer the material, the smaller the interparticle channels). Oxidation of maucherite to form an arsenate layer (peak II) would involve an increase in volume which might be sufficient to close the interparticle channels associated with the finer material, but not the larger channels in the case of the coarser material. This could confine the reaction to the top layer of the finest sample, resulting in a small DTA peak.

For peak III, the exothermic activity increased with the decrease in particle size illustrating that the sum of peaks I and III represents the completion of reaction (5).

For peak IV, there was a decrease in the exothermic activity for the smallest particle size. This behaviour indicates that, for the smallest particle size (Fig. 6c), peak III is the result of a runaway oxidation reaction. The heat given off by the oxidation of most of the niccolite to maucherite is sufficient to raise the local surface temperature above 635°C and initiate the next reaction. The sample thermocouple registered a transient increase in temperature of 55°C for peak III of Fig. 6c. Localized heating of the particles could be substantially higher.

The effect of oxygen partial pressure on oxidation

Earlier investigators studied oxidation reactions of niccolite in an air atmosphere. In the present work, the oxidation reactions were examined by subjecting the samples, in the thermal analyser, to oxygen/nitrogen gas mixtures of various ratios. It was suspected that the sequence of interdependent oxidation reactions might be dependent on the oxygen partial pressure in the atmosphere and hence on the amount of oxygen available at the reaction site.

There is evidence of this dependency in the DTA diagrams shown in Fig. 7. It is apparent that, as the oxygen partial pressure decreases, peak I increases in height, peak III diminishes, and peaks I, III and IV shift to lower temperatures. The increase in size for peak I can be accounted for by the fact that at lower oxygen partial pressures there is less surface oxidation of $\text{Ni}_{11}\text{As}_8$ to inhibit the volatilization of As_4 . Consequently, reaction (5) approaches completion during the first oxidation stage (peak I) and thus, peak III decreases in size.

The shift in the exothermic peaks is explained in light of Fig. 8 which shows TG diagrams for synthetic niccolite in oxygen, air and argon. The weight-change steps associated with the oxidation of NiAs in Fig. 8 may be explained as follows.

Step A. Niccolite heated in argon exhibited a gradual weight loss starting at ~ 370°C. The weight losses in air and oxygen did not begin until ~ 440°C and ~ 460°C, respectively. Since the weight loss in argon is due to volatilization of As_4 (as a result of dissociation of NiAs), it is postulated that the

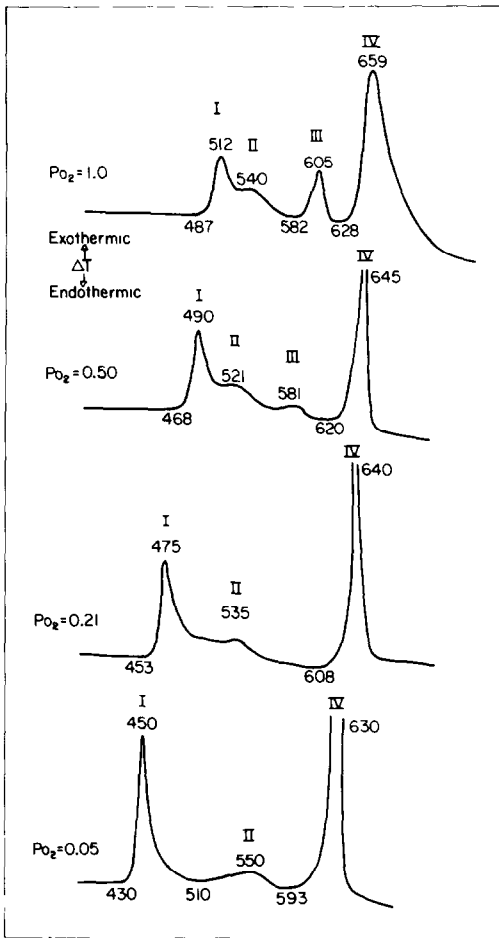


Fig. 7. DTA diagrams for natural niccolite (45–53 μm) in different oxygen partial pressures.

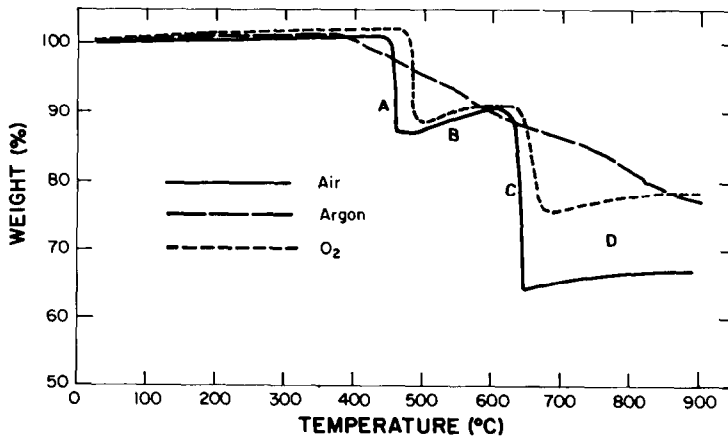


Fig. 8. TG diagrams for synthetic niccolite in oxygen, air and argon.

retardation of weight loss in air or oxygen is due to the formation, during heating, of a thin impervious oxidation layer on the surface of the particles. The eventual rupture of the layer, probably due to reaction with dissociated arsenic, and hence the release and oxidation of the arsenic (DTA peak I), would seem to be the cause of the sharp weight loss. More surface oxidation may occur during heating in pure oxygen, relative to air, resulting in a thicker product layer; this would explain the further delay in the initiation of weight loss for the higher oxygen partial pressure.

To verify the formation of the oxidation layer, a sample of niccolite was heated in oxygen to 450°C (just before the initiation of the first weight loss, Fig. 8) and then cooled to room temperature. After several hours of purging with argon, the sample was reheated in argon to determine whether the volatilization of As_4 was delayed by surface oxidation. Indeed, the weight loss was delayed to ~ 420°C. This result is consistent with the formation of an impervious layer of oxidation product on the surface of the particles during heating in oxygen.

The synthetic NiAs is similar in size to the largest particle size of the natural mineral. The third DTA peak is almost non-existent for this particle size since the oxidation of NiAs to $\text{Ni}_{11}\text{As}_8$ is nearly complete in one step. Hence, weight-loss step A represents completion of reaction (5) and the weight loss associated with peak III in Fig. 4 does not appear in Fig. 8.

Step B. The initial weight loss in air or oxygen was followed by a gradual weight gain which may be associated with the surface oxidation of $\text{Ni}_{11}\text{As}_8$ (as discussed previously for DTA peak II). In Fig. 8, the weight gain does not overlap with weight-loss step A, as was observed with natural niccolite (Fig. 4), since the initial reaction for synthetic NiAs was shifted to a lower temperature (as discussed with respect to dissociation).

Step C. The second weight loss in Fig. 8 (which corresponds to DTA peak IV) was initiated by the dissociation of $\text{Ni}_{11}\text{As}_8$ to Ni_5As_2 and As_4 (reaction (4)). The evolution of As_4 , however, would be inhibited by the impervious layer formed during oxidation of maucherite (step B). The slight delay in the rupturing of the layer and the initiation of the weight loss in oxygen relative to air may be due to the formation of a thicker oxidation layer in oxygen than in air.

As previously discussed, the final oxidation reactions result in the formation of both NiO and nickel arsenate. Fig. 8 clearly illustrates that the greater the oxygen partial pressure, the smaller the weight loss, and hence the larger the amount of arsenate formation relative to NiO formation.

Step D. In Fig. 8, a gradual weight gain is apparent above 700°C. This phenomenon illustrates the continued formation of arsenates at higher temperatures, as previously noted.

Oxidation in air

DTA diagrams for different particle sizes of natural niccolite in air are

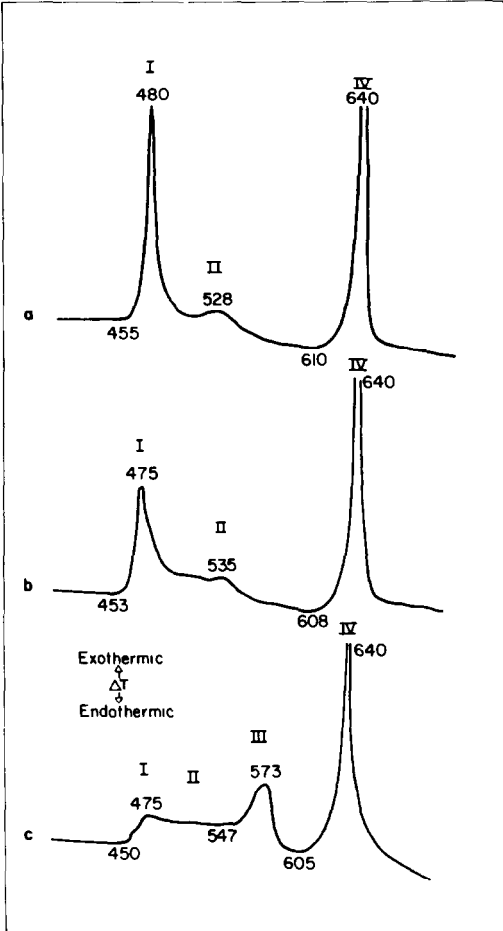


Fig. 9. DTA diagrams for different particle sizes of natural niccolite in air: (a) 74–105 μm ; (b) 45–53 μm ; (c) < 38 μm .

shown in Fig. 9. Comparing this figure with Fig. 6 illustrates the differences between oxidation in air and in oxygen for each particle size. These differences can be explained by the phenomena discussed above.

CONCLUSIONS

The oxidation of niccolite was studied by using differential thermal analysis and thermogravimetry. The principal oxidation reactions were identified as:

- (a) oxidation of NiAs to $\text{Ni}_{11}\text{As}_8$ and As_4O_6 ;
- (b) some oxidation of $\text{Ni}_{11}\text{As}_8$ to an unidentified product (probably a nickel arsenate);

- (c) oxidation of $\text{Ni}_{11}\text{As}_8$ to Ni_5As_2 and As_4O_6 ;
- (d) oxidation of Ni_5As_2 to NiO and As_4O_6 ;
- (e) oxidation of Ni_5As_2 to nickel arsenate.

The thermal dissociation of niccolite in an inert atmosphere was also examined. Appreciable dissociation of niccolite to maucherite and of maucherite to Ni_5As_2 occurred upon heating in a dynamic system. The resulting volatilization of arsenic played an important role in several of the oxidation processes. Arsenic reacted with, and thus disrupted, protective product layers on the surface of the particles and, therefore, allowed oxidation to proceed.

The effects of niccolite particle size and of oxygen partial pressure on the oxidation of niccolite were studied. The course of oxidation was found to be critically dependent on these factors. The niccolite particle size influenced the degree of oxidation since it determined the size of the interparticle channels which could be blocked by oxidation product formation. The oxygen partial pressure determined the degree of formation of protective product layers which interrupted oxidation reactions; it also determined the degree of formation of nickel arsenate.

The above results imply that a clean removal of arsenic from niccolite-bearing ores in a roasting operation is not readily achievable under either oxidizing or inert conditions. Under oxidizing conditions, NiAs undergoes stepwise oxidation to form a mixture of NiO and nickel arsenate, thus retaining arsenic in the solid product. Under inert conditions, NiAs dissociates sequentially to $\text{Ni}_{11}\text{As}_8$ and Ni_5As_2 but further removal of arsenic is difficult.

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