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METHODS FOR PREPARATION OF EXTREMELY FINE SUPERALLOY POWDERS AND FABRICATION TO SUPERALLOY PARTS

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Introduction

The use of reducing agents such as sodium borohydride have been used in a wide variety of chemical reactions from organic compounds synthesis (1) to metal production (2). In order to reduce metal ions into the metallic state, the solution electrochemical potential must be sufficiently low to allow the metal to accept electrons from the reducing agent. One information source that gives important information regarding the conditions necessary for spontaneous aqueous nickel metal reduction is the electroless nickel plating literature. Although nickel is not the only desired metal, it provides an important starting point in metal reduction, and it is useful because of its resistance to corrosion.

The electroless nickel plating literature indicates that sodium hypophosphite, sodium borohydride, and hydrazine are all used as reductants [3, 4]. Sodium hypophosphite is usually used at 30-95°C in a bath containing dissolved nickel sulfate and other additives such as oxalic acid and ammonium chloride. Sodium borohydride is usually used with sodium hydroxide in a similar temperature range. Hydrazine is also used with sodium hydroxide in a similar temperature range. However, in order to make the transition from electroless nickel deposition to spontaneous metal powder production requires different conditions. In this research program, a number of different conditions were examined to determine optimum conditions for the production of metal and metal alloy powders in aqueous solutions.

Experimental Procedures

The general procedures followed in performing the tests in this study are as follows:

1. Add 40 ml of deionized water to a 250 ml beaker.
2. Add the specified amount of metal salt.
3. Add other nonreducing additives as specified.
4. Adjust the pH to the specified level using HCl or KOH as needed.
5. Heat to 70°C.
6. Carefully and gradually add the reducing agent to the solution.
7. Let the sample stir for approximately 1 hour.
8. Take a small sample of the slurry for microscopic size analysis.
9. Perform the size analysis.
10. Weigh a piece of filter paper.
11. Filter the slurry (filter top, clear section first, before adding the rest to speed filtration).
12. Measure the volume of the filtered solution.
13. Save one sample vial full of the solution - label the vial with the appropriate test number.
14. Dry the filtered solids at 25°C in the oven to avoid dust contamination.
15. Weigh the dried solids.
16. Save the solids in a sample vial - label the vial.
17. Weigh 0.10 gram sample of solids in a 250 ml beaker.

18. Place the 0.10 gram sample of solids in a 250 ml beaker.
19. Slowly add 5 ml of 7:1 water:HNO₃.
20. Mix.
21. Gradually add 10 ml of concentrated HNO₃.
22. If solids do not dissolve in 30 minutes, add a few drops of conc. HCl.
23. Dilute the solution to 100 ml total volume in a volumetric flask.
24. Analyze the solution from step 23 for the metal of interest.

The size analyses were performed by capturing microscopic images using a light microscope, video camera, image data transfer equipment, and image analysis software. Note that the size analyses were performed in-situ using a drop of the colloidal suspension during the metal powder production. The size analyses were performed at 400 X magnification, whereas the images of powders shown later in this summary were obtained on the dried samples with no magnification.

Results and Discussion

Nickel Powders

Experiments were conducted using nickel sulfate along with different additives and either hydrazine, sodium borohydride, or sodium hypophosphite. Test results with hydrazine as the reducing agent did not appear to result in metal powder formation as shown in Figure 1, thus further testing with hydrazine was suspended. Testing using sodium borohydride and sodium hypophosphite

resulted in metal-like powders as shown in Figures 2 and 3 when the proper amount of reducing agent and other additives was present. Chemical analyses on the final powders show that a final powder of *at least 80 % nickel* can be produced using either *sodium borohydride* or *sodium hypophosphite* as the reducing agent. Results also show that recoveries using either of these reducing agents can be *greater than 90%* under proper conditions. In most tests involving sodium hypophosphite, a small (50 mg) chip of magnesium was added in order to initiate the powder formation. Tests with sodium borohydride did not require the use of the magnesium chip.

Both the *chemical additive(s) and quantity and type of reducing agent* had a significant effect upon both the nickel powder grade and recovery. In general, nickel recovery *increased* as the concentration of reducing agent increased. Increasing sodium hydroxide content resulted in higher grade and recovery when used with sodium borohydride. Increasing the ammonium chloride concentration *increased* both grade and recovery when used with sodium hypophosphite.

Figure 1: Test performed With 20 g/l Hydrazine Monohydrate with 5 g/l Nickel sulfate hexahydrate And 69 g/l potassium Phosphate.

Figure 2: Test performed with 30 g/l nickel sulfate hexahydrate, 1.5 g/l sod. hydroxide, and 80 g/l sodium borohydride

Figure 3: Test performed with 90 g/l nickel sulfate Hexahydrate, 53 g/l sod. citrate, 50 g/l ammonium chloride, 450 g/l sod. hypophosphite

Nickel-Iron Powders

Several experiment were performed to produce a nickel-iron alloy powder using sodium hypophosphite. Although only a few tests were performed, the chemical analyses showed that an iron nickel alloy consisting of 36% iron and 30% nickel can be produced using sodium hypophosphite. However, the yields from these tests were generally less than 10%.

Iron Powders

Tests designed to produce iron powders was also performed. The tests using sodium borohydride have been the most successful with grades of 60% and recoveries of 97%. Tests conducted with sodium hypophosphite have yielded much lower grades (13 - 41%) and recoveries (1 - 19%). It is believed that the sodium hypophosphite is an inadequate reducing agent to produce iron powder, since the standard reduction potential for iron is -0.44 V and the final solution potential obtained using hypophosphite was near 0.2 V (The potential in the borohydride tests is typically less than -0.6 V). The final powder produced using sodium borohydride is a fine black powder that is indistinguishable from that shown in Figure 2 for nickel.

Future Work

The testing performed to date has provided considerable insight into the potential for producing metal powders from solution; however, considerable improvements are likely in the areas of metal grades and alloy production. With respect to metal grades, optimization work has not been performed to determine the highest degree of purity that can be obtained using reducing agents. In particular, it is believed that pH control and additive concentration play a very important role in determining the final metal powder grade. The effect of both of these variables should be explored further.

Also, only a few tests have been performed with regard to alloy production using sodium hypophosphite. Results from the iron powder production tests clearly show that sodium hypophosphite is an inadequate reducing agent for iron. Thus, additional alloy powder production tests should be performed using sodium borohydride.

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