

Heat of Reaction of Niobium in Buffered Chemical Polish

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7/7/00

Abstract

The heat of reaction of niobium in BCP was determined by a lab-scale experiment performed in a vent hood. The reaction was allowed to occur over a temperature range of 20 °C to 25 °C over a five to seven minute time scale in a nearly adiabatic container. One milliliter of BCP was found to heat up 0.37 °C for every gram of niobium etched. This corresponds to an approximate heat of reaction of 770 kJ/mol of niobium etched.

Introduction

In order to determine the design parameters for a large scale etching system for Niobium, it was important that the heat of reaction of niobium in buffered chemical polish (BCP) be determined. This information can be used to determine the required cooling load for an etching tank, or to determine how much an uncooled acid tank will heat up during an etching process. Information on the heat of reaction of niobium with BCP could not be found in the literature, but it was known that the process was significantly exothermic and had to be monitored in the production of RF cavities. Therefore, a lab-scale etching experiment was performed in which the temperature rise of the acid solution being used to etch the niobium was measured.

Experimental

BCP solution was created by mixing 40 mL of phosphoric acid, 20 mL of nitric acid and 20 mL of hydrofluoric acid in a 100 mL polypropylene beaker. All chemicals were purchased from the chemistry store on MSU's campus and were reagent grade. The sides of the 100 mL beaker were covered in 3/8th inch black, tubing insulation and wrapped in teflon tape in order to reduce heat loss in the container. Also, the 100 mL beaker was attached to the inside of a 1000 mL polypropylene beaker in order to increase the stability and safety of the containers and also reduce heat loss from the BCP due to air currents. Size 25 Norprene food grade tubing was looped twice through the acid and connected by Tygon tubing to a cold water spigot and to a drain. The niobium wafer used in a previous etching experiment¹ was also used in this experiment. In review, a 3/16" hole was drilled through a 16.7 g niobium wafer with the dimensions of 1" by 1" by .125". Teflon string was tied through the hole and used to suspend the wafer in the acid solution. Due to the effects of the first experiment, the weight of the niobium wafer had been reduced to 15.0 grams.

The temperature of the BCP solution was reduced to 20 °C by placing the Norprene tubing in the 100 mL beaker and running cold water through the tubing. The tap water had previously been determined to have a temperature of 14.5 °C. The temperature of the solution was measured using a Teflon covered thermometer. When the acid had been cooled to the desired temperature, the tubing was quickly removed from the beaker and the niobium wafer suspended in the bath. In order to lightly agitate the solution and maintain an even temperature inside the beaker, the wafer was slowly swung back and forth and the thermometer was swirled in the beaker. After the temperature had increased by 5 °C to produce an overall temperature of 25 °C, the niobium was removed from the beaker and rinsed thoroughly with water. The wafer was then measured using an analytical scale. The experiment was repeated twice using the same acid solution cooled back down to 20 °C.

Results

The results for the three tests can be found in Figure 1.

Figure 1: Heat of Reaction Experiment Results

Test	Mass change (g)	Time (min)	etch ($\mu\text{m}/\text{min}$)	H_{rxn} ($^{\circ}\text{C}/\text{gNb mLBCP}$)	H_{rxn} (kJ/mol)
1	0.1608	5.3	2.20	0.389	809
2	0.1791	6.2	2.09	0.349	726
3	0.1692	7	1.75	0.369	769
average:			2.01	0.369	768

The first heat of reaction column refers to the increase in temperature in $^{\circ}\text{C}$ of a milliliter of BCP for every gram of niobium reacted. In order to determine the heat of reaction in kJ/mol, the density and the heat capacity of BCP were calculated assuming an ideal solution. The heat of reaction was determined to be 770 kJ/mol and the etch rate to be 2.0 $\mu\text{m}/\text{min}$.

Discussion

The average etch rate determined, 2.01 $\mu\text{m}/\text{min}$, compares well to the literature data² and to the etch rate found in the experiment mentioned previously. During this experiment, the average etch rate for a non-agitated solution at approximately 30 $^{\circ}\text{C}$ was determined to be 1.48 $\mu\text{m}/\text{min}$. When the niobium was swirled in the acid, the etch rate increased to 3.48 $\mu\text{m}/\text{min}$ at the same temperature. While the acid was also agitated in the experiments performed for this report, it was done to a smaller extent due to the lower quantity of acid being used. Furthermore, the temperature was lower than in the non-temperature controlled experiments. Both of these factors would be expected to lead to a reduced etch rate.

The heat of reaction determined was in the range of the value expected. The heat of reaction was approximated using heat of formation data and led to an expected value of around 500 kJ/mol niobium etched. The calculation did not include the heat of solution of the niobium compounds or nitrogen dioxide produced, and assumed that the only products were nitrogen dioxide, water, and niobium pentafluoride. The extra heat released in the actual reaction is due to lower energy products being created and heat being given off by dissolution of the products.

The initial plans for the experiment called for the acid to be cooled down to 15 $^{\circ}\text{C}$ before starting the etching process. Unfortunately, the low thermal conductivity of the Norprene tubing and the relatively high temperature of 14.5 $^{\circ}\text{C}$ of the cold water made it difficult bring the acid down to this temperature. The heat of reaction at 15 $^{\circ}\text{C}$, however, should not be significantly different than the value determined for this experiment because the product composition should not be noticeably different.

The conditions for this experiment were not entirely adiabatic. The top of the 100 mL container was open to the air. The lip of the outer 1000 mL container, however, helped to keep the air flow of the hood from blowing over the top of the solution. In addition, the experiments only took five minutes and the mid-point of the temperature range change was at room temperature. In the non-temperature controlled experiments performed in an open 1000 mL container, the average temperature drop of the acid solution at 30 $^{\circ}\text{C}$ over a ten minute period of inactivity in the hood was only about a half of a degree.

Another source of error could be found in the way the solution was agitated. A consistent, quantifiable method was not employed for each experiment. This, however, should not effect the heat of reaction, and the randomness of the agitation only produced a standard deviation of 12% in the etch rate.

Conclusions

The heat given off by the niobium reaction should not be a safety concern. The etch rate is not severely temperature dependant as seen by the fact that the etch rate at the temperature range studied in this experiment was similar to the rate found at 30 °C. Furthermore, the heat given off is not large relative to the amount of liquid that will be used in the production of niobium cavities. Therefore, a runaway reaction should be easy to prevent.

Recommendations

Effort needs to be put into finding a suitable method of cooling the BCP. The temperature of the tap water makes it nearly impossible to cool the acid solution down to the desired 15 °C using the tap water in a simple heat exchanger. In addition, suitable tubing needs to be found. Plastic tubing such as the Norprene used in this experiment is resistant to the acid solution, but its heat transfer properties characterize it as an insulator. Stainless steel is a very good conductor of heat, but its resistance to BCP is questionable. 316 stainless may hold up for limited periods, but a hastelloy alloy is probably required for the best results³.

¹ C. Preston et al, "Non-Temperature Controlled Etching of Niobium in BCP", Internal NSCL report, June 2000.

² Hasan Padamsee, Jens Knobloch, Tom Hays, RF Superconductivity for Accelerators, John Wiley & Sons, Inc., 1998, pg. 105-127.

³ R. Perry et al., Perry's Chemical Engineers' Handbook, 7th ed., McGraw Hill, 1997, pg. 28-30 to 28,34.