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MICROWAVE-MONOMODE ENERGY TRANSFER: CHEMICAL SYNTHESES, CRYSTALLOGRAPHIC AND THERMAL PROPERTIES OF MINERAL POWDERS

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ABSTRACT

The high energy transfer produced by means of the electromagnetic beam of microwave apparatus is used more and more to carry out chemical syntheses of numerous chemical compounds. This paper draws particular attention to the formation of metals, viz. copper and silver, and carbides, viz. TaC, carried out at ambient atmosphere. The monomode technique is highly available; in this case, the beam was nearly focused at the center of the test tube containing the powder. The compounds copper hemioxide, copper hemisulfide, tantalum pentoxide, titanium dioxides (anatase and rutile), palladium black powder, and mixed vanadium pentoxide and zirconium dioxide were studied. The crystallographic structures of these materials were systematically determined by X-ray diffraction before and after treatment. A scanning electron micrograph is given for copper metal, and the value of the dielectric absorption parameter is evaluated for silver oxide and sulfide. The measurement of temperature in the case of incandescent red powders is addressed, because it leads to various controversies.

KEYWORDS: A. oxides, D. crystal structure, D. phase transitions, D. thermodynamic properties

INTRODUCTION

Microwave (MW) apparatus are now used by numerous research teams in experimental procedure for chemical syntheses (inorganic, metalloorganic, and organic materials). In the

field of the solid state chemistry, the first MW works were carried out by Ford and Pei, (1), who showed that numerous oxides and sulfides were easily heated by means of a multimode MW oven. More recently, Walkiewicz et al. (2) and Gasgnier et al. (3,4) have reported very important results induced by the energy transfer of either a multimode or a monomode MW. Another technique, MW hydrothermal procedure, has been used by Roy et al. (5,6).

Numerous results are reported in the literature, some of which were obtained using far from conventional experimental procedures. The production of copper metal from the reduction of Cu_2O at ambient atmosphere (or argon) after a treatment of 7 min and for a temperature close to 500 K (measured by pyrometer and thermocouple) (4); the synthesis of pure metals and alloys such as Cu, Ni, Co, and Ag (6), Sn (7), Nd and Cu (8), Fe, Sn, Zn, Pb, and Si (9), Fe (10), and NdFe (11); and the synthesis of carbides such as TiC (12,13), TaC (13), and SiC (14), and of various oxides (2-6,15) are now well known.

Various physical and chemical phenomena occur during MW experiments, often unexpectedly. The redox reactions observed after treatment by means of a monomode MW either at air or under argon are very difficult to explain (3,4). The low temperatures at which the powders turn incandescent red in color at the impact of the electromagnetic beam lead to controversies on the true recorded value of the temperature. The physical parameters which induce these phenomena are difficult to measure. The dielectric absorption parameter ε " and the electrical conductivity σ , for example, are poorly known at the very high frequency scale, not only at low temperature but overall above 473-573 K. Other parameters, such as grain size, shape and abundance of defects of particles, presence of water vapor, and bond mode of the chemical compounds, must also be taken into account. From a thermodynamic point of view, it is possible for the state of the material to be considered as far from a thermodynamic equilibrium. Worner (16) observed that "MW energy stimulates endothemic reactions apparently just as it hastens exothermic reactions" and that "chemical reactions (as smelting) seem to take place at significantly lower temperature than when conventional means of heating are involved."

The aim of this paper is to describe the behavior of various compounds after mixing, or not, with a carbon powder, under the same experimental conditions than those carried out previously (3,4).

EXPERIMENTAL

The experiments were carried out by means of a monomode MW (Prolabo Maxidigest 350, 2.45 GHz) fitted to a computer in order to choose the beam power (300 W) and to record the temperature. Temperature is measured by means of a pyrometer located in front of a mirror positioned under the test tube containing the powder. Such a set-up does not allow direct measurement of the IR radiation. Indeed, one may consider that the powder not heated at the bottom of the tube shields part of the IR radiation and that there is some radiation waste throughout the glass and on the mirror. Therefore, we have used an IR pyrometer (Raytek Thermalert SL 230 BC) which allows measurement at temperatures between 338 and 588 K. It was gauged according to a corrective factor, as a function of the emissivity of a heated powder, by comparison to a volume of methane annealed at the same temperature. In this case, the vibrating stretching of the C–H bonding at 3.43 μ was used. For each thermic equilibrium, the temperature was detected at the same time on a mercury thermometer and the pyrometer gauge. For the experiment the pyrometer was plumbed with the bottom of the test tube.

RESULTS

Copper Hemioxide. The pyrometer has been used to measure the temperature of a Cu_2O powder during the energy transfer of an electromagnetic beam. Two experiments were carried out with 6 and 7 gr of the oxide, respectively. For each experiment, a shift of about 70-80 °C was recorded between the pyrometer (higher temperature) and the MW in situ measurement (lower temperature). The direct measurement indicated a value of 643-663 K just at the moment when the powder turned incandescent red in color. The pyrometer gauge indicated that the temperature increased progressively up to 588 K as a function of time and did not increase abruptly.

Previously (4) it was demonstrated that copper hemioxide powder is reduced to copper metal. This material presents two particular characteristics: first, the copper crystallites present a gray-black metallic aspect and, second, at the impact of the beam they form as a solid spherolite which is very difficult to desegregate into small particles. Scanning electron microscopy observations show that the metal appears compacted and that the surface of the grains is formed by small craters and very small pores. The experiment reported in ref 4 was carried out again, this time adding 0.090 gr of carbon to 2.50 gr of Cu₂O powder. Very quickly (about 20 sec) after the power as turned on, green flashes were observed and bursts heard, and the powder turned incandescent red in color. The mixture was heated up to a maximum of 750 K (measured by means of the monomode in situ pyrometer) after 90 sec (Fig. 1). After cooling down, it was observed that big pieces and small nuggets of metal had formed in the heart of the mixture. At that time, the metal (always very difficult to desegregate) had taken on a bright golden-brown color. A scanning electron microscopy image of the metal so formed is given in Figure 2. Another new characteristic is that all the powder had turned black (whereas previously it remained claret red) and, as revealed by Xray diffraction pattern (XDP), was mainly (about 90%) constituted of fine copper metal particles. It should be noted that the diffraction lines relative to the carbon are not observed on the pattern and, therefore, CO₂ and/or CO probably formed during MW exposure.

Silver Hemioxide. This commercial black powder (Jansen Chimica, purity 99%) is crystallized according to the primitive cubic cell of Ag_2O ($a_p = 0.473$ nm). Five gr of powder were put into a test tube and exposed to the MW beam. Surprisingly, such material cannot be heated at temperatures higher than 328 K. This is explained by a very low value of the absorption coefficient ε ", which is close to zero between 293 and 393 K. The experimental procedure which relates the measurement of this coefficient is described elsewhere (4). One should note that, among all the black powders studied in our laboratory, silver hemioxide is the first which does not absorb the MW beam (3,4).

The first set of experiments showed that the mixture $Ag_2O(5.00 \text{ gr.}) + C(0.03 \text{ gr.})$ cannot be heated at temperatures higher than 351 K. For the second set of experiments, the Ag_2O powder was mixed with carbon graphite according to the three following proportions: (i) 1.90 gr + 0.50 gr, (ii) 4.00 gr + 0.40 gr, and (iii) 2.00 gr + 0.05 gr, respectively. The experimental reactions were equivalent in the three cases: overheating of the carbon particles as soon as the powder was exposed to the beam, then the apparition of green gleams and flashes, and simultaneously strong bursts were heard. After about 70 sec (Fig. 3), a thermal runaway occurred. The recorded temperature reached 600-700 K after about 90 sec. At this point, the material inside the test tube appeared compacted. It was constituted by a gray powder and near spherical granules covered by a white cuticle (0.73 gr. and 1.10 gr. respectively for the third experiment). Compared to the initial weight there was a loss of



FIG. 1

Temperature-time curve of a $Cu_2O + C$ mixture; after 2 min a thermal runaway occurs. At this moment the copper metal is formed.

matter of about 11% for the three experiments. The loss is probably due to the reduction of the oxide and to the formation of CO and/or CO₂. The silver spherolites show the particular aspect of a smelted metal; moreover, they are very hard and do not look like the pure metal, which is rather malleable. For the third set of experiments the following components were put into the test-tube: $Ag_2O/Ag/Ag_2O + C$ (2 gr of each). After a very short exposure to the beam (20 sec), strong bursts were heard and intense green flashes were observed. The experiment was stopped quickly (30 sec later) and at that time the formation of a thin silver film along the tube walls was noted.

XDP relative to the second set of experiments revealed the coexistence of different chemical species, of which Ag metal, Ag₂O, and C were the main constituents. The white cuticle, isolated by scraping it off from the granules, is characterized by a body-centered cubic lattice such as $a_e = 0.444$ nm. It is probably a silver suboxide, which is not known in the literature. Additional diffraction lines with interplanar distances of 0.289, 0.248, 0.212, and 0.166 nm are also observed. They correspond neither to the various known silver oxides (i.e., Ag₂O₃, AgO, Ag₃O₄, Ag₄O₅, and Ag₃O) nor to the silver carbonates reported elsewhere (17-22).

The reduction of Ag_2O by graphite was studied by Ashin et al. (23,24). They reported that the reaction occurs at low temperature (443-463 K) and that it progresses autocatalytically. In this experiment, it appears that MW energy transfer and thermal heating show some similarities. However, Ashin et al. (23) did not indicate the time necessary to form the silver metal or the aspect of the mixture after heating.

Silver Hemisulfide. The black commercial powder (Jansen Chimica, purity 99.9%) is characterized by small particles which crystallized according to the well-known monoclinic structure a = 0.423, b = 0.693 and c = 0.786 nm, and $\beta = 99.60^{\circ}$. MW treatment did not allow us to heat the powder at high temperature (about 400 K). It is difficult to measure the



FIG. 2

Scanning electron micrograph of the so-formed copper metal; one can observe two types of aggregates. (The white segment is equal to 1 micron.)

absorption coefficient because the signal given by this material is included inside a strong background. After 15 min of exposure, XDP only revealed that the intensity of the diffraction lines was reduced about 25%. This indicates that the material is directed toward an amorphous state.

During exposure, we observed green glimmers and heard strong bursts after adding carbon (0.3 gr) to Ag_2S (2 gr). The recorded temperature 70 sec later was close to 643 K (Fig. 4). Just after that observation, a strong SH_2 odor was detected at the open top of the



Temperature-time curve of a $Ag_2O + C$ mixture (rich in C). After 70 sec a thermal runaway occurs. At this moment the silver metal is formed.



Temperature/time of a $Ag_2S + C$ mixture; after 70 sec the temperature reaches a value of 623 K and after 10 min it exceeds 673 K.

tube. However, the weight of the mixture was always equal to 2.2 gr, and XDP revealed that the silver metal was not formed, the lone constituent, Ag_2S , being badly crystallized. One must recall that MW devices are used industrially to desulfurize various sulfide compounds. However, such a phenomenon does not occur, as evident in the case of strontium sulfide (SrS), which cannot be heated at more than 400 K after 10 min of treatment.

For another mixture, 0.5 gr C + 7 gr Ag₂S, the experimental characteristics appeared closely equivalent. However, it was observed that friable aggregates were formed inside the powder. XDP revealed that this powder, as with Ag₂S, was badly crystallized, and that the aggregates were constituted by chemical compounds that, to our knowledge, are not reported elsewhere. From 18 diffraction lines, it was only possible to index a primitive cubic cell with $a_p = 0.498$ nm (8 lines); the remaining diffraction lines were not indexable.

Tantalum Pentoxide. In a previous experiment it was not possible to heat Ta_2O_5 at more than 430 K³. In the case of a mixture such as 0.5 gr C + 0.5 gr Ta_2O_5 , the powder could be heated at about 573 K after 50 sec (Fig. 5) and 813 K after 70 sec. XDP revealed the formation of the compound TaC, well-defined by an intense set of diffraction lines, in coexistence with small amounts of Ta_2O_5 and carbon. It is strongly possible that after heating at higher temperatures, the remaining carbon could react completely with Ta_2O_5 to form a pure TaC material. An identical result was obtained by Binner and Cross (13) in a classical MW oven.

Titanium Dioxides. It was previously demonstrated (3,4) that titanium dioxides rutile and anatase behaved completely different during exposure to the MW beam. Both rutile and anatase were mixed with carbon in an equivalent weight (0.85 gr). The recorded curves for temperature/time have corroborated earlier results: TiO₂ anatase was heated at higher temperature (800 K) than rutile (600 K), during the same time of exposure to the beam (4).



Temperature/time of a $Ta_2O_5 + C$ mixture. After 50 sec the temperature reaches a maximum value of 573 K; at this moment the TaC compound is formed.

We must add that the former powder becomes incandescent red in color. However, in the two cases, XDP revealed, surprisingly, that each mixture was almost amorphous (only one faint diffraction line is observed, and it corresponds to the (101) intense line of the anatase phase). One should note that Binner et al. (12,13) have observed the formation of the crystallized TiC compound. It is possible that the amorphous powder might contain TiC.

Palladium Black Powder. Palladium black powder metal (1.2 gr) was put in the test tube and heated by means of the MW beam. Immediately, green sparks and flashes were observed and strong bursts were heard. They then decreased in intensity and stopped at a recording temperature of about 453 K. The temperature/time curve shows clearly that the heating rate decreased and was directed toward a plateau (Fig. 6). It was observed that the powder volume was reduced by 50% and that its weight was equivalent to the initial one. XDP revealed the coexistence of palladium metal (as a very intense set of diffraction lines) and of PdO (about 10% in weight). The very fine particles of the black powder turned to metallic particles having a non-negligible size.

Mixtures of Vanadium Pentoxide and Zirconium Dioxide. V_2O_5 (orange powder) is very quickly heated to high temperature at the impact of the beam (3). After cooling, an agglomerate of long V_2O_5 monocrystals is formed. These monocrystals remained bright metallic after exposure to air for 2 years, whereas in normal conditions they turn garnet red at their surface and finally desegregate as fine powder.

One of the ceramist's problems is to obtain colored pigments. It is possible to form yellow pigments by mixing V_2O_5 and ZrO_2 . That was tentatively carried out by mixing 2.5 gr of each oxide. At the impact of the beam the mixture was quickly heated. After 2 min the mixture turned incandescent red in color, and after 10 min the temperature reached a



FIG. 6

Temperature/time curve for black Pd powder. After about 2 min the temperature reaches a maximum value of 523 K and metallic particles are then formed.

maximum value of 545 K. After cooling down, the mixture was again heated from 363 up to 673 K during 5 min. At this point, a thermal runaway occurred and a solid aggregate was formed. After a small part extracted from the heart of this solid was crushed off, XDP showed the coexistence of V_2O_5 , ZrO₂ (monoclinic), and V_2ZrO_7 (primitive cubic with $a_p = 0.876$ nm).

CONCLUSION

Obtaining metals, alloys, and carbides from various compounds treated by means of MW is studied more and more. The more prominent results relate that either the reactions are strongly activated (rate of synthesis increased by at least an order of magnitude) or the temperatures of reaction are lower than in the case of classical thermodynamic experiments. But, the measurement of temperature is obviously controversial. Indeed, one can think of it as either a surface effect or a volume effect. One can add that when the powder is incandescent red in color, the glass tube does not melt. Moreover, whatever the thermocouple, the temperature measured at the heart of the bulk incandescent material just after that the electromagnetic beam is switched off is always close to the one recorded with the pyrometer.

In our case, the use of a monomode MW oven fitted with low power (P = 300 W) appeared very interesting, because as the electromagnetic beam is nearly focused, the interaction beam/material is enhanced. Therefore, for various materials, the heart of the powder inside the test tube quickly becomes incandescent red in color. Such a phenomenon is difficult to explain; however, it might be correlated to the absorption coefficient and also to the electrical conductivity coefficient (that is the case for the nonpolar carbon element, where eddy currents are observed at the external surface of the powder). Lastly, if obtaining

metals by the way of a reaction of an oxide with graphite appears easy to understand, this is not the case for the synthesis of copper at ambient atmosphere or at very low temperature.

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