

[54] **FORMATION OF METAL FILAMENTS BY SOLID STATE REACTIONS**

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[22] Filed: **June 25, 1973**

[21] Appl. No.: **359,400**

[52] U.S. Cl. **75/5 B, 75/5 R, 75/200, 75/213, 75/DIG. 1**

[51] Int. Cl. **B22f 9/00**

[58] Field of Search **75/5 R, .5 B, 125, 153, 75/DIG. 1, 213, 200; 148/126**

[56] **References Cited**
UNITED STATES PATENTS

3,060,013 10/1962 Harvey 75/5 B

3,529,954 9/1970 Cech 75/5 B

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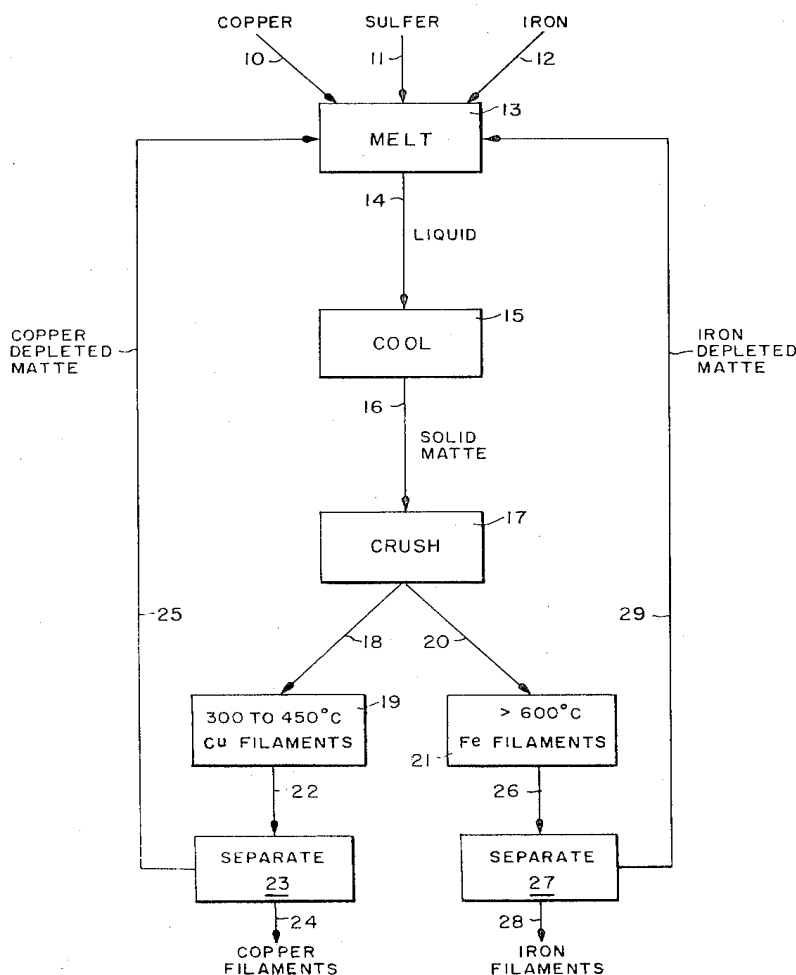
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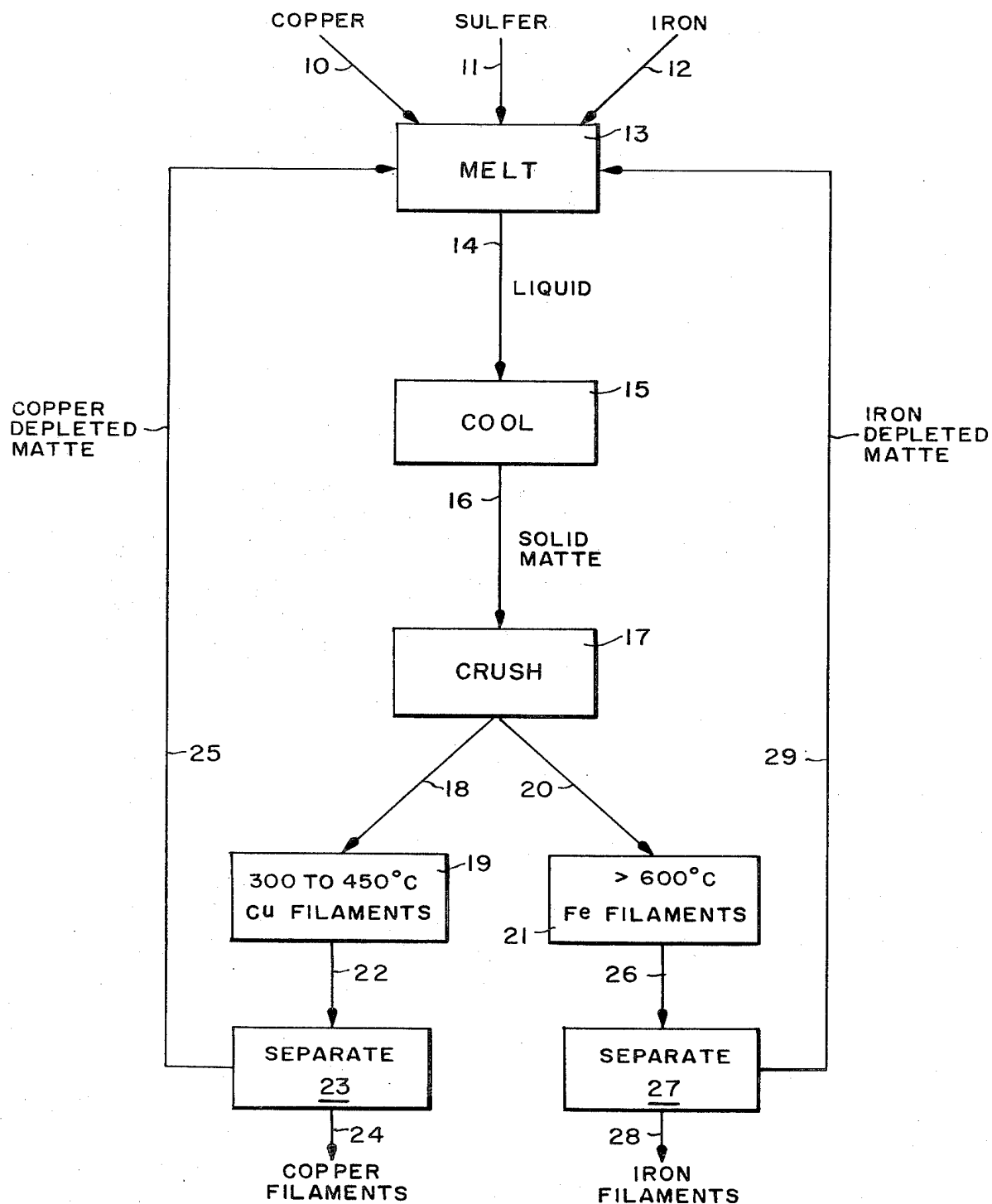
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[57] **ABSTRACT**

Metal filaments are grown by solid state reactions from a matrix or matte of copper, iron and sulfur. Copper filaments, iron filaments or copper-iron duplex filaments may be produced by adjustment of temperature and growth conditions. The copper-iron duplex filaments consist of copper at one end and iron at the other with a sharp junction between the two compositions. Individual filaments are typically on the order of 1 micron in diameter and the filaments grow in bundles often about 10 microns in diameter. Growth is extremely rapid; lengths of 2 to 3 centimeters being attained in a few minutes.

17 Claims, 1 Drawing Figure





FORMATION OF METAL FILAMENTS BY SOLID STATE REACTIONS

BACKGROUND OF THE INVENTION

Very fine metal filaments commonly have extremely high strengths and other unusual physical properties. Such filaments have often been incorporated into a matrix, such as another metal, to impart greater strength or other desirable physical characteristics to the composite.

Metal filaments have been grown in the past from metal alloy compositions in which one component of the alloy is caused to grow as a filament under the influence of high temperatures and thermal gradients. An example of this technique as applied to the growth of copper filaments is found in U.S. Pat. No. 3,060,013.

SUMMARY OF THE INVENTION

When copper, iron, and sulfur are heated together, there is formed a matte which contains a variety of copper and iron sulfides and usually some free or elemental metals depending upon the proportions of the matte. If the matte is stoichiometrically deficient in sulfur, that is, if less sulfur is present than that required to satisfy the requirements of the copper and iron for the formation of simple sulfides, then the sulfur will partition between the iron and copper in the solid matte. Simple sulfides are defined for the purposes of this disclosure as CuS and FeS . Depending upon temperature, the sulfur will partition with the copper leaving free iron or will partition with the iron leaving free copper. When such a sulfur deficient matte is crushed so as to create a large surface area and is thereafter heated in a nonreactive atmosphere, filaments of copper or iron grow outwardly from the surfaces of the matte particles. The filaments easily break free from the matte surfaces and may be separated from the metal-depleted matte by conventional techniques.

Hence, it is an object of our invention to produce metal filaments.

It is another object of our invention to extract metals in the form of filaments from sulfide mattes.

Another object of our invention is to grow iron filaments and copper filaments.

Yet another object of our invention is to produce copper-iron duplex filaments.

BRIEF DESCRIPTION OF THE DRAWINGS

For a fuller understanding of the invention, reference is made to the following description taken in connection with the accompanying drawing in which:

The single FIGURE shows schematically the process for producing metal filaments described in this specification.

DETAILED DESCRIPTION OF THE INVENTION

We have found that copper, iron, or copper-iron duplex filaments may be readily grown from a solid matte of copper, iron, and sulfur which is stoichiometrically deficient in sulfur. Filament growth is extremely rapid; growth rates of 2 to 3cm in 5 minutes being commonplace. Filament growth requires a nonreactive atmosphere which may be an inert gas such as nitrogen or a vacuum. The vacuum need not be good, 0.05 Torr or less will suffice, but care must be taken to insure that

the atmosphere will not oxidize metals at the surface of the matte and that iron carbides do not form as will occur if oil from a vacuum pump is allowed to contaminate the matte. If either oxides or carbides form on the matte surfaces, filament growth will stop.

Depending upon the temperatures, either copper filaments or iron filaments may be grown from matte surfaces. The filaments grow outwardly from the matte surfaces as bundles of fibers. Individual filaments or fibers are typically slightly less than 1 micron in diameter and filament bundles are usually about 10 microns in diameter. A temperature gradient is not necessary for filament growth. However, a temperature gradient will cause orientation of the growing filaments causing them to grow toward the cold area.

Referring now to the FIGURE, copper 10, sulfur 11, and iron 12 are melted in heating means or furnace 13. All three components may be in their elemental form or may be added in the form of either copper or iron sulfides or both. The metal sulfides may be in the form of ore concentrates such as chalcopyrite (CuFeS_2), as a mixture of covellite (CuS), and pyrite or marcasite (FeS_2), or as combinations of other copper, iron, or copper-iron sulfides, or as combinations of metals and metal sulfides. Impurities, such as the normal gangue constituents of sulfide ore concentrates, do not normally interfere with the process.

An ore concentrate, such as chalcopyrite, is not stoichiometrically deficient in sulfur. Upon heating chalcopyrite to a relatively high temperature, above about 800°C , some elemental sulfur is driven off. This is best accomplished in a vacuum furnace provided with a condenser to collect the evolved sulfur. Heating a chalcopyrite concentrate to a temperature of 800°C for 2 hours in a vacuum furnace results in a lowering of the sulfur content from about 32 to about 27 percent to form a sulfur deficient matte from which filaments may be grown. Pyrite will also decompose with the evolution of free sulfur at these temperatures.

While it is not absolutely necessary to melt the mixture of copper, iron, and sulfur provided the three components are in intimate physical admixture, a melting step to prepare the sulfur deficient matte is strongly preferred. A melting step introduces a number of advantages to the process even when using a copper-iron sulfide such as chalcopyrite as the raw material. Melting chalcopyrite will drive off along with the sulfur most of the sulfides of lead, zinc, and the alkali metals which tends to purify the matte and allows recovery of valuable metals associated with the chalcopyrite. Further, melting a chalcopyrite charge and allowing it to cool as an ingot or within the furnace results in the formation of a siliceous slag which solidifies above the matte. This slag layer cleanly separates from and does not adhere to the matte, thus allowing its separation after cooling. As a result, the matte is further concentrated and purified.

When iron, copper, or sulfur are added in a physical form which precludes intimate mixing with the other components, then melting the components to form a matte becomes a necessity. Metallic iron may be added in the form of scrap such as shredded sheet or can stock; copper may be added in the form of wire or other scrap forms, and sulfur may be added as a solid or liquid or in the form of a metal sulfide. Dissolution of copper or iron in sulfur is rapid at high temperatures. Temperature level required to form a molten matte is

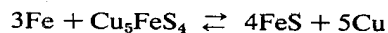
above about 900°C. Chalcopyrite, which can be considered an equimolar mixture of cupric sulfide (covellite) and ferrous sulfide (troilite) melts at about 915°C, and this represents about the minimum temperature at which a matte deficient in sulfur may be melted since the melting point increases as sulfur content decreases.

A liquid, sulfur deficient matte 14, is allowed to solidify and cool in zone 15. Composition of the sulfur deficient matte 14 may broadly range from 10 to 30 weight percent sulfur, 20 to 50 weight percent iron, and 30 to 60 weight percent copper. A more preferred matte composition contains from 15 to 25 weight percent sulfur, 25 to 40 weight percent iron and 40 to 55 weight percent copper. Our most preferred matte composition contains from 16.5 to 21.5 weight percent sulfur, 32.5 to 37.5 weight percent iron, and 42.5 to 47.5 weight percent copper. While copper and iron filaments can be grown at the extremes of these composition ranges, yield of filaments increases substantially as the matte composition approaches and enters the most preferred range. As was explained previously, zone 15 may comprise the furnace itself or may be an ingot mold or similar device. After cooling to below about 300°C and preferably to near ambient temperatures, solid matte 16 is removed from cooling zone 15 and is crushed to form relatively fine particles in means 17. Purpose of the crushing step is to create a large surface area from which the metal filaments can grow. Particle size of the crushed matte is not critical but a size range of approximately -5+20 mesh works well in the process.

Crushed matte from zone 17 may be used to grow either copper filaments, iron filaments, or in some cases both. When it is desired to grow copper filaments, a crushed matte fraction 18 is passed to heating means 19. Means 19 comprises a closed device having temperature control capabilities. Filament growth requires a nonreactive atmosphere which may either be an inert gas or vacuum. Hence, means 19 may comprise a temperature controlled vacuum furnace, oven, or similar device. Upon heating the matte particles to a temperature within the range of about 300° to 450°C., copper filaments grow upon the matte surfaces. It is not necessary to precisely control the temperature during filament growth since temperature variations within the growth range appear to affect only the rate of filament growth. A preferred temperature range for copper filament growth is between 375° and 425°C.

When it is desired to grow iron filaments, crushed matte fraction 20 from means 17 is passed to heating means 21. Means 21 may be similar to or identical with means 19 except that means 21 must be capable of maintaining a higher temperature. Iron filament growth occurs at a temperature above about 600°C but below the melting point of the matte. It is preferred that the growth temperature for iron filaments be within the range of 600° to 700°C. Little advantage is gained by exceeding 700°.

In order to understand why both iron and copper filaments can be grown from the same matte, it is instructive to examine the equilibrium relationships between iron, copper, and sulfur at various temperatures. Assume, for example, a matte composition which is 33.4 weight percent iron, 47.5 weight percent copper, and 19.1 weight percent sulfur. This particular composition can be represented by the following reaction equation:



The equilibrium relationship depicted by the equation is temperature dependent; below about 475°C the reaction tends to proceed to the right and above that temperature, the reaction tends to proceed to the left. Hence, metallic copper is formed at relatively low temperatures, while metallic iron is formed at somewhat higher temperatures. Exactly why and how the metallic iron or copper grows in the form of filaments from the matte surfaces is not fully understood.

After filament growth is complete, a matte fraction 22, having copper filaments adhering to the surface of the matte particle, is passed to separation zone 23. In zone 23, filaments may be detached from the matte by tumbling the matte particles as the filaments readily break free of the matte surface. Filaments 24 may then be separated from matte particles by screening, air elutriation, tabling, or similar conventional methods. A recycle matte stream 25, depleted in copper, may be recycled to melt zone 13 to provide at least part of the iron and sulfur requirements of the process.

When growing iron filaments, the recovery procedure is somewhat more critical. After iron filament growth is complete, a matte fraction 26, having iron filaments adhering to the surface of the matte particles, is passed to separation zone 27. At this point, extra precautions must be taken in recovering iron filaments compared to those taken in the recovery of copper filaments. Growth of the iron filaments must be stopped as the matte particles are removed from growth zone 21. This is most easily accomplished by rapidly cooling the matte particles to a temperature below about 300°C. If the matte particles are cooled slowly through the transformation temperature of about 475°C, iron filaments redissolve into the matte. Upon further cooling to a temperature within the range of about 300° to 450°C, copper filaments will start to grow. Growth of the copper filaments occurs below the base of the iron filaments to form a duplex filament, iron on one end and copper at the other with a sharply defined junction between the two sections. In like fashion, if copper filaments are grown upon matte particles and the temperature is raised above the transformation temperature of about 475°C, to a level of about 525°C for example, copper filaments are redissolved into the matte. Raising the temperature even higher, to 600°C or above, before copper filaments are completely redissolved causes iron filaments to grow under the base of the copper filaments, thus, again producing a copper-iron duplex filament. These duplex filaments display interesting physical and electrical characteristics and may find use in electronic components, miniature thermocouples, and the like as well as being useful generally in other applications where fine wires and filaments presently are employed.

But in order to recover iron filaments in good yield, it is necessary to stop the filament growth-filament dissolution mechanisms. This is most easily accomplished by cooling the matte particles and attached filaments at a rate sufficiently rapid so as to prevent iron filament dissolution and growth of copper filaments. Cooling of the filaments and surfaces of the matte particles to temperature levels below about 300°C must be accomplished in substantially less time than required for filament growth. In practical terms, cooling must be accomplished within a minute or so but preferably even

faster. Cooling may readily be accomplished by subjecting the matte particles to a flowing stream of relatively cold inert gas. It is also possible to stop filament growth and prevent dissolution of the filaments by introducing small quantities of a reactive gas such as air into the growth chamber. This method is less favored because filament surfaces are also affected.

Iron filaments may be detached from matte particles in zone 27 by tumbling or other mild physical treatment. The filaments may then be easily separated from the matte by magnetic means or by other physical separation techniques, such as those used with copper filaments, to recover an iron filament fraction 28. An iron-depleted matte fraction 29 may be recycled back to melt zone 13 to provide at least a part of the sulfur and copper requirements for the process.

The following examples will serve to more thoroughly illustrate specific embodiments of our invention.

EXAMPLE 1

A chalcopyrite flotation concentrate was obtained which assayed 28.4 percent copper, 28.0 percent iron, 31.9 percent sulfur, 0.60 percent zinc, 0.06 percent lead, 0.3 percent molybdenum, 0.43 percent calcium oxide, and 7.0 percent insoluble. All values are in weight percent. In addition, the concentrate assayed 0.003 ounces gold and 3.3 ounces silver per ton. Spectrographic analysis showed the presence of silicon and aluminum in significant amounts and small quantities of titanium, bismuth, manganese, barium, cobalt, lithium, nickel, and strontium.

A sample of the chalcopyrite concentrate was heated in a vacuum furnace equipped with a condenser. Evolution of free sulfur began at a temperature of about 550° to 550°C. The furnace charge was raised to a maximum temperature of 800°C and held at that temperature for about 2 hours or until all sulfur evolution ceased. Sulfur content of the matte produced was about 27 percent compared to an original concentration of about 32 percent.

Another charge of the chalcopyrite concentrate was melted in the vacuum furnace. Some free sulfur and a number of different metal sulfides including lead sulfide, zinc sulfide, and alkaline sulfides were condensed and collected on the condenser surfaces. Some Mo and Ag sulfides were entrained by the other volatile sulfides but for the most part they remained with the matte. Upon cooling, a silica slag formed above a Cu-Fe-S matte. The slag layer did not adhere to the matte and was easily removed. Additional melting tests of the same ore concentrate were performed and the sulfur content of the recovered mattes ranged from about 27 to 30 percent. It was observed that neither prolonged heating above the melting point nor raising the temperature to as high as 1,450°C had a significant effect upon the sulfur content of matte compositions produced.

EXAMPLE 2

Sulfur deficient mattes produced in Example 1 were cooled to ambient temperature and crushed to a relatively small particle size. The matte particles were then heated in a vacuum to temperatures in the range of about 350° to 430°C. Copper filaments grew from the surfaces of the matte particles. Maximum filament growth was obtained in about half an hour at 350°C and in much shorter times at 430°C. The matte particles

and copper filaments were then cooled to ambient conditions in the vacuum. Copper filaments were detached from the matte particles by tumbling and a copper filament fraction was recovered by screening. The copper filaments analyzed over 99.3 percent copper metal and the impurities appeared to be derived from small amounts of matte contamination.

EXAMPLE 3

A sulfur deficient matte similar to those produced in Example 1 was crushed and the matte particles were then rapidly heated in a vacuum to a temperature of about 625°C. Iron filaments grew upon the matte surfaces. Lowering the temperature to a level below about 475°C caused the iron filaments to redissolve into the matte. Raising the temperature to about 625°C caused iron filaments to again grow upon the matte surfaces. Rapid cooling of the matte and associated iron filaments to a temperature below about 300°C prevented dissolution of the filaments and allowed their later recovery.

EXAMPLE 4

A sulfur deficient matte, similar to those produced in Example 1, was crushed and the matte particles were heated in a vacuum to a temperature of about 400°C. Copper filaments grew upon the matte surfaces. The matte and copper filaments were then heated to about 525°C whereupon the filaments were redissolved into the matte. The temperature of the matte was then lowered to 400°C and copper filaments once again grew from the matte.

Rapid heating of the matte particles and attached copper filaments to a temperature of about 625°C resulted in little if any dissolution of the copper filaments but upon holding the matte particles at 625°C for a few minutes, iron filaments began to grow beneath and attached to the copper filaments. The matte and attached filaments were then rapidly cooled to a temperature below about 300°C and there was recovered from the matte copperiron duplex filaments.

EXAMPLE 5

Examples 2 and 3 were repeated using a nitrogen atmosphere rather than a vacuum. Essentially identical results were obtained.

EXAMPLE 6

A sulfur deficient matte was obtained by heating a pelletized homogeneous mixture of elemental iron, copper, and sulfur to a temperature of about 800°C. This matte was then used to grow both iron and copper filaments. Essentially equivalent results were obtained using this matte as were obtained by use of the mattes of Example 1.

EXAMPLE 7

Shredded tin cans were added to a copper sulfide material and the mixture was melted to form a Cu-Fe-S matte deficient in sulfur. The cans were not de-tinned prior to use. This matte was then used to grow both iron and copper filaments. It was found that metallic tin tended to vaporize from the matte when iron filaments were grown in a vacuum environment and that the tin tended to inhibit filament growth. However, tin did not interfere with the growing of copper filaments nor did it interfere with the growing of iron filaments when iron

filament growth was conducted in a nitrogen atmosphere rather than in a vacuum.

EXAMPLE 8

A particle of matte was placed in an evacuated quartz tube which was then inserted horizontally into a muffle furnace held at 400°C. One end of the quartz tube extended to the exterior of the furnace which was at ambient temperature. Thus, there was created a temperature gradient over the length of the tube.

Copper filaments grew quickly from the matte. Filaments were long and straight and grew toward the cold end of the tube. No filaments formed on the side of the matte particle facing the hot end of the tube. In contrast, heating matte particles uniformly without a temperature gradient resulted in filaments growing in random directions and sometimes becoming entangled.

As may be appreciated, our invention may also be viewed as a metallurgical process to extract copper, iron, or both from their sulfide ores. It may also be used as an extraction technique to recover either elemental copper or iron in a substantially pure form.

We claim:

1. A process for making metal filaments which comprises:

heating a mixture of copper, iron and sulfur to a temperature above about 800°C to form a matte which is stoichiometrically deficient in sulfur;

cooling the matte;

comminuting the cooled matte to form matte particles having a substantial surface area;

heating the matte particles to a temperature above about 300°C in a nonreactive atmosphere to grow metal filaments from the surfaces of the matte particles;

cooling the matte, now depleted in metal, and the metal filaments to a temperature below 300°C;

detaching metal filaments from the metal-depleted matte surfaces, and

separating metal filaments from the metal-depleted matte.

2. The process of claim 1 wherein the sulfur-deficient matte contains from 10 to 30 weight percent sulfur, 20 to 50 weight percent iron and 30 to 60 weight percent copper.

3. The process of claim 2 wherein the mixture of copper, iron and sulfur is melted to form a matte which is stoichiometrically deficient in sulfur.

4. The process of claim 3 wherein at least one component of the mixture is in the elemental form prior to melting and formation of the matte.

5. The process of claim 3 wherein the copper, iron

and sulfur are in the form of copper and iron sulfides prior to melting and formation of the matte.

6. The process of claim 5 wherein the copper and iron sulfides are naturally occurring minerals.

7. The process of claim 3 wherein the metal filaments are chosen from the group consisting of copper filaments, iron filaments and copper-iron duplex filaments.

8. The process of claim 7 wherein the metal filament is copper and wherein the sulfur-deficient matte is heated to a temperature in the range of 300° to 450°C during filament growth.

9. The process of claim 7 wherein the metal filament is iron and wherein the sulfur-deficient matte is heated to a temperature above about 600°C but below the melting point of the matte during filament growth.

10. The process of claim 9 wherein the matte particles and attached iron filaments are cooled to a temperature below about 300°C at a rate sufficiently rapid as to preclude dissolution of the iron filaments and growth of copper filaments during cooling.

11. The process of claim 7 wherein the metal filament is copper-iron duplex and wherein the sulfur-deficient matte is heated to a temperature in the range of 300° to 450°C for a time sufficient to grow copper filaments and thereafter the temperature is increased to above about 600°C at a rate sufficiently rapid as to preclude dissolution of copper filaments into the matte whereby iron filaments grow at the base of and joined to the copper filaments.

12. The process of claim 11 wherein the matte particles and attached copper-iron duplex filaments are cooled to a temperature below about 300°C at a rate sufficiently rapid as to preclude dissolution of the filaments.

13. The process of claim 7 wherein the matte particles are subjected to a temperature gradient during filament growth.

14. The process of claim 7 wherein the non-reactive environment is a vacuum.

15. The process of claim 7 wherein the non-reactive environment is an inert gas.

16. The process of claim 7 wherein the sulfur-deficient matte contains from 15 to 25 weight percent sulfur, 25 to 40 weight percent iron and 40 to 55 weight percent copper.

17. The process of claim 7 wherein the sulfur-deficient matte contains from 16.5 to 21.5 weight percent sulfur, 32.5 to 37.5 weight percent iron and 42.5 to 47.5 weight percent copper.

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