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The "Bent Copper Tube": A New Inexpensive and Convenient Reactor for Fluorides of Metals in Suboxidation States

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Bent copper tubes have been successfully used for solid state reactions at high temperature, under nonoxidizing atmosphere. They provide an inexpensive and convenient alternative to gold and platinum for reactions between fluorides, and do not reduce some elements such as tin(II), as nickel does. Solid state NMR studies of fast fluoride ion conductors $Pb_{1-x}Sn_xF_2$ prepared in copper tubes show that contamination by paramagnetic Cu^{2+} is minimal. ^{119}Sn Mössbauer spectroscopy is used as a sensitive probe for the formation of SnO_2, and indicates that no oxygen leaked in the tubes. Like any reaction carried out in a sealed container, those resulting in a gas being evolved and/or highly exothermic reactions can lead to explosions and thus must be avoided. An attempt to synthesize TiI_4 in a sealed copper tube is described, as an example of a dangerous uncontrollable reaction by this method.

Introduction

Solid state reactions between intimately mixed powdered reagents are often carried out in open containers, under air for oxides or under flow of an inert or reactive gas as appropriate. When an inert atmosphere is required or when some reagents are volatile at high temperature, sealed containers are best suited.

The most inexpensive and convenient type of sealed container is a tube that is sealed at one end, loaded with the starting reagent mixture, and then sealed at the other end under the appropriate atmosphere. Not many materials are suitable and the choice depends on the type of reagents and reaction temperature. Only glass and vitreous silica (often improperly called "quartz") tubes can be easily evacuated and sealed under vacuum. Glass tubes are limited to 300–400°C, while quartz tubes can be used well above 1000°C (quartz mp = 1610°C). For reactions between fluorides, it is common to use gold or platinum tubes. These are about the only metals totally unreactive to fluorides at high temperatures; however, they suffer from two main disadvantages: (i) they are very expensive, and (ii) they have poor mechanical properties, such that they cannot usually withstand the high pressure created just by heating the inert gas they contain. The most common way to prevent leakage is to enclose them in a vitreous silica tube, under one atmosphere pressure (at room

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temperature) to counterbalance the pressure created upon heating. However, when quenching is desired in order to stabilize high-temperature phases, fast cooling rates cannot be obtained because of the low thermal conductivity of silica and the poor physical contact between silica and the inner tube. Finally, the two ends of the tubes must be welded with an acetylene torch (mp: Au = 1063°C, Pt = 1772°C), and in welding the second end, precautions must be taken not to overhead the reagents because of the high conductivity of the metals.

This paper presents an inexpensive and convenient alternative to gold and platinum for high-temperature reactions of halides, namely, copper. Although copper is restricted to moderately high temperatures, it allows a larger number of reactions and at a much larger scale, because of its low price. Two main types of reactions are presented: (i) reaction of halides, and (ii) oxidation of titanium by iodine in an attempt to prepare TiI_4. While reactions of the first type are perfectly safe, the second type results in violent explosions and should not be attempted in sealed tubes unless a special procedure is used. A known alternative, nickel, is compared to copper, as sealed tube material, for reactions of halides; however, nickel presents redox stability problems for metals in suboxidation states, such as with divalent tin halides, and for highly oxidized metals, such as U(VI), Nb(V), Ta(V), or V(V), for example.

The Sealed Copper/Nickel Tube Technique

Both nickel and copper tubes are cleaned in a dilute HCl solution to remove surface oxide, rinsed with distilled water, then with acetone (or ethanol and diethyl ether) to remove water, and dried at room temperature (Fig. 1a). The nickel tubes are sealed at one end after hammering in order to have a flat

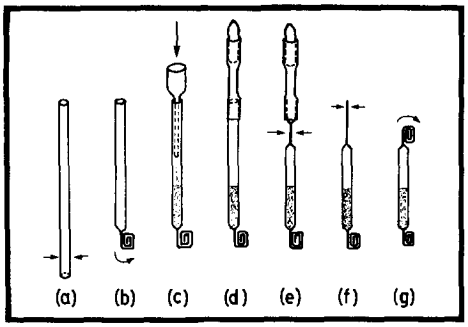

FIG. 1. Successive steps for loading and sealing a copper tube for solid state reactions by the bending technique. See text for details.

regular joint, filed to have a clean smooth surface for welding, then arc-welded under flow of argon to avoid oxidation of the molten nickel. Welding must be done very carefully in order to avoid leakage at high temperature. Copper cannot be welded because a layer of black cupric oxide always forms on the surface of the metal, even under flow of argon. An alternative way of sealing the copper tubes, which we have developed, consists of flattening them and bending the end around itself three or four times (Fig. 1b). Soft, i.e., nonannealed, copper must be used for this because otherwise the tubes split upon hammering and bending. Next, the tubes are loaded with the reagent mixture (Fig. 1c) in a glove box under controlled atmosphere if one or more reagents are air sensitive, outside the glove box otherwise. Temporary sealing is done inside the glove box (Fig. 1d) using a rubber or plastic tube stopped at one end. Figure 2 shows the detail of a copper tube after temporary sealing. Then the tubes are removed from the glove box and the area above the reaction mixture (area C on Fig. 2) is hammered flat over ca. 3 cm length (Fig. 1e). This makes another temporary sealing, such that the rubber tube can be removed and the tube is flattened all the way to the upper end (Fig. 1f). Then, for a nickel tube, the excess flattened part is cut off and the

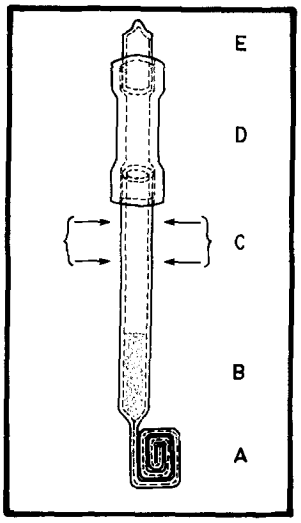

FIG. 2. Detailed picture of a copper tube after loading and temporary sealing in the glove box. (A) Sealed end, (B) sample area, (C) empty area for sealing second end, (D) rubber or plastic tube, (E) metal rod or closed tube.

cut is filed and arc-welded. For a copper tube, the upper end is bent several times following the same procedure as for the lower end (Fig. 1g). Now the tubes are ready to be heated. When cutting the reaction tube open after reaction care must be taken not to allow metal chips to fall inside and contaminate the product. Nickel particles can be removed using a magnet because Ni is ferromagnetic at room temperature, but copper particles cannot. Use of shears to open the tubes reduces this problem but does not totally eliminate it.

Reaction of Halides in Bent Copper Tubes

Because most of our research is concerned with reactions of fluorides, few materials, besides gold and platinum, offer the required lack of reactivity. Teflon can be used but is hard to seal, although we have successfully used it for the ^{19}F and ^{119}Sn NMR study of molten SnF_2 (*1*). Sealing was performed by applying one layer of Teflon tape in the thread of the screw cap. However, Teflon cannot be used above 400°C. Monel is a Ni (≅ 60%)–Cu (≅ 40%) alloy, which is highly unreactive to fluorides and is often used for reactions with fluorine and anhydrous HF. Nickel metal is also unreactive to many fluorides and has been used successfully for the synthesis of rare-earth fluorozirconates (*2*) and rare-earth–uranium(IV) mixed fluorides (*3*). However, when we tried reactions of stannous fluoride, SnF_2, with other fluorides in nickel tubes, corrosion of the wall of the tube was observed, due to reduction of some of the tin(II) to tin metal and oxidation of some of the nickel(0) to nickel(II), which contaminates the samples. Therefore, in the presence of species in oxidation states easily reduced, nickel cannot be used.

Other unreactive elements in the same groups as platinum and gold are palladium and silver; however, they are also very expensive. On the other hand, copper, with the same valence electronic structure as gold and silver, i.e., $(n - 1)d^{10}ns^1$, can be called a "seminoble" metal in nonoxidizing environment. Using sealed copper tubes, we were able to carry out the synthesis of many types of SnF_2-based fluorides and oxifluorides, under nitrogen atmosphere. For example, $MSnF_4$ (M = Pb, Sr, Ba) fast ion fluoride conductors have been prepared, up to 600°C with no corrosion or leakage problem (*4*). These materials have been studied by a variety of techniques, including X-ray and neutron diffraction, ^{19}F solid state NMR, electrical conductivity and transport number measurements, and ^{119}Sn Mössbauer spectroscopy (*5–8*), which show no evidence of contamination by copper. This is corroborated by examination of the inner wall, which is nicely shiny red after reaction, showing no evidence of corrosion.

Leakage upon heating would result in fast hydrolysis of tin(II) fluoride to black SnO (*9*), followed by oxidation to SnO_2. This does not occur because formation of

SnO or SnO_2 would be very easily detected by Mössbauer spectroscopy as the recoil-free fraction of SnO_2 [$f_a(SnO_2) = 0.44$] (*10*) at room temperature is almost 13 times as large as that of α-SnF_2 [$f_a(SnF_2) = 0.034$] (*11*). As a result, oxidation of 1% of the tin(II) of α-SnF_2 to SnO_2 would give a signal for SnO_2 of 13% of the total signal. Because the SnO_2 signal never exceeded 4% in our samples, we can safely assume that only ca. 0.3% of the total tin was in the stannic form. In addition, at least half of that tin(IV) was already present in the stannic form in the starting stannous fluoride material, whoever the supplier was (Omnium Scientific Industrial, Alfa, or Ozark Mahoning) (*12*). We can therefore conclude that only about 0.15% of the total tin was oxidized to SnO_2 in the worst case of copper tube showing no sign of leakage. This minute oxidization can be attributed to traces of moisture contained in the nitrogen gas and in the starting materials.

Up to ca. 400°C, leakage was never observed. Above, leakage frequency increases with reaction time. However, we were successful in carrying out 1-hr reactions at up to 800°C, even though at that temperature about 50% of the tubes leaked. This is not surprising considering that copper melts at 1083°C. Leakage was more frequent when the tubes were quenched in water, probably because uneven thermal contraction distorted the bent flattened tube, allowing water in.

Attempted Synthesis of Titanium Tetraiodide in Bent Copper Tubes

In the course of a ^{47,49}Ti NMR study of titanium compounds (*13*), the direct synthesis of TiI_4 by solid state reaction in a sealed copper tube was attempted. This is not the standard method of preparation of titanium tetraiodide, but was considered a possible alternative. The most common synthetic procedure is probably the reaction of powdered titanium at room temperature with iodine gas, in a closed vessel, under vacuum at temperatures as high as 425°C.

The thermal stability of the titanium iodides has also been well established and the two following reactions are reported to take place:

—at 480°C: $TiI_4 + Ti \rightarrow 2TiI_2$ (I);

—at 350°C: $TiI_4 + TiI_2 \rightarrow 2TiI_3$ (II).

These equilibria play an important role in the well-known method of purification of titanium by the Van Arkel–de Boer process (*14*).

In a first attempt, stoichiometric amounts of iodine and titanium powder, for a theoretical yield of 5 g of TiI_4, were weighed and mixed together, in a glove box, under dry nitrogen. Exact stoichiometry is hard to achieve because of the volatility of iodine. The mixture was loaded in a copper tube under nitrogen and sealed following the procedure described in Fig. 1. The tube, which was about a quarter filled with the reaction mixture, was held almost vertical in a narrow beaker that contained enough water to have about half of the tube immersed; i.e., the water level in the beaker was well above the level of the reaction mixture in the copper tube to ensure uniform heating. The temperature of the water bath was raised slowly. As it reached ca. 90°C, a violent explosion occurred, splitting the copper tube open, shattering the beaker, and splashing the reagents. The reaction was repeated at a much smaller scale (500 mg TiI_4), under the same conditions. Again at about 90°C, an explosion occurred, so violent that the top end of the copper tube, that was bent four times, unbent and split open. The reaction mixture was thrown out, splashing the fume hood, and the beaker broke. Obviously, even small amounts of reaction mixtures are very dangerous and no further attempt to control the reaction was done.

We found no report in the literature on the danger of explosion during the synthesis of TiI_4 from the elements. The only warnings reported are about their high sensitivity to air (hygroscopicity leading to hydrolysis, which results in HI being evolved) and their violent reaction with water upon dissolution. One must also be very careful when removing the product from the reaction vessel as unreacted powdered titanium may be pyrophoric. However, warning about possible explosions have been given for the synthesis of low-valence metal halides (*15*). We published a warning letter about the explosions encountered in the above experiments (*16*).

It is clear that solid–gas reactions, with iodine and the metal contained in different sections of the sealed systems, are much safer.

Obviously, it seems much harder to control the solid state reaction at ca. 90°C than the solid–gas reaction at 400°C. The temperature of the water bath was purposely kept below the melting point of iodine; however, the vapor pressure of iodine at 90°C must have been high enough to allow a significant amount of iodine gas to react with solid titanium. One could, however, have expected the reaction rate to be slow at that temperature. It is most likely that the reaction of iodine and titanium is highly exothermic, such that heating at 90°C allows the reaction kinetics to reach an explosive rate.

Conclusion

Copper can be considered the "poor man's gold" for high-temperature solid state reactions of halides under unreactive atmosphere. Reactions up to 700°C have been carried out between SnF_2 (mp = 215°C) and ZrF_4 (sublimes at ca. 600°C) in bent copper tubes. No significant copper contamination of the products or loss of ZrF_4 were observed. Sealed copper tubes allow quenching of the product in order to isolate high-temperature phases. However, copper cannot be welded and therefore sealing is performed by flattening and bending several times both ends of the tubes. Surprisingly, this method is efficient for leak-free reactions under moderate heating (e.g., 1 hr at 400–500°C) as shown by ^{119}Sn Mössbauer spectroscopy, which is very sensitive to the formation of SnO_2, for reactions of SnF_2, which easily oxidizes at high temperature. Some leaks occur at higher temperatures, such that 800°C seems to be about the upper limit. However, absence of welding seems to have been a blessing in the above unfortunate attempts to prepare TiI_4 by solid state reactions between the elements. Indeed, if the tubes were welded, they would probably have allowed a significantly higher pressure to build up, leading to much more violent explosions. Therefore, the bending seal, in some way, must have acted as a safety valve, preventing worse damage. For example, a nickel tube would have been much worse because the metal is harder and would have sustained a much higher pressure.

However, highly exothermic reactions and those leading to the formation of highly volatile compounds must be avoided because the kinetics may be hard to control and they may lead to explosions. Pressure buildup does not seem to be prevented by having a colder zone, because for the attempted syntheses of TiI_4 half of the copper tube was not in the water bath. The cold end could have become hot because of the high thermal conductivity of copper. However, a vacuum system is probably necessary for condensing volatile products at the cold end of the tube because inert gases hinder gaseous molecule transport due to collisions between molecules. Of course, copper tubes sealed by the technique described here cannot be evacuated. On the other hand, they provide a cheap and convenient

alternative to gold and platinum and allow reactions between halides of metals in suboxidation states such as divalent tin which are reduced in nickel tubes, but they must never be used for reactions such as oxidizing metals with halogens.

In summary, bent copper tubes are inexpensive and convenient reactors for moderately high-temperature reaction of fluorides. They are unreactive to fluorides and do not contaminate the samples. They do not generate redox instabilities of some elements in suboxidation states such as divalent tin. They allow easy fast quenching for stabilizing high-temperature phases.

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