(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 452 079 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **91303101.9**

(22) Date of filing: **09.04.91**

(51) Int. Cl.^{5}: **C22C 1/04,** B22F 3/14, B22F 3/20, C22C 27/06

(30) Priority: **12.04.90 JP 95160/90**
11.06.90 JP 150043/90
19.06.90 JP 158569/90

(43) Date of publication of application:
16.10.91 Bulletin 91/42

(84) Designated Contracting States:
AT DE FR GB

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(54) High chromium-nickel material and process for producing the same.

(57) A high chromium-nickel material containing from 50 to 90% by weight of chromium and not more than 0.5% by weight of impurities, with the remainder substantially comprising nickel, whose metallurgical structure consists of two phases of a hard phase and a soft phase and whose crystal grains have a diameter of not more than 50 μm. The material is excellent in workability, abrasion resistance, and corrosion resistance. The material is produced by preparing an ingot having a packing density of 7 g/cm^3 or more by using chromium powder having a purity of 99% or higher and nickel carbonyl powder, heating the ingot in vacuo or in an inert gas, and subjecting the heat treated ingot to hot working.

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FIELD OF THE INVENTION

This invention relates to high chromium-nickel materials and a process for producing the same. Moreover, this invention relates to high chromium-nickel wires produced from the above-described high chromium-nickel materials and a process for producing the same.

BACKGROUND OF THE INVENTION

A high chromium-nickel material is widely used as various targets, abrasion resistant protectors, materials for switching, various electrodes, and welding spray materials.

Conventional processes for producing a high chromium-nickel material are roughly divided into a melt and molding method and a powder metallurgy method. The melt and molding method includes a high frequency induction heating method, an arc melting method, etc.

Arc melting is a process for producing an ingot which generally comprises arc melting metals in an inert gas using a water-cooled mold. An ingot obtained by arc melting has a metallurgical structure showing development of dendrites to large grains. Since ferrochromium or low purity chromium powder is used as a chromium raw material, the resulting ingot contains a phase which causes reduction in workability in addition to a hard phase and a soft phase. Such an ingot is so brittle and inferior in workability that it requires care in handling and encounters difficulty in forging or rolling. Further, voids in the ingot, such as molding defects, deteriorate properties of final products. Furthermore, cooling after melting tends to induce cracks, making it difficult to obtain a large-sized ingot.

In powder metallurgy, on the other hand, since chromium has a high melting point and a high vapor pressure, it has been difficult to obtain a dense and crack-free sintered product by general molding and sintering techniques. Even hot pressing being adopted, products obtained are limited in size, and productivity is poor. These difficulties are enhanced with an increase in chromium content.

Thus, chromium-nickel materials, particularly high chromium-nickel materials, produced by conventional processes are so brittle due to internal defects that they are apt to be broken on cutting or other handling. Further, it was impossible for these materials to be molded by general hot working operations.

In production of, for example, wires, where low-melting chromium-nickel materials having a chromium content of less than 50% by weight are used, a melting process has been predominantly adopted. However, high chromium-nickel materials with a chromium content of 50% by weight or more cannot be melted without difficulty due to their high melting point, only to provide wires suffering from cracks or internal defects, containing coarse grains, and having deteriorated workability. Also by powder metallurgy, the high melting point and high vapor pressure of chromium have made it difficult to obtain dense and crack-free wires by usual swaging from a molded and sintered body. Accordingly, a wire has been frequently obtained by hot swaging, forging or rolling using an ingot obtained by a hot press method or a hot isotropic hydrostatic press (hereinafter abbreviated as HIP) method. However, HIP, etc. cause excessive solid phase diffusion between chromium powder and nickel powder to induce grain growth, failing to form a homogeneous fine structure. As a result, the ingot is likely brittle because of an increased chromium content in soft phases thereof and encounters with difficulty in wire working. In some cases, a mixture of chromium powder and nickel powder in a capsule is subjected to wire drawing. However, conditions for obtaining wires having a fine and uniformly dispersed structure free from defects, e.g., cracks, are strictly limited due to differences between a capsule material and the chromium-nickel in strength, thermal expansion, working degree, etc. This tendency increases with an increase in chromium content.

Thus, chromium-nickel materials obtained by conventional processes, particularly high chromium-nickel materials, contain coarse grains, phases causing reduction in workability, and internal defects and are, therefore, very brittle and have inferior workability.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a high chromium-nickel material having a dense structure free from internal defects, exhibits excellent workability, and undergoes no cracking during later handling.

In order to accomplish the above-described object, the inventors have conducted extensive studies and, as a result, found that the object of the present invention is accomplished by a high chromium-nickel material satisfying certain conditions and then completed the present invention.

A first embodiment of the present invention relates to a high chromium-nickel material containing from 50 to 90% by weight of chromium and not more than 0.5% by weight of impurities, with the remainder substantially comprising nickel, whose metallurgical structure consists of two phases of a hard phase and a soft phase and whose crystal grains have a diameter of not more than 50 μm.

A second embodiment of the present invention relates to a process for producing a high chromium-nickel material containing from 50 to 90% by weight of chromium and not more than 0.5% by weight of impurities, with the remainder substantially comprising nickel, whose metallurgical structure consisting of two phases of a hard phase and a soft phase and whose crystal grains having a diameter of not more than 50 μm, which comprises preparing an ingot having a packing density of 7 g/cm^3 or more by using chromium powder having a purity of 99% or higher and nickel carbonyl powder, heating the ingot in vacuo or in an inert gas, and subjecting the heat treated ingot to hot working.

A third embodiment of the present invention relates to a high chromium-nickel wire containing from 50 to 90% by weight of chromium and not more than 0.5% by weight of impurities, with the remainder substantially comprising nickel, whose metallurgical structure consisting of two phases of a hard phase and a soft phase and whose grains having a diameter of not more than 50 μm.

A fourth embodiment of the present invention relates to a process for producing a high chromium-nickel wire containing from 50 to 90% by weight of chromium and not more than 0.5% by weight of impurities, with the remainder substantially comprising nickel, whose metallurgical structure consisting of two phases of a hard phase and a soft phase and whose grains having a diameter of not more than 50 μm, which comprises preparing an ingot having a packing density of 7 g/cm^3 or more by using chromium powder having a purity of 99% or higher and nickel carbonyl powder, heating the ingot in vacuo or in an inert gas, filling the heat treated ingot in a capsule, and subjecting the ingot-containing capsule to hot wire drawing at a temperature of from 300 to 800°C at a degree of hot wire drawing of not more than 30% per pass.

A fifth embodiment of the present invention relates to a process for producing a high chromium-nickel wire for coating containing from 50 to 90% by weight of chromium and not more than 0.5% by weight of impurities, with the remainder substantially comprising nickel, which comprises preparing an ingot having a packing density of 7 g/cm^3 or more by using chromium powder having a purity of 99% or higher and nickel carbonyl powder, heating the ingot to a temperature of 1300°C or lower in vacuo or in an inert gas, filling the heat treated ingot in a cylindrical metal capsule, subjecting the ingot-containing capsule to hot wire drawing at a temperature of from 300 to 800°C at a degree of hot wire drawing of not more than 10% per pass, removing the capsule, and rolling the resulting wire to further reduce the diameter by means of a tandem grooved roll mill.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph showing tensile values (maximum tensile breaking deformation and maximum tensile elongation) of high chromium-nickel materials according to the present invention at varying temperatures.

Figures 2(a) and (b) are scanning electron micrographs (1000X magnification) showing microstructures of the materials obtained in Comparative Example 2 and Example 1, respectively.

Figures 3(a) and (b) are scanning electron micrographs showing microstructures of the wires obtained in Comparative Example 18 and Example 7, respectively.

DETAILED DESCRIPTION OF THE INVENTION

Raw materials which can be used in the present invention include a mixed powder of metallic chromium and nickel carbonyl and a high chromium-nickel alloy powder. Metallic chromium powder to be used should have a purity of 99% or higher. If chromium having a purity of less than 99% is used, the content of impurities in the resulting material would exceed 0.5% by weight to form a segregated phase mainly comprising the impurities in addition to a hard phase and a soft phase. If nickel sources other than nickel carbonyl or chromium-nickel alloys hereinafter described, such as metallic nickel powder, are used, since the degree of size reduction of the raw material is limited, sintering reaction becomes insufficient only to provide a material with defects or a material having reduced bond strength between the two phases.

High chromium-nickel alloy powder which is used as a raw material has a structure comprising a soft phase and a finely dispersed lamellar hard phase. If the distance between lamellar hard phases is 10 μm or more, the ingot filled in a capsule has so poor workability that sufficient ductility cannot be obtained at the time of hot working to cause cracks during working of the resulting material. In order to avoid this, workability of the material can be improved by using an alloy powder having a distance of not more than 10 μm between the lamellar hard phases. Inert gas atomizing is the best method for obtaining such an alloy powder having a so controlled structure. Further, it is preferable to use raw material powders having a particle size of not more than 50 μm. If the particle size exceeds 50 μm, the resulting material suffers from troubles such as cracking on hot working due to insufficient workability. It is more preferable to use raw material powders having a particle size of not more than 20 μm. A material obtained from such a raw material exhibits improved uniformity of dispersion of hard phases, which leads to improved workability during hot working and improved abrasion resistance.

The raw material powders are thoroughly mixed by stirring, if desired, together with a binder, e.g., an alcohol, diethyl ether, and ethylene glycol, and molded in a cold isotropic hydrostatic press, etc. to prepare an ingot having a density of 7 g/cm^3. The resulting ingot is then heat treated in vacuo or in an inert gas. If the density of the ingot is less than 7 g/cm^3, a gap is apt to be formed between a capsule wall and the ingot during the subsequent hot working to produce a difference in draft degree between the capsule and the ingot, causing cracks from the surface. If the above-described heat treatment is omitted, the ingot would have internal defects, or diffusion between the two phases becomes partially insufficient, leading to breaks during hot working, for example, hot swaging.

The thus heat treated ingot is filled in a capsule. Although capsules to be used are not limited in material, it is recommended to choose a capsule material which has a coefficient of thermal expansion close to that of the ingot material and withstands the subsequent hot working. For example, where a metallic material is used as a capsule material, stainless steel and mild steel are generally employed. If there is a gap between the capsule wall and the ingot, the capsule and the ingot would not have equality in work elongation or workability on pressure application from the outside by swaging, forging, and the like. As a result, the capsule is broken or the bonding strength between the hard phase and the soft phase necessary for ingot molding is reduced, which finally results in cracks or internal defects. It is desirable that the capsule after being filled with the ingot is sealed in vacuo or in an inert gas to thereby prevent surface oxidation of the chromium-nickel ingot and to improve workability.

The ingot-containing capsule is then subjected to hot working to obtain a desired size. Hot working is usually carried out by hot swaging, hot forging, or hot rolling. The working temperature is from 300 to 800°C, and preferably around 600°C. The ingot is likely broken at a working temperature of less than 300°C. If the working temperature exceeds 800°C, the capsule component is heat diffused into the ingot, resulting in production of a material having an increased content of impurities and suffering from cracks due to a difference in coefficient of thermal expansion between the hard phase and the soft phase. It is apparent from Fig. 1 that satisfactory workability is manifested in the above-specified working temperature range of from 300 to 800°C. In Fig. 1, curves 1 to 5 each shows temperature dependency of maximum tensile breaking deformation (the upper graph) and maximum tensile elongation (the lower graph) of high chromium-nickel materials having a chromium content of 50, 60, 70, 80, or 90% by weight, respectively, a content of impurities of not more than 0.5% by weight, with the remainder substantially comprising nickel. It can be seen from Fig. 1 that the materials exhibit the highest deformation and the highest elongation, i.e., greatest plastic workability, in the temperature range of from 300 to 800°C.

The thus produced high chromium-nickel material can be further worked into plates, tubes, wires, and other complicated shapes by generally known working techniques, such as mold casting, hot rolling, perforation, extrusion, wire drawing, deep drawing, roll forming, swaging, and the like.

A process for producing wires by using the high chromium-nickel material of the present invention is described below.

In this process, the heat treated ingot is subjected to hot wire drawing as the above-described hot working. Hot wire drawing is conducted at least once and usually through several passes to obtain a desired diameter. What is important here is to conduct hot wire drawing at a degree of hot wire drawing of not more than 30% per pass. It is generally recognized that easily workable iron-based alloys, etc. can be drawn at a degree of hot wire drawing of from 5 to 30% per pass, while sparingly workable materials or high-melting materials should be drawn at a degree of hot wire drawing of from 1 to 10% per pass. However, sparingly workable materials like the materials of the present invention can be effectively drawn similarly to easily workable materials such as iron-based alloys as long as the above-described specific conditions are satisfied. In the present invention, if a degree of hot wire drawing exceeds 30% for each pass, the resulting wires suffer from cracks.

In the production of high chromium-nickel wires for coating, wire drawing is carried out through two stages. That is, as a first step of the above-described hot working, the ingot is subjected to hot wire drawing. In this first step, hot wire drawing is performed at least once and usually through several passes. It is essential that each hot wire drawing operation should be conducted at a degree of hot wire drawing of not more than 10%. It is generally recognized that workable iron-based alloys, etc. may be drawn at a degree of hot wire drawing of from 5 to 20% per pass, while sparingly workable materials or materials having a high melting point should be drawn at a degree of hot wire drawing of up to 5% per pass. However, the material of the present invention which is included in sparingly workable materials can be effectively drawn similarly to easily workable materials such as iron-based alloys as long as the above-described specific conditions are satisfied. If each drawing operation for obtaining a desired wire diameter is conducted at a degree of hot wire drawing exceeding 10%, the resulting wire tends to have cracks.

The resulting wire is then subjected to a second wire drawing step in which the wire diameter is further reduced by means of an economical excellent tandem grooved roll mill. The second wire drawing is carried out at a temperature of not higher than 500°C, and usually from 200 to 500°C from the viewpoint of workability and at a degree of hot wire drawing of not more than 10% per pass from the same reason as described above. Further, in order to maintain a prescribed temperature, the drawing is carried out at a feed rate of 10 m/min or more.

The above-described process for producing wires for coating is characterized in that the first wire drawing step is followed by the second wire drawing step whereby slight surface micro cracks, defects, etc., if any produced during the first step, can be modified.

The thus obtained wire for coating usually has a diameter of from 1 to 10 mm.

The composition and structure of the thus obtained high chromium-nickel material according to the present invention are explained below in detail.

Although chromium is an element excellent in corrosion resistance and abrasion resistance under various environmental conditions, it is poor in workability. On the other hand, nickel is an effective element for improving working characteristics. Chromium-nickel materials composed of these two elements form a two-phase structure comprising a hard phase mainly comprising chromium and a soft phase mainly comprising nickel. Chromium-nickel materials having a total chromium content of less than 50% by weight have reduced resistance to corrosion and abrasion, failing to accomplish the objects of the present invention.

Chromium-nickel materials having a total chromium content of 90% by weight or more have reduced plastic workability, and the working of such materials into wires become difficult because of formation of internal defects or surface cracks. From this reason, a total chromium content should fall within a range of from 50 to 90% by weight.

It is necessary that the crystal grains of the material of the present invention should have a diameter of not more than 50 µm. If the grain diameter exceeds 50 µm, the material suffers from troubles such as cracking on hot working due to insufficient workability. The grain diameter is more preferably not more than 20 µm. With a grain size being controlled to 20 µm or less, uniformity of dispersion of the hard phase during the preparation of the material is enhanced, which leads to improved workability and improved abrasion resistance.

The crystal grain size can be so controlled by using a raw material powder having a particle size of not more than 50 µm or by conducting hot working of an ingot within the above-specified range, i.e., from 300 to 800°C.

Should the total content of impurities, e.g., C, Mn, Fe, and Ni, exceed 0.5% by weight, a segregated phase mainly comprising the impurities is formed in addition to a hard phase and a soft phase. Besides causing reduction in workability of the material, such a segregated phase locally produces portions which are inferior in corrosion resistance. For this reason, the material should have a two-phase structure consisting of a hard phase and a soft phase, with the total content of components other than chromium and nickel being controlled not to exceed 0.5% by weight. The content of impurities can be controlled by, for example, use of high purity raw materials.

The high chromium-nickel material according to the present invention are suitable for use not only as wires as above exemplified but also as anti-corrosion materials for molten carbonates. That is, since the material of the present invention has excellent workability and very high corrosion resistance against molten carbonates containing traces of impurities, e.g., salts, it is particularly suitable as a vessel (electrolytic cell) for anode and cathode active substances in a molten carbonate type fuel electric cell. Carbonates to which the material of the present invention is applicable include sodium carbonate, potassium carbonate, lithium carbonate, cesium carbonate, magnesium carbonate, calcium carbonate, strontium carbonate, and barium carbonate. Impurities which may be present in these carbonates include chlorides, bromides, iodides or fluorides of the above-enumerated alkali metals or alkaline earth metals. No case has been reported in which a corrosion resistant material having the composition specified in the present invention is applied to various kinds of molten carbonates. Further, since the material of the present invention is excellent in workability, it can be directly subjected to secondary processing into complicated shapes or structures for various applications.

Thus, the high chromium-nickel material according to the present invention has excellent plastic workability and can be produced by a relatively simple process.

The present invention is now illustrated in greater detail with reference to Examples, but it should be understood that the present invention is not deemed to be limited thereto. All the percents are by weight unless otherwise indicated.

EXAMPLES 1 TO 6

A mixed raw material powder (a mixture of metallic chromium powder and nickel carbonyl powder) or an alloy powder (high chromium-nickel alloy powder) having a composition shown in Table 1 below was mixed with 2% of ethyl alcohol and compressed in a cold isotropic hydrostatic press to prepare an ingot having a density of 7.5 g/cm^3. The ingot was sintered in an vacuum heating furnace at 1250°C for 2 hours and then filled in a stainless steel tube having a length of 125 mm, a diameter of 33 mm, and a wall thickness of 5 mm so tightly that no space was left. After being kept in an argon gas for about 15 minutes, the tube was evacuated to 10^{-4} mmHg at room temperature, and the exhaust vent was closed by welding.

The thus prepared capsule was externally heated to 750°C and hot rolled through 11 passes to a degree of reduction of area of 50%, followed by gradually cooling. After being maintained at 800°C for 2 hours, the material was again hot rolled at 600°C in a direction perpendicular to the above rolling direction to obtain a degree of reduction of area of 93%.

The microstructure, workability, abrasion resistance, and corrosion resistance of the resulting material were measured in accordance with the following methods. The results obtained are shown in Table 1.

1) Microtructure:

The material was buffed and electrolytically etched with oxalic acid. The etched surface was observed under an optical microscope. A micrograph of the sample of Example 1 is shown in Fig. 2(b).

2) Workability:

With both ends of the material being fixed, a load of 50 kgf was imposed on the center. The angle of bend under load was measured.

Workability was evaluated according to the following rating system:

Good ...	Bendable to an angle of 45°
Medium ...	Cracking occurred after bending to 45°
Poor ...	Unbendable to 45°

3) Abrasion Resistance:

Hardness of hard and soft phases was measured with a Vickers hardness tester. A higher hardness was taken as an indication of higher abrasion resistance.

3) Corrosion Resistance:

The material was buffed and weighed. It was then soaked in a mixed aqueous solution of 10% nitric acid and 3% hydrofluoric acid at 50°C or in a 30% sodium hydroxide aqueous solution at 150°C, and a rate of corrosion (mm/year) was determined from weight changes. The test in a sodium hydroxide aqueous solution was conducted in an autoclave.

TABLE 1

Example No.	Composition*		Material Characteristics**		Abrasion Resistance (Hardness/Hv)	Rate of Corrosion		Remarks
	Cr (wt%)	Impurities (wt%)	Workability (45° bend)	Crystal Grain Size (μm)		10% Nitric Acid/3% Hydrofluoric Acid 50°C (mm/year)	30% NaOH 150°C (mm/year)	
1	50.5	0.4	good	40	198-368	0.1	0.05	mixed powder
2	50.5	0.38	good	40	200-360	0.1	0.04	alloy powder
3	60.8	0.3	good	40	210-402	0.08	0.03	mixed powder
4	60.9	0.3	good	40	206-392	0.08	0.03	alloy powder
5	79.9	0.05	good	35	210-412	0.05	0.02	mixed powder
6	79.9	0.05	good	30	210-410	0.03	0.02	alloy powder

Note: *: The remainder was Ni.

The particle size was not more than 50 μm in each example.

**: In each case, the surface of the material was free from micro cracks and had a two-phase structure.

As can be seen from Table 1 and the micrograph of Fig. 2(b), the material according to the present invention was apparently free from cracks or defects and had a two-phase structure in which a hard phase and a soft phase are uniformly dispersed, with the grain size being not more than 50 µm. It is also seen that the material exhibited excellent workability in 45° bending test, excellent abrasion resistance, and excellent corrosion resistance against both a strong acid solution and a strong alkali solution.

COMPARATIVE EXAMPLES 1 TO 11

Chromium-nickel materials were produced in the same manner as in Examples 1 to 6, except for using the raw material powder(s) shown in Table 2 below. Differences from the conditions specified in the present invention are shown in a separate table.

In Comparative Example 11, an alloy powder prepared by hydraulic atomizing was used as a raw material powder. The powder had a particle size of not more than 50 µm and had a sharply angular shape but not a spherical shape.

The resulting materials were evaluated in the same manner as in Example 1, and the results obtained are shown in Table 2. A micrograph showing the metallurgical microstructure of the sample of Comparative Example 2 is shown in Fig. 2(a).

TABLE 2

Comp. Ex. No.	Composition*		Powder Particle Size (µm)	Surface Condition**	Material Characteristics			Abrasion Resistance (Hardness/Hv)	Rate of Corrosion		Remarks
	Cr (wt%)	Impurities (wt%)			Workability (45° bend)	Metallurgical Structure	Crystal Grain Size (µm)		10% Nitric Acid/3% Hydrofluoric Acid 50°C (mm/year)	30% NaOH 150°C (mm/year)	
1	20.3	0.4	<50	no MR	good	two-phase	49	160-201	2.5	0.8	MP ***
2	99.7	0.4	<50	cracks	poor	two-phase	45	200-350	0.5	0.1	"
3	50.5	0.9	<50	MR	poor	three-phase	45	200-320	1.0	0.3	"
4	50.8	0.5	>50	MR	poor	two-phase	75	210-355	0.9	0.3	"
5	70.8	0.5	>50	MR	poor	two-phase	80	220-395	0.6	0.3	"
6	88.5	0.05	>50	cracks	poor	two-phase	100	220-410	0.5	0.2	"
7	50.5	0.55	<50	MR	poor	three-phase	45	200-310	1.5	0.5	"
8	50.5	0.4	<50	MR	medium	two-phase	50.5	200-290	1.5	0.35	"
9	50.5	0.4	>50	MR	medium	two-phase	100	200-295	1.1	0.3	AP ****
10	91.5	0.4	<50	MR	poor	two-phase	45	225-450	0.5	0.2	"
11	50.5	0.4	<50	cracks	poor	two-phase	46	200-280	1.2	0.3	

Note: *: The remainder was Ni. **: MR means micro cracks.

: MP means a mixed powder. *: AP means an alloy powder

Difference from the Invention

Comparative Example No.	
1	Cr content less than 50 wt%
2	Cr content more than 90 wt%
3	Total content of impurities more than 0.5 wt%
4	Raw material powder size greater than 50 μm
5	Raw material powder size greater than 50 μm
6	Raw material powder size greater than 50 μm
7	Cr powder purity less than 99.0%
8	Metallic nickel as raw material
9	Raw material powder size greater than 50 μm
10	Cr content more than 90 wt%

Since the composition of the materials of Comparative Examples 1 to 3, 7, and 10 is out of the scope of the present invention, a black segregated phase was formed in addition to a hard phase and a soft phase as shown in the micrograph of Fig. 2(a). Further, micro cracks appeared on the surface of these comparative materials, and cracks occurred during hot working. In Comparative Examples 4 to 6 and 9 in which raw material powders had a particle size exceeding 50 μm and in Comparative Example 11 in which a non-spherical raw material powder prepared by a different method was used, a crystal grain had a size of more than 50 μm, workability was inferior, and cracks or micro cracks developed on the surface. Further, these samples showed scatter of hardness in abrasion test, indicating tendency to undergo local abrasion. Furthermore, it is seen that a non-uniform structure produces a potential difference between two phases or among three phases in a corrosive solution, resulting in deterioration of corrosion resistance.

COMPARATIVE EXAMPLES 12 TO 15

Chromium-nickel materials were produced from raw material powders shown in Table 3 below by the process shown in the remarks of Table 3. In Comparative Example 12, the material was produced by melt and molding. In Comparative Example 13, the material was produced by compressing a raw material powder by means of a cold isotropic hydrostatic press to form an ingot having a density of 7.5 g/cm^3, subjecting the ingot to HIP (1200°C, 1.2 ton/f, 30 minutes, in argon atmosphere) instead of heat treatment, and further subjecting the ingot to hot working. In Comparative Example 14, an ingot having a density of 7.5 g/cm^3 was directly subjected to hot working without conducting heat treatment. In Comparative Example 15, an ingot having a density of 6.5 g/cm^3 was subjected to heat treatment followed by hot working.

The surface condition, workability, metallurgical structure, and crystal grain size of the resulting material were evaluated in the same manner as in Example 1, and the results obtained are shown in Table 3.

TABLE 3

Comp. Ex. No.	Composition* Cr (wt%)	Composition* Impurities (wt%)	Powder Particle Size (µm)	Material Characteristics Surface Condition**	Material Characteristics Workability (45° bend)	Material Characteristics Metallurgical Structure	Grain Size (µm)	Remarks
12	47.0	0.9	-	cracks	poor	three-phase	>50	melting method
13	50.3	0.7	<50	no MR	medium	two-phase	>50	packing density >7.0 + HIP
14	50.5	0.4	<50	MR	poor	three-phase	<50	packing density >7.0 + no heat treatment
15	50.8	0.41	<50	MR	poor	two-phase	<50	packing density >7.0 + heat treatment

Note: *: The remainder was Ni. **: MR means micro cracks.

The metallurgical structure of the material obtained in Comparative Example 12 showed development of the hard phases to dendrites so that the material was very difficult to work and liable to undergo cracking. In Comparative Example 13 wherein the ingot had a density of 7.5 g/cm^3 but was subjected to HIP instead of heat treatment, although the resulting material showed reduced cracks and internal defects, the pressing at a high temperature caused crystal grains to grow, resulting in deterioration of workability. Also in Comparative Examples 14 and 15, micro cracks developed on the surface of the material due to shortage of bonding strength between two phases and shortage of packing density of the ingot. Internal defects were also observed.

EXAMPLES 7 TO 12

A mixed raw material powder (a mixture of metallic chromium powder and a nickel carbonyl powder) or an alloy powder (high chromium-nickel alloy powder) having a composition shown in Table 4 below was mixed with 2% of ethyl alcohol and compressed in a cold isotropic hydrostatic press to prepare an ingot. The ingot was sintered in an vacuum heating furnace at 1110°C for 2 hours and then filled in a stainless steel tube having a length of 125 mm, a diameter of 60 mm, and a wall thickness of 5 mm so tightly that no space was left. After being kept in an argon gas for about 15 minutes, the tube was evacuated to 10^{-4} mmHg at room temperature, and the exhaust vent was closed by welding.

The thus prepared capsule was externally heated to 750°C and subjected to hot swaging through 11 passes to a degree of reduction of area of 50% (degree of hot wire drawing of 5% per pass in the 1st to 6th passes and 10% per pass in the 7th to 11th passes), followed by gradually cooling. The surface stainless steel of the resulting wire was removed by lathing. After being maintained at 250°C for 30 minutes, the wire was swaged with a die heated to 200°C to a degree of reduction of area of 85% (degree of hot wire drawing of 25% per pass) to obtain a wire having a diameter of 3.1 mm.

The metallurgical structure, workability, abrasion resistance, and corrosion resistance of the resulting wire were measured in the same manner as in Example 1. The results obtained are shown in Table 4. The micrograph showing the metallurgical structure of the material of Example 7 is shown in Fig. 3(b).

TABLE 4

Example No.	Composition*		Material Characteristics**		Abrasion Resistance (Hard-ness/Hv)	Rate of Corrosion		Remarks
	Cr (wt%)	Impu-rities (wt%)	Work-ability (45° bend)	Crystal Grain Size (µm)		10% Nitric Acid/3% Hydrofluoric Acid 50°C (mm/year)	30% NaOH 150°C (mm/year)	
7	51.5	0.4	good	40	208-368	0.09	0.05	mixed powder
8	52.5	0.38	good	30	220-360	0.09	0.04	alloy powder
9	61.8	0.3	good	40	230-402	0.07	0.03	mixed powder
10	61.9	0.3	good	20	226-394	0.06	0.03	alloy powder
11	79.9	0.05	good	35	230-422	0.05	0.01	mixed powder
12	80.2	0.05	good	20	230-410	0.03	0.01	alloy powder

Note: *: The remainder was Ni.

The particle size was not more than 50 µm in each example.

**: In each sample, the surface of the material was free from micro cracks, and had a two-phase structure.

As can be seen from Table 4 and the micrograph of Fig. 3(b), the material according to the present invention was apparently free from cracks or defects and had a two-phase structure in which a hard phase and a soft phase were uniformly dispersed, with the grain size being not more than 50 μm. It is also seen that the material exhibited excellent workability in 45° bending test, excellent abrasion resistance, and excellent corrosion resistance against both a strong acid solution and a strong alkali solution.

COMPARATIVE EXAMPLES 16 TO 25

Chromium-nickel materials were produced in the same manner as in Examples 7 to 12, except for using the raw material powder(s) shown in Table 5 below. Differences from the conditions specified in the present invention are shown in a separate table.

In Comparative Example 25, the wire was prepared from an ingot prepared by a melting method because the chromium content was less than 50%. The resulting wire showed a structure in which the hard phase developed to dendrites.

The resulting wires were evaluated in the same manner as in Example 1, and the results obtained are shown in Table 5. The microstructure of the wire obtained in Comparative Example 18 is shown in Fig. 3(a).

TABLE 5

Comp. Ex. No.	Composition*		Powder Particle Size (µm)	Surface Condition**	Material Characteristics			Abrasion Resistance (Hardness/Hv)	Rate of Corrosion		Remarks
	Cr (wt%)	Impurities (wt%)			Workability (45° bend)	Metallurgical Structure	Crystal Grain Size (µm)		10% Nitric Acid/3% Hydrofluoric Acid 50°C (mm/year)	30% NaOH 150°C (mm/year)	
16	39.3	0.4	<50	no MR	good	two-phase	49	170-201	3.0	1.6	MP ***
17	99.7	0.4	<50	cracks	poor	two-phase	45	190-250	0.8	0.3	"
18	50.5	0.9	<50	MR	poor	three-phase	45	290-320	1.0	0.5	"
19	50.8	0.8	>50	MR	poor	two-phase	55	230-355	0.9	0.3	"
20	70.8	0.5	55	MR	poor	two-phase	80	240-395	0.6	0.3	"
21	68.5	0.65	60	cracks	poor	two-phase	100	240-310	0.5	0.2	"
22	35.5	0.55	<50	MR	medium	two-phase	35	220-310	2.5	1.0	AP ****
23	92.5	0.4	<50	MR	poor	two-phase	42	290-490	0.9	0.3	"
24	50.5	0.87	>50	MR	poor	three-phase	80	200-295	1.1	0.3	"
25	46.1	0.4	100	MR	poor	two-phase	45	225-450	1.2	0.9	"

Note: *: The remainder was Ni. **: MR means micro cracks.

: MP means a mixed powder. *: AP means an alloy powder.

Difference from the Invention

Comparative Example No.	
16	Cr content less than 50 wt%
17	Cr content more than 90 wt%
18	Total content of impurities more than 0.5 wt%
19	Raw material purity less than 99%
20	Raw material powder size greater than 50 µm
21	Metallic nickel as raw material powder
22	Cr content less than 50%
23	Cr content more than 90%
24	Total content of impurities more than 0.5%
25	Melting method

Since the composition of the materials of Comparative Examples 16 to 18 and 22 to 24 is out of the scope of the present invention, a black segregated phase was formed in addition to a hard phase and a soft phase as shown in the micrograph of Fig. 3(a). Further, micro cracks appeared on the surface of these comparative materials, and cracks occurred during hot wire drawing. In Comparative Example 20, in which raw material powders had a particle size exceeding 50 µm, and in Comparative Example 25 in which the raw material powder prepared by a melting method had dentrites, the resulting wire had poor workability and suffered from cracks or micro cracks on the surface thereof. Further, these samples showed scatter of hardness in abrasion test, indicating tendency to undergo local abrasion. It is also seen that a non-uniform structure produces a potential difference between two phases or among three phases in a corrosive solution, indicating inferior corrosion resistance.

COMPARATIVE EXAMPLES 26 TO 30

Chromium-nickel materials were produced in the same manner as in Examples 7 to 12, except that the preparation conditions were altered as shown in Table 6 below.

The ingot was filled in a stainless steel tube having a length of 125 mm, a diameter of 40 mm, and a wall thickness of 2 mm so tightly that no space was left. After being kept in an argon gas for about 15 minutes, the tube was evacuated to 10^{-4} mmHg at room temperature, and the exhaust vent was closed by welding.

The thus prepared capsule was subjected to hot wire drawing through 20 passes to obtain a wire having a diameter of 1.5 mm.

In Comparative Example 26, the ingot had a packing density of 7.5 g/cm^3 but was directly subjected to hot wire drawing without conducting heat treatment. In Comparative Example 27, the ingot having a packing density 6.5 g/cm^3 was heat treated at 800°C for 1 hour and then subjected to hot wire drawing. In Comparative Example 28, the ingot had a packing density of 7.4 g/cm^3, and wire drawing was carried out at 800°C to at a degree of hot wire drawing of 35% per pass. In Comparative Example 29, hot wire drawing was carried out at 250°C at a degree of hot wire drawing of 15% per pass. In Comparative Example 30, hot wire drawing was carried out at 1000°C at a degree of hot wire drawing of 25% per pass.

The metallurgical structure, workability, abrasion resistance, and corrosion resistance of the resulting wire are shown in Table 6. Test methods were the same as in Example 1.

In Comparative Examples 26 and 27, since voids were formed between the capsule wall and the chromium-nickel material during working, cracks developed in the capsule, and the chromium-nickel material also underwent cracking. In Comparative Example 28, because the degree of hot wire drawing per pass was as high as 35%, the material underwent cracking during the 3rd pass. The wires obtained in Comparative Examples 29 and 30 developed micro cracks at the end of the final drawing operation.

TABLE 6

Comp. Ex. No.	Composition*		Powder Particle Size	Material Characteristics			Grain Size	Remarks
	Cr (wt%)	Impurities (wt%)	(µm)	Surface Condition**	Workability (45° bend)	Metallurgical Structure	(µm)	
26	57.0	0.4	<50	cracks	poor	two-phase	<50	ingot density: >7.0 + no heat treatment
27	50.3	0.3	<50	micro cracks	poor	two-phase	<50	ingot density: <7.0 + heat treatment
28	50.5	0.4	<50	cracks	poor	two-phase	<50	degree of hot wire drawing: 35% per pass
29	50.8	0.5	<50	micro cracks	poor	two-phase	<50	wire drawing temp.: <300°C
30	50.8	0.5	<50	micro cracks	poor	two-phase	<50	wire drawing temp.: >800°C

Note: *: The remainder was Ni.

EXAMPLES 13 TO 18

A mixed raw material powder (a mixture of metallic chromium powder and a nickel carbonyl powder) or an alloy powder (high chromium-nickel alloy powder) having a composition shown in Table 7 below was mixed with 2% of ethyl alcohol and compressed in a cold isotropic hydrostatic press to prepare a cylindrical ingot having a density of 7.5 g/cm^3 and a diameter of 84 mm. The ingot was heat treated in a vacuum heating furnace at 1110°C for 2 hours and then filled in a stainless steel tube having a length of 125 mm, a diameter of 90 mm, and a wall thickness of 5 mm. After being kept in an argon gas for about 15 minutes, the tube was evacuated to 10^{-4} mmHg at room temperature, and the exhaust vent was closed by welding.

First Wire Drawing:

The thus prepared capsule was externally heated to 750°C and subjected to hot swaging through 11 passes to a degree of reduction of area of 30% (degree of hot wire drawing of 5% per pass in the 1st to 6th passes and 10% per pass in the 7th to 11th passes), followed by gradually cooling. The surface stainless steel of the resulting wire was removed to a thickness of 2 mm by lathing.

2nd Wire Drawing:

After being maintained at 140°C for 30 minutes, the wire was rolled by means of a 4-tandem grooved roll while heating an octagonal grooved roll die at 200°C to a degree of reduction of area of 85% (degree of hot wire drawing: 8.5% per pass; feed rate: 10 m/min) to obtain a wire having an outer diameter of 3.1 mm.

The metallurgical structure, workability, abrasion resistance, and corrosion resistance of the resulting wire were measured in the same manner as in Example 1. The results obtained are shown in Table 7.

TABLE 7

Example No.	Composition*		Abrasion Resistance (Hard-ness/Hv)	Rate of Corrosion		Remarks
	Cr (wt%)	Impurities (wt%)		10% Nitric Acid 50°C (mm/year)	30% NaOH 150°C (mm/year)	
13	53.5	0.4	238-368	0.11	0.06	mixed powder
14	55.5	0.38	230-360	0.11	0.05	alloy powder
15	62.8	0.3	250-402	0.15	0.04	mixed powder
16	62.9	0.3	256-394	0.16	0.04	alloy powder
17	89.9	0.05	280-422	0.16	0.02	mixed powder
18	89.2	0.05	280-410	0.15	0.02	alloy powder

Note: 1) * The remainder was Ni.

The particle size was not more than 50 µm in each example.

2) All the samples were bendable through 45°.

3) All the wires were free from micro cracks and revealed a two-phase structure.

As can be seen from Table 7, the wire materials according to the present invention were apparently free from cracks or defects. The materials were also proved excellent in abrasion resistance and corrosion resistance against a strong acid solution and a strong alkali solution.

COMPARATIVE EXAMPLES 31 TO 37

Wires were produced in the same manner as in Examples 13 to 18, except for using the raw material powder(s) shown in Table 8 below. Differences from the conditions specified in the present invention are shown in a separate table.

Workability, corrosion resistance, and abrasion resistance of the resulting wires as determined in the same manner as in Example 1 are shown in Table 8.

TABLE 8

Comp. Ex. No.	Composition*		Characteristics of Wire			Abrasion Resistance (Hardness/Hv)	Rate of Corrosion		Remarks
	Cr (wt%)	Impurities (wt%)	Surface Condition**	Workability	Metallurgical Structure		10% Nitric Acid 50°C (mm/year)	30% NaOH 150°C (mm/year)	
31	39.9	0.4	no MR	good	two-phase	180-201	3.1	1.8	mixed powder
32	99.5	0.4	cracks	poor	two-phase	200-250	0.9	0.5	"
33	50.5	1.3	MR	poor	three-phase	290-320	1.2	0.7	"
34	50.8	0.9	MR	poor	two-phase	240-355	1.0	0.5	"
35	39.5	0.55	MR	medium	two-phase	230-310	2.6	1.2	alloy powder
36	95.5	0.4	MR	poor	two-phase	300-490	1.2	0.5	"
37	51.5	0.87	MR	poor	three-phase	220-295	1.5	0.5	"

Note: *: The remainder was Ni.

**: MR means micro cracks.

Difference from the Invention

Comparative Example No.	
31	Cr content of 39.9 wt%
32	Cr content of 99.5 wt%
33	Total content of impurities of 1.3 wt%
34	Cr powder purity of 98%
35	Cr content of 39.5 wt%
36	Cr content of 95.5 wt%
37	Content of impurities more than 0.87 wt%

As is apparent from Table 8, since the composition of the materials of Comparative Examples 31 to 33 and 35 to 37 is of the scope of the present invention, micro cracks developed on the surface of these comparative materials, and cracks occurred during hot wire drawing. Further, these samples showed scatter of hardness in abrasion test, indicating tendency to undergo local abrasion. Furthermore, it is also seen that a non-uniform structure produces a potential difference between two phases or among three phases in a corrosive solution, indicating inferior corrosion resistance.

COMPARATIVE EXAMPLES 38 TO 45

Chromium-nickel wires were produced in the same manner as in Examples 13 to 18, except that the preparation conditions were altered as shown in Table 9 below.

The ingot (diameter: 35 mm) was filled in a stainless steel tube having a length of 125 mm, a diameter of 40 mm, and a wall thickness of 2 mm. After being kept in an argon gas for about 15 minutes, the tube was evacuated to 10^{-4} mmHg at room temperature, and the exhaust vent was closed by welding.

1st Wire Drawing:

The thus prepared capsule was subjected to hot swaging through 5 passes to obtain a wire having a diameter of 25 mm. The surface stainless steel layer was removed by centerless grinding to obtain a wire having a diameter of 23 mm.

2nd Wire Drawing:

The wire was subjected to rolling by means of a 6-tandem grooved roll mill to obtain a wire having a diameter of 2.0 mm.

In Comparative Example 38, the ingot having a packing density of 7.5 g/cm^3 was directly subjected to hot wire drawing without conducting heat treatment. In Comparative Example 39, the ingot having a packing density 6.5 g/cm^3 was heat treated at 800°C for 1 hour and then subjected to hot wire drawing. In Comparative Example 40, the ingot having a packing density of 7.4 g/cm^3 was drawn by swaging at 800°C at a degree of hot wire drawing of 15% per pass and then by second wire drawing. In Comparative Example 41, hot wire drawing was carried out at 250°C at a degree of hot wire drawing of 8% per pass. In Comparative Example 42, hot wire drawing was carried out at 1000°C at a degree of hot wire drawing of 8% per pass. In Comparative Examples 43 to 45, the second wire drawing by the tandem grooved roll mill was conducted at a temperature of 700°C, at a degree of hot wire drawing of 15% per pass, and at a feed rate of 5 m/min.

The surface condition and workability of the resulting wire are shown in Table 9. Test methods were the same as in Example 1.

TABLE 9

Comp. Example No.	Composition*		Charateristics of Wire		Remarks
	Cr	Impurities	Surface Condition**	Work-ability	
38	58.0	0.4	cracks	poor	ingot density: >7.0 + no heat treatment
39	51.3	0.3	MR	poor	ingot density: <6.5 + heat treatment
40	51.5	0.4	cracks	poor	degree of swaging wire drawing: >15% per pass
41	51.8	0.5	MR	poor	swaging temp.: 250°C
42	52.8	0.5	MR	poor	swaging temp.: 1000°C
43	52.6	0.5	MR	medium	rolling temp.: 750°C
44	51.9	0.2	cracks	poor	rolling degree: >15% per pass
45	57.0	0.2	cracks	poor	rolling feed rate: <5 m/min

Note: *: The remainder was Ni.

**: MR means micro cracks.

In Comparative Examples 38 and 39, because voids were formed between the capsule wall and the chromium-nickel material during working, cracks developed in the capsule, and the chromium-nickel material also underwent cracking. In Comparative Example 40, because the degree of hot wire drawing per pass was as high as 15%, the material underwent cracking during the 3rd pass. The wires obtained in Comparative Examples 41, 42, 44 and 45 developed micro cracks at the end of the final drawing operation. Surface observation of the material of Comparative Example 43 revealed considerable cracks of the oxidized film formed on the surface of the material.

EXAMPLES 19 TO 23

A mixture of 99.9% pure metallic chromium powder and nickel powder was melted in an inert gas arc melting furnace (Max: 1000 A, 20 V) in a 1 atm. argon atmosphere to obtain an ingot. An alloy mass for rolling was cut out of the ingot.

The alloy mass was put in a hot roll mill (roll diameter: 200 mm; rotation of roll: 17 rpm), and hot rolling was conducted at 40°C to obtain a high chromium-nickel material having a composition shown in Table 10 below.

The resulting material was dipped in a molten salt shown in Table 10, and polarization curves of the anode and cathode were determined by potential scanning to obtain a corrosion current. The results obtained are shown in Table 10.

COMPARATIVE EXAMPLES 46 TO 48

Corrosion test was carried out in the same manner as in Examples 19 to 23 using each of 99.9% pure nickel (Comparative Example 46), SUS 347 (Comparative Example 47), and SUS 316 (Comparative Example 48) which are anti-corrosion materials conventionally employed for molten carbonates. The results obtained are shown in Table 10.

COMPARATIVE EXAMPLES 49 AND 50

Chromium-nickel materials having a composition shown in Table 10 were produced in the same manner as in Example 19, and the resulting materials were subjected to corrosion test in the same manner as in Example 19. The results obtained are shown in Table 10.

TABLE 10

Example No.	Composition (wt%) Cr	Ni	Mo	Fe	Nb	Corrosion Current (mA/cm^2) Na_2CO_3 500°C	Na_2CO_3 800°C	10% NaCl-Na_2CO_3 700°C
Example 19	50.0	49.8				0.03	0.08	0.42
" 20	59.8	39.8				0.03	0.07	0.35
" 21	69.9	29.9				0.02	0.06	0.28
" 22	79.9	19.8				0.01	0.03	0.19
" 23	90.0	9.8				0.01	0.03	0.18
Comparative Example 46	-	99.9				0.09	0.8	1.1
" 47	18.0	11.0		BL*	0.6	0.14	1.8	10 or more
" 48	18.0	12.0	2.0	BL		0.15	1.6	10 or more
" 49	30.1	69.8				0.07	0.3	0.9
" 50	40.2	59.7				0.07	0.2	0.7

Note: *: BL means a balance.

The results in Table 10 prove that the materials according to the present invention applied as anti-corrosion material for molten carbonates are by no means inferior to nickel or other Ni-Cr-based alloys.

While the invention has been described in detail and with reference to specific examples thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A high chromium-nickel material containing from 50 to 90% by weight of chromium and not more than 0.5% by weight of impurities, with the remainder substantially comprising nickel, whose metallurgical structure consists of two phases of a hard phase and a soft phase and whose crystal grains have a diameter of not more than 50 μm.

2. A process for producing a high chromium-nickel material containing from 50 to 90% by weight of chromium and not more than 0.5% by weight of impurities, with the remainder substantially comprising nickel, whose metallurgical structure consisting of two phases of a hard phase and a soft phase and whose crystal grains having a diameter of not more than 50 μm, which comprises preparing an ingot having a packing density of 7 g/cm^3 or more by using chromium powder having a purity of 99% or higher and nickel carbonyl powder, heating the ingot in vacuo or in an inert gas, and subjecting the heat treated ingot to hot working.

3. A process as claimed in Claim 2, wherein a high chromium-nickel alloy powder is used as a raw material powder.

4. A high chromium-nickel wire containing from 50 to 90% by weight of chromium and not more than 0.5% by weight of impurities, with the remainder substantially comprising nickel, whose metallurgical structure consisting of two phases of a hard phase and a soft phase and whose grains having a diameter of not more than 50 μm.

5. A process for producing a high chromium-nickel wire containing from 50 to 90% by weight of chromium and not more than 0.5% by weight of impurities, with the remainder substantially comprising nickel, whose metallurgical structure consisting of two phases of a hard phase and a soft phase of and whose grains having a diameter of not more than 50 μm, which comprises preparing an ingot having a packing density of 7 g/cm^3 or more by using chromium powder having a purity of 99% or higher and nickel carbonyl powder, heating the ingot in vacuo or in an inert gas, filling the heat treated ingot in a capsule, and subjecting the ingot-containing capsule to hot wire drawing at a temperature of from 300 to 800°C at a degree of hot wire drawing of not more than 30% per pass.

6. A process as claimed in Claim 5, wherein a high chromium-nickel alloy powder is used as a raw material powder.

7. A process for producing a high chromium-nickel wire for coating containing from 50 to 90% by weight of chromium and not more than 0.5% by weight of impurities, with the remainder substantially comprising nickel, which comprises preparing an ingot having a packing density of 7 g/cm^3 or more by using chromium powder having a purity of 99% or higher and nickel carbonyl powder, heating the ingot to a temperature of 1300°C or lower in vacuo or in an inert gas, filling the heat treated ingot in a cylindrical metal capsule, subjecting the ingot-containing capsule to hot wire drawing at a temperature of from 300 to 800°C at a degree of hot wire drawing of not more than 10% per pass, removing the capsule, and rolling the resulting wire to further reduce the thickness by means of a tandem grooved roll mill.

8. A process as claimed in Claim 7, wherein a high chromium-nickel alloy powder is used as a raw material powder.

Fig. 1

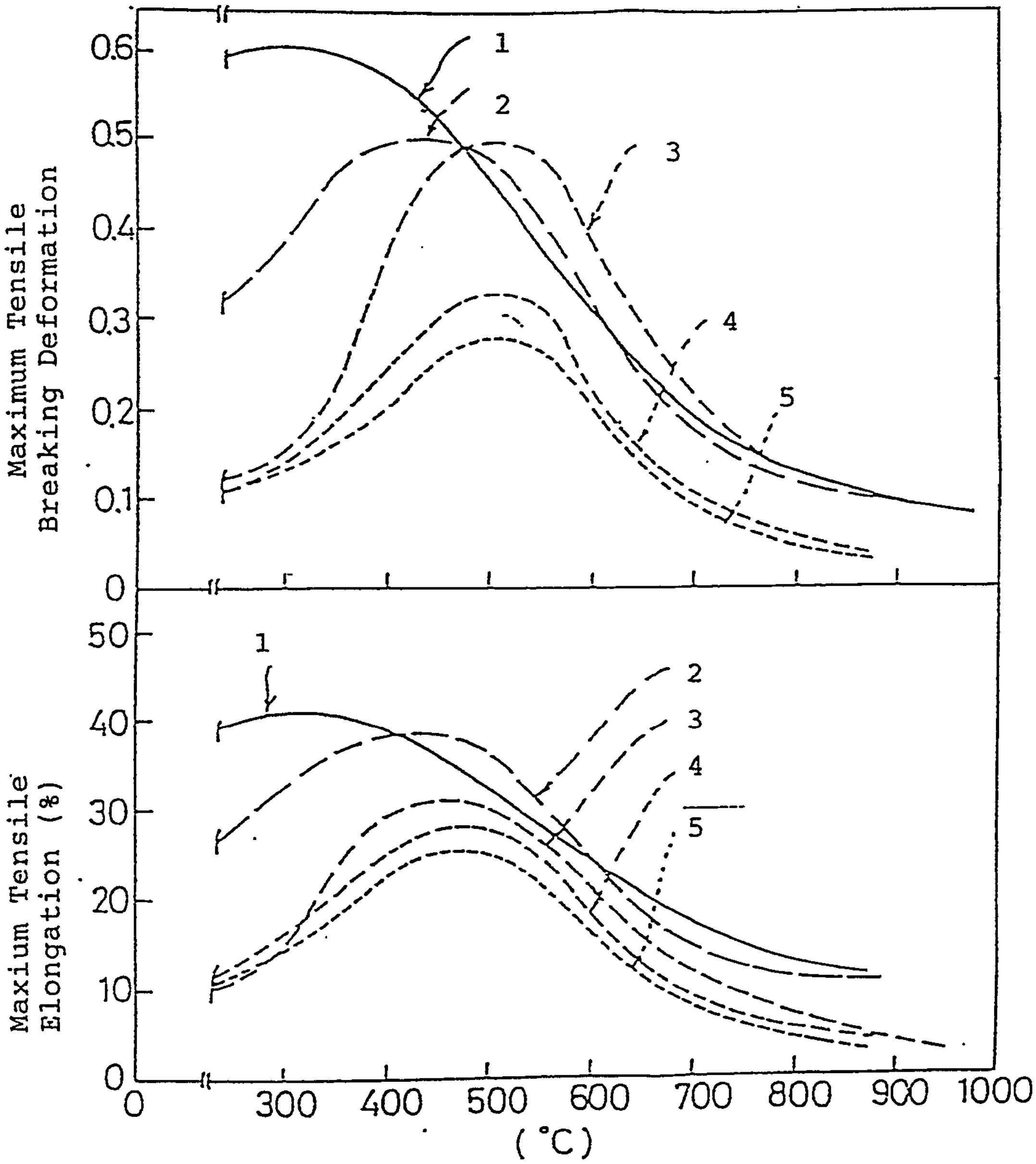
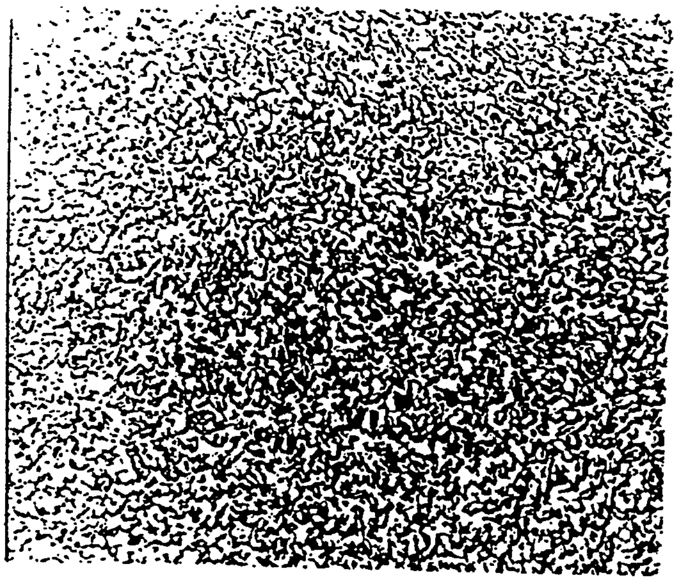

Maximum Tensile Breaking Deformation
0.6
0.5
0.4
0.3
0.2
0.1
0
1
2
3
4
5
Maxium Tensile Elongation (%)
50
40
30
20
10
0
0
300
400
500
600
700
800
900
1000
(°C)

Fig. 2

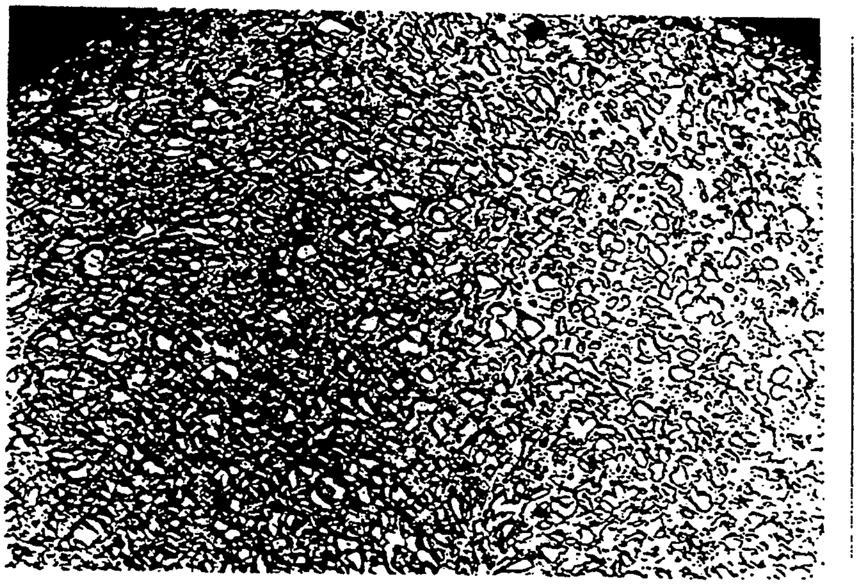
(a)



(b)

Fig. 3

(a)



(b)

European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 91 30 3101

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	ERZMETALL vol. 38, no. 3, 1985, STUTTGART DE pages 129 - 133; R.ECK ET AL: 'Properties and production of powder-metallurgical PVD sources ' * page 129, left column, line 35 - page 132, left column, line 7 *	1	C22C1/04 B22F3/14 B22F3/20 C22C27/06
Y		2-8	
Y	CHEMICAL ABSTRACTS, vol. 78, no. 24, June 18, 1973, Columbus, Ohio, US; abstract no. 150371, SOLONIN, S. M. 'Sintering of binary alloys with limited solubility in the solid state ' * abstract * & POROSH. MET. vol. 13, no. 2, 1973, KIEV,USSR	2-8	
Y	US-A-1 760 367 (J.W.MARDEN ET AL) * page 4, line 69 - page 5, line 16; claim 7 *	2-8	
Y	US-A-3 162 530 (R.W.HARRISON) * claim 4 *	5,7	TECHNICAL FIELDS SEARCHED (Int. Cl.5) C22C B22F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	25 JULY 1991	SCHRUERS H.J.

CATEGORY OF CITED DOCUMENTS

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