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Collector for Recovering Gallium from Weapons Plutonium

C.V. Philip, R.G. Anthony, and S. Chokkaram
Department of Chemical Engineering
Texas A&M University

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Edited by

Angela L. Woods
Technical Editor

600 South Tyler • Suite 800 • Amarillo, TX 79101
(806) 376-5533 • Fax: (806) 376-5561
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A Report on

Collector for Recovering Gallium from Weapons Plutonium

C. V. Philip, R. G. Anthony, and S. Chokkaram
Department of Chemical Engineering
Texas A&M University
College Station, TX 77843

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Collector for Recovering Gallium from Weapons Plutonium

C. V. Philip, R. G. Anthony, and S. Chokkaram
Department of Chemical Engineering
Texas A&M University, College Station, TX 77843

Abstract

Currently, the separation of gallium from weapons plutonium involves the use of aqueous processing using either solvent extraction or ion exchange. However, this process generates significant quantities of liquid radioactive wastes.

A Thermally Induced Gallium Removal process, or TIGR, developed by researchers at Los Alamos National Laboratories, is a simpler alternative to aqueous processing. This research examined this process, and the behavior of gallium suboxide, a vapor that is swept away by passing hydrogen/argon over gallium trioxide/plutonium oxide heated at 1100°C during the TIGR process. Through experimental procedures, efforts were made to prevent the deposition of corrosive gallium onto furnace and vent surfaces.

Experimental procedures included three options for gallium removal and collection: (1) collection of gallium suboxide through use of a "cold finger"; (2) collection by in situ air oxidation; and (3) collection of gallium on copper.

Results conclude all three collection mechanisms are feasible. In addition, gallium trioxide exists in three crystalline forms, and each form was encountered during each experiment, and that each form will have a different reactivity.

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1. INTRODUCTION

Currently, separation of gallium from weapons plutonium involves the use of aqueous processing using either solvent extraction or ion exchange, but this process generates significant quantities of liquid radioactive waste. At Los Alamos National Laboratory, researchers have been developing a simpler alternative referred to as the Thermally Induced Gallium Removal (TIGR) process. In this process, vaporized gallium suboxide is swept away by passing hydrogen/argon over gallium trioxide/plutonium oxide heated at 1100°C or higher. During the TIGR process some of the gallium suboxide prematurely decomposes to gallium metal and gallium trioxide and deposits on furnace and vent surfaces. The deposition of this corrosive gallium must be prevented. The efforts at Texas A&M University are directed towards learning more about the behavior of gallium suboxide and determining how the reduction of vaporized gallium suboxide on a copper surface can be used to develop an effective "gallium collector," which could be incorporated into the TIGR process. It was discovered that copper catalyzes the reduction of vaporized gallium suboxide to gallium and the droplets of gallium collect on the copper forming a Ga/Cu alloy[2]. When a copper wire was placed in a stream of gallium suboxide vapors, gallium metal was collected on the tip of the wire forming droplets that dropped off as they gained weight. Gallium collected mostly on the tip of the wire, suggesting that by placing a copper collector above the oxide bed, all the gallium could be collected as an alloy with copper. Deposition of gallium suboxide on a "cold finger," and in situ vapor phase oxidation of gallium suboxide to nonvolatile gallium trioxide are the other two options under consideration. Experiments were conducted to test and evaluate these options.

The copper-collector is believed to be the best choice because of its clean gallium collection without the formation of any suboxide or trioxide dust, which could deposit on parts of the furnace and vent. Ga/Cu alloy is chemically stable as well as easier to handle than the oxides. Since the reduction of gallium suboxide takes place on the tip of the copper wire, the reaction is very fast and does not need a large copper surface area. A large copper rod could be used as the collector and the drippings from the rod will have high Ga content.

Incorporation of a copper-collector in the TIGR process is an attractive option. Several experiments were conducted to identify the benefits of a copper-collector as well as the reactions of other materials in gas streams with vapors of gallium suboxide. Elemental analysis by atomic absorption (AA) spectrometry, FT-IR (both mid and far IR) spectrometric analysis, BET surface area and pore size distribution measurements, and powder X-ray diffraction scanning were used for the characterization of materials.

2. EXPERIMENTAL PROCEDURE

Cerium Oxide powder (< 5 micron), Gallium trioxide and copper wire (AA standard grade) were obtained from Aldrich Chemical Company, Inc. The experimental setup is shown in Figure 1. Two Lindberg Blue/M furnaces were used so that two experiments could be run simultaneously. The Lindberg Blue/M furnace has a 10 X 10 X 10 cm uniformly heated zone. The furnace vessel, a quartz "U" tube, was made by bending 61 cm long, 6 mm O.D. X 4 mm ID quartz tubing (Heraeus Amersil Inc., Austin, TX, Tubinger, HSQ300, 4 X 6 X 1220); the sides were 2 cm apart. About 10 cm of the quartz "U" tube was inside the heated zone, 9 cm of the reactor was outside the heated zone but inside the insulation and the outer metal cabinet of the furnace. About 10 cm of the quartz 'U' tube was outside in air. Figure 2 shows temperature profile of the furnace and the quartz "U" tube. When the quartz "U" tube was inside furnace, which was maintained generally at 900^0C, the ends were cool enough to touch. The use of 1/8" Teflon tubing for the gas lines to and from the quartz "U" tube, made handling easier. Swagelok 1/4 to 1/8 reducing unions and Graphite/Vespel ferrules (Altech Associates) were used to connect the Teflon tubes to the quartz "U" tube. The outlet of the quartz "U" tube was connected to a gas flow meter (J&W scientific, ADM 1000). The flow meter displayed the gas flow and the digital signal from the flow meter was connected to a PC using RS232 ports. Soft Wedge software was used to collect the flow meter data into an Excel spreadsheet. The loaded quartz "U" tube was easily placed in and taken out of the furnace as needed. Either pure hydrogen or 10% hydrogen in Argon was used as the feed gas. Hydrogen was added to a cylinder with Argon to obtain the latter. The feed gas was always purified with a High Capacity Gas Purifier from Supelco that uses a heated proprietary material for removing O_2 and H_20 from the feed gas. Typically 200mg of Ga_2O_3/CeO_2 or Ga_2O_3 was positioned on one side of the quartz "U" tube using two quartz wool plugs. Copper wire was placed on the other side. The system was pressurized with helium and tested for leaks using a Gow Mac Helium Leak Detector (Gow Mac Model 21-250). The success of each experiment depends on a leak free system, as well as oxygen free feed gas.

The reducing gas (H_2 or H_2/Ar) was allowed to flow first through the oxide bed, and then around the copper wire. Generally a flow rate of 10ml/minute was used for hydrogen and a flow rate of 35ml/min was used for H_2/Ar. The feed gas and the flow rates were changed as needed. For each experiment the loaded quartz "U" tube with reducing gas-flow was heated in the furnace for several hours at a constant temperature. Experiments were performed for the temperature range of 700-1000°C. An analytical balance (Sartorius model BP11OS) was interfaced with a PC using a special cable from Sartorius for connecting the RS232 ports. The software, Soft Wedge, allowed balance readings to be directly recorded in an Excel spreadsheet.

First, the quartz "U" tube was weighed. A quartz wool plug was placed at the bottom of the tube and weighed. The oxide mixture (200mg) was placed above the plug and the tube was weighed again. Another quartz wool plug was placed above the oxide and then the tube was weighed again. A copper wire (about 2g) was weighed and positioned in the other side of the quartz tube. The quartz tubing with the contents were weighed before and after each experiment. If any oxide mixture was left at the end of an experiment, it was referred to as gallium trioxide treated with reducing gas and was carefully removed from the tube and weighed. Copper wire and Ga/Cu alloy droplets were weighed. The weight gain by the copper wire and the Ga/Cu alloy represents the gallium removed from the oxide bed. The weight gain was used for calculating the TIGR conversion. In experiments where copper was not used, gallium suboxide was collected at the cooler (> 700°C) parts of the quartz tube; this was referred to as TIGR condensed product. It was carefully removed, weighed and used for calculating the conversion. The chemical composition of TIGR condensed product is unknown. Each experiment was associated with a number of recorded weights, which were used to calculate the weight of oxide mixture before and after the reaction, the weight of gallium collected on copper wire, and the weight of gallium in Ga/Cu alloy droplets. A Varian AA30 atomic absorption spectrometer was used for the determination of copper in the Ga/Cu alloy. It is assumed that Ga was the only other element in the alloy; the weight of Ga in the alloy was determined by subtracting the weight of Cu from the weight of the alloy. The samples were also sent to Texas Tech University for ICP analysis. We have also sent samples to Galbraith Laboratory for elemental analysis by ICP; however, they could not determine the composition of the alloy due to matrix interference. They were getting a higher value for copper (78%) and lower value for gallium (35%) with a total of more than 100%.

The FT-IR spectrometer (Nicolet Magna 560), was equipped with two beam splitters (KBr for mid IR and Solid Substrate for far IR) and three detectors (DTGS with KBr window for Mid IR, DTGS with polyethylene window for far IR and MCTA for Diffuse Reflectance and mid IR studies). The FT-IR setup allows the analysis of samples in the form of pellets, films, and powders. Powder samples were filled in micro cups and scanned for the Mid IR spectrum using the MCTA detector and the Diffuse Reflectance (DRIFT) accessory (SpectraTech). Almost all the samples were analyzed as cesium chloride pellets using the transmission spectrometry. Each pellet (13-mm dia.) was prepared by pressing 100 mg of 1 to 10% well-mixed sample in cesium chloride (99.999%, Aldrich Chemical Co.). The pellets were placed in the sample holder and scanned for both mid and far IR spectra while changing the beam splitter and detector as needed. BET surface area and pore size distributions of each sample was measured using a Micrometric ASAP 2000 analyzer. X-ray diffraction spectrometer (Scintag, XDS 2000) was used for scanning the powder XRD pattern of each sample.

2.1 THREE OPTIONS FOR GALLIUM REMOVAL AND COLLECTION

During the TIGR process some of the gallium suboxide prematurely decomposes to gallium metal and gallium trioxide and deposits on furnace and vent surfaces. To prevent such deposition of this corrosive gallium three options were suggested. They are "cold finger collection" of gallium suboxide, vapor phase oxidation of gallium suboxide to nonvolatile gallium trioxide, and use of a "copper collector." The following experiments were conducted to test and evaluate these options.

2.1.1 Collection of Gallium Suboxide by "Cold Finger"

The experiments were conducted to study the TIGR condensed white powder on the cooler areas of the quartz "U" tube as shown in Figure 3. Mid and far IR spectra of the white powder and gallium trioxide is shown in Figure 4. The white powder has a different IR spectrum compared to gallium trioxide as received. Of the three oxides of gallium (Ga_2O_3, GaO, Ga_2O), GaO is very unstable and not expected to form. Ga_2O is volatile and deposits on the cooler areas of the quartz tube. Later, it decomposes or gets oxidized to more stable products. Most of the white power could be gallium trioxide, but with a crystal structure different from that of gallium trioxide as received. Sometimes the deposit was gray-colored or turned gray. The powder XRD patterns of the white and gray products are shown in Figure 5 and listed in Table 1. Chemical reactions responsible for the color change are not well understood. Mid and far IR spectra of the gray product are shown in Figures 6 a and b, respectively. The spectrum is almost identical with that of white powder (Figure 4). It is reasonable to assume that most of the gray material is gallium trioxide. There may be a small amount of gallium present, which could cause the gray color. Gallium suboxide is known to decompose into gallium and gallium trioxide. Oxygen, even at extremely low levels, is capable of oxidizing gallium suboxide to gallium trioxide. Most of the time the TIGR condensed product was pure white and crystalline. Long reaction times converted all the gallium trioxide to vapors of gallium suboxide and deposited it on the cooler parts as gallium suboxide, which is later oxidized to gallium trioxide. The reaction was also stopped when half of the oxide was converted and the samples of gallium trioxide remaining in the tube were analyzed using FT-IR and powder XRD scanning. Mid and far IR spectra of gallium trioxide left in the quartz reactor are shown in Figures 7 and b, respectively. The IR spectrum of gallium trioxide left after some reaction is different from that of TIGR condensed product, as well as from that of gallium trioxide as received (Figure 4). Heating gallium trioxide in a reducing atmosphere causes the volatilization of gallium suboxide, while changing the structure gallium trioxide left behind. It is unknown whether gallium trioxide is merely dehydrated or has undergone phase transformation. It appears that a material with new crystal structure is produced. The powder XRD pattern of gallium trioxide before and after heating in a reducing atmosphere are shown in Figure 8 and listed in Table 2. Sometimes gallium trioxide also turned gray when heated in a reducing atmosphere. When H_2 was used instead of H_2/Ar, shiny flakes or droplets of gallium were formed. So the gray color could be due to tiny amounts of elemental gallium. It could be concluded that under certain conditions, gallium suboxide could further be reduced to metallic gallium by hydrogen. Since all the oxides of gallium are white, the gray color should be due to elemental gallium. Hydrogen can convert some of the gallium suboxide deposited to elemental gallium. The conditions under which gallium suboxide is reduced to metallic gallium are not clearly understood.

2.1.2 Collection by In Situ Air Oxidation of Gallium Suboxide Vapors

The experimental setup is shown in Figure 9. An airflow of 5 ml/minute was introduced into the stream of feed gas and gallium suboxide vapors. A white powder deposited near the air-feed gas (H_2/AR) mixing zone. No white powder deposited at the cooler parts of the tube as in the case of "cold finger" experiments. The IR spectrum and powder XRD pattern of the white powder were obtained. The IR spectrum (Figure 10) is similar to that of TIGR condensed white product (Figure 4). Neither IR spectra nor the XRD patterns (Figure 8) indicate the presence of any gallium trioxide in the as received form or the form obtained after heating in a reducing gas. The gallium trioxide could be further reduced by hydrogen back to gallium suboxide and finally brought into the cooler parts of the tube and deposited as gallium suboxide. Apparently this was not happening. Even the reduction of gallium trioxide to gallium suboxide is inhibited by traces of oxygen. That is why there was no deposition of gallium suboxide on the cooler areas of the quartz tube. If heavier grains fell below the air-mixing zone, the hydrogen rich zone could reduce and produce gallium suboxide vapors. It is not known whether the latter is happening.

2.1.3 Collection of Gallium on Copper

The experimental setup is shown in Figure 11. A coiled copper wire is kept in the path of gallium suboxide vapors. Copper catalyzes the reduction of gallium suboxide to elemental gallium, which was collected at the copper wire tip as droplets that melt at 650^{O}C (50% Ga based on phase diagram). It is quite probable that during the melting point experiments, the droplet melting observed is surface melting while the interior could still be solid. There may be more copper inside the droplet. The copper in the droplet was estimated at about 60% by elemental analysis using atomic absorption (AA) spectrometry. It is concluded that the droplets contained about 40% gallium. The inner part of the droplet is rich in Cu and the outer part is rich in Ga. When the droplet breaks off it may have an inner core rich in Cu. The use of a larger rod of copper may result in Ga/Cu alloy rich in Ga, which would drop off rather than breaking off parts of the thinner wire. When copper is used as a collector, no white deposit was collected in the cooler areas of the quartz "U" tube. Several experiments were conducted to study various aspects of gallium collection on copper; they are discussed in detail later.

The three current options for improving the TIGR process, which could be used for Ga removal from weapons plutonium, are tested by the three types of experiments discussed above. Copper collector is believed to be the best choice because of the clean collection of Ga without gallium suboxide or trioxide that can be carried away into other parts of the furnace and vent. Ga/Cu alloy is also easier to handle than the oxides. Since the reduction of gallium suboxide takes place at the tip of the copper wire, the reaction is very fast and does not need a high copper surface area. A heavy copper rod could be use as the collector, and drippings from the rod will have higher Ga content. Experiments should be performed to determine the relationship between the geometry of the copper collector and the Ga/Cu alloy composition.

The Oxidation and Reduction Reactions of Gallium Species

$$Ga_2O_3 + 2H_2 \rightarrow Ga_2O + 2H_2O \quad (1)$$

$$Ga_2O + 2Cu \rightarrow Cu_2O + 2Ga \quad (2)$$

$$Cu_2O + H_2 \rightarrow 2Cu + H_2O \quad (3)$$

$$Ga_2O_3 + 3H_2 \rightarrow 2Ga + 3H_2O \quad (4)$$

$$3Ga_2O \rightarrow 4Ga + Ga_2O_3 \quad (5)$$

$$Ga_2O_3 + H_2 \rightarrow 2GaO + H_2O \quad (6)$$

$$2Ga + O_2 \rightarrow 2GaO \quad (7)$$

$$Ga_2O + O_2 \rightarrow Ga_2O_3 \quad (8)$$

$$4Ga + 6O_2 \rightarrow 3Ga_2O_3 \qquad (9)$$

$$2Ga + N_2 \rightarrow 2GaN \qquad (10)$$

Heat of Formation of Gallium Oxides

$$2Ga + 3/2O_2 \rightarrow Ga_2O_3 + 257\ 61\ \text{kcal/mole} \qquad (11)$$

$$Ga_2O + O_2 \rightarrow Ga_2O_3 + 175\ 62\ \text{kcal/mole} \qquad (12)$$

$$2Ga + 1/2O_2 \rightarrow Ga_2O_{solid} + 82\ 62\ \text{kcal/mole} \qquad (13)$$

$$3Ga_2O \rightarrow 4\,Ga + Ga_2O_3 + 11\ 6\ 6\ \text{kcal/mole} \qquad (14)$$

Equations 1-9 list all the possible reactions of gallium species in the presence of hydrogen, nitrogen, oxygen and copper. Even a small amount of oxygen can suppress the Ga removal process. The system must be leak proof and oxygen free. Nitrogen is known to react with Ga to produce Gallium nitride, which is easily oxidized to Ga_2O_3. More study is needed in this area.

2.2 REACTIONS OF METALS AND ALLOYS IN GALLIUM SUBOXIDE VAPOR

Experiments were conducted by replacing the copper wire in Figure 12 with wires of other metals and alloys. The experimental conditions were the same as the "copper collector" experiments using H_2/Ar as the feed gas and a temperature of 900^0 C. Several metals and alloys were tested to determine their activity towards gallium suboxide vapors. The XRD pattern of powder product from the two experiments are shown in Figure 13 and listed in Table 3. All of these experiments with corresponding observations or comments are listed in Table 4. Platinum and rhodium/ platinum (10%) alloy has some Ga collecting ability but not as good as a copper collector. A gray powder deposition was observed on most materials including stainless steal. Zirconium crumbled in gallium vapor forming a gray granular material. Tungsten and molybdenum were found to be very inert. It could be concluded that copper is the best material for gallium collection. Tungsten and molybdenum possibly could be used for building the furnace vessel for the TIGR process since they are the mostly inert.

2.2.1 Effect of Reaction Temperature on Gallium Removal

Figure 14 shows the effect of temperature on gallium removal using H_2/Ar and copper collector. Figure 15 shows the effect of temperature on gallium removal using H_2 and copper collector. The lowest temperature at which gallium could be collected on copper is 800^0C. Highest temperature tested was 1000^0C.

2.2.2 Effect of Copper to Ga_2O_3 Bed Distance on Gallium Collection

A series of experiments were conducted using the setup in Figure 11 to determine if the distance between the copper and the gallium oxide bed has any effect on gallium collection on copper. Figure 16 shows the result of the experiments using H_2/Ar. Figure 17 shows the result of the experiments using H_2. The distance apparently has no effect on the conversion as long as the copper is within the hot zone.

2.2.3 BET Surface Area Measurements

The change in the surface area of gallium trioxide with respect to reaction conditions shown are in Figure 18 and also listed in Table 5.

2.3 VOLATILIZATION OF GALLIUM SUBOXIDE

Beta-gallium oxide was prepared by reducing gallium trioxide in a quartz reactor using either hydrogen or hydrogen/argon using the "cold finger" experiment. Gallium suboxide first condenses on the cooler parts of the quartz tube and then undergoes chemical changes to produce a white powder that is sometimes mixed with gray color. Gallium suboxide is very unstable and could easily be oxidized to gallium trioxide. Both the IR spectrum and the XRD pattern of TIGR condensed product is very different from that of gallium trioxide as received. The Ga_2O_3 bed in the "cold finger" (Figure 4) was replaced by TIGR condensed product. In one series of experiments, pure hydrogen was passed. Another series of experiments used the conditions of copper collector experiments (Figure 12). The disappearance of TIGR condensed product and the weight gain due to the formation of Ga/Cu alloy on copper tip were monitored. The results of these two experiments are listed in Table 6. Gallium suboxide is initially volatilized from Ga_2O_3 bed by passing hydrogen or H_2/Ar. The vapor condenses on cooler parts of the furnace. The volatilization of gallium suboxide, once condensed, is a slow process probably due to the chemical changes it is undergoing. Gallium suboxide is very unstable and exposure to air probably oxidizes it to gallium trioxide but with a different crystal structure and IR absorption spectrum. The chemical nature of the product is unknown and it is referred to as TIGR condensed product on "cold finger." The volatilization of suboxide from TIGR condensed product is favored by a flow of a reducing gas such as H_2 and H_2/Ar. Figure 19 shows the effect of reaction time on conversion of TIGR condensed product in H_2 and Figure 20 shows the effect of flow rate on conversion of TIGR condensed product in H_2.

3. CONCLUSIONS

Gallium trioxide exists in α, β, and γ crystalline forms. The alpha form is stable and commercially available. It appears that the three forms are encountered during the experiments. It is quite likely that all of these forms will have different reactivity. For example β-gallium trioxide could easily be reduced to gallium suboxide. If the most reactive form of gallium trioxide is producing during the HYDOX process, the gallium removal could be accomplished in short and less rigorous conditions.

The distance between copper collector and the oxide bed does not have an effect on gallium removal or conversion. In addition, hydrogen gives a better conversion than H_2/Ar. The rate of conversion increases with increase in temperature and gas flow rates.

When gallium trioxide is heated in H_2 or H_2/Ar, gallium suboxide vaporized and deposited cooler parts of the quartz "U" tube and a white powder is produced. However, sometimes the powder is gray colored. When heating at 950°C in a reducing gas (H_2 or H_2/Ar), both white and gray powders sublimed in about thirty minutes. This is a significant decrease in reaction rate compared to the as-received powder.

Air oxidation of gallium suboxide vapors produces a nonvolatile white powder which deposits on the quartz "U" tube inside the furnace. The far IR spectrum of the oxidized product is very similar to that of the white deposit collected on the cooler parts of the quartz during the heating of Ga_2O_3 in H_2 or H_2/Ar. It should be noted that trace amounts of oxygen and perhaps nitrogen could be affecting the TIGR process. An oxygen sensor capable of monitoring very low levels of oxygen is needed to better quantify this effort.

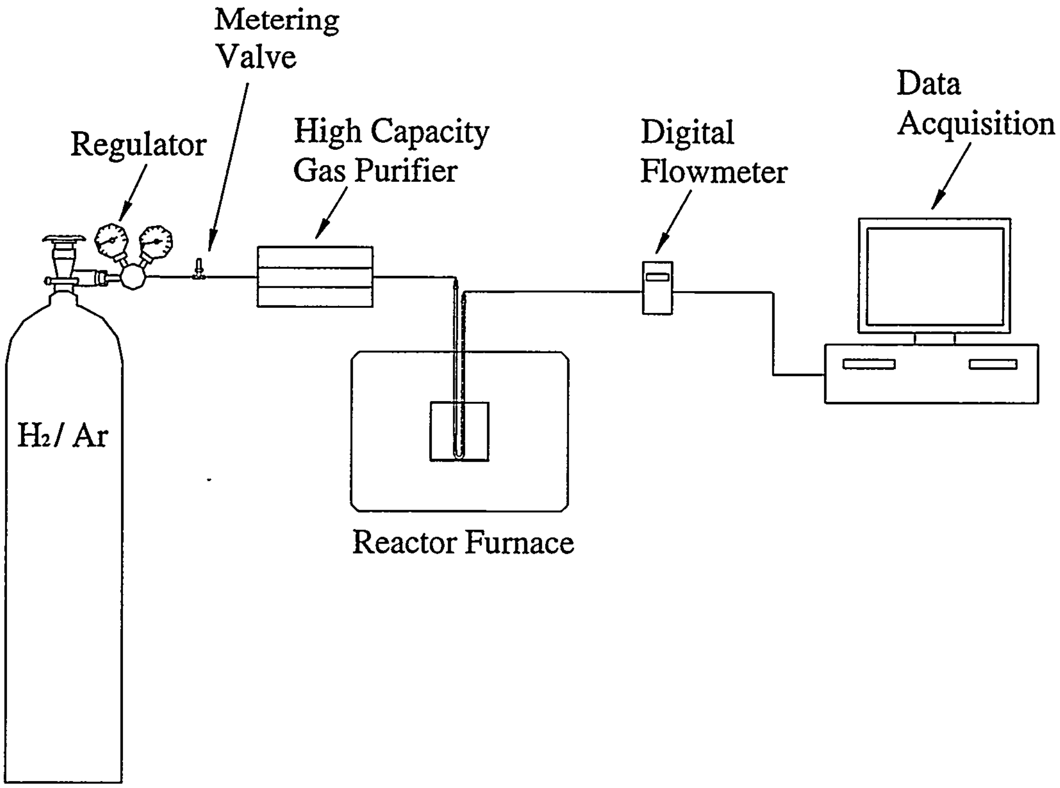

Figure 1: Schematic Diagram of the Experimental Setup used for Gallium Removal

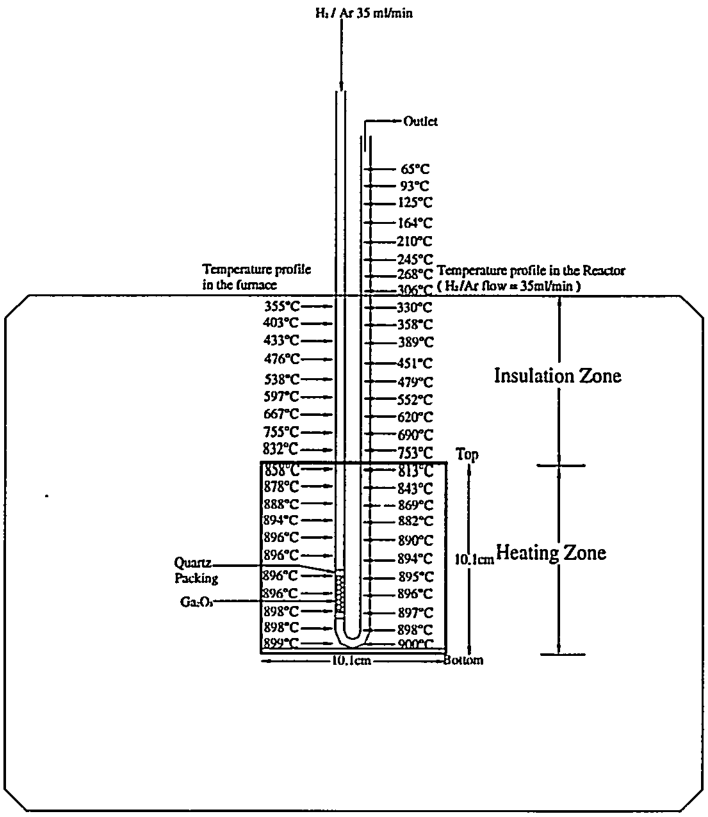

Figure 2: Experimental Setup for Gallium Removal

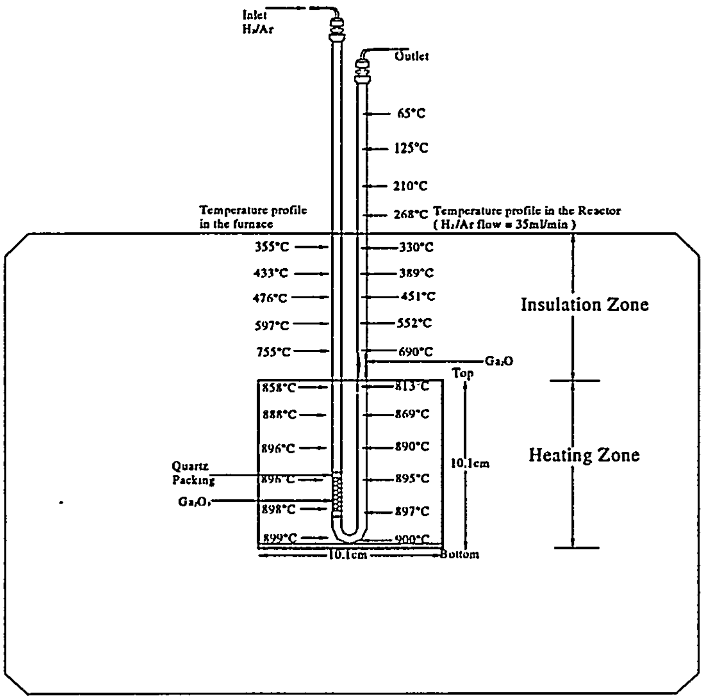

Figure 3: Experimental Setup for Gallium Removal by "Cold Finger" Deposition of Product

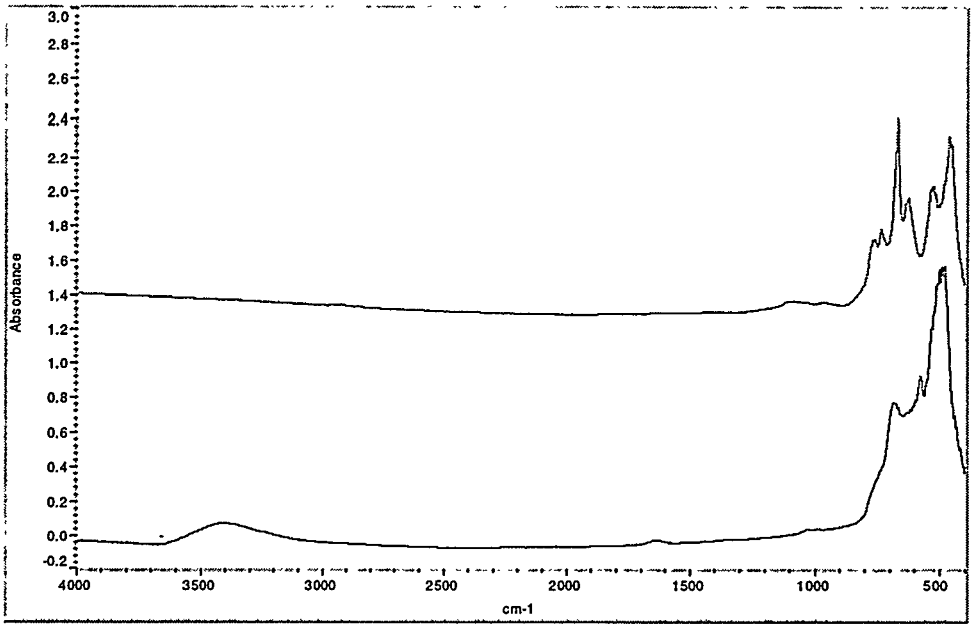

Figure 4a: Mid-IR Spectra of Deposited White Product (top) and Gallium Trioxide (bottom), Respectively

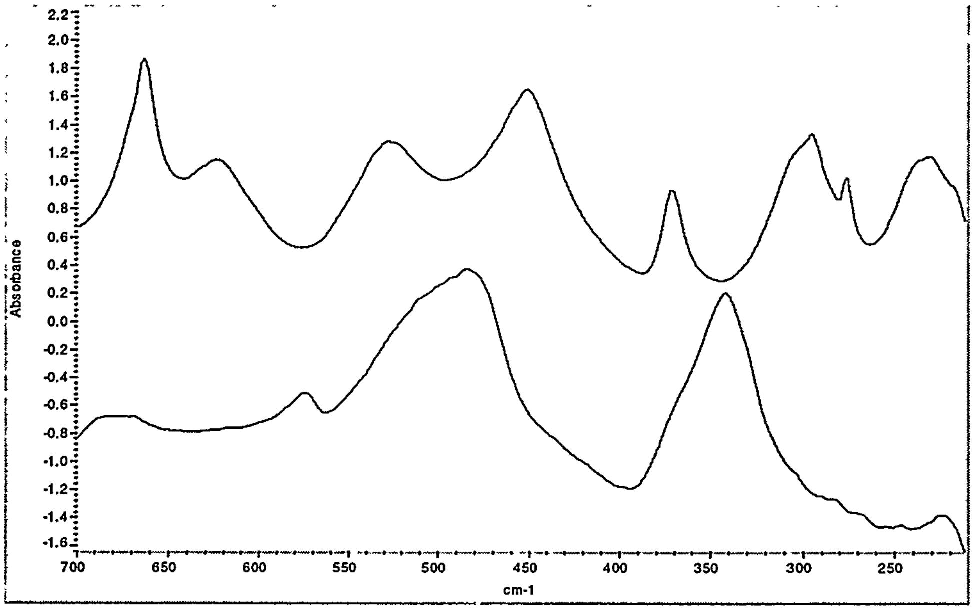

Figure 4b: Far-IR Spectra of Deposited White Product (top) and Gallium Trioxide (bottom), Respectively

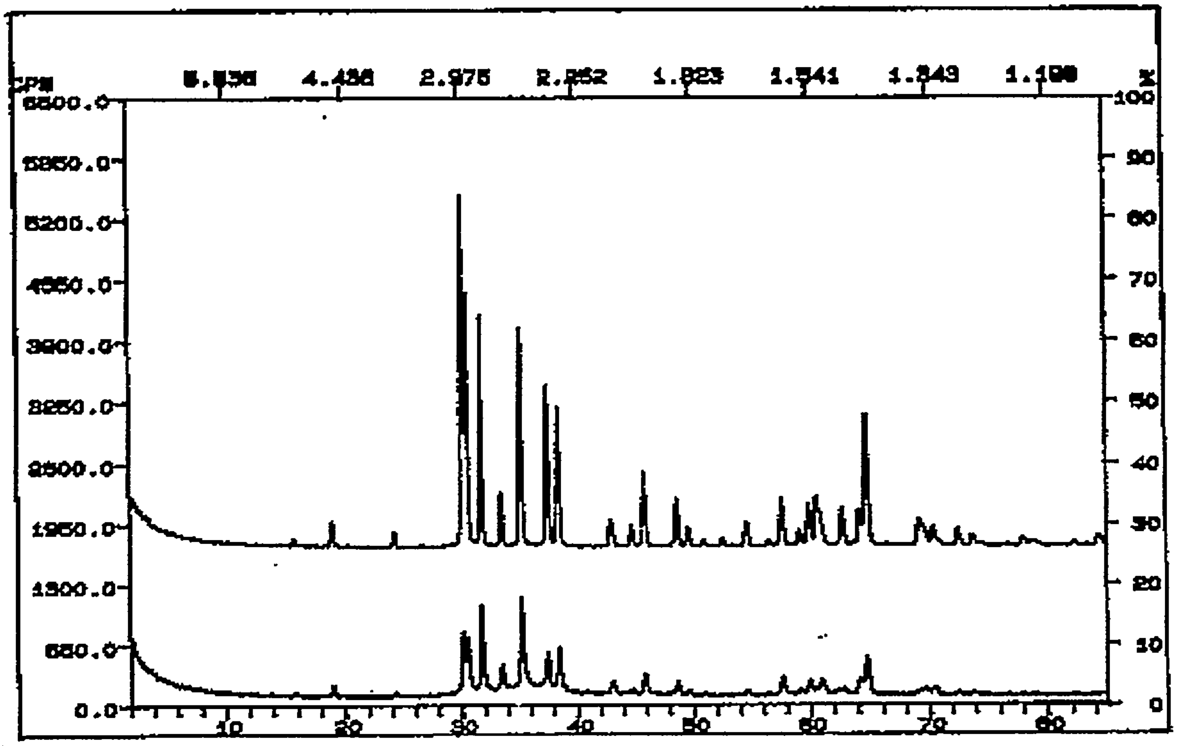

Figure 5: X-Ray Diffraction Pattern of White Product (top) and Gray Product (bottom), Respectively. [White Product is from Run 50 and the Gray Product is from Run 69.]

Table 1: XRD Peak Positions, d-Spacing Values of White and Gray Products

White Product				Grey Product			
Two Theta	d Spacing, A	Intensity	I/Imax	Two Theta	d Spacing, A	Intensity	I/Imax
30.14	2.96	208752	100.0	30.10	2.97	33202	66.6
30.51	2.93	149150	71.4	30.48	2.93	26943	54.1
31.75	2.82	133579	64.0	31.74	2.82	47417	95.1
33.51	2.67	29677	14.2	33.48	2.67	14092	28.3
35.23	2.55	125696	60.2	35.22	2.55	49835	100.0
37.49	2.40	94724	45.4	37.45	2.40	19847	39.8
38.43	2.34	81441	39.0	38.42	2.34	23662	47.5
45.85	1.98	44435	21.3	43.05	2.10	6004	12.0
48.66	1.87	29448	14.1	45.82	1.98	11703	23.5
57.62	1.60	29087	13.9	48.65	1.87	8000	16.1
59.93	1.54	25628	12.3	57.62	1.60	10198	20.5
60.58	1.53	29334	14.1	59.91	1.54	7416	14.9
62.71	1.48	23566	11.3	60.96	1.52	8163	16.4
64.14	1.45	23713	11.4	64.13	1.45	7968	16.0
64.71	1.44	77935	37.3	64.68	1.44	19632	39.4

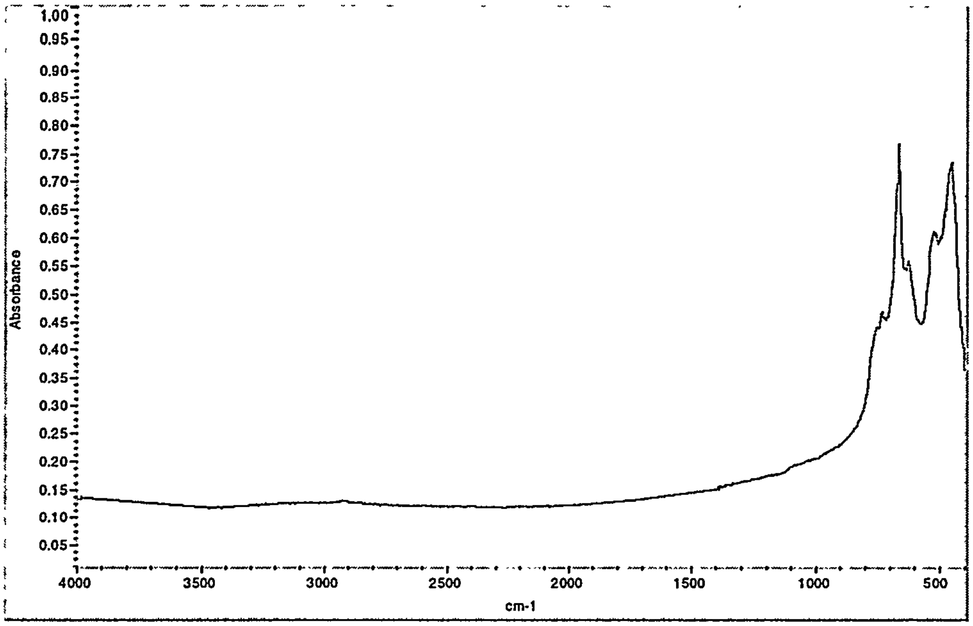

Figure 6a: Mid-IR Spectrum of Deposited Gray Product. Conditions: Reaction Temperature = 950°C, Treatment Gas = H_2/Ar (35 ml/min) and Reaction Time = 2.0 hr.

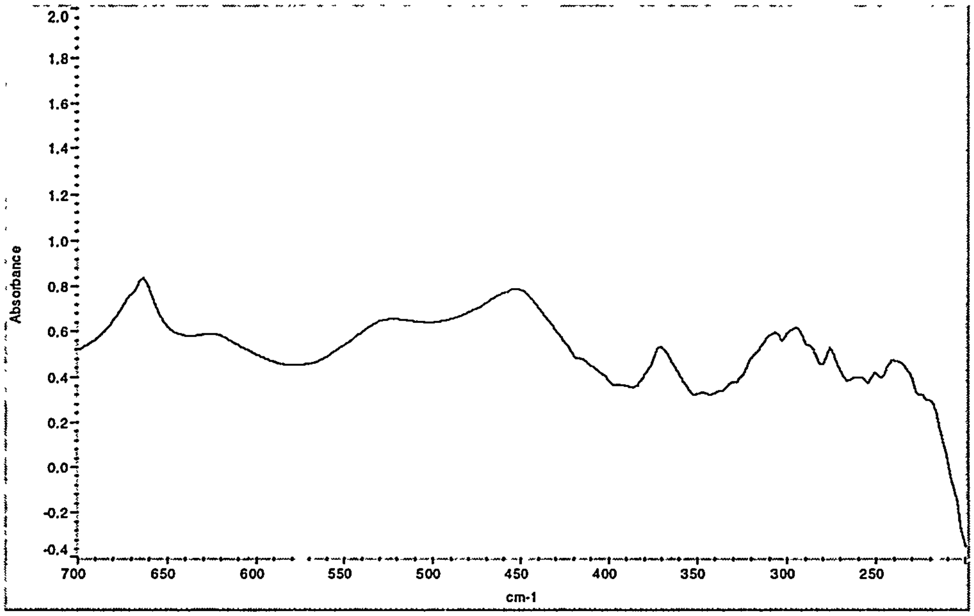

Figure 6b: Far-IR Spectrum of Deposited Gray Product. Conditions: Reaction Temperature = 950°C, Treatment Gas = H_2/Ar (35 ml/min) and Reaction Time = 2.0 hr.

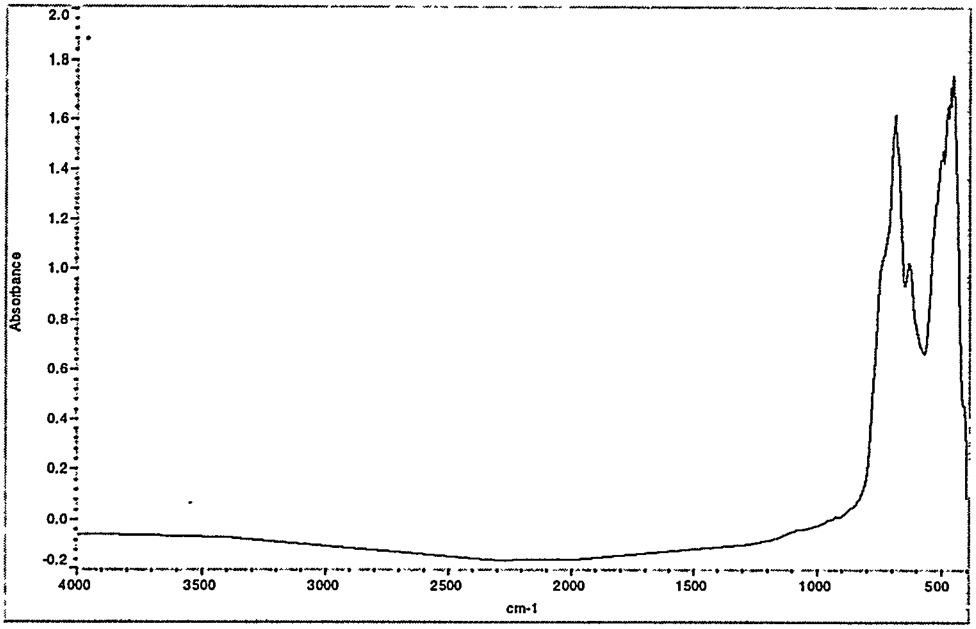

Figure 7a: Mid-IR Spectrum of Gallium Trioxide after the Reaction. Conditions: Reaction Temperature = 950°C, Treatment Gas = H_2/Ar (35 ml/min) and Reaction Time = 2.0 hr.

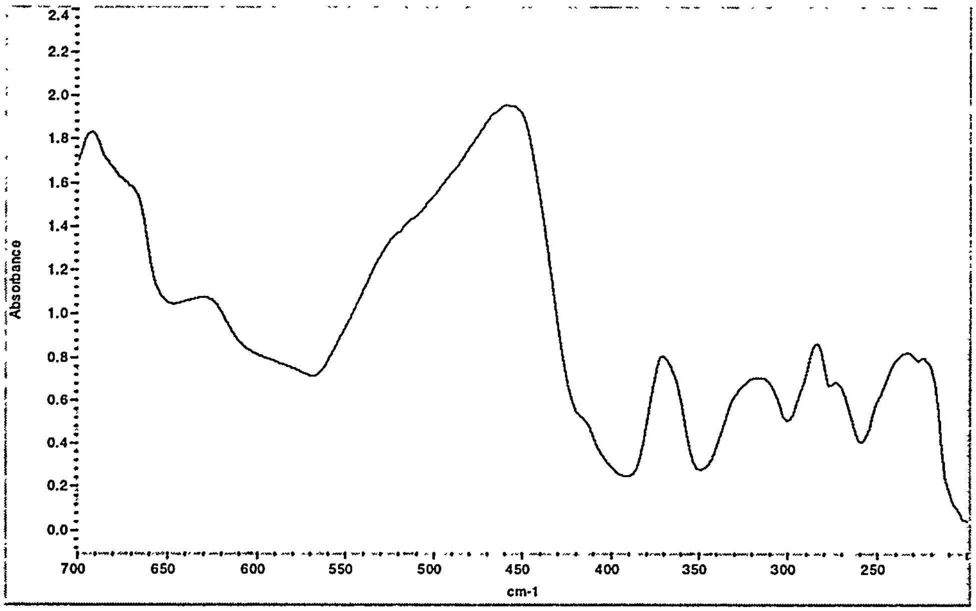

Figure 7b: Far-IR Spectrum of Gallium Trioxide after the Reaction. Conditions: Reaction Temperature = 950°C, Treatment Gas = H_2/Ar (35 ml/min) and Reaction Time = 2.0 hr.

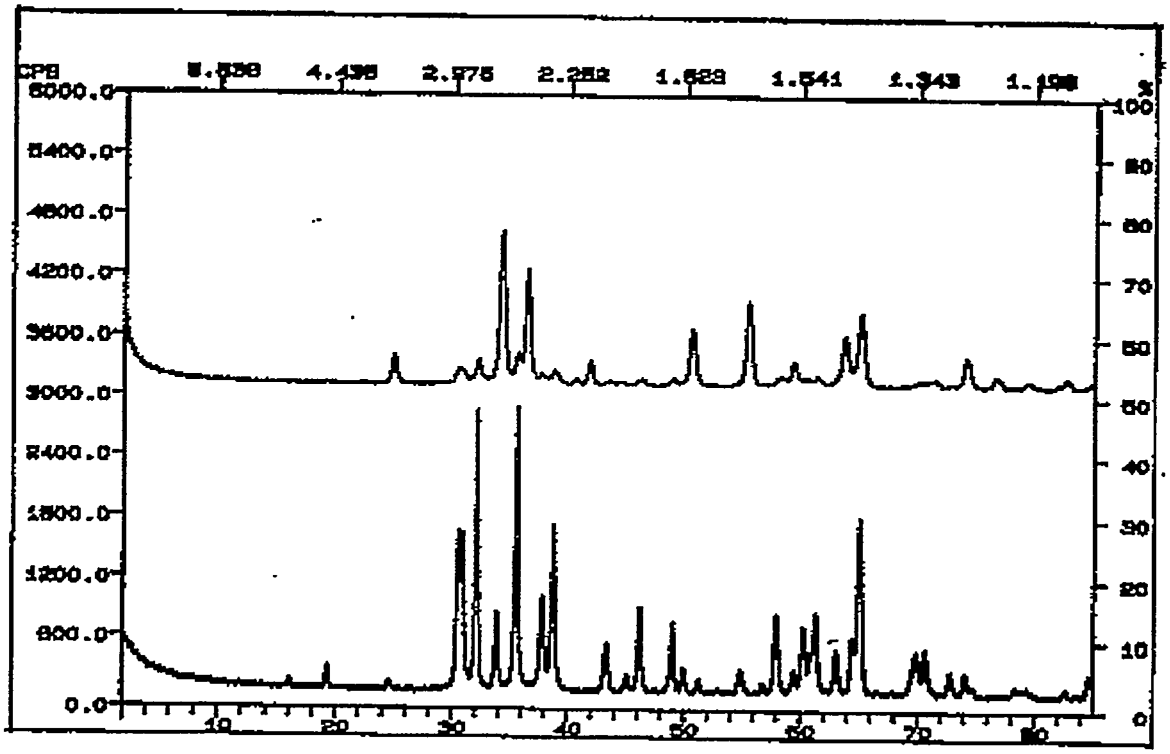

Figure 8: X-Ray Diffraction Pattern of Gallium Trioxide Before Reaction and Gallium Trioxide after Reaction from Run N-23 (bottom)

Table 2: XRD Peak Positions (2θ), d-Spacings and Relative Intensities of Gallium Oxides

Gallium Trioxide Before Reaction				Gallium Trioxide After Reaction (Run N-23)			
Two Theta	D Spacing, A	Intensity	I/Io	Two Theta	D Spacing, A	Intensity	I/Io
24.88	3.58	11796	19.6	30.42	2.94	63618	52.3
30.57	2.92	4832	8.0	30.78	2.90	62273	51.2
32.10	2.79	8640	14.3	32.03	2.79	121612	100.0
34.14	2.62	60314	100.0	33.78	2.65	30610	25.2
35.62	2.52	8356	13.9	35.51	2.53	119589	98.3
36.37	2.47	45803	75.9	37.76	2.38	34828	28.6
41.80	2.16	10655	17.7	38.71	2.32	69851	57.4
50.54	1.80	23921	39.7	43.29	2.09	16533	13.6
55.38	1.66	35527	58.9	46.14	1.97	35898	29.5
59.29	1.56	8825	14.6	48.94	1.86	31500	25.9
63.59	1.46	17265	28.6	57.87	1.59	34639	28.5
65.04	1.43	27827	46.1	60.18	1.54	26661	21.9
74.04	1.28	13652	22.6	61.22	1.51	34378	28.3
76.60	1.24	4262	7.1	64.38	1.45	23815	19.6
82.57	1.17	4262	7.1	64.97	1.43	82125	67.5

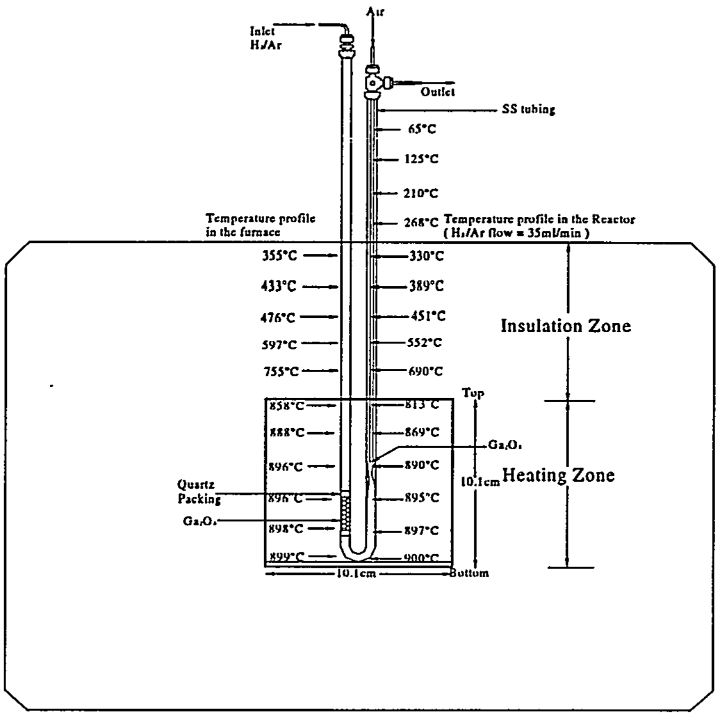

Figure 9: Experimental Setup for Gallium Removal by In-Situ Oxidation of Ga_2O

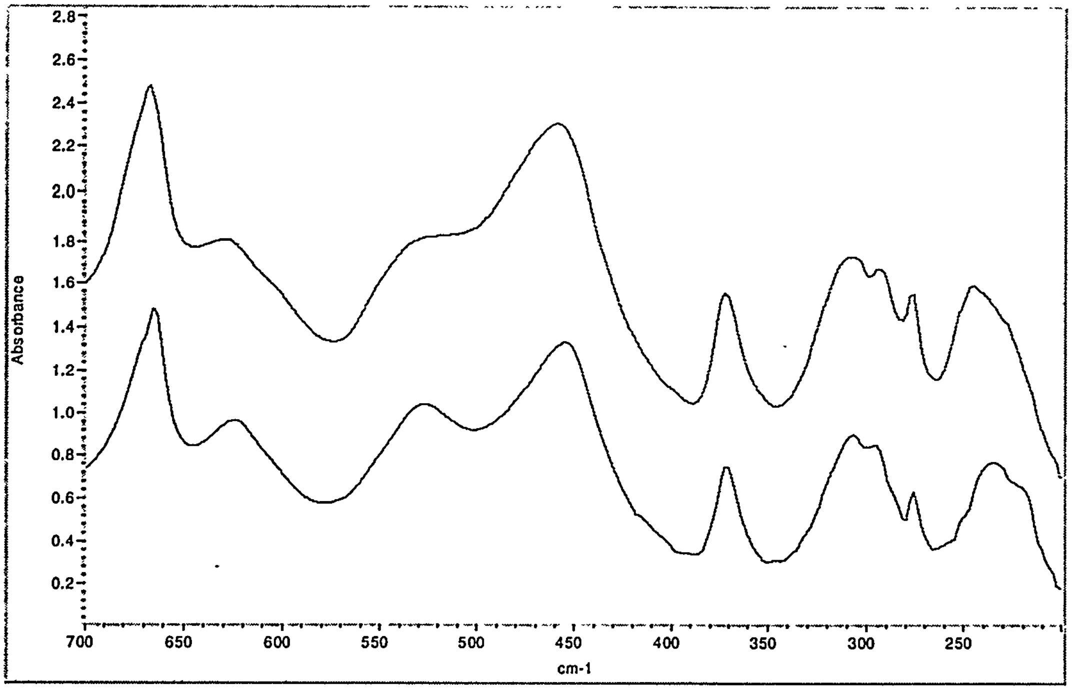

Figure 10: Far-IR Spectra of Reoxidized (In-Situ) Product (top) and White Product (bottom). Conditions for Reoxidized Product: Reaction temperature (RT) = 1000°C, Treatment Gas = H_2/Ar (35 ml/min), Reoxidation Gas = Air (5 ml/min) and Reaction Time = 2 hr. Conditions for Deposited White Product: Reaction Temperature = 950°C, H_2/Ar (35 ml/min) for 2 hr.

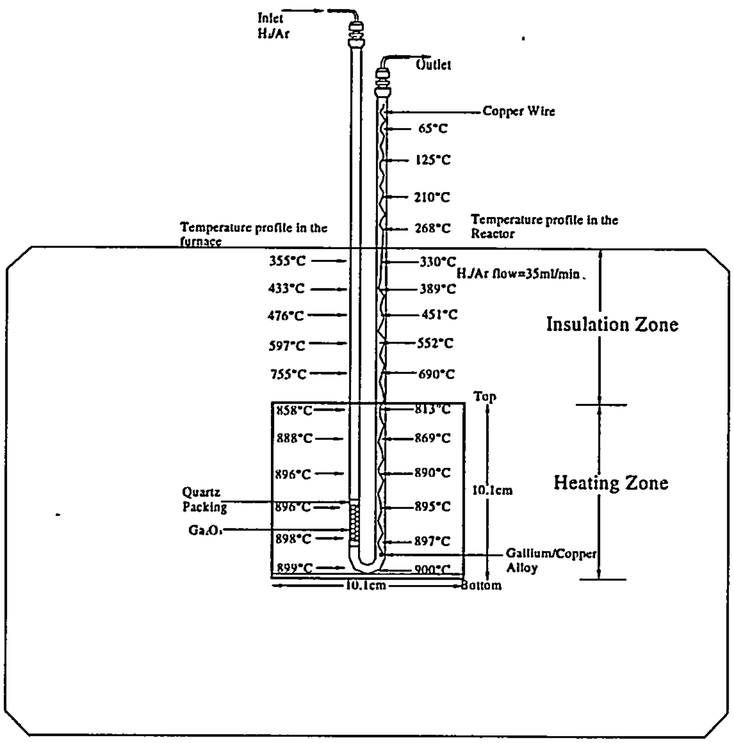

Figure 11: Experimental Setup for Gallium Removal using Copper Collector

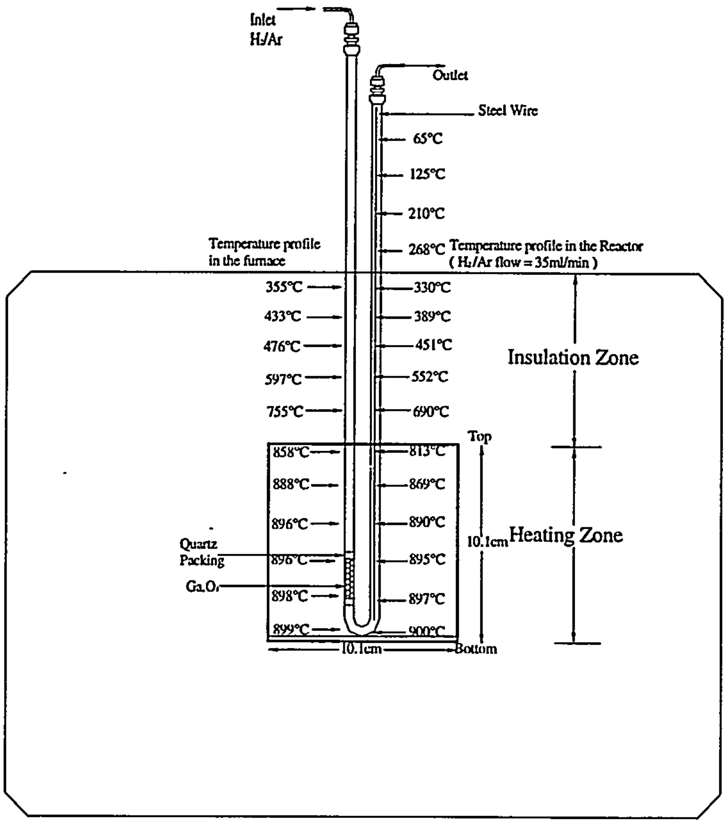

Figure 12: Experimental Setup for Gallium Removal using Stainless Steel Collector

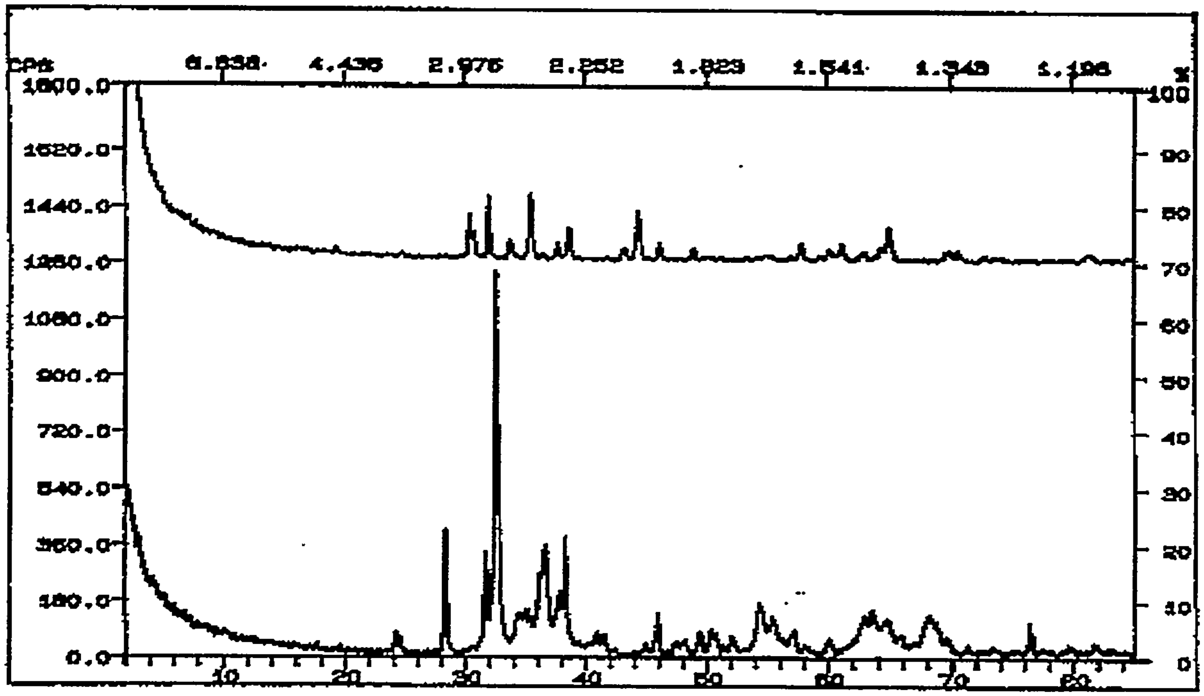

Figure 13: X-Ray Diffraction Pattern of the Scratch from Stainless Steel Wire from Run N-4 (top) and Crumbled Zirconium Wire from Run 42 (bottom), Respectively

Table 3: XRD Peak Positions and d Spacing Values for the Deposited Products on Stainless Steel and Zirconium Wires

Scratch from Stainless Steel Wire				Crumbled Zirconium Wire			
Two Theta	d Spacing, A	Intensity	I/Imax	Two Theta	d Spacing, A	Intensity	I/Imax
30.11	2.97	7871	70.9	28.29	3.15	17727	34.3
30.49	2.93	3903	35.1	31.58	2.83	13550	26.2
31.72	2.82	11106	100.0	32.53	2.75	51648	100.0
33.48	2.67	3142	28.3	36.08	2.49	7057	13.7
35.22	2.55	10852	97.7	36.19	2.48	7421	14.4
37.47	2.40	2753	24.8	36.58	2.45	11243	21.8
38.39	2.34	4885	44.0	37.81	2.38	6145	11.9
43.02	2.10	1910	17.2	38.23	2.35	17802	34.5
44.09	2.05	7036	63.4	45.84	1.98	8529	16.5
45.83	1.98	3058	27.5	54.20	1.69	5398	10.5
48.66	1.87	2154	19.4	54.35	1.69	5112	9.9
57.61	1.60	3334	30.0	55.35	1.66	4529	8.8
60.92	1.52	2627	23.7	63.47	1.46	4379	8.5
64.07	1.45	2095	18.9	67.96	1.38	4360	8.4
64.69	1.44	5848	52.7	76.40	1.25	7659	14.8

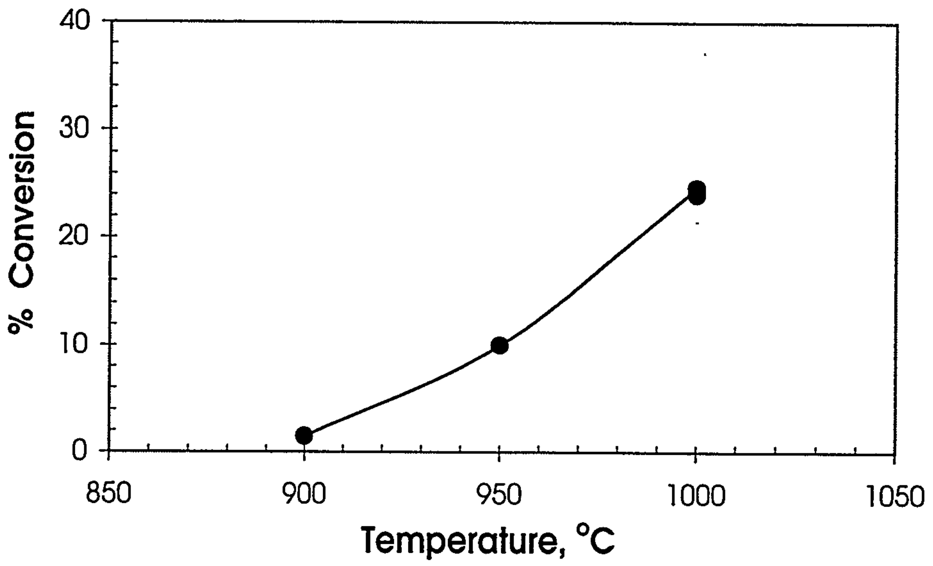

Figure 14: % Ga_2O_3 Conversion as a Function of Reaction Temperature in H_2/Ar Flow. Conditions: Flow rate =35 ml/min, sample wt=200 mg and reaction time=2 hr.

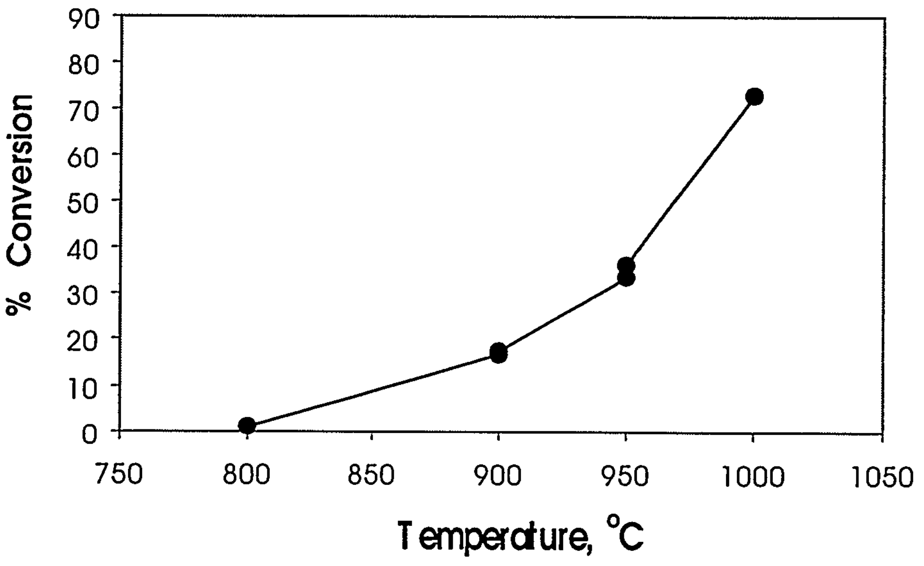

Figure 15: % Ga_2O_3 Conversion as a Function of Reaction Temperature in H_2 Flow. Conditions: Flow rate=35 ml/min, sample wt =200 mg and reaction duration = 2 hr.

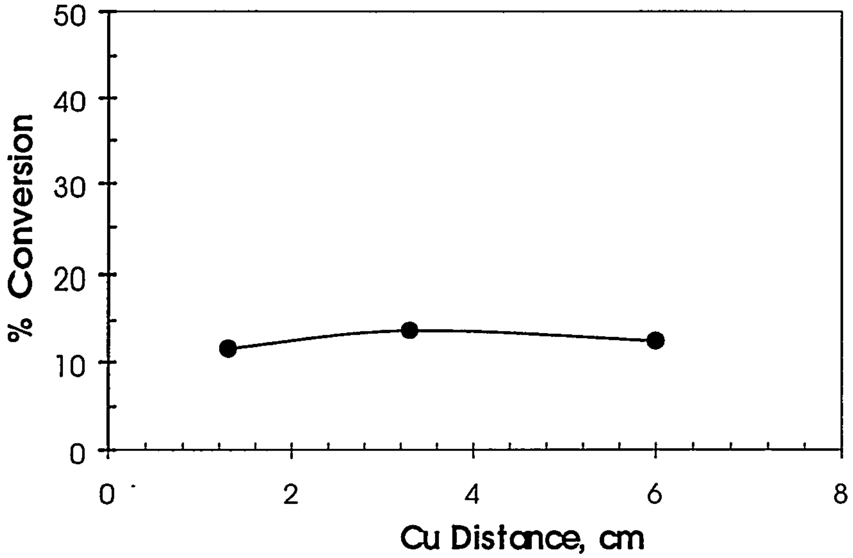

Figure 16: % Ga_2O_3 Conversion as a Function of Copper Distance. Conditions: Pretreatment gas=H_2/Ar (35 ml/min) reaction duration=2 hr.

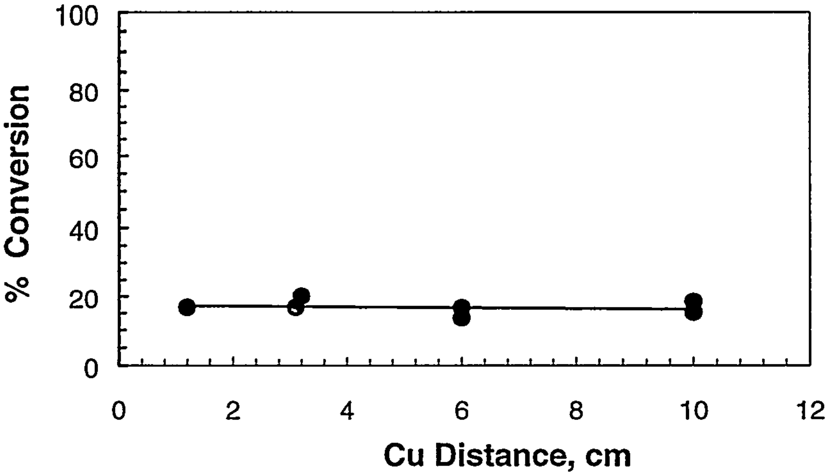

Figure 17: % Ga_2O_3 Conversion as a Function of Copper Distance. Conditions: Reaction Temperature=900°C, Pretreatment Gas=H_2 (35 ml/min), and Reaction Duration=2 hr.

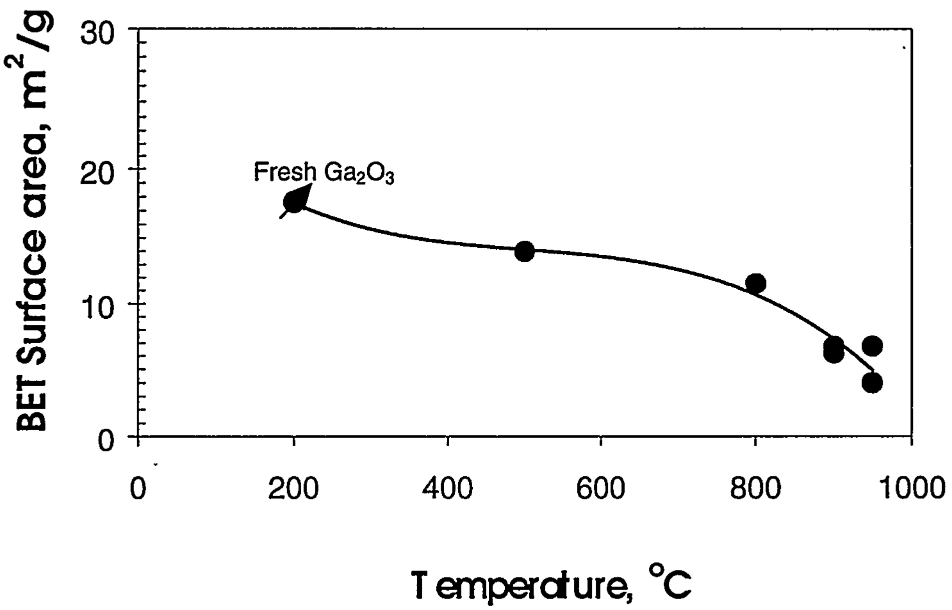

Figure 18: Effect of Hydrogen Pretreatment on BET Surface Area of Gallium Trioxide. Condition: Pretreatment Gas=H_2 (35 ml/min) Reaction Duration=2 hr.

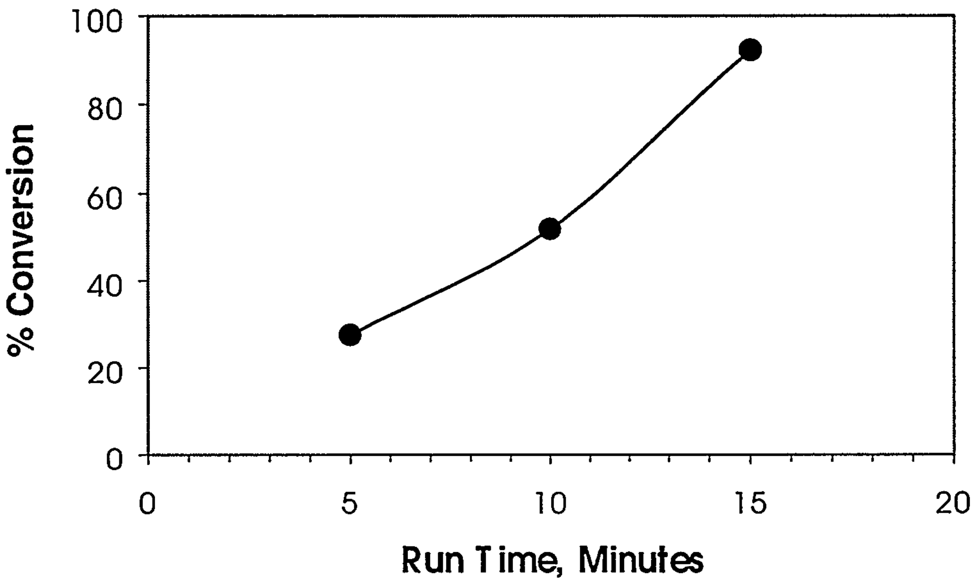

Figure 19: %Conversion of TIGR Process Product as a function of Reaction Time Conditions: Reaction Temperature=1000°C, H_2 flow=35 ml/min, Cu distance=1.2 to 1.3 cm and sample size =20 mg.

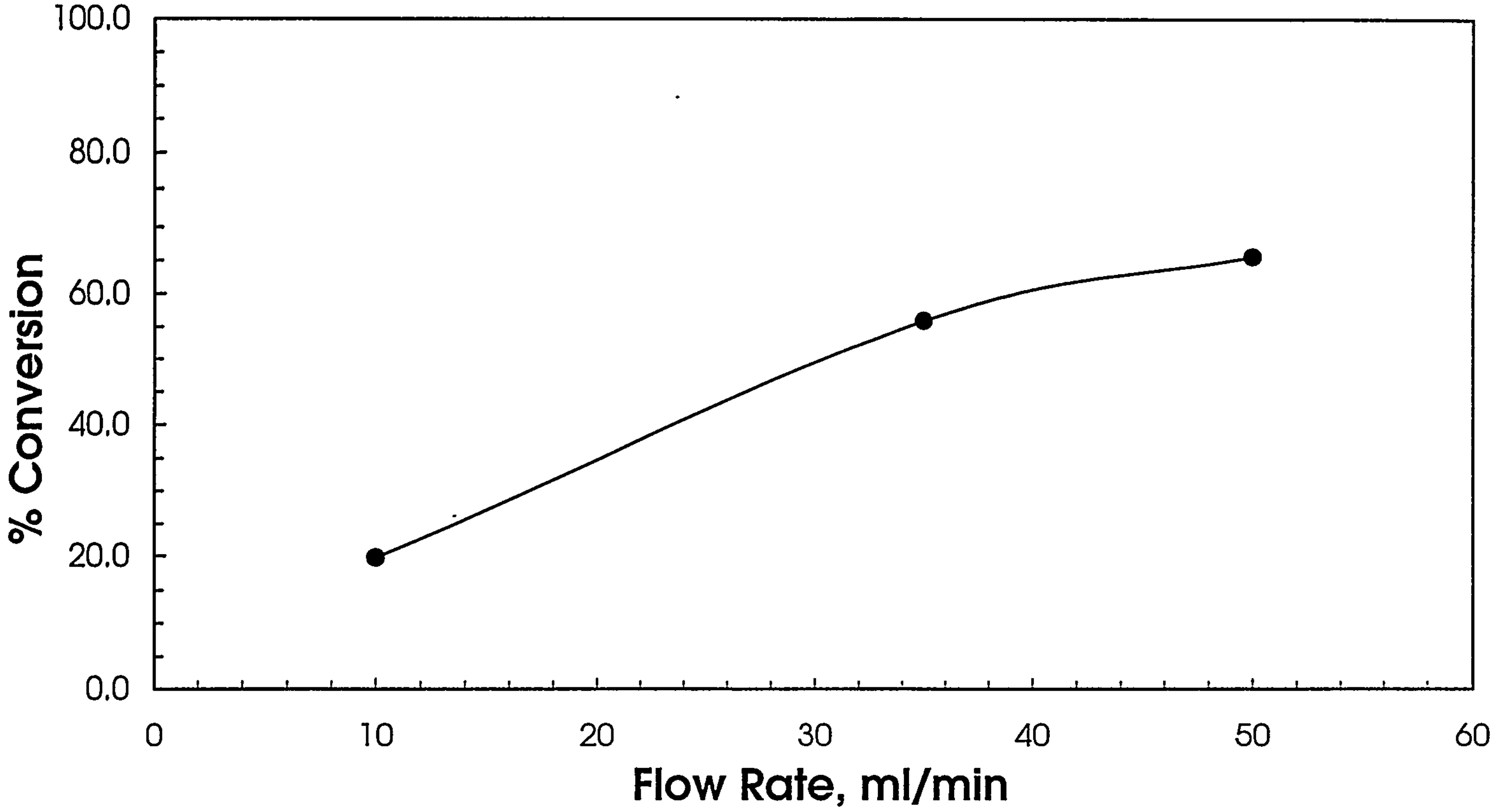

Figure 20: % Conversion of TIGR Process Product as a function of Flow Rate. Conditions: Reaction temperature = 1000°C, Reaction Time = 10 minutes, Sample Size = 20 mg and Pretreatment Gas = H_2.

Table 4: Summary Table for the Gallium Experiments Conducted with Different Metals

Run #	Type of Metal Substrate	Reaction Temperature, °C	Type of Gas & (Flow Rate, ml/min)	Duration of Pretreatment	Comments
69	304 SS wire	900	H_2/Ar (35)	24	SS wire a stable and small amount of dark product was deposited on the ss wire.
70	316 SS wire	900	H_2/Ar (35)	24	SS wire a stable and small amount of dark product was deposited on the sswire.
26	Zirconium wire	900	H_2/Ar (15)	24	Zirconium wire crumbled
27	Pt-Rh	900	H_2 (35)	24	Small droplets of gallium formed.
28	Pt-Rh	900	H_2/Ar (35)	24	Very small Gallium droplets formed.
37	Titanium	900	H_2/Ar (35)	24	Titanium wire was stable but turned into dark.
38	Nb foil	900	H_2/Ar (35)	24	Nb foil was stable but turned into dark.
41	Sterling silver	900	H_2/Ar (35)	25	Sterling silver melted and also gained some weight during the reaction and appears to somewhat reactive with gallium suboxide.
127	Tungsten filament	950	H_2 (20)	5	Tungsten filament was stable and there is no weight gain on the filament.
N-27	Molybdenum wire	1000	H_2 (20)	5	Molybdenum was stable and a white deposits of gallium suboxide was deposited on the cooler parts of Molybdenum wire.

Table 5: Effect of Pretreatment on the BET Surface Area* of Gallium Trioxide

Sample Description	Temperature, °C	Pretreatment Gas	BET Surface Area, m^2/g	Run #
Ga_2O_3 Before Reaction	200	None	17.6	N/A
Ga_2O_3 After Reaction	500	H_2 (2 hr)	14.0	Run N-37
Ga_2O_3 After Reaction	800	H_2 (2 hr)	11.5	Run 146
Ga_2O_3 After Reaction	900 900	H_2 (4 hr) H_2 (2 hr)	6.7 6.2	Run 74 Run 79
Ga_2O_3 After Reaction	950 950	H_2 (5.5 hr) H_2 (2 hr)	6.7 4.0	Run 92 Run 87
Ga_2O_3 After Reaction	1000	Air (5 hr)	10.9	Run 139

* Prior to BET measurements the samples were degassed under vacuum at 200°C for 10 hr.

Table 6: Effect of H_2 Flow Rate on the % Conversion of TIGR Process Product

(Conditions: Temperature = 1000°C, Pretreatment Gas = H_2 and Sample Size = 20 mg.)

Run ##	Flow Rate, ml/min	Run Time, minutes	% Conversion based on	
			Cu wt gain	Sample wt loss
111	35	5	27.6	30.4
110	35	15	92.4	98.1
113	10	30	59.2	64.8
109	35	10	55.9	49.5
112	50	10	65.5	77.2

Table 7: Experimental Results for Thermally Induced Gallium Removal (TIGR) Process Using "Cold Finger"

Run	Reaction Temperature, °C	Reducing Gas	Gas Flow Rate, ml/min	Reaction Duration, hr	% Conversion based on Deposited	% Conversion based on Sample Wt loss
99	900	H_2	10	2	6.3	6.4
76	900	H_2	35	2	16.6	18.1
64	950	H_2/Ar	30	2	6.3	5.5
57	950	H_2/Ar	35	2	11.8	10.3
63	950	H_2/Ar	35	2	10.6	9.3
87	950	H_2	25	2	24.4	26.6
84	950	H_2	35	2	41.4	39.1
91	950	H_2	35	2	39.9	39.6
89	950	H_2	35	4	55.5	52.8
66	1000	H_2/Ar	35	2	29.3	24.2