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[54] **CHLORINATION OF TUNGSTEN-BASE ALLOYS**

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[58] **Field of Search** 423/492, 60, 136, 149, 423/341, 493, 495; 75/176

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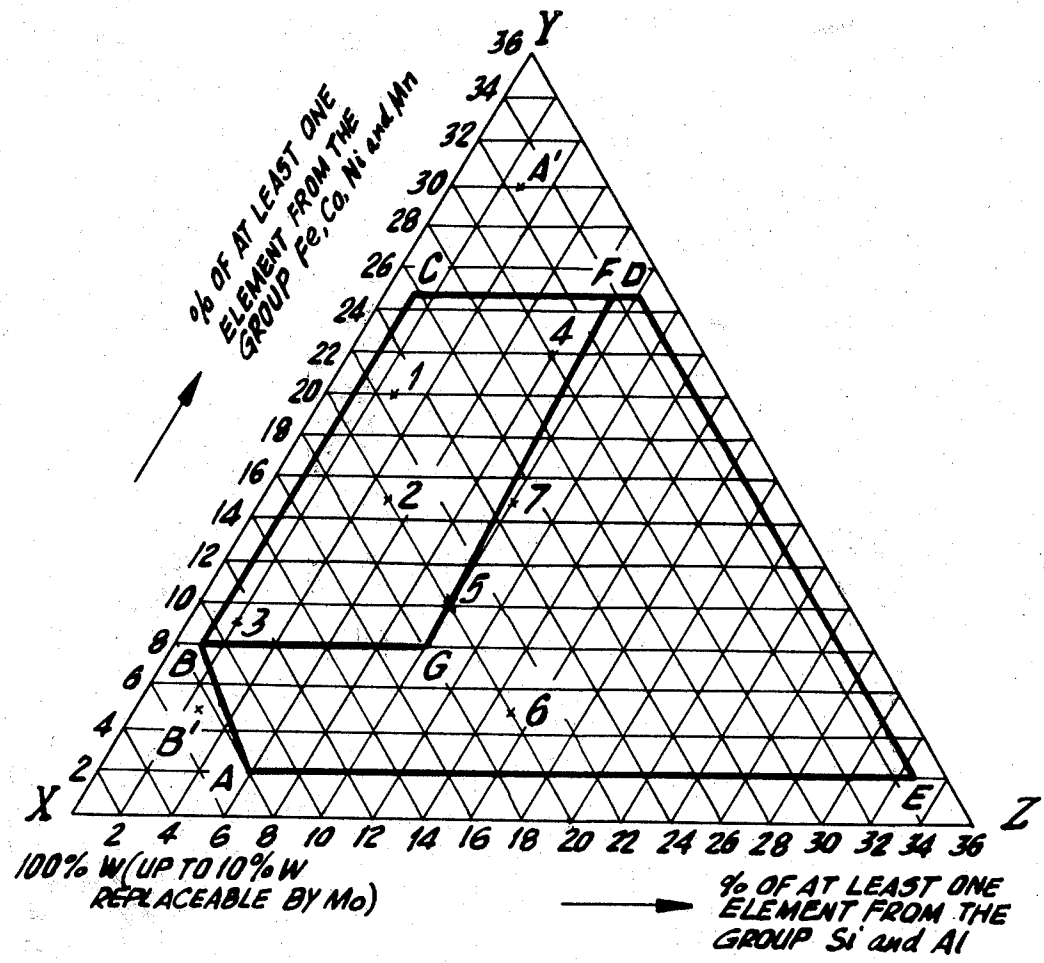
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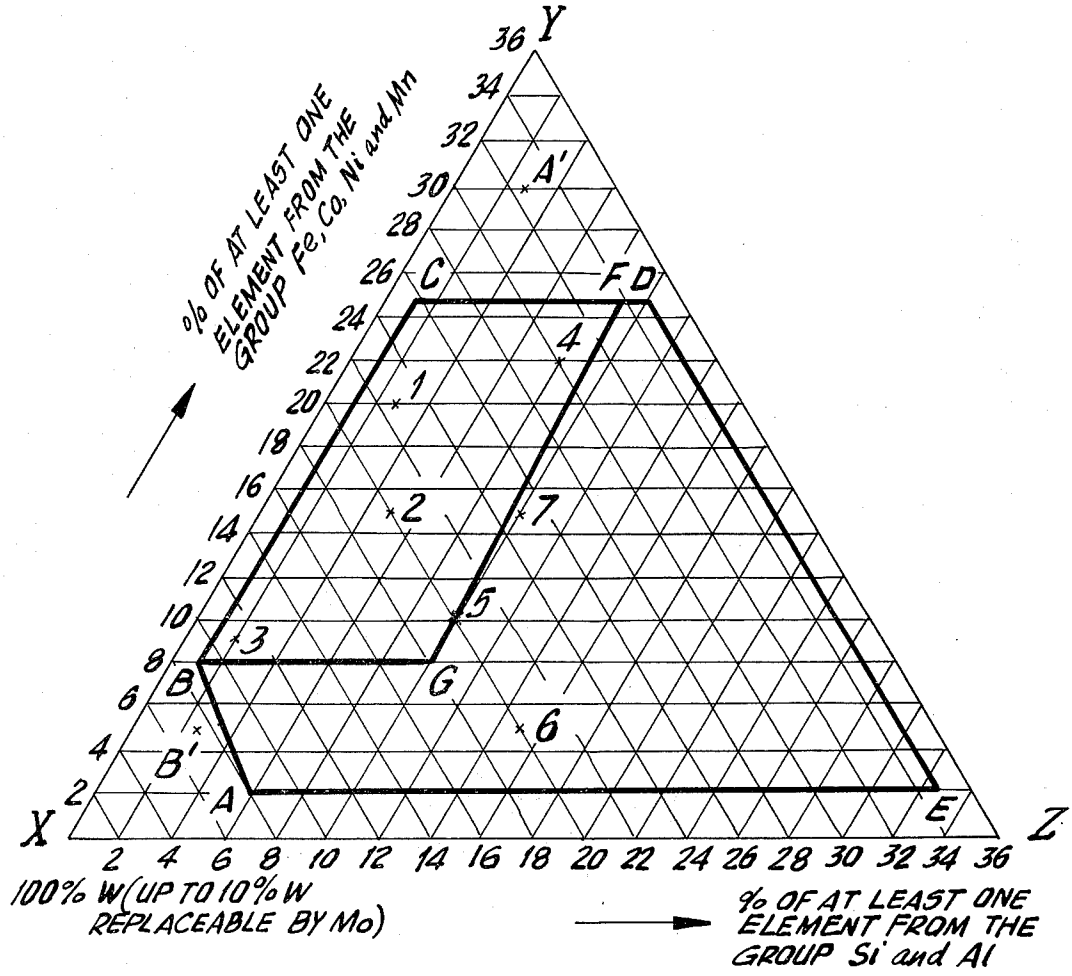
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[57] **ABSTRACT**

A tungsten-base alloy is provided capable of being easily halogenated to form volatile halides from which tungsten values are easily recovered. The tungsten-base alloy contains at least one metal from the group Fe, Co, Ni, Mn and at least one metal from the group consisting of Si and Al. One embodiment resides in halogenating the aforementioned alloy in particulate form with, for example, chlorine while leaving behind very little residues.

2 Claims, 1 Drawing Figure




Y
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
% OF AT LEAST ONE ELEMENT FROM THE GROUP Fe, Co, Ni and Mn
A'
C
F
D
4
1
2
7
5
3
G
B
6
B'
A
E
X
Z
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36
100% W (UP TO 10% W REPLACEABLE BY Mo)
% OF AT LEAST ONE ELEMENT FROM THE GROUP Si and Al

CHLORINATION OF TUNGSTEN-BASE ALLOYS

This is a division of copending application Ser. No. 205,059, filed Dec. 6, 1971, now abandoned.

This invention relates to a tungsten-base alloy suitable for use as a starting material in the production of tungsten values e.g. tungsten powder, by the halogenation of the alloy followed by recovery of tungsten halide which is subseqently reduced to tungsten. The alloy in particulate form is preferably halogenated using chlorine.

Tungsten metal is an important new material in the production of refractory tungsten metal compounds, e.g. tungsten carbide, for use in the hard metal industry. The metal tends to be expensive due to the difficulties entailed in recovering the metal at high yields from tungsten-bearing ores. In copending application Ser. No. 813,746, filed Apr. 4, 1969, now U.S. Pat. No. 3,701,649 issued Oct. 31, 1972 a process is disclosed for recovering tungsten from oxidic tungsten-bearing ores by reducing the ore with silicon and/or aluminum in either the elemental form or in the form of ferrosilicon and/or ferro-aluminum, the cast alloy being thereafter crushed into particulate form and then halogenated with a halogen, such as chlorine, or halogen or halide equivalents thereof, to convert the metal values in the alloy to volatile halides from which tungsten halide is subsequently selectively recovered and reduced to metallic tungsten.

The aforementioned process of converting the tungstenbearing ore to an alloy which is thereafter treated to recover the tungsten in the metallic state has economic advantage, despite the fact that certain of the tungsten alloy compositions tend to react slowly with the halogen during the halogenation process. Thus, some reactions tend to take a long time to complete, even where high temperatures are employed. Moreover, in many instances, large amounts of residues have remained in the reactor.

It would be desirable in reducing certain tungsten ores into tungsten alloys to produce alloys within a controlled composition range which are capable of being easily halogenated with little, if any, residue remaining in the reactor.

It is thus the object of the invention to provide a tungsten-base alloy which is suitable for use in the halogenation thereof for the selective recovery of tungsten therefrom.

Another object of the invention is to provide a tungstenbase alloy of a controlled composition containing, in addition to tungsten, at least one metal in effective amounts selected from the group consisting of Fe, Co, Ni and Mn together with at least one metal in effective amounts selected from the group consisting of Si and Al.

A further object of the invention is to provide a method for improving the halogenation of tungsten-bearing alloys.

These and other methods will more clearly appear from the following disclosure and the accompanying drawing which is a triaxial diagram showing the boundary conditions for assuring the desired alloy compositions suitable for halogenation.

STATEMENT OF THE INVENTION

In its broad aspects, the invention provides a tungstenbase alloy suitable as a starting material for the preparation of metallic tungsten by the halogenation of an alloy composition defined by the area enclosed by polygon ABCDEA and, more preferably, by the area BCFGB.

As will be noted from the diagram, the tungsten content may range from as low as about 65% by weight to as high as about 92% by weight, essentially the balance of the alloy being at least one metal selected from the group consisting of Fe, Co, Ni and Mn, together with at least one metal from the group consisting of Si and Al.

Thus, in producing the alloy composition from an oxidic tungsten ore in accordance with copending application Ser. No. 813,746, filed Apr. 4, 1969, using silicon and/or aluminum as the reducing agent, the ultimate mixture with the ore is determined in the well known manner to assure the alloy composition desired capable of being easily halogenated. Of course, scrap metallic materials can be melted together to provide the desired alloy. Thus, it makes no difference how the desired alloy is produced.

What has been surprisingly discovered is that a tungsten alloy containing either or both of Si and Al as a reducing agent and one or more of the metals Fe, Co, Ni and Mn within substantially the limits set forth in the triaxial diagram can be easily halogenated with very little residue remaining in the reactor.

In this connection, the metals iron, cobalt, nickel and manganese are equivalent and give analogous results, and for the same reason silicon can be replaced with aluminum. The metals iron and manganese often occur in tungsten ores and need possibly only be added to a minor extent during the reduction of the ore in order to obtain a composition of the alloy according to the invention. Cobalt and nickel have been shown in tests to have the same effect on the halogenation ability of the alloy as iron and manganese, but cobalt and nickel seldom occur in tungsten ores. Therefore, these metals are generally added in one form or another when desired.

Tungsten ores sometimes also contain molybdenum which is similar to tungsten as an alloying component. According to the invention, molybdenum can replace up to about 10% of the tungsten content.

Thus, the invention relates substantially to an alloy containing approximately 100% of the enumerated alloy components. These alloy components (metals) substantially determine the halogenation properties of the alloy. However, it will be appreciated that the alloy may also contain in addition to the foregoing metals minor amounts of impurities or small amounts of other substances which do not substantially adversely affect the halogenation of the resulting alloy. Thus, the presence of other substances is included as coming within the scope of the invention. Such substances, for instance carbon and copper, may occur in concentrations of several % by weight, even though they are not taken into consideration in calculating the alloy composition.

DETAILS OF THE INVENTION

The invention will now be described with reference to the accompanying drawing showing part of a ternary diagram of a tungsten alloy. The corner of the diagram at "X" depicts 100% of W and the other corners not shown relate to 100% Fe, Co, Ni and/or Mn and 100% Si and/or Al, respectively, the cut-off being at corners "Y" and "Z".

The present alloy is characterized in that it has a composition defined by polygon ABCDEA, the corner points having the composition (in % by weight).

A:	92% W,	6% Si,	2% Fe
B:	91% W,	1% Si,	8% Fe
C:	74% W,	1% Si,	25% Fe
D:	65% W,	10% Si,	25% Fe
E:	65% W,	33% Si,	2% Fe

Si can totally or partly relpaced with Al, while Fe can be totally or partly replaced with one or more of Co, Ni and Mn. Up to 10% of the tungsten content can be replaced by molybdenum.

An alloy, whose composition is within the polygon ABCDEA can be easily halogenated in a reactor, with very little residue, if any, of non-halogenated metals remaining. An alloy of a composition outside the polygon is more or less difficult to halogenate. The difficulties are apparently chiefly due to the fact that certain phases are halogenated more slowly than others. These phases often occur in a fine-granular form and cause the pressure to increase in the reactor which leads to inhibiting or stopping of the reaction. To make provisions to remove the fine-granular product from the reactor would require a somewhat complicated reactor construction. On the other hand, by using halogenatable alloys of the invention, very simple reactor constructions can be used.

Alloys which are particularly easy to halogenate include those defined by polygon BCFGB in the triaxial diagram. The corner points in this polygon in % by weight are as follows:

B:	91% W,	1% Si,	8% Fe
C:	74% W,	1% Si	25% Fe
F:	66% W,	9% Si,	25% Fe
G:	82% W,	10% Si,	8% Fe

Even within this narrower field, silicon can be replaced with aluminum and iron with the other metals indicated. Alloys with a composition within the polygon BCFGB can be halogenated at lower temperatures. In order to illustrate the difference in halogenation ability between alloys in particulate form within the preferred polygon BCFGB and outside this area but within polygon ABCDEA, a number of tests were conducted. These are described in the following illustrative examples (Examples 1 to 7), in which also for the sake of comparison alloys have been tested whose compositions are outside the larger polygon ABCDEA (Examples A' and B'). At these tests, the temperatures employed were relatively low so that the differences between various compositions could be easily measured. With all the tests, a certain amount of residue was obtained with each alloy tested. Generally, it has not been possible to halogenate such residues at the test temperature. The amounts of residue measured are given for each example. The temperature employed for all the tests was 450°C, the reaction time being 3 hours. Halogen chlorine gas was used, the flow being about 2.82 l/Min. About 0.05 l/Min of oxygen gas was added at the same time. During the heating and cooling of the reactor, nitrogen gas was used as a flush through the reactor. Similar tests have been carried out with other halogens and the results have, as to their tendency, been equivalent. Thus, the term "chlorination" used herein and in the claims is meant to cover other equivalent halogenation processes using other halogens.

As illustrative of the various embodiments of the invention, the following examples are given:

EXAMPLE 1

Alloy with a composition within BCFGB according to diagram:
77.5% W
20.0% Fe
2.5% Si
Residue after chlorination: 1% of weighed sample.

EXAMPLE 2

Alloy with a composition within BCFGB according to diagram:
80.0% W
6.0% Fe
2.5% Co
2.5% Ni
4.0% Mn
2.0% Si
3.0% Al
Residue after chlorination: 1.5% of weighed sample.

EXAMPLE 3

Alloy with a composition within area BCFGB according to the diagram:
84.0% W
5.0% Mo
9.0% Fe
2.0% Si
Residue after chlorination: 2.5% of weighed sample.

EXAMPLE 4

Alloy with a composition within area BCFGB according to the diagram:
70.0% W
20.0% Fe
2.0% Mn
2.0% Si
6.0% Al
Residue after chlorination: 2.5% of weighed sample.

EXAMPLE 5

Alloy with a composition on the line FG according to diagram:
80.0% W
10.0% Fe
10.0% Si
Residue after chlorination: 3.0% of weighed sample.

EXAMPLE 6

Alloy with a composition within ABCDEA but outside BCFGB according to diagram:
80.0% W
5.0% Fe
15.0% Si
Residue after chlorination: 5.0% of weighed sample.

EXAMPLE 7

Alloy with a composition within ABCDEA but near line FG according to diagram:
75.0% W
15.0% Fe
10.0% Si
Residue after chlorination: 7.0% of weighed sample.

EXAMPLE A'

Alloy with a composition outside ABCDEA according to diagram:

67.5% W
30.0% Fe
2.5% Si

Residue after chlorination: 34.4% of weighed sample.

EXAMPLE B'

Alloy with a composition outside ABCDEA according to diagram:

92.5% W
5.0% Fe
2.5% Si

Residue after chlorination: 55.0% of weighed sample.

All of the alloys tested were in the particulate form, such as by crushing the alloy ingot. Generally, in chlorinating tungsten-base alloys of the invention, the chlorinating temperature may range from about 400° to 1000°C, preferably about 600° to 900°C.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and the appended claims.

What is claimed is:

1. In a method of chlorinating tungsten-base alloys containing at least one metal selected from the group consisting of Fe, Co, Ni and Mn and at least one metal from the group consisting of Si and Al, wherein said alloy is converted to a gaseous mixture of metal chlorides, the improvement of minimizing the amount of residue remaining from said chlorination which comprises,

selecting said tungsten-base alloy in a crushed, particulate form and having a controlled composition defined by area BCFGB of the accompanying drawing,

and then chlorinating in a reactor said particulate alloy at a temperature within the range of 400° to 1000°C wherein said alloy is converted substantially to a gaseous mixture of metal chlorides, said reactor being flushed with nitrogen gas during the heating and subsequent cooling of the reactor.

2. The method of claim 1, wherein up to 10% of the tungsten in the alloy subjected to chlorination is replaced by molybdenum.

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