JOURNAL OF SOLID STATE CHEMISTRY **136,** 51–55 (1998)
ARTICLE NO. SC977651

Low-Energy Mechanochemistry Formation of Silver and Copper Metals from Hemioxides

H. Szwarc[1]

Laboratoire de Chimie Physique des Matériaux Amorphes, URA D1104, CNRS, Bâtiment 490, Université Paris-Sud, 91405 Orsay, France

and

M. Gasgnier

Laboratoire des Réactions Sélectives sur Support, ICMO, URA 478, CNRS, Bâtiment 410, Université Paris-Sud, 91405 Orsay, France

Received February 13, 1997; in revised form September 30, 1997; accepted October 7, 1997

A number of oxides and mixtures of oxides with or without carbon were ball-milled in homemade stainless steel vessels and the resulting compounds examined by X-ray powder diffraction. The expected trend to amorphization was systematically observed. Moreover, chemical action developed in most cases. Copper oxides tend to be reduced from CuO to Cu_2O and metallic copper forms at the surface of the balls and diffuses a few micrometers within the ball steel as revealed by energy-dispersive X-ray spectroscopy. Mixtures of Ag_2O with carbon lead to small nuggets and square platelets of metallic silver, and YBCO superconductor is decomposed into Y_2O_3, Cu_2O, and some unidentified compounds. The behavior of the balls was observed visually: in the powder, an overall rotating motion takes place, revealing a crushing process instead of the expected smashing one.

INTRODUCTION

Mechanochemistry has been known since "striking flint against pyrites or a spark made by friction while drilling a hole in wood gave man the idea for producing fire" (1) in neolithic times. Recently, it has generated new interest and problems in mechanochemistry, or mechanical activation of solids, have been extensively analyzed by Boldyrev (2) and Butyagin (3). These authors introduce a number of hypotheses to explain different unexpected phenomena that occur during the various experimental procedures that have been used for the past 50 years. Among the many results reported by these authors are the changeover from stable to metastable states of calcite to aragonite (4), α-PbO_2 (orthorhombic) to PbO_2 (tetragonal) (5), and α-Ca_2SiO_4 to γ-Ca_2SiO_4 (6) and the stabilization of monocrystalline or amorphous structures (7). Another reported result is the lowering of synthesis and sintering temperatures. A survey of the recent literature indicates that mechanochemistry is mainly devoted nowadays to forming metallic and hydrogenated alloys. In the field of mineral oxides, most experiments aim to form stabilized zirconia compounds (8). Recently, polymorphic transformations in SnO_2, TiO_2, WO_3, and heavy rare earth sesquioxides (Y_2O_3, Dy_2O_3, Er_2O_3, and Yb_2O_3) were reported by Michel *et al.* (8) and Begin-Colin *et al.* (9). Various suboxide syntheses were carried out by Gaffet *et al.* (10) by adding some metal to higher oxides (for instance, $2Nb_2O_5 + Nb \rightarrow 5NbO_2$). To our knowledge, only Begin-Colin *et al.* (9) point out that after treatment the SnO_2 compound decomposes into SnO_x and metallic β-Sn: the steel balls were coated by a bright layer consisting of a mixture of the two compounds. On the other hand, Gilman (11) examined how strains can trigger chemical reactions. He drew a Walsh energy-level diagram to show the effect of bending shear on the LUMO–HOMO gap in the case of H_3^- for periodic crystals.

To our knowledge, no pure oxide → metal transition has ever been observed in this way.

The aim of the present paper is to describe some very simple experiments and their results. These experiments involve various oxides that are ground with a homemade device that develops far less energy than usual industrial mill apparatuses.

EXPERIMENTAL PROCEDURE

Mineral oxide powders (either pure or as mixtures, or added with Mg or C) were placed inside cylindrical steel containers terminated by a polished hemisphere. Twenty steel balls (weight 4 or 2 g, diameter 11 or 8 mm, respectively) were

---

[1] To whom correspondence should be addressed.

0022-4596/98 $25.00

then added to the ampullae, which were finally closed by means of a nut.

Two types of containers were used. The first (hereafter called A) was 16 cm deep, with a 6-cm inner diameter. The second (hereafter called B) was 8-cm deep with a 4-cm inner diameter, and was homemade. Eight of the latter arranged in two parallel rows were fastened on a special assembly line. Finally, the A and B containers were placed on a shaker (IKA-VIBRAX-VXR) that produced a horizontal ~0.5-cm-amplitude vibrating motion driven by a rotating eccentric gear (~2000 rotations/min).

Mechanical shaking lasted from 1.50 to 90 hr. Even after long grinding times, the temperature of the steel containers had only increased a few degrees. Thus, from a macroscopic point of view, the temperature did not increase over the course of the experiments.

Before and after mechanical treatments, the powders were studied by X-ray diffraction (Guinier–de Wolff Camera II, Enraf-Nonius apparatus, fitted with a quartz monochromator). Such an apparatus allows four patterns to be obtained in parallel; one of them is always dedicated to KBr, which is used as a standard. Complementary energy-dispersive X-ray spectroscopy (EDX) studies were carried out on a Philips 502 scanning electron microscope.

RESULTS

Silver Hemioxide

(a) *Formation of metallic silver.* Black Ag_2O powder was ground in container B, either pure or added with carbon. The starting material is characterized by a primitive cubic structure ($a = 0.473$ nm, space group O_h^4-$Pn3m$). X-ray diffraction patterns (XDP) show that the longer the treatment, the more broadened and weak the initially intense (111) diffraction line becomes. After 60 hr of milling, the pattern transforms into a near halo.

On the other hand, milling a (Ag_2O (2 g) + CH (1 g)) mixture for 10 hr produces bright nuggets and thin bright (unmetallic-like) square platelets whose sides are as long as 2 mm within the black powder.

XDP revealed the coexistence of two diffraction line systems. The first, with blurred and broadened lines, corresponds to Ag_2O. The second, characterized by intense and well-defined lines, is related to metallic Ag. It should be noted that accurate positioning of the KBr (220) line allows one to distinguish the Ag_2O (200) line ($4\theta = 76°$) from the Ag (111) line ($4\theta = 76.20°$). Moreover, the intensity of the Ag_2O (200) line is very weak with respect to the Ag lines, especially the (111) line, which is intense and narrow. The pattern is shown in Fig. 1.

However, platelets and nuggets disappear almost entirely after 7–8 months in air. X-ray measurements show that metallic silver is still everywhere in the powder but five new diffraction lines (at *d*-values of 0.479, 0.462, 0.435, 0.266, and 0.263 nm) are observed: they can possibly be associated with an orthorhombic unit cell but we could not assign them to any previously reported likely silver compounds.

(b) *Formation of an unknown material.* After a (Ag_2O (2.20 g) + C (0.60 g)) mixture was milled for 30 hr, bright nuggets and platelets were formed inside the black powder. XDP exhibit the coexistence of three different diffraction line systems.

Two of the systems appear very weak in intensity with broadened diffraction lines. They belong to Ag_2O and Ag metal. The third system (which is different from a new peak system observed after several months have elapsed since treatment) is characterized by intense and narrow lines and can be easily indexed according to a centered cubic unit cell with $a_c = 0.408$ nm. The pattern shows very intense (110) and (200) lines and moderately intense (211), (220), (310), and (222) lines. One should note that the lattice parameter is equal to that of metallic Ag (which is face-centered cubic). To explain the formation of this material, not previously reported in the literature, we may hypothesize that displacements of Ag atoms from their initial lattice sites take place, leading to a less symmetrical cubic structure for silver. Then, seven Bragg peaks of the XRD pattern correspond to interplanar spacings of the primitive cubic lattice ($a = 0.498$ nm) of Ag_2O_3.

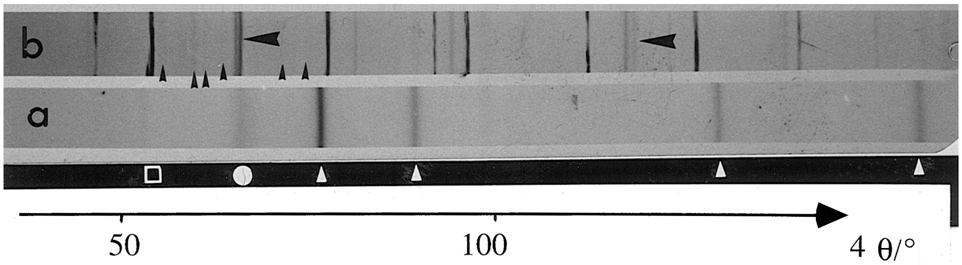

FIG. 1. X-ray diffraction patterns (a) of a (Ag_2O + C) mixture after 10 hr of mechanical treatment, exhibiting lines corresponding to (□) graphite, (○) Ag_2O, and (△) Ag, and (b) of YBCO after 30 hr of treatment: left-pointing arrows, YBCO double lines; up-pointing arrows, lines of products formed during treatment. The very intense lines corespond to KBr internal standard.

Copper Monoxide and Hemioxide

(a) All the following experiments were carried out in B ampullae with the smaller balls. After pure CuO (30 g) was ground for 29 hr, XDP showed diffuse halos, indicating the formation of ill-crystallized Cu_2O. Moreover, the steel balls were coated with a thick gangue that was difficult to remove. After removal of this thick layer, the balls lost their metallic gloss and were coated with a green-black film (probably CuO). On the other hand, pure Cu_2O (5–20 g) ground for 29 hr also became ill-crystallized. Finally, a (Cu_2O (2 g) + C (1 g)) mixture did not yield Cu metal after 39 hr of treatment.

(b) A (CuO (80%) + Cu_2O (20%)) mixture was ground in ampulla A. XDP showed that the amount of Cu_2O increased as the treatment progressed, and after 23 hr the CuO/Cu_2O ratio had become 20/80. The powder was red-brown, and dark brown agglomerates had formed at the bottom of the container. When crushed in a mortar, the latter showed the characteristic Cu_2O red color. The steel balls were covered with a thick black gangue. After removal of this layer, a red-bronze color was observed all over the surface of the balls: such a color is characteristic of copper, and not of oxide. To check this contention, a ball was cut into two parts and studied by EDX. Five chemical analyses were carried out from the surface to a depth of $\sim 10\ \mu m$ (Fig. 2). The Cu content decreases from 4.33% at point 1 to 0.66, 0.65, and 0.64% at points 2, 3, and 4 to 0% at point 5 (below the threshold of detection). In these conditions it can be considered that copper has diffused about 8 μm into the steel ball. One must add that, after several months in air, some of the balls retained the red-bronze color, whereas others turned green-black, suggesting the formation of CuO.

Other Compounds: Oxides and Telluride

To look for other possible phase transitions, a variety of compounds were milled inside ampulla B with the smaller balls.

(a) *YBCO superconductor.* After 30 hr of grinding, the XDP exhibits the coexistence of the orthorhombic YBCO phase with several other compounds (Fig. 1). The former is well defined by intense doublets such as (103) and (013), (006) and (200), and (116) and (213). The latter compounds exhibit two important characteristics: the longer the grinding, the more numerous the diffraction lines are. These lines are either wide and diffuse or very narrow with a medium intensity, indicating the formation of several compounds. The more intense diffraction lines may be assigned to Y_2O_3 and Cu_2O, whereas the other lines cannot be attributed to the well-known binary oxides that generally form when YBCO is synthesized or decomposed.

(b) *Treatments without change.* Some oxides and oxide mixtures were not transformed by ball-milling. For instance, V_2O_5, (V_2O_5 (1.50 g) + ZrO_2 (1.50 g)), and (Nb_2O_5 (2.75 g) + ZrO_2 (2.75 g)) ground for 25, 45 and 90 hr, respectively, do not lead to phase transition or formation of some binary compound. Also, anatase-type TiO_2 was not

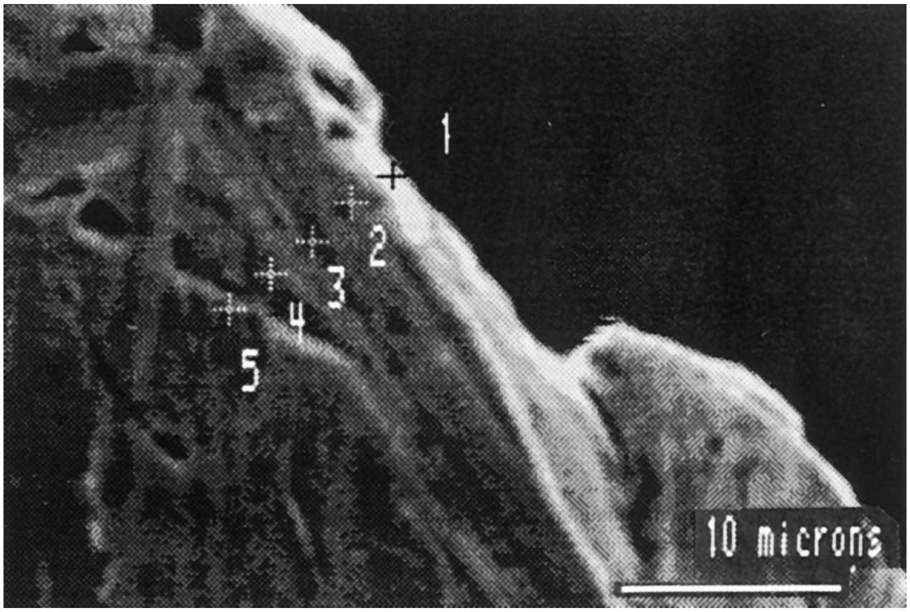

FIG. 2. Photograph of a section of a steel ball after mechanical treatment of a (Cu_2O + CuO) mixture: the crosses indicate the places where energy-dispersive X-ray analysis was performed.

observed after grinding the rutile form for 45 hr (8). In the same way, calcite-type CO_3Ca ground for 17 hr in ampulla A does not yield the aragonite form (stable above 673 K) (4).

(c) *Crystalline → amorphous transition.* MnO_2, Co_3O_4, η-Al_2O_3, and As_2Te_3 were ground 29, 45, 55, and 30 hr, respectively. No phase transition was observed. However, XDP revealed that the more intense diffraction lines became blurred and that the less intense lines totally disappeared.

This suggests a transition stage toward an amorphous state. Indeed, As_2Te_3 lost its brilliant metallic aspect and became dull black-gray.

DISCUSSION AND CONCLUSION

Mechanical Process

To observe the ball motion, two B vessels were covered with a transparent Plexiglas plate with O-ring sealing. One vessel (B1) contained only 20 balls; the other (B2) contained 20 balls and about 5 g of Pb_3O_4. The vibration frequency was set at its maximum value.

In vessel B1, elastic shocks apparently occur between the balls that move in straight lines in between as in the usual description of gas motion. However, the maximum height attained by the balls does not exceed ~1 cm above the maximum level of the balls at rest. During the few minutes we watched the process, no ball reached the Plexiglas cover ~8 cm higher. It should be noted that 20 balls form only one layer on the hemispherical bottom of the container at rest, or a layer of 17 balls plus another layer of 3 balls after shaking, the overall rest height remaining almost the same.

In vessel B2, linear motions no longer exist. As in the previous case, the maximum height attained by the (ball + powder) system does not exceed 1 cm above the rest level and there are no sudden jumps of the balls. There are almost no shocks, and we observed an overall softened slow rotating (either clockwise or anticlockwise) motion of the balls with respect to one another and to the vessel wall. At the same time, the balls undergo a rotating motion in vertical planes which slowly drives them sporadically into and out of the powder. As the down-moving balls completely disappear inside the powder, they probably move closer to the bottom of the vessel. These observations were confirmed by means of a magnifying video camera system.

The powder motion is reminiscent of the fluidification of powdered catalysts in many industrial processes such as petroleum refining.

All in all, the resulting process can be described as crushing instead of smashing. This can be an explanation for the lack of macroscopic temperature increase. In these conditions, the masses of the balls probably play a negligible part in the mechanical action. Compared to other ball-milling devices, ours develops very low energy indeed. The shock frequency either between the balls or with the ampulla walls is low. This induces a low kinetic energy. Moreover, as temperature does not increase over the course of the treatment, it can be concluded that, on the macroscopic scale, ΔP and ΔT are negligible. However, the overall rotating motion of the balls could induce important variations at the mesoscopic scale. In particular, these motions may be very efficient for surface action (as large specific areas are involved) and defect formation. Such changes could favor unexpected chemical reactions.

Furthermore, within a few minutes, in spite of the fact that no ball ever reaches the cover, an impalpable layer of minium accumulates along the sealing O-ring. An experiment with two pieces of cigarette paper suspended at the end of two fine sewing threads reveals no ascentional or pendular motion so there is probably no convection motion acting on the air inside the vessel. A sensible explanation is that the powder, which is rapidly crushed to nanometer size, is ejected from the treated sample by the moving balls. In some cases, at the end of the treatment, there is some powder outside the vessels in spite of the O-rings and screw caps. Thus, the cap tightness cannot be fully trusted and slight air leaks could exist, such that a faint continuous air renewal inside the containers could occur. Chemical reactions due to some dynamical motion should therefore be considered.

During the same time, some balls become spotted with almost circular islands of Pb_3O_4, whose diameters may attain 2 mm.

Aspects of the Powders

The initial powders are more or less coarse. However, all resulting powders exhibit an analogous range of aspects.

After unscrewing the covers of vessels in which (Ag_2O + C), YBCO, Pb_3O_4, or (Cu_2O + CuO) is treated, one can witness a smoke, which can also be observed by hand-shaking the vessel. In particular, the initial powder of CuO, which consists of millimeter-size aggregates, yields plenty of smoke after mechanical treatment. The smoke is evidence for the formation of nanoparticles.

Some very fine powder has generally deposited on the inner side of the closure cap. It can easily be blown off.

Up to the level that, according to the previously described visual observation, corresponds to the maximum height attained by the moving balls, the vessel inner wall and bottom are coated with a ~0.5–1-mm-thick densely agglomerated powder layer. The coating strongly sticks to the steel surface and it is necessary to scrape it with a metallic tool to get rid of it. Usually the final cleaning is performed by means of mechanical milling with microballs.

Above the previous level, some fine powder has also deposited. It is easily blown off. In the lower part of the vessel, the balls are embedded within a mixture of free powder and aggregates which easily break up into fine powder. Granulometric measurements (Coulter Laser LS apparatus) show that the initial Cu_2O powder is made of two grain populations whose diameters lie around 0.8 and 10 mm, respectively. After 24 hr of ball-milling and rapid deaggregation by sonication, only one population with $\sim$5-mm-diameter was observed. Possible explanations are that the finer particles are ejected at the very beginning of the treatment or that they stick on the balls. In any case, this is another example of reducing grain sizes through ball-milling.

The balls themselves are coated with a very sticky millimeter-thick crust. In most cases, it is almost impossible to scrape it off entirely. We have seen that, for ($CuO + Cu_2O$) mixtures, copper has diffused ~ 8 μm deep into the steel balls through a mechanism we do not understand. No analyses were performed for the other mixtures and the reasons for the sticking of the crusts are yet to be understood.

Finally, only one (number of balls)/(amount of powder) ratio was used. Other ratios could lead to quite different results and observations.

Some Final Comments on the Results

We have seen that in most systems the X-ray patterns become blurred, revealing a tendency to amorphization. This of course conforms with the general trend in systems mechanically treated, a trend that is used to generate new amorphous systems (8). It can result in very obvious changes such as the dullness of initially metal-like As_2Te_3.

Several chemical modifications were also observed. In the case of copper oxides, CuO tends to be reduced to Cu_2O. We thought that the addition of carbon to these oxides would favor the reduction process and hence the formation of pure copper, but X-ray measurements revealed no copper in the powder itself. Copper formed only on the surface of the balls, perhaps through an electrochemical mechanism favored by the presence of moisture in the initial mixtures. One may wonder whether such a mechanism can force copper diffusion ~ 8 μm deep into the balls.

The reduction trend also acts in the case of silver hemioxide and it is even more efficient as ($Ag_2O + C$) mixtures transform into pure silver. However, it is difficult to grasp how the almost perfectly square platelets described earlier can form and grow in this ever moving and crushing medium. However, the fact that platelets are found down to the bottom of the vessels can be explained by the up and down rotating motion of the balls. Their disappearance after a few months is also puzzling, all the more so as metallic silver is still present according to X-ray diffraction patterns.

The case of YBCO is another example of chemical action. It has to be stressed that Y_2O_3 and Cu_2O do not usually form thermally from YBCO before 1100 K. Another puzzling fact is the absence of the tetragonal form of this compound, which is generally observed when YBCO is reduced.

Some chemical modifications are reminiscent of the action of microwaves. For instance, under the influence of a focused 2.45-GHz 300-W beam, ($Ag_2O + C$) yields metallic silver, CuO transforms into Cu_2O, and Cu_2O leads to copper (12). There are also some analogies in the YBCO modifications (13). One may wonder whether some common mechanism underlies microwave- and mechanical-driven chemistry.

So far, it is difficult to explain the chemical reactions. It may be assumed that, with carbon, there should be formation of CO_2 and/or CO during oxide reduction. However, because of the dynamic ambient atmosphere, the reduction reactions (from Cu_2O and Ag_2O) and the dissociative reaction (YBCO) cannot be accurately explained. Thus, experiments will be carried out either under a vacuum or under inert gases to detect the possible formation of oxygen during ball-milling and chemical analysis techniques will be used.

ACKNOWLEDGMENTS

The authors are grateful to Dr. E. Gaffet, CNRS, Belfort, France, for valuable discussions and comments.

REFERENCES

1. "Encyclopedia Britannica," Vol. 9, p. 293, 1967.
2. V. V. Boldyrev, *J. Chim. Phys.* **83,** 821 (1986).
3. P. Yu. Butyagin, *Russ. Chem. Rev.* **63,** 965 (1994).
4. J. H. Burns and M. A. Bredig, *J. Chem. Phys.* **25,** 1281 (1956).
5. R. Schrader and A. Weigelt, *Z. Anorg. Allg. Chem.* **372,** 228 (1970).
6. R. Schrader and H. Schumann, *Z. Chem.* **7,** 322 (1967).
7. I. Tsukushi, O. Yamamuro, and H. Suga, *J. Therm. Anal.* **45,** 905 (1995).
8. D. Michel, L. Mazerolles, P. Berthet, and E. Gaffet, *Eur. J. Solid State Inorg. Chem.* **32,** 673 (1995).
9. S. Begin-Colin, F. Wolf, and G. Le Caër, *J. Phys. III* **7,** 473 (1997).
10. E. Gaffet, D. Michel, L. Mazerolles, and P. Berthet, *Mater. Sci. Forum* **235–238,** 103 (1997).
11. J. J. Gilman, *Science* **274,** 65 (1996).
12. M. Gasgnier, A. Petit, H. Jullien, and A. Loupy, *Mater. Res. Bull.* **31,** 1101 (1996).
13. M. Gasgnier, unpublished results.