United States Patent Office 3,529,954 Patented Sept. 22, 1970

3,529,954

METAL FIBERS

Robert E. Cech, Scotia, N.Y., assignor to General Electric Company, a corporation of New York

No Drawing. Filed Apr. 22, 1968, Ser. No. 723,313
Int. Cl. B22f 9/00
U.S. Cl. 75—.5 8 Claims

ABSTRACT OF THE DISCLOSURE

A metal sulfide is reduced with hydrogen in the presence of a scavenging agent to produce metal fibers. These fibers can be sintered to produce a product having numerous interstices useful as a filter.

This invention relates to the art of preparing metal fibers and is more particularly concerned with a novel method of producing metal filaments from metal sulfides and with the unique products of this process.

The thermodynamics for hydrogen reduction of metal sulfides is unfavorable. For example, the reaction:

$$Cu_2S+H_2 \rightleftarrows 2Cu+H_2S$$

has a value for the equilibrium constant of only about 1×10^{-3} in the temperature range of interest (about 300°–900° C.). Equilibrium is attained when the gas stream contains only 0.1% H_2S, and reduction kinetics are undoubtedly established by the rate of transport of H_2S out of the system. For this reason, direct hydrogen reduction of a metal sulfide has never been seriously considered as a metal production process.

I have discovered that the shortcomings of the prior art can be overcome and that hydrogen can be used to advantage under certain circumstances by using a scavenging agent for hydrogen sulfide gas. Specifically the scavenging agent, in a finely divided form, is initially admixed with the metal sulfide particles prior to treatment with hydrogen. During reduction, as hydrogen sulfide is produced, it is quickly removed by the scavenging agent which is in close physical proximity to the sulfide. By this technique, hydrogen sulfide gas is removed at a point close to the point of generation rather than being carried through and out of the system. Accordingly, the use of the scavenging agent under these conditions brings about a significant increase in reduction kinetics to substantially completely reduce the sulfide and enable the formation of metal fibers.

Briefly stated, the present invention provides a process for reducing a metal sulfide to form metal fibers wherein said sulfide is selected from the group consisting of a copper sulfide, a nickel sulfide, a cobalt sulfide and a nickel-cobalt alloy sulfide, which comprises contacting said sulfide with a hydrogen reducing gas in the presence of a scavenging agent for hydrogen sulfide gas. This process is carried out in the temperature range of a minimum temperature at which metal fibers form and a maximum temperature corresponding to the eutectic temperature of the metal-metal sulfide system.

The particular chemical composition of the sulfide can vary, i.e. it may vary from metal-rich to sulfur-rich. The sulfide, however, should be substantially free of the metallic phase. The sulfide may contain non-metallic impurities since their presence does not deteriorate to any great extent the filament-forming mechanism. As the impurity content of the sulfide is increased, however, the amount of filament produced is decreased. Substantially pure metal sulfides are therefore preferred since they yield the largest amount of metal fibers.

In carrying out the instant process, the metal sulfide should be in a particulate form. Particle size of wide range can be used because the coarser particles break up as reduction progresses. Particles of a finely-divided form, i.e. less than about 10 mesh, are preferred since they provide a large surface area for contact with the reducing gas thereby promoting quick reduction of the sulfide particles. In addition, finer fibers are usually produced from the finer metal sulfide particles.

A number of scavenging agents for hydrogen sulfide gas may be used. These agents should form sulfides which are removable by conventional techniques. Representative of such agents is calcium oxide, calcium carbonate and calcium hydroxide. Calcium hydroxide and calcium carbonate are effective only after decomposition by heat to calcium oxide. To obtain maximum absorption of the hydrogen sulfide, the scavenging agent should be used in at least a stoichiometric amount. Amounts in excess of the stoichiometric amount are satisfactory. The scavenging agent should also be in a particulate form. Particle size may vary widely. However, particles of a finely divided form, i.e., less than about 10 mesh, are preferred since the scavenging agent has to pick up the hydrogen sulfide at a rate faster than the rate at which it is produced. This is generally accomplished by using a finer particle size to obtain a larger surface area. Specifically, when calcium oxide is mixed with the metal sulfide particles, hydrogen sulfide gas will be removed by the reaction:

$$CaO+H_2S \rightleftarrows CaS+H_2O$$

The hydrogen reducing gas used may be any commercial grade of hydrogen or a gas mixture containing hydrogen. The hydrogen gas mixture is useful for the reduction of cobalt sufide and nickel-cobalt alloy sulfides containing significant amounts of cobalt since pure hydrogen is too strong a reducing agent for these sulfides converting them generally to sponge metal with only an occasional filament in evidence. A gas mixture comprised of 10% hydrogen and 90% nitrogen is satisfactory. The reducing gas may contain impurities which would not significantly interfere with the process, i.e. carbon monoxide, hydrocarbons and nitrogen. The hydrogen may also be used in a form such as cracked ammonia gas. Generally, in a given physical apparatus, the highest gas flow rate consistent with keeping the products in the hot zone of the furnace is used to shorten the period of reduction.

A number of conventional techniques can be used to carry out the instant process. Preferably, the scavenging agent is initially thoroughly mixed with the metal sulfide so that the hydrogen sulfide gas is removed at a point close to the point of generation. The mixture can be reduced in any closed system which is suitable for contracting particulate solids with a gaseous reducing agent. For example, the mixture may be spread in a layer in trays which are passed through a furnace or a rotary hearth furnace may be used.

The metal fibers of the instant process are produced within a certain temperature range. The minimum temperature is one at which fibers will form. The maximum reducing temperature is the eutectic point of the metal-metal sulfide system which is a composition dependent point. It varies depending on the impurities present. The eutectic temperature for nickel sulfide is about 637° C., and for cobalt sulfide it is about 880° C. The nickel-cobalt alloy sulfides used herein may contain any proportion of nickel or cobalt and their eutectic temperature will lie between about 637° C. and about 880° C. Copper sulfide has a eutectic temperature of about 1067° C. At temperatures higher than the eutectic temperature, each metal sulfide particle melts to form a sphere of liquid, and as the sulfur is removed during the reduction process, a skin of metal forms over the particle resulting eventually in a hollow sphere of metal.

The minimum temperature at which fibers will form

within a reasonable period of time, generally no longer than about an hour, depends somewhat on the specific metal sulfide composition. Generally, nickel sulfide has a minimum temperature of about 535° C., copper sulfide has a minimum temperature of about 400° C., cobalt sulfide has a minimum temperature of about ten degrees below the eutectic point and the nickel-cobalt alloy sulfide has a minimum temperature of above about 535° C.

The specific structure of the metal fibers depends on the particular metal sulfide used and the process temperature. The maximum amount of metal fibers is generally produced at a temperature close to the eutectic point, usually within about one to ten degrees of the eutectic point. At the eutectic point, the production of fibers is inhibited to some extent due to formation of the eutectic liquid. At temperatures close to the minimum temperature at which metal fibers initially form, smaller amounts of fibers form because more metal sulfide particles remain inert to the reducing system.

Generally, in the present invention, copper sulfide reduced in the presence of a scavenging agent produced a profuse growth of filaments which were largely irregular in character. By the term irregular it is meant a fiber of varying thickness. Nickel and cobalt sulfides and a nickel-cobalt alloy sulfide reduced in the presence of a scavenging agent produced a variety of fibrous or columnar crystal growth forms. By the terminology columnar crystal growth form it is meant a straight fiber of substantially uniform thickness. Reduction at a temperature equal to the metal-metal sulfide eutectic temperature and over a few degrees of temperature below this point produced columnar single crystals, i.e. fibers of 10 to 100 microns diameter and 0.1 to 1.0 mm. in length of metal. Below this temperature thinner single crystals, i.e. straight filaments of 1 to 5 microns diameter and 1.0 to 10 mm. in length were formed by the reduction treatment. At still lower temperatures irregular polycrystalline fibers were formed.

The fibers produced by the present process are useful for a number of applications. For example, they can be sintered to produce an interlocked structure of porosity and density which may be varied depending on the final use of the product. Specifically, a highly porous structure is useful as a filter. The fibers can also be used to form composites with other materials such as plastics or other metals. For example, the fibers can be used in substantially the same manner as fillers to reinforce plastic. Although metal fibers have been prepared mechanically, they are more expensive to produce, and they cannot be made in a significant amount in as fine a form as the present fibers.

All parts and percentages used herein are by weight unless otherwise noted.

The invention is further illustrated by the following examples.

The conditions used in the following examples were as follows unless otherwise noted:

The reduction furnace was a horizontal electrical resistance tube furnace 1¾ inch inside diameter x 30 inches long with a tapered winding to lengthen the constant temperature zone. A fused silica tube extended through the furnace.

Experiments were performed by placing a thin layer of the sample particles in a porcelain boat and pushing it into the furnace pre-heated to the desired reduction temperature.

During the reduction period the hydrogen reducing gas was passed over the specimen at a flow rate of 100 cm.^{3} per minute.

100% of all the scavenging agent used was in powder form having a particle size under 325 mesh.

EXAMPLE 1

In this example, a series of runs was made wherein copper sulfide was reduced by hydrogen gas and a second series of runs was made in substantially the same manner except that a scavenging agent was used.

Copper sulfide was prepared by reacting conductivity grade copper and resublimed sulfur at the boiling point of sulfur, 444.6° C. Following this, the excess sulfur was driven off in a flowing stream of hydrogen. The sulfide was not fused prior to its use in reduction experiments. Weight gain measurements on the reacted material showed that it was comprised of 90% Cu_2S and 10% CuS. The copper sulfide was crushed to a particle size of 0.5 to 1.0 mm.

In the first series of runs, without the scavenging agent, long incubation periods were required. Specifically, at a reduction temperature of 600° C. copper filaments grew from 0.5 to 1.0 mm.-diameter sulfide particles after an incubation period of 60 to 90 minutes. Approximately 48 hours were required to bring about complete conversion to a fibrous metal product. Reduction treatments of 48 hours at 400° and 500° C. caused only an occasional filament to form on the otherwise unreacted sulfide particles.

Reduction of copper sulfide at 700° C. produced a porous incompletely reduced product with a bright film of copper coating all surfaces of the sulfide. No indications of fiber formation were found.

In the second series of runs, copper sulfide particles, 1 mm. in diameter, were mixed with a stoichiometric excess of finely divided calcium oxide and heated to 600° C. in hydrogen for varying periods of time. The incubation period for the appearance of copper fibers was less than 3 minutes. The presence of calcium oxide, therefore, reduced the incubation period by 57 minutes. A photomicrograph of a partially reduced particles showed that a large number of fine, closely spaced copper filaments were formed over the entire surface of the sulfide particle. The fibers were curly and irregular in cross-section ranging in thickness from about 25 to 100 microns.

EXAMPLE 2

A number of nickel sulfide melts ranging from 70.0% to 78.3% nickel, balance sulfur, were prepared by reacting Inco electrolytic nickel sheet and redistilled sulfur in a fused silica tube under a hydrogen atmosphere. After the reaction was completed the sulfide was heated to a fully molten condition, violently agitated to homogenize it and rapidly solidified by running it into the cold end of the tube. The compositions of the samples were, for the most part, within the Ni_3S_2 single phase field. The nickel sulfide was crushed to a particle size of 0.5 to 1.0 mm.

Reduction was performed by mixing small samples of the crushed nickel sulfide with a stoichiometric excess of calcium oxide or calcium carbonate and heating the mixture to 600° C. in hydrogen for varying periods of time. Upon completion of the reduction treatment, the scavenging agent was removed either magnetically or by screening. Final cleanup was accomplished with a wash in dilute acid.

Reduction treatments of one hour produced complete reduction of 0.5 mm. to 1.0 mm. diameter nickel sulfide particles to a mass of nickel filaments. A shadowgraph of a small amount of the material was made. Individual fibers appeared to be only a few microns in cross-section, a millimeter or less in length, and perfectly straight. A second shadowgraph was evidence that the straight fibers grew from the base, not from the tip as do the "whiskers" produced by reduction of metal halides.

EXAMPLE 3

A cobalt sulfide ingot with a composition corresponding to Co_9S_8 was produced by reacting electrolytic cobalt sheet and resublimed sulfur in a fused silica tube under a hydrogen atmosphere. The reacted mass was brought to the fusion point, agitated to homogenize the melt, and

allowed to solidify in place. After cooling, the ingot was crushed to 0.5 mm. to 1.0 mm. diameter particles.

Reduction runs were carried out by placing 0.1 gram samples of the cobalt sulfide in a small molybdenum boat. After thirty minutes, upon completion of the reduction treatment, the samples were withdrawn from the furnace and examined microscopically.

Additional reduction runs were carried out in the same manner except that the 0.1 gram sample of cobalt sulfide was premixed with 0.12 gram of calcium hydroxide.

It was found that with pure hydrogen alone, in the reduction furnace, either with or without the scavenging agent, and with reduction temperatures ranging from 780° to 880° C., cobalt sulfide was reduced to a coarse, semi-fibrous, i.e. sponge-like material. In this case the eutectic temperature occurs at 880° C. between cobalt and Co_4S_3. Additional runs carried out at still higher temperatures produced the same type of material. This was strong evidence that the particles became completely reduced while being heated to the reduction temperature.

Further experiments were then carried out using a gas mixture containing 10% hydrogen and 90% nitrogen.

Reduction experiments carried out above the eutectic temperature then produced agglomerates of equiaxed metal crystals that were indistinguishable from those produced by reduction of nickel sulfide under similar conditions. Reduction at 878° to 880° C. with calcium hydroxide produced coarse short fibers about 0.5 to 2 mm. in length. A few extremely long and fine filaments approximately 5 mm. in length and 3 to 5 microns in cross-section were found in the reduced material. Many of the filaments were in the form of a thin ribbon rather than a square cross-section. Only irregular fibers were produced when the reduction temperature was more than a few degrees below the eutectic point, i.e. 878° C. When reduction occurred more than 10° below the eutectic point, or when the calcium hydroxide was omitted, the product consisted entirely of non-fibrous metal.

EXAMPLE 4

In this example, nickel-cobalt alloy fibers were formed by reducing a nickel-cobalt alloy in the presence of calcium hydroxide.

A nickel-cobalt alloy sulfide of the composition $(Ni_{0.5}Co_{0.5})S$ was prepared. The sulfide was crushed to a particle size of about 0.5 to 1.0 mm. Samples were prepared by thoroughly mixing a portion of the alloy sulfide with twice the stoichiometric amount of the calcium hydroxide.

A series of thirty minute reduction runs was performed using a 10% hydrogen-90% nitrogen reducing gas and a variety of reduction temperatures. The upper temperature limit for filament formation was found to be 805° C. and the lower temperature limit about 750° C. At temperatures lower than this the incubation period for fiber nucleation exceeded one hour. Above 805° C. only spherical metal particles were produced. Within the 55° temperature range for fiber formation the fibers were observed to be almost exclusively of the straight single crystal filament type and frequently quite long, occasionally exceeding 1 cm. in length.

EXAMPLE 5

A comparison was made between −325 mesh and −100 +200 mesh nickel sulfide particles. Samples were prepared by mixing a portion of the nickel sulfide of specified particle size with calcium oxide in excess stoichiometric amount. Each sample was reduced by hydrogen by identical reduction treatments of 60 minutes at 600° C. Following the separation procedure to remove calcium salts the fibers of each reduced sample were pressed into pellets in order to facilitate metallographic examination. The metallographic structure of sections taken through the fibrous material showed a very significant size effect with the finer sulfide particles reducing to finer fibrous material.

EXAMPLE 6

This example illustrates the different types of fibers which can be produced under various process conditions. Nickel sulfide of Ni_3S_2 composition having a particle size of 0.5 to 1.0 mm. was used. Samples were prepared by mixing a portion of the sulfide with a 1.2 x stoichiometric amount of calcium hydroxide. The reduction was carried out under hydrogen at 1° intervals of temperature from 640° to 637° C. and at 10° intervals lower in temperature. Each reduction run was about 120 minutes. The upper temperature limit for fiber formation was found to be 638° C. Fibers were formed at all temperatures lower than this to 535° C. Reduction at 532° C. produced only irregular masses of nickel.

Three distinct types of crystalline or fibrous nickel growth were observed. At and near the eutectic temperature, columnar crystals were formed by crystallization from a completely liquid sulfide phase. Visual examination of partially reduced particles shows globular particles of sulfide studded with partially grown columnar crystals.

As the reduction temperature was lowered, columnar crystals appeared less frequently and the structure was composed of a fibrous product comprised mainly of straight-sided filaments and ribbons.

The nickel fibers produced by reduction of Ni_3S_2 at 567° C. and lower are almost entirely of the irregular type. Reduction at 577° and 587° C. produced a mixture of straight and irregular fibers.

EXAMPLE 7

The metal fibers prepared in Example 2 were sintered by heating in hydrogen to a temperature of 700° C. The resulting structure had numerous small interstices and was useful as a filter.

EXAMPLE 8

This example illustrates that a minute quantity of hydrogen sulfide in the gas stream prevents the formation of metal fibers. A number of nickel sulfide particles 0.5 mm. in diameter were placed in a row on a small strip of mica in a stainless steel boat. The boat was pushed into the center of the uniform temperature region of the furnace with the temperature set 2° below the eutectic temperature, i.e. 635° C. Hydrogen gas was flowed over the specimen and no scavenging agent was used in the system. After treating for a time to allow only partial reduction to occur the boat was withdrawn and the particles were examined. It was noted that the first few particles were completely decomposed to fine filamentary metal with much of it in the form of straight sided filaments. The remaining particles were only partially reduced and showed only slight indications of a tendency for filament formation. While a few indications of filament formation could be seen, most of the metallic phase had deposited on grains which were completely immersed in the nickel sulfide. Apparently, the filament forming process was inhibited by the slight pressure of H_2S resulting from reduction of particles ahead of it in the flowing reducing gas stream.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. A process for reducing a metal sulfide to form metal fibers wherein said sulfide is selected from the group consisting of a copper sulfide, a nickel sulfide, a cobalt sulfide, and a nickel-cobalt alloy sulfide which comprises contacting said sulfide with a hydrogen reducing gas in the presence of a scavenging agent for hydrogen sulfide gas, said process being carried out in the temperature range of a minimum temperature at which metal fibers form and a maximum temperature corresponding to the eutectic temperature of the metal-metal sulfide system.

2. A process according to claim 1 wherein said metal sulfide has a particle size less than 10 mesh.

3. A process according to claim 1 wherein said reducing gas is selected from the group consisting of hydrogen and a gas mixture containing hydrogen.

4. A process according to claim 1 wherein said scavenging agent is selected from the group consisting of calcium oxide, calcium hydroxide and calcium carbonate.

5. A process according to claim 1 wherein said sulfide is a nickel sulfide and said minimum temperature is about 535° C.

6. A process according to claim 1 wherein said sulfide is a copper sulfide and said minimum temperature is about 400° C.

7. A process according to claim 1 wherein said sulfide is a cobalt sulfide and said minimum temperature is about ten degrees below the eutectic point.

8. A process according to claim 1 wherein said sulfide is a nickel-cobalt alloy sulfide and said minimum temperature is above about 535° C.

References Cited

UNITED STATES PATENTS

2,879,154	3/1959	Campbell	75—0.5
3,060,013	10/1962	Harvey	75—0.5
3,132,022	5/1964	Luborasky et al.	75—0.5

HYLAND BIZOT, Primary Examiner

W. W. STALLARD, Assistant Examiner