Properties of Nickel Fume Generated in a Plasma Jet

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The possibilities of chemical processing in a plasma jet have been intriguing ever since the advent of commercially available arc plasma generating equipment several years ago. Processes such as nitrogen fixation, acetylene, and carbon black formation from hydrocarbon vapors have been reported. However less work has been done on exploring the possibilities of forming solid materials with unique surface properties. The Vitro Corporation (*1*) has pioneered in the formation of silica fume by vaporizing consumable electrodes in a high-intensity arc and has extended this work to purification of beryllium (*2*) and manganese ores (*3*) and aluminum powder (*4*).

This investigation was initiated to determine what features could be incorporated in an inorganic crystal lattice formed by condensation from the vapor state in a highly ionized plasma. Because of the thorough literature coverage and ease of working with the nickel-nickel oxide system it was chosen as the system for study. The volatile liquid nickel carbonyl was chosen as the feed material and was used in all subsequent work in preparing nickel fume. Since the nickel is already a vapor when it enters the electrode chamber, a much higher degree of thermal ionization can be achieved than by going through an initial electrode vaporization step.

A plasma generating system with a head operated on argon was used in all of this work. Electrodes in this system are water cooled and nonconsumable as compared with the Vitro electrode system. Four rectifiers capable of producing 48 kw. were connected in parallel to supply the electrical power.

EXPERIMENTAL PROCEDURE

Fume and Arc Characterization

Nickel fume is the ultrafine powder condensed out of the argon plasma jet containing decomposed nickel carbonyl vapor. It consists of a physical mixture of nickel, nickel oxide, and electrode impurities. The effects of various arc operating parameters on the fume were evaluated by measuring chemical and physical properties of the powder.

The usual solid state measurements such as electrical conductivity, Seebeck effect, or Hall effect would be difficult to make and even more difficult to interpret because the fume is not a pure material and is quite sensitive to its pressure and thermal environment. Hence surface area was used to help characterize the fume, and within the scope of this paper it is the most important property.

Surface areas were measured by gas chromatographic techniques with a modified Burrell Kromo-Tog and an adaptation of the Brunauer-Emmett-Teller method (*5*). Surface areas measurements as a function of time at fixed temperature were used to characterize sintering rates in air, oxygen, and hydrogen.

In measuring the surface areas of representative samples made with two different plasma generating anodes, several sample preparation techniques were tried to see if the physical form of the powder had any bearing on the values. The results of these treatments are shown in Table 1. Because of the marked influence of pressure on room temperature sintering all further surface areas were measured on unpressed fume. The outgassing step was also adopted as standard procedure.

Chemical activity due to available or nonstoichiometric oxygen was measured by titrating the iodine liberated from an acidic starch-KI solution of the sample with standard sodium thiosulfate. At sufficiently high temperature, oxygen is reversibly taken up by the bulk oxide, and for each mole of excess oxygen two nickel vacancies (2 Ni^{+2}) and four Ni^{+3} ions are created to maintain neutrality and form a p-type of semiconductor NiO_{1+x}. The value of x can be determined when the impurity concentration and ratio of nickel to nickel oxide are known.

There is still considerable debate among solid state physicists studying oxygen excess semiconductors about the interpretation of nonstoichiometric oxygen content. Whether a clear-cut distinction between chemisorbed and lattice bound oxygen can be made has not been resolved. Nevertheless the amount of excess oxygen is related to the method of treatment in the plasma jet. Distinction in advantage between high surface area or high available oxygen was not made owing to the previously mentioned problem. It would also depend on the ultimate use of the fume.

The metal to metal oxide ratio was determined qualitatively by X-ray diffraction on the crystalline fraction of the sample. Owing to considerable line broadening and no knowledge of the amorphous content of the fume the ratio is only an estimate of the true value. Chemical analysis for the nickel content was made by gravimetric and X-ray fluorescence techniques. Carbon was determined volumetrically. Electrode impurities were tungsten from the cathode, boron from a boron nitride insulator ring for the cathode, and copper from the anode. Electrode contamination and erosion rate are two of

TABLE 1. SAMPLE TREATMENT EFFECT ON SURFACE AREA

Treatment	Sg(sq. meter/g.) 5/16 in.*	Sg(sq. meter/g.) 7/16 in.*
1. None-powder as collected	72	165
2. Outgassed in helium for 2 min. at 120°C.	69	167
3. Original powder pelleted and crushed	62	93
4. Crushed pellets outgassed	64	121

* Anode hole diameter (arc variable).

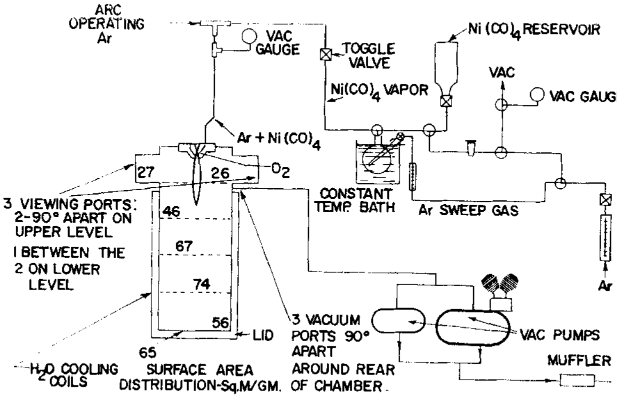

Fig. 1. Fume production system.

the prime considerations in use of the plasma jet as a preparative tool.

Arc stagnation enthalpy has been shown to be a relatively simple but valuable parameter to measure and correlate with fume properties. It was determined by measuring the net electrical energy content of the arc when corrected for 5% radiation loss and heat loss to the electrode cooling water. The heat content is expressed as reduced stagnation enthalpy which is a dimensionless parameter defined by the relation

$$\frac{H_T^o}{RT_o} = \frac{H_T^o - H^o_{298}}{RT_o} + \frac{H^o_{298} - H_o^o}{RT_o} = \frac{(9.5 \times 10^{-4}VA) - L}{q\,RT_o} + 3$$

Values of H_T^o/RT_o can be used in conjunction with an argon Mollier diagram to define arc stagnation temperatures when no other gases are present in the plasma and arc pressure is known.

Carbonyl Injection Technique

A schematic diagram of the system used in producing the fume is shown in Figure 1. The nickel carbonyl feed system is maintained in an inert atmosphere at all times to prevent decomposition of the liquid. The vapor pressure of the liquid in the feed flask is adjusted to change the feed rate.

The plasma jet is run inside a brass environment chamber maintained at roughly 0.2 atm. during the nickel carbonyl vapor injection period. The chamber dimensions are 8 in. I.D., 20 in. high, with five equal height subdivisions marked off in Figure 1. When the water-cooled chamber walls overheated, the arc was turned off and the chamber cooled in argon at 1 atm. When run under vacuum the arc is about 6 in. long as compared with about 2 in. at 1 atm.

Residence time for a typical run in the subatmospheric arc is 88 μsec. and is about 85% longer than in an atmospheric arc run at the same power level. This comparison is based on calculated aerodynamic velocities in the throat of the converging anode nozzle and assumes constant velocities over the entire jet length for simplicity. The real situation is difficult to define without elaborate velocity measurements. Nevertheless the arc run under reduced pressure insures longer contact time for the nickel vapor which results in more time for electronic energy equipartition. As a result of this and the decreased pressure the degree of nickel ionization is higher than in an atmospheric arc. High ion concentrations create a high nucleation center density which will lead to condensation of very fine particles from the supersaturated vapor.

To insure continuous operating without plugging the vapor was injected by passing the argon swept feed through a pipe tee where it mixed with the main argon arc operating gas flowing at above 0.7 std. cu. ft./min. The gas mixture then entered the electrode gap in a tangential swirl followed by carbonyl decomposition (Figure 2). Gaseous products in the jet were swept out through the anode orifice and condensed out on the chamber wall as nickel fume with a surface area of 91 sq. meter/g. Since this injection technique worked so efficiently the first time, it was used in all further studies.

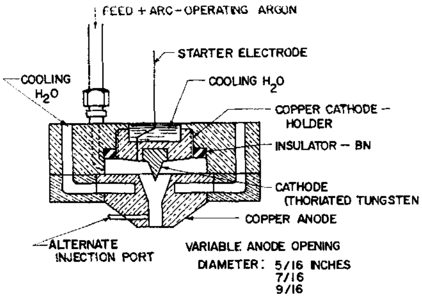

Fig. 2. Electrodes and feed injection system.

Fume Recovery and Sampling

To determine the distribution of fume on the chamber wall a carefully controlled run was made, and samples were taken from 4-in. vertical sections on the chamber wall, the bottom lid, and the viewing ports. The surface areas of these samples are shown in Figure 1. Since the high area powder was concentrated on the lower 12-in. wall section, this area, excluding the lid, was sampled in all further tests. The range of areas in this section is 65 ± 9 sq. meter/g. which is not a big spread. Sampling included the entire circumference of this 12-in. vertical section followed by uniform mixing and quartering. Between 65 to 75% of the fume was deposited on the lower 12-in. section.

The powder is black owing to the nonstoichiometric oxygen content of the nickel oxide. Black nickel oxide is characteristic of a material prepared by thermal decomposition of nickel carbonate at 400°C., whereas decomposition of nickel carbonate at 1,000°C. gives a stoichiometric green nickel oxide. Here is a case where nickel oxide prepared at much higher than 1,000°C. is black, contrary to what would have been predicted.

The fume can easily be rubbed off the brass wall with rubber gloves for collection. There is considerable static charge associated with the powder because of its particle size and method of preparation. In general it has a bulk density of about 14 lb./cu. ft.

VARIABLE STUDY

The effects of five arc operating parameters on fume properties were investigated. There was no preconceived notion about the importance of these five, but it turned out they all were. Operating data and results of pertinent runs to be compared are tabulated in the Appendix.* Listed are run conditions, composition, and surface area of the fume.

Anode Hole Diameter

The influence of the diameter of the anode hole was the first variable studied. The variation in fume properties with hole diameter at H^o_T/RT_o = 45 to 185 is shown in Figure 3. Increasing the diameter from 7/16 in. has very

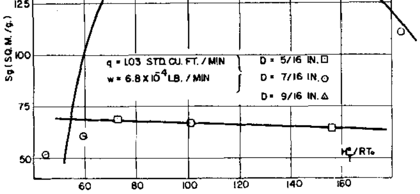

Fig. 3. Stagnation enthalpy effect on surface area.

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* Tabular material has been deposited as document 7761 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or for 35-mm. microfilm.

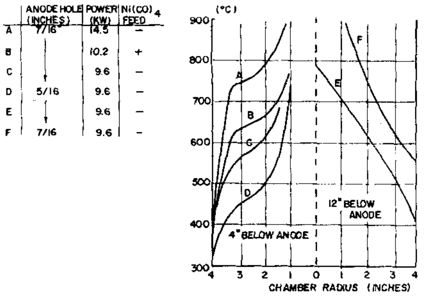

Fig. 4. Quench chamber temperature profile.

little effect on surface area. This is important from a practical standpoint because it means normal anode erosion leading to an enlarged nozzle will not significantly decrease the surface area.

Variation in anode hole diameter does not change the carbon content or nickel-nickel oxide ratio. The effect on available oxygen was inconclusive.

To determine why a decrease in diameter from 7/16 to 5/16 in. should change the surface area so much the temperature of the gas in the brass chamber was measured as a function of distance from the arc center to the chamber wall. Two sets of four thermocouples at the two positions in Figure 4 measured the profile. Curve D shows a much more rapid drop off in temperature for the 5/16-in. anode than curve C for the 7/16-in. anode. The same is true in curves E and F at a distance of 8 in. lower in the chamber. Arc power input increases the temperature in the 4-in. gap from the arc core.

Addition of nickel carbonyl to the arc increases the temperature in the gap over that without nickel carbonyl in the arc. This is a result of the nickel vapor releasing its heat of vaporization as it condenses in the region between the arc and the wall. As a result of the different cooling rates with the two anodes the vapor from the 5/16-in. anode becomes supersaturated and condenses to solid nickel oxide nuclei closer to the arc than with the larger anode. As a result of this the condensed fume has a longer time to sinter in hot gaseous atmosphere before hitting the water-cooled wall when the small anode is used. A two-color optical pyrometer gave a temperature of 2,700°C at the bottom tip of the arc jet 6 in. from the anode when nickel carbonyl is fed at 12-kw. power input and q = 1.03 std. cu. ft./min.

Stagnation Enthalpy

Since the temperature varied continuously throughout the arc and was difficult to measure for use in chemical reaction characterization, the arc enthalpy was used as a measure of the thermal environment through which the nickel vapor passed. The results of fourteen runs with three anodes at different reduced stagnation enthalpy are plotted in Figure 3. All variables are fixed except enthalpy and anode diameter.

The region for maximum surface area is quite broad for the 7/16-in. anode, but it shows a definite drop off on either extreme. As long as $H^o{}_T/RT_o$ is in the range 80 to 150, the surface area will be over 150 sq. meter/g. With the 5/16-in. anode there is no variation in area throughout the range studied.

Low enthalpy results in low carbon and very high nickel-oxide nickel ratio with the 7/16-in. anode. High enthalpy produces high carbon and an intermediate nickel oxide-nickel ratio. Nonstoichiometric oxygen content is higher for high enthalpy.

Nickel Carbonyl Concentration in Arc Gas

Surface area is inversely proportional to the concentration of nickel carbonyl in the arc gas. Figure 5 shows this correlation with data from runs having $H^o{}_T/RT_o$ between 78 to 126, a range where enthalpy has little effect on surface area for the 7/16-in. anode. High nickel carbonyl concentration generates a high nickel-nickel oxide ratio in the product. Increasing carbonyl rate at fixed argon rate increases the tungsten cathode erosion due to high temperature sputtering by the gaseous nickel ions and erosion due to carbon. Carbon content and oxygen excess are not influenced by concentration.

Turkevich (*6*) reported a concentration effect in thermal decomposition of a nitrogen stream of iron pentacarbonyl at high temperature. The lower the iron pentacarbonyl concentration the smaller the particles which condensed out downstream. Particle morphology was also influenced by iron pentacarbonyl concentration. Particle shape has not been investigated in this work.

Oxygen Injection

The effect of oxygen injection was studied by adding it to the arc gas through the anode injection port shown in Figure 2. As would be expected the addition of oxygen lowers the carbon content, raises the nickel oxide-nickel ratio, and increases the excess oxygen content of the fume.

Since the definition of arc enthalpy is ambiguous with oxygen dilution, the surface area results were compared on the basis of fixed power input at either equal total argon rates or equal total argon plus oxygen rates. In either case the addition of oxygen lowers the surface area markedly, in some cases from 160 to 80 sq. meter/g.

In order to determine whether possible air leakage into the chamber had any influence on the arc reaction when run at 0.2 atm. a sample was taken of the chamber off gas during a typical nickel carbonyl feed run and analyzed by mass spectrometer. The result was 1.5% nitrogen, 0.3% oxygen, 0.3% carbon monoxide, 0.1% carbon dioxide, 97.8% argon. It is difficult to say on the basis of this analysis whether the oxygen from dissociated carbon monoxide or leaking air causes the greatest part of the nickel oxidation because the rate of oxygen appearance from either source is about the same.

Rapid Quench

The last one of the variables studied was rapid quenching of the arc tip. Isopropyl alcohol cooled down to − 65°C. with dry ice was rapidly pumped to the inside of a nickel pipe cap suspended below the arc anode. Temperature measurements of the coolant and the cap while the arc was running without carbonyl feed showed that the surface of the cap and the exit coolant never went above 125°C. when 4 in. below the anode. As soon as nickel carbonyl was added to the arc, the pipe cap temperature rose above 400°C. owing to liberation of the nickel heat of vaporization.

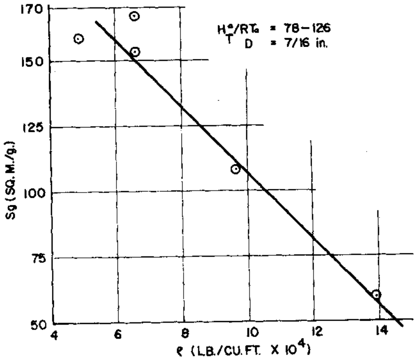

Fig. 5. Influence of nickel carbonyl concentration in argon arc gas on surface area.

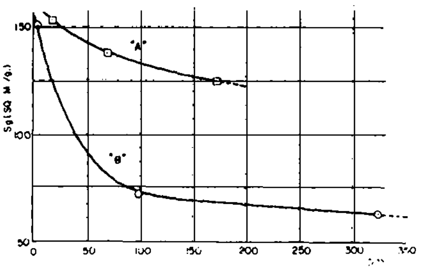

Fig. 6. Room temperature sintering of nickel fume.

Surface area of the powder quenched in this way was 82 sq. meter/g. or about half that formed with regular brass wall cooling. The same effect was observed when the cap was lowered three more inches. Inability to rapidly remove the quenched fume from the pipe cap resulted in loss of surface area owing to sintering. The most significant change was the unusually high carbon content. At 11.3% this was ten times higher than the next highest run with conventional quench. Rapid quenching also raised the available oxygen content to seven to ten times the value with regular quenching.

FUME SINTERING

The particle size of nickel fume with a surface area of 150 sq. meter/g. has been measured with an electron microscope. The size ranged from 30Å. to 300Å. with the majority of the particles below 100Å. The geometric surface area of a cubic nickel oxide particle 54Å. on an edge is 150 sq. meter/g. Thus the correlation between measured surface area and calculated value based on particle size shows the fume surface is mainly geometric with little pore structure. A 54Å. particle of nickel oxide has 29% of its molecules on the cube surface.

The effect of impurities on sintering has not been determined. The range of impurities is carbon 0.2 to 11.3%, boron 0.1 to 1.0, tungsten 1.1 to 11.5, copper 0.7 to 2.7, nickel 65+. The excess oxygen content of one sample has been translated into a stoichiometry of $NiO_{1.008}$.

Various theories have been postulated to account for the solid state sintering process. Most of these agree on surface diffusion as the principal phenomenon occurring below the Tamman temperature ($0.5 \times T_{MP}$ in °K.). Some of the fume samples prepared in this work show measurable surface area decrease at room temperature which is only 0.13 T_{MP} of nickel oxide. In Figure 6 this phenomenon is shown for two samples with the same initial area. This is conclusive evidence for a high degree of excess surface energy which is slowly released in attaining a more thermodynamically stable crystal structure. The difference between the two curves has not been completely explained but may be related to the nickel-nickel oxide ratio. No satisfactory theory for explaining the observed kinetics of surface area decrease has been developed as yet. Most probably there is a spectrum of activation energies dependent on the concentration of defects present at any time.

The nature of the gaseous environment has been shown to influence sintering rates at moderate temperature (below 550°C.). Nickel fume is more resistant to sintering at high temperature in an oxygen atmosphere than in hydrogen. Nuclear irradiation of nickel oxide has been shown to reduce the induction period for reduction at 250°C. by a factor of 4 and increases the rate by a factor of 2 (7). The formation of point defects and dislocations by plasma treatment is presumably a similar type of high energy treatment, although of much lower magnitude.

CONCLUSION

The influence of ionized plasma on formation of a high surface energy fume has been established. The high surface area, small particle size, and defect state as reflected in room temperature sintering are definite evidence of unusual features in powdered nickel oxide. Surface areas of commercially available nickel-nickel oxide powders range from 0.4 sq. meter/g. carbonyl nickel prepared by decomposing nickel carbonyl at 250°C. through pyrophoric nickel at 72 sq. meter/g. to stabilized nickel on aluminum oxide at 187 sq. meter/g. Quantitative evaluation of the three stages of fume formation characterized by reactions in the arc, condensation, and solid particle growth remain for future studies.

ACKNOWLEDGMENT

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NOTATION

A = d.c. current, amp.
D = anode hole diameter, in.
H^o = ideal gas stagnation enthalpy, kw./std. cu. ft./min.
L = power loss to cooling water, kw.
O_{xs} = nonstoichiometric or excess oxygen content, weight %
p = chamber pressure, atm.
q = arc operating gas rate, std. cu. ft. argon/min.
ρ = nickel carbonyl concentration in argon arc gas, lb./cu. ft.
R = gas constant, 1.75×10^{-4} kw./std. cu. ft./min./°K.
Sg = surface area per gram, sq. meter/g.
T_o = 273.16°K.
V = d.c. voltage, v.
w = nickel carbonyl feed rate, lb./min.

Dimensionless Groups

$$\frac{H^o{}_T - H^o{}_o}{RT_o} = \text{reduced stagnation enthalpy at } T°\text{K.} = H^o{}_T/RT_o \text{ for argon}$$

$$\frac{H^o{}_{298} - H^o{}_o}{RT_o} = 2.73 \text{ for argon}$$

X_{Ni} = relative X-ray line intensity for 2.04Å nickel line
X_{NiO} = relative X-ray line intensity for 2.09Å nickel oxide line

Subscript

H_T = enthalpy at reference temperature, T°K.

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