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(54) **Composite material having a low thermal expansivity.**

(57) A composite material having a low thermal expansivity obtained by combining 10 to 60 wt. % of a powdery Li_2O-Al_2O_3-SiO_2 mineral with 40 to 90 wt. % of one or more members selected from the group consisting of metals of Fe, Cu, Ni, Co, Mo, Ti. Cr, Al, Mn, Si, Zn, Ben and W and alloys of two or more of these metals to form the composite material containing the metal(s) having a reduced coefficient of thermal expansion.

Croydon Printing Company Ltd.

Title of the Invention:

COMPOSITE MATERIAL HAVING A LOW THERMAL EXPANSIVITY

Field of the Invention:

The present invention relates to a composite material having a low thermal expansivity. More particularly, the invention relates to a composite material having a low thermal expansivity, prepared by combining a metal with a lowly expansive powdery $Li_2O-Al_2O_3-SiO_2$ mineral to lower the coefficient of thermal expansion of the metal.

Prior Art:

Metal materials having a low thermal expansivity used heretofore include an invar alloy used as a material for parts of various measuring instruments, bimetals and watches. However, it has a specific gravity of as high as 8 to 8.5 and is expensive and its processability is unsatisfactory.

Known ceramic materials having a low thermal expansivity include aluminum titanate, indialite and petalite. However, the use of them in the production of parts of precision machines is difficult, since they have only a poor mechanical strength and thermal hysteresis.

It is believed in general that the properties of a composite material comprising two or more starting materials are determined by properties of the respective materials in proportion to volume fractions of them. This is the so-called "composite rules". For example, the thermal expansion coefficient α_c of a composite comprising n materials is calculated as follows:

$$\alpha_c = \frac{K_1\alpha_1V_1 + K_2\alpha_2V_2 + \cdots\cdots + K_n\alpha_nV_n}{K_1V_1 + K_2V_2 + \cdots\cdots + K_nV_n} \quad \ldots\ldots (1)$$

wherein α represents the thermal expansion coefficient, V represents a volume fraction, K represents a bulk modulus of elasticity and numerals of 1 to n refer to the first to the n-th material, respectively.

When a powder of a mineral having a low coefficient of thermal expansion is combined with a metal and/or its alloy to form a composite material, the above formula (1) may be employed and the resulting metallic composite material has a low coefficient of thermal expansion.

However, the above-mentioned composite rules are formulated on the assumption that the constituent materials are utterly free from the mutual action. In practice, it is difficult to obtain a composite material having desired properties, since the properties vary depending on various factors such as interfacial diffusion phase, residual stress phase formed in the course of the production process and differences in the coefficient of thermal expansion and modulus of elasticity between the starting materials constituting the composite material. For example, it is difficult to obtain a metal composite material having a high processability, high strength and low coefficient of thermal expansion even from a metal and a powder of a mineral having a low thermal expansivity. Therefore, attempts were scarcely made in the prior art at producing a composite material having properties of both metal and mineral powder having a low thermal expansivity by combining them.

Object of the Invention:

An object of the present invention is to provide a composite material having a low thermal expansivity, a specific gravity far lower than that of an invar alloy, a high processability, a low thermal hysteresis and a high strength which can be obtained at a low cost.

To attain the above-mentioned object, the composite material of the present invention having a low thermal expansivity comprises 40 to 90 % of one or more members of the group consisting of metals of

Fe, Cu, Ni, Co, Mo, Ti, Cr, Al, Mn, Si, Zn, Be and W and alloys of two or more of these metals and 10 to 60 % of a Li_2O-Al_2O_3-SiO_2 mineral powder.

The composite material having a low thermal expansivity according to the present invention may further contain one or more powdery substances selected from the group consisting of carbons, carbides, oxides and borides.

In addition, the composite material of the present invention may comprise reinforcing fibers.

In the present invention, the percentage are given by weight unless otherwise stated.

Detailed Description of the Invention:

The metals and alloys thereof used in the present invention include Fe, Cu, Ni, Co, Mo, Ti, Cr, Al, Mn, Si, Zn, Be and W as well as alloys of two or more of these metals. These metals and their alloys may be used either alone or in the form of a combination of two or more of them according to the use of the composite material.

The composite material of the present invention may be produced by mixing the powdery meal(s) and/or alloy(s) with the mineral powder, molding the mixture and sintering the moldings as described below. In this process, the particle size of the powdery metal or alloy is preferably up to 50 μm, particularly the average diameter of the particles is preferably up to 20 µm. When a major part of the particels of the metal and/or alloy powder(s) has a particle diameter of larger than 50 µm, it becomes difficult to obtain the composite material having a high density. When the metal and/or alloy powder used contains a large amount of the powder having a particle diameter of up to 5 µm, the metal and/or alloy powder is easily oxidized unfavorably.

The powdery Li_2O-Al_2O_3-SiO_2 minerals usable in the present invention are those having an Li_2O/Al_2O_3/SiO molar ratio of 1/1/2-10. Examples of them include Li_2O-Al_2O_3-$2SiO_2$ (ß-eucryptite), Li_2O-Al_2O_3-$4SiO_2$ (ß-spodumene) and Li_2O-Al_2O_3-$8SiO_2$ (petalite). The powdery Li_2O-Al_2O_3-SiO_2 mineral may be selected suitably depending on desired properties of the composite material.

The powdery mineral used in the production of the composite material has a particle size of preferably up to 500 µm, particularly, an average particle diameter of 10 to 200 µm. When a large amount of the particles having a size of larger than 500 µm is contained therein, an adverse influence is exerted on the sinterability. An average particle diameter of less than 10 µm is not preferred, since the average particle diameter of the metal is less than 5 µm in such a case, because the particle diameter of the powdery mineral is preferably at least twice as large as that of the powdery metal or alloy in the production of the composite material having a low thermal expansivity as described below.

The composite material of the present invention may comprise, in addition to said metal and/or alloy and Li_2O-Al_2O_3-SiO_2 mineral, one or more powdery substances selected from the group consisting of carbons, carbides, oxides, nitrides and borides.

The carbons include acetylelene black, carbon black, and graphite. The carbides include SiC, TiC, WC, TaC, NbC, Mo_2C and VC. The nitrides include Si_3N_4, TiN, AlN and TaN. The oxides include Al_2O_3, BeO, TiO_2, ZrO_2, MgO, Y_2O_3, WO_3, Ta_2O_3 and MoO_3. The borides include BN, B_4C and TiB_2. These additives may be used either alone or in the form of a combination of two or more of them depending on the desired properties of the composite material.

These carbons, carbides, nitrides, oxides and borides are in the form of a powder having a particle size of preferably up to 50 µm, particularly up to 20 µm. When the particle size is larger than 50 µm, the strength of the resulting composite material is reduced. When the particles having a size of less than 1 µm are used in a large amount, they exert an adverse influence on the moldability.

According to the present invention, amatrix composition comprising the above-mentioned metal and/or alloy and Li_2O-Al_2O_3-SiO_2 mineral may be reinforced with various fibers.

The usable reinforcing fibers are one or more members of the group consisting of glass fibers, ceramic fibers, metal fibers, metal/ceramic fibers and whiskers.

The glass fibers include both long and short ones.

The ceramic fibers include those of rock wool, mullite, silica, alumina, SiC, BN, carbon, zirconia (ZrO_2), thoria (ThO_2), and yttria (Y_2O_3).

The metal fibers include those of stainless steel, steel, molybdenum (Mo), and tungsten (W)'.

The metal-ceramic composite fibers include those of boron-tungsten (B-W) and SiC-W.

The whiskers include those of SiC, Si_3N_4, and alumina.

These fibers may be used either alone or in the form of a combination of two or more fibers suitably according to the desired properties of the composite material.

The diameter of both short and long fibers is preferably up to 100 µm, particularly up to 20 µm. When the diameter of the fiber exceeds 100 µm, problems of the interfacial adhesion between the metal and mineral powder are caused to reduce the strength of the composite material. The aspect ratio (ratio of the diameter to the length of the fiber) of the short fibers is preferably 20 to 100. When the aspect ratio of the short fibers exceeds 100, the fibers are entangled with one another in the mixing step to make homogenenous dispersion difficult. When the aspect ratio of said fibers is less than 20, no effect of reinforcing the composite material can be obtained.

Generally, in the composite materials comprising two or more different materials, the offset of difference in the thermal expansion between the constitutent materials becomes non-steady due to an interfacial thermal stress, as represented by the product of (strain among the crystal particles due to a difference in the thermal expansion between the materials) and (modulus of elasticity), and the residual stress generated in the production process.

Namely, when the composite rules can be applied to a composite material comprising two or more starting materials, a property such as thermal expansivity coincides substantially with a value calculated according to the above formula (1). However, under the influence of the thermal stress and residual stress as described above, the thermal expansivity of the composite is not always proportional to the volume fraction of the coefficient of the thermal expansion and said composite rules cannot be applied thereto.

Also in the composite material of the present invention, the effect of the powdery Li_2O-Al_2O_3-SiO_2 mineral in reducing the coefficient of thermal expansion of the metal and/or alloy matrix cannot easily be obtained under the influence of the thermal stress or residual stress.

After intensive investigations, the inventors have found that the influences of the thermal stress and residual stress on the thermal expansion can be eliminated by controlling the particle diameters of the powders of the metal and/or alloy and Li_2O-Al_2O_3-SiO_2 mineral.

More particularly, as the ratio of the particle diameter of the powdery mineral to the particle diameter of the powdery metal or alloy is increased, the effect of the powdery mineral in reducing the coefficient of thermal expansion of the metal or alloy is increased. This effect is remarkable when the average particle diameter of the powdery mineral is at least twice as large as that of the metal or alloy. When the average particle diameter of the former is less than twice as large as that of the latter, the effect of reducing the coefficient of thermal expansion is reduced under the influence of the interfacial thermal stress between the metal constituent materials and the residual stress as described above.

It has also been found that when the particle diameter of the powdery mineral is more than 10 times as large as that of the powdery metal or alloy, the particle diameter of $Li_2O-Al_2O_3-SiO_2$ mineral becomes too large and the metal composite material of a high density cannot be obtained easily.

Therefore, in the production of a fiber-reinforced composite material having a low thermal expansivity from the metal and/or alloy, powdery $Li_2O-Al_2O_3-SiO_2$ mineral, fibers and a carbon, carbide, nitride, oxide or boride according to the present invention, it is preferred that the ratio of the average particle diameter of the powdery mineral to that of the metal or alloy is controlled within the range of 2/1 to 10/1.

The particle diameters of the carbons, carbides, nitrides, oxides and borides are controlled preferably to a value equal to or smaller than that of the metal or alloy, since when the particle diameter of the former is larger than that of the latter, the strength of the composite material is unsatisfactory.

In the production of the metal composite material of the present invention, the relative amounts of the metal and the powdery Li_2O-Al_2O_3-SiO_2 mineral are 40 to 90 % and 10 to 60 %, respectively.

The amount of the carbon, carbide, nitride, oxide or boronide powder is preferably up to 10 % based on the total amount ofhte composite material.

In reinforcing the composite material of the present invention with the fibers, it is preferred to use 1 to 30 vol. % of the glass fibers, ceramic fibers, metal fibers, metal-ceramic composite fibers and/or whiskers for 70 to 99 vol. % of the matrix composition comprising 40 to 90 % of the metal and/or its alloy aad 10 to 60 % of the powdery LiO_2/Al_2O_3-SiO_2 mineral.

When the amount of the metal and/or its alloy is less than 40 % or when that of the powdery Li_2O-Al_2O_3-SiO_2 mineral exceeds 60 %, the amount of the metal and/or the alloy dispersed among the mineral particles is insufficient and the metallic properties of the composite material are damaged extremely and strength and processability thereof are reduced.

When the amount of the metal and/or the alloy exceeds 90 % or when that of the powdery mineral is less than 10 %, the effect of reducing the coefficient of thermal expansion to be obtained by using the powdery mineral is hardly obtained.

When the amount of the carbon, carbide, nitride, oxide and/or boride used for the purpose of imparting a high elasticity and abrasion resistance to the resulting composite material exceeds 10 %, the sinterability is damaged seriously.

When the amount of the fibers in the composite material is less than 1 vol. %, the intended reinforcing effect cannot be obtained. As this amount is increased to at least 1 vol. %, the strength of the composite material is increased in proportion to this amount and the strength reaches the maximum with the fiber content of 30 vol. % and can be no more increased.

Though a slight diffusion reaction proceeds between the Li_2O-Al_2O_3-SiO_2 mineral and the metal or alloy in the composite material of the present invention, the extent of the reaction is only small and no influence is exerted on the properties of the metal, alloy or Li_2O-Al_2O_3-SiO_2 mineral. In a broad sense, the crystals of the constituent materials are principally physically bound to one another and the crystal phase comprises only the metal or alloy and the powdery Li_2O-Al_2O_3-SiO_2 mineral. Accordingly, no interfacial diffusion phase which causes a deviation of the composite effects on the coefficient of thermal expansion is formed.

The composite material having a low thermal expansivity of the present invention is produced generally by molding a previously homogeneously dispersed mixture by a known means and heating the resulting molding at 600 to 1300°C in vacuum or in a non-oxidizing atmosphere to sinter the product. As a matter of course, the composite material having a high density and a high strength can be obtained easily by other means such as a known hot press method or hot isostatic pressing method. In another process, the powdery mineral and, if necessary, one or more members selected from the group consisting of carbons, carbides, nitrides, oxides and borides and/or the reinforcing fibers are dispersed in the molten metal, and the dispersion is cooled to obtain a solid.

In producing the composite material reinforced with the fibers by using short fibers, a mixture previously homogenized in a roll mill or ball mill is molded by a known process such as compression molding with a mold. When long fibers are used, the oriented long fibers and mixed slurry of the metal and/or its alloy and the powdery mineral are molded by slip casting. The resulting molding is heated at 600 to 1300°C in vacuum or non-oxidizing atmosphere to sinter it. By employing the hot press method, HIP method or the like, the composite material having a high density nad a further improved strength can be obtained easily.

Thus, the coefficient of thermal expansion of the metal can be reduced by combining the metal and/or its alloy with the powdery Li_2O-Al_2O_3-SiO_2 mineral having a low coefficient of expansion.

Further, by incorporating the carbon, carbide, nitride, oxide or boride in the composite material, a high elasticity can be realized. When the carbide, nitride, oxide or boride is incorporated therein, the abrasion resistance is also improved.

By reinforcing the composite material with the glass fibers, ceramic fibers, metal fibers, metal-ceramic composite fibers or whiskers, high strength and elasticity can be obtained.

Thus, according to the present invention, composite materials having any desired coefficient of thermal expansion ranging from that of the metal or its alloy to nearly zero is provided. Further, by incorporating the carbon, carbide, nitride, oxide or boride therein, the composite material having a low coefficient of expansion or both low coefficient of expansion and excellent abrasion resistance is provided. By reinforcing with fibers, the composite material having a low coefficient of thermal expansion, a high strength and a high elasticity is provided.

The above-mentioned composite material of the present invention having a low coefficient of thermal expansion and a composition containing said composite material have a coefficient of thermal expansion lower than that of an invar alloy and they are lighter in weight than the latter and obtainable at a lower cost. Their strength is higher than that of a aluminum titanate (at least about 10 kg/mm^2).

Therefore, the composite material of the present invention is most suitable for the production of parts to be fitted into various machineries and tools, particularly measuring instruments and precision instruments which parts necessitate at least a given strength, modulus of elasticity, light weight and a low thermal expansivity. Further, they can be clamped together with other metals.

The composite material of the present invention can be used for the production of members having a complicated shape which require a high dimensional accuracy by the steps of (1) forming a product having a size larger than an intended size from the composite material of the present invention and (2) cutting the product.

When the starting materials of the composite material of the present invention are in the form of powders and fibers, the above-mentioned product having a considerably complicated shape can be produced. The exposed surface of the product is glossy, since it is made of a metal. The outer surface of the product may be plated or coated.

Thus, the fiber-reinforced composite material of the present invention having a low thermal expansivity is suitable for use in the production of parts of measuring and precision instruments, since it is inexpensive and has a light weight, high strength, high elasticity and excellent processability. It is of a high utility value.

The following examples and comparative examples will further illustrate the present invention, which by no means limit the invention.

Example 1

A commercially available powdery iron (having a purity of above 99 % and a particle diameter of up to 44 µm) was finely divided into particles having an average diameter of 5 or 10 µm. The resulting iron powder in an amount which varied in the range of 40 to 90 % as shown in Table 1 was mixed with ß-eucryptite (having a purity of at least 99 % and average particle diameter of 15 or 20 µm) or ß-spodumene (having a purity of 99 % and average particle diameter of 15 µm) by means of a ball mill (alumina balls and an alumina pot) using isopropyl alcohol as the solvent and sodium hexametaphosphate (1 %) as the dispersant for 3 h. Another mixture comprising the above-mentioned iron and ß-eucryptite and, in addition, Ti or Mo was prepared in the same manner as above.

The resulting powdery mixture was molded under a pressure of 1500 kg/cm^2 and the molding was treated in a hot hydrostatic press device (hereinafter referred to as HIP device) under the treatment conditions shown in Table 1 (Nos. 1 to 10). Separately, the moldings were sintered in a non-oxidizing atmosphere under atmospheric pressure (Nos. 11 to 13).

The properties of the obtained samples are given in Table 1.

It may be understood from Table 1 that, for example, the coefficients of thermal expansion of samples Nos. 1 to 4 are reduced significantly to

6.2×10^{-6} to -1.8×10^{-6}/°C and the flexural strengths of them are as high as at least 10 kg/mm^2, while the coefficient of thermal expansion of iron is 11.7×10^{-6}/°C. It may be also understood that when a small amount of Mo or Ti is incorporated therein as in Nos. 9 and 10, the strength is improved.

Example 2

Commercially available powdery electrolytic copper (having a purity of above 99 % and an average particle diameter of 5 µm) and ß-eucryptite (having a purity of above 99 % and average particle diameter of 15 or 20 µm) were mixed together in a ratio as shown in Table 2 and the mixture was molded in the same manner as in Example 1.

The resulting moldings were treated in the HIP device under the conditions shown in Table 2 (Nos. 14 to 19). Separately, the moldings were sintered in a non-oxidizing atmosphere under atmospheric pressure (Nos. 20 to 22).

The properties of the obtained samples are given in Table 2.

It may be understood from Table 2 that, for example, the coefficients of thermal expansion of samples Nos. 14 to 17 are reduced to as low as 12.5×10^{-6}/°C to -1.3×10^{-6}/°C and the strengths of them are high, while the coefficient of thermal expansion of copper is $16.5 \times 10^{-6}/°C$.

Example 3

Moldings were produced in the same manner as in Example 1 except that Ti, Co, Ni, Cr or Al having a particle diameter of 5 µm was used as the metal and the mixing ratio was altered as shown in Table 3. The resulting moldings were subjected to the HIP treatment under the conditions shown in Table 3 (Nos. 23 to 27).

The properties of the obtained samples are given in Table 3.

Example 4

A metal or alloy (having an average particle diameter of 5 µm) shown in Table 4 was mixed with ß-eucryptite (having a purity of above 99 % and an average particle diameter of 15 µm) in a ratio shown in Table 4. Isopropyl alcohol as the solvent and sodium hexametaphosphate (1 %) as the dispersant were added to the mixture and the mixture was stirred in a ball mill (alumina pot and alumina balls) for 3 h.

The resulting powdery mixture was molded under 1500 kg/cm^2 and the moldings were treated in the HIP device under conditions shown in Table 4 (Nos. 28

to 37).

The properties of the obtained samples are given in Table 4.

Comparative Example 1

The same procedure as in Example 4 was repeated except that Fe or Cu having a particle diameter of 5 µm was used and the mixing ratio was altered as shown in Table 4. The moldings were subjected to the HIP treatment under the conditions shown in Table 4 (Nos. 38 to 45).

The properties of the obtained samples are shown in Table 4.

It may be understood from Tables 1 to 4 that the composite material of the present invention has a light weight, high strength and low thermal expansivity.

Example 5

A mixture of the following components was prepared as shown in Table 5:

40 to 90 % of one or more members of the group consisting of powdery metals of Fe, Cu, Ni, Co, Mo, Ti, Cr, Al, Mn, Si, Zn and Be and alloys thereof (average particle diameter: 5 µm), and up to 10 % of one or more members of the group consisting of carbons, carbides, nitrides, oxides and borides (average particle diameter: 3 µm).

Isopropyl alcohol as the solvent, sodium hexametaphosphate (1 %) as the dispersant and zinc stearate (1 %) as the lubricant were added to the mixture and mixed homogeneously in a ball mill (alumina pot and alumina balls) for 3 h.

The resulting powdery mixture was molded under 1500 kg/cm^2 and the moldings were subjected to the HIP treatment under conditions shown in Table 5 (Nos. 46 to 48 and 50 to 63). Separately, the moldings were sintered in a non-oxidizing atmosphere under atmospheric pressure (No. 49).

The properties of the obtained samples are given in Table 5.

Comparative Example 2 and Referential Example 1

Moldings were produced in the same manner as in Example 5 using the metal or its alloy, powdery mineral and carbon, carbide or the like as shown in Table 6. The moldings were subjected to the HIP treatment.

The properties of the obtained samples are given in Table 6.

It is apparent from Tables 5 and 6 that the strength and elasticity are improved by the incorporation of the carbon, carbide or the like.

Example 6

A mixture of the following components was prepared as shown in Table 7:

70 to 90 vol. % of a matrix comprising 40 to 60 % of one or more members of the group consisting of powdery metals of Fe, Cu, Ni, Co, Mo, Ti, Cr, Al, Mn, Si, Zn and Be and alloys of them (average particle diameter: 5 um) and 40 to 60 % of a powdery $Li_2O-Al_2O_3-SiO_2$ mineral (average particle diameter: 15 µm), and

10 to 30 vol. % of one or more members of the group consisting of glass fibers, ceramic fibers, metal fibers, metal-ceramic composite fibers and whiskers.

Isopropyl alcohol as the solvent and zinc stearate (0.5 %) as the lubricant were added to the mixture and mixed homogeneously in a ball mill for 5 h.

The resulting powdery mixture was molded under 2000 kg/cm^2 and the molding was treated in the HIP device under the conditions shown in Table 7.

The properties of the obtained samples (Nos. 69 to 83) are given in Table 7.

Example 7

0.5 % of sodium alginate and 1 % of acrylic polymer were added to a matrix composition shown in

Table 8 to obtain a slurry having a pH of about 4.5 to 5 and a specific gravity of about 1.6.

On the other hand, long fibers shown in Table 8 were placed in a mold in such a manner that (1) they were oriented in the same direction (Nos. 85 to 87) or (2) they were oriented in two directions perpendicular to each other (Nos. 84 and 88). The slurry was placed in the mold by the slip method so that the slurry penetrated into the gaps between the fibers. The charge was compressed to obtain a molding. The mixing ratio was as shown in Table 8. The resulting molding was dried and treated in the HIP device under the conditions shown in Table 8.

The properties of the obtained samples (Nos. 84 to 88) are given in Table 8. The tensile strength was measured by applying a force in the same direction as that of the orientation of the fibers.

Comparative Example 3 and Referential Example 2

Moldings were produced in the same manner as in Example 6 with the mixing ratio of the powdery metal or alloy to the powdery mineral in the matrix composition and the mixing ratio of the matrix composition to the fibers altered as shown in Table 8. The moldings were treated in the HIP device under the conditions shown in Table 8.

The properties of the obtained samples (Nos. 89 to 93) are given in Table 8.

It may be understood from Tables 7 and 8 that the strength and elasticity of the composite material of the present invention having a low thermal expansivity are improved by the reinforcement with the fibers.

Table 1

Ex.	Sample No.	Particle diameter of starting materials (μm)			Composition (wt. %)			
		Iron, etc	β-eucryptite	β-spodumene	Iron	Other metal	β-eucryptite	β-spodumene
Ex.1	1	5	15	-	90	0	10	0
	2	5	15	-	70	0	30	0
	3	5	15	-	50	0	50	0
	4	5	15	-	40	0	60	0
	5	10	20	-	50	0	50	0
	6	5	20	-	50	0	50	0
	7	5	20	-	50	0	50	0
	8	5	-	15	50	0	0	50
	9	5	15	-	55	Ti 5	40	0
	10	5	15	-	55	Mo 5	40	0
	11	5	15	-	90	0	10	0
	12	5	15	-	70	0	30	0
	13	5	15	-	50	0	50	0

Table 1 (Cont.)

Ex.	Sample No.	Treatment conditions			Properties			
		Temp. (°C)	Pressure (kg/cm^2)	Time (hr)	Density ratio (%)	Flexural strength (kg/mm^2)	Specific strength (x10^5·cm)	Coefficient of thermal expansion (x10^{-6}/°C) *1
Ex.1	1	1200	1000	1	97.7	26.3	4.12	6.2
	2	1200	1000	1	96.3	18.1	3.80	2.0
	3	1200	1000	1	96.4	12.3	3.21	0.0
	4	1200	1000	1	96.0	10.2	2.94	-1.8
	5	1200	1000	1	95.1	10.3	2.92	-0.5
	6	1200	1000	1	96.8	11.3	2.93	-0.2
	7	800	1000	1	95.4	10.0	2.63	-0.7
	8	1200	1000	1	94.7	11.4	2.78	4.1
	9	1200	1000	1	96.7	15.8	3.78	0.5
	10	1200	1000	1	95.8	16.7	3.93	0.4
	11	1150	Atmospheric pressure	2	92.1	13.2	2.19	7.5
	12	1150	"	2	90.7	9.8	2.18	2.2
	13	1150	"	2	88.3	7.3	2.08	-1.0

*1: at room temp. to 200°C

Table 2

Ex.	Sample Nol	Particle diameter of starting materials (μm)		Composition (wt.%)	
		Copper	β-eucryptite	Copper	β-eucryptite
Ex.2	14	5	15	90	10
	15	5	15	70	30
	16	5	15	50	50
	17	5	15	40	60
	18	5	20	50	50
	19	5	20	50	50
	20	5	20	90	10
	21	5	15	70	30
	22	5	15	50	50

*1: at room temperature to 200°C

Table 2 (Cont.)

Ex.	Sample No.	Treatment conditions			Properties			
		Temp. (°C)	Pressure (kg/cm^2)	Time (hr)	Density ratio (%)	Flexural strength (kg/mm^2)	Specific strength (x10^5·cm)	Coefficient of thermal expansion (x10^{-6}/°C)
Ex.2	14	1000	1000	1	98.0	20.7	2.90	12.5
	15	1000	1000	1	97.8	15.0	1.96	6.3
	16	1000	1000	1	96.4	12.7	2.00	0.0
	17	1000	1000	1	96.5	10.1	1.48	-1.3
	18	1000	1000	1	97.1	10.0	1.32	-0.2
	19	1000	1000	1	96.1	13.1	2.04	0.5
	20	1050	Atmospheric pressure	2	93.4	10.7	1.58	10.8
	21	1050	Atmospheric pressure	2	92.1	8.4	1.74	2.9
	22	1050	Atmospheric pressure	2	89.8	5.3	0.70	-0.8

*1: at room temperature to 200°C

Table 3

Ex.	Sample No	Particle diameter of starting materials (µm)		Composition (wt.%)	
		Metal	ß-eucryptite	Metal	ß-eucryptite
Ex.3	23	Ti 5	15	55	45
	24	Co 5	15	55	45
	25	Ni 5	15	55	45
	26	Cr 5	15	75	25
	27	Al 5	15	40	60

*1: at room temp. to 200°C

Table 3 (Cont.)

Ex.	Sample No	Treatment conditions			Properties			
		Temp (°C)	Pressure (kg/cm^2)	Time (hr)	Density ratio (%)	Flexural strength (kg/mm^2)	Specific strength (x10^5·cm)	Coefficient of thermal expansion (x10^{-6}/°C)
Ex.3	23	1250	1000	1	94.7	-	-	0.3
	24	1100	1000	1	95.6	-	-	0.7
	25	1100	1000	1	96.8	-	-	-0.1
	26	1300	1000	1	96.2	-	-	0.5
	27	600	1000	1	92.4	-	-	3.8

*1: at room temp. to 200°C

Table 4

Ex.	Sample No.	Composition (wt. %)				
		Metal or alloy			β-eucryptite	
				*1		*1
Ex.4	28	18Cr-8Ni-Fe	(5µm)	50	50	(15µm)
	29	2Ni-0.5Mo-0.2Mn-Fe	(5µm)	50	50	(15µm)
	30	20Zn-Cu	(5µm)	40	60	(15µm)
	31	3.5Be-Cu	(5µm)	50	50	(15µm)
	32	8Mn-Ti	(5µm)	50	50	(15µm)
	33	18Fe-22Cr-Ni	(5µm)	55	45	(15µm)
	34	4W-4Mo-20Ni-Co	(5µm)	55	45	(15µm)
	35	2Cu-Al	(5µm)	40	60	(15µm)
	36	Mn	(5µm)	40	60	(15µm)
	37	Si	(5µm)	50	60	(15µm)
Comp. Ex,1	38	Fe	(5µm)	50	50	(5µm)
	39	Fe	(5µm)	100	-	
	40	Fe	(5µm)	95	5	(5µm)
	41	Fe	(5µm)	35	65	(5µm)
	42	Cu	(5µm)	100	-	
	43	Cu	(5µm)	95	5	(15µm)
	44	Cu	(5µm)	30	70	(15µm)
	45	Cu	(5µm)	50	50	(5µm)

* 1 Numerals in the parentheses indicate particle diameters

* 2 at room temp. to 200°C

Table 4 (Cont.)

Ex.	Sample No.	Treatment conditions			Properties			
		Temp. (°C)	Pressure (kg/cm^2)	Time (hr)	Density ratio (%)	Flexural strength (kg/mm^2)	Specific strength (x10^5·cm)	Coefficient thermal expansion (x10^{-6}/°C) *2
Ex.4	28	1100	1000	1	97.4	20.7	5.43	1.9
	29	1100	1000	1	98.1	15.4	4.05	0.4
	30	800	1000	1	98.4	10.5	2.89	0.5
	31	750	1000	1	98.7	15.2	3.69	1.2
	32	1250	1000	1	95.8	-	-	0.4
	33	1100	1000	1	98.0	-	-	0.7
	34	1100	1000	1	97.4	-	-	0.3
	35	600	1000	1	93.0	-	-	3.6
	36	1200	1000	1	92.3	-	-	-0.5
	37	1100	1000	1	94.7	-	-	1.1
Comp. Ex,1	38	1200	1000	1	97.5	14.7	3.79	4.3
	39	1200	1000	1	98.0	42.3	5.53	11.7
	40	1200	1000	1	96.8	31.7	4.60	10.5
	41	1200	1000	1	95.9	7.8	2.34	-2.7
	42	1000	1000	1	98.7	25.7	2.90	16.0
	43	1000	1000	1	98.1	22.3	2.83	13.6
	44	1000	1000	1	90.0	3.0	0.98	-2.8
	45	1000	1000	1	93.8	6.4	1.63	2.1

*1 Numerals in the parenthese particle diameters

*2 at room temp. to 200°C

Table 5

*1 at room temp. to 200°C

Ex.	No.	Composition (wt. %)					
		Metal or alloy		Mineral powder		Carbon, carbide, etc.	
Ex. 5	46	Fe	49.5	β-eucryptite	49.5	Carbon black	1
	47	Fe	47.5	"	47.5	SiC	5
	48	Fe	47.5	"	47.5	TiN	5
	49	Fe	77.5	"	17.5	Al_2O_3	5
	50	Fe	47.5	β-spodumene	47.5	TiC	5
	51	18Cr-8Ni-Fe	48.5	β-eucryptite	48.5	AlN	3
	52	4Ti-Fe	48	"	48	TiC	6
	53	2Ni-0.5Mo-0.2Mn-Fe	48.5	"	48.5	Mo_2C	3
	54	2Si-Fe	47	"	47	Si_3N_4 SiC	3 3
	55	5Cu-Fe	50	"	49	B_4C	0.5
	56	Cu	48	"	47	VC	5
	57	20Zn-Cu	40	"	55	WC	5
	58	3.5Be-Cu	45	"	50	BN	5
	59	Ti	50	"	45	TiC	5
	60	Co	50	"	45	Tic Tac	3 2
	61	Ni	50	"	45	TiN	5
	62	Cr	70	"	25	TiN	5
	63	Al	40	"	57	AlN	3

Table 5 (Cont.)

Ex.	No.	Treatment conditions			Properties		
		Temp. (°C)	Pressure (kg/cm²)	Time (hr)	Flexural strength (kg/mm²)	Modulus of elasticity (x10⁴·kg/mm²)	Coefficient of thermal expansion (x10⁻⁶/°C) *1
Ex. 5	46	900	1500	2	27.3	1.7	-0.5
	47	900	"	"	24.8	1.8	-0.1
	48	900	"	"	25.1	1.8	0.2
	49	1150	Atm.pres.	"	18.4	1.4	4.3
	50	900	1500	"	25.7	1.7	4.1
	51	1100	"	"	30.1	1.9	2.0
	52	1000	"	"	29.7	1.7	0.3
	53	1000	"	"	20.3	1.6	0.7
	54	900	"	"	24.5	1.7	0.4
	55	1050	"	"	28.0	1.6	0.5
	56	800	"	"	18.4	1.0	-0.1
	57	800	"	"	15.2	0.8	0.5
	58	750	"	"	18.7	1.1	1.0
	59	1250	"	"	-	1.1	0.3
	60	1100	"	"	-	1.7	0.7
	61	1100	"	"	-	1.7	0.0
	62	1300	"	"	-	1.9	0.5
	63	600	"	"	-	0.6	3.8

*1: at room temp. to 200°C

Table 6

Ex.	No.	Composition (wt. %)					
		Metal or alloy		Mineral powder		Carbon, carbide, etc.	
Comp. Ex.2	64	18Cr-8Ni-Fe	95	β-eucryptite	5	AlN	3
Ref. Ex. 1	65	Fe	50	"	50	-	-
	66	18Cr-8Ni-Fe	45	"	44	AlN	11
	67	Cu	30	"	65	VC	5
	68	20Zn-Cu	40	"	60	-	-

*1: at room temp. to 200°C

Table 6 (Cont.)

Ex.	No.	Treatment conditions			Properties		
		Temp. (°C)	Pressure (kg/cm²)	Time (hr)	Flexural strength (kg/mm²)	Modulus of elasticity (x10⁴ kg/mm²)	Coefficient thermal expansion (x10⁻⁶/°C) *1
Comp. Ex.2	64	1100	1500	2	18.5	2.6	9.9
Ref. Ex. 1	65	900	"	"	12.4	1.2	-0.5
	66	1100	"	"	10.1	1.5	1.8
	67	800	"	"	5.2	0.7	-2.2
	68	800	"	"	12.7	0.6	0.6

*1: at room temp. to 200°C

Table 7

*1 at room temp. to 200°C

Ex.	No.	Matrix composition (wt. %)				Composite material Composition (wt. %)		
		Metal and alloy		Mineral powder		matrix	Fibers and whiskers	
Ex. 6	69	Fe	50	β-eucryptite	50	70	Sic whiskers	30
	70	"	40	"	60	80	Si_3N_4 whiskers	20
	71	"	40	"	60	80	Steel fibers	20
	72	"	60	"	40	70	Carbon fibers	30
	73	"	40	β-spodumene	60	70	"	30
	74	18Cr-8Ni-Fe	40	β-eucryptite	60	90	Stainless steel fibers	10
	75	"	40	"	60	70	Carbon fibers glass fibers	20 10
	76	"	40	β-spodumene Petalite	30 30	80	Carbon fibers	20
	77	Fe Ti	46 4	β-eucryptite	50	80	SiC fibers	20
	78	2Ni-0.5Mo-0.2Mn-Fe	50	"	50	90	Stainless steel fibers	10
	79	Fe Si	48 2	"	50	90	Silica fibers	10
	80	Fe Cu	45 5	"	50	80	Alumina fibers	20
	81	Cu	50	"	50	80	Carbon fibers	20
	82	20Zn-Cu	50	"	50	90	"	10
	83	3.5Be-Cu	50	"	50	90	"	10

Table 7 (Cont.)

Ex.	No.	Treatment conditions			Properties		
		Temp. (°C)	Pressure (kg/cm^2)	Time (hr)	Tensile strength (kg/mm^2)	Modulus of elasticity (x10^{4}kg/mm^2)	Coefficient of thermal expansion (x10^{-6}/°C) *1
Ex. 6	69	900	1500	2	35.4	2.7	1.5
	70	900	1500	2	30.6	2.5	-0.3
	71	900	1500	2	22.1	1.7	0.4
	72	900	1500	2	32.4	2.6	1.8
	73	900	1500	2	30.2	2.5	3.7
	74	1100	1500	2	27.4	1.8	0.8
	75	1100	1500	2	32.4	2.6	1.2
	76	1100	1500	2	30.6	2.6	3.3
	77	1000	1500	2	36.7	2.7	1.2
	78	1000	1500	2	25.6	1.6	0.8
	79	1000	1500	2	20.3	1.5	0.4
	80	1050	1500	2	24.3	1.8	2.3
	81	800	1500	2	22.7	1.8	0.1
	82	800	1500	2	21.4	1.5	0.7
	83	750	1500	2	23.1	1.6	1.2

*1 at room temp. to 200°C

Table 8

Ex.	No.	Matrix composition(wt.%)				Composite material Composition(vol.%)		
		Metal and alloy		Mineral powder		Matrix	Fibers and whiskers	
Ex.7	84	Fe	50	β-eucryptite	50	70	Carbon fibers	30
	85	"	50	"	50	70	Steel fibers	30
	86	18Cr-8Ni-Fe	40	"	60	70	Stainless steel fibers	30
	87	2Ni-0.5Mo-0.2Mn-Fe	40	"	60	80	"	20
	88	Cu	50	"	50	70	Carbon fibers	30
Comp. Ex. 3	89	18Cr-8Ni-Fe	95	"	5	90	Stainless steel fibers	10
Ref. Ex.2	90	Fe	50	"	50	100	-	-
	91	18Cr-8Ni-Fe	40	"	60	50	Stainless steel fibers	50
	92	Cu	30	"	70	80	Carbon fibers	20
	93	20Zn-Cu	50	"	50	100	-	-

*1: at room temp. to 200°C

Table 8 (Cont.)

Ex.	No.	Treatment conditions			Properties		
		Temp (°C)	Pressure (kg/cm^2)	Time (hr)	Tensile strength (kg/mm^2)	Modulus of elasticity (x10^{4}kg/mm^2)	Coefficient of thermal expansion (x10^{-6}/°C) *1
Ex.7	84	900	1500	2	62.3	2.8	1.9
	85	900	1500	2	48.5	1.8	2.4
	86	1100	1500	2	50.5	2.0	1.0
	87	900	1500	2	49.7	1.7	0.4
	88	800	1500	2	30.4	1.8	0.1
Comp. Ex. 3	89	1100	1500	2	18.4	2.5	9.7
Ref. Ex.2	90	900	1500	2	6.7	1.2	-0.5
	91	1100	1500	2	28.7	2.1	5.4
	92	800	1500	2	10.2	1.2	-2.2
	93	800	1500	2	6.1	0.6	0.6

*1: at room temp. to 200°C

What is Claimed is:

(1) A composite material having a low thermal expansivity which comprises a matrix composition containing 40 to 90 wt. % of one or more members selected from the group consisting of metals of Fe, Cu, Ni, Co, Mo, Ti, Cr, Al, Mn, Si, Zn, Be and W and alloys of two or more of these metals and 10 to 60 wt. % of a powdery $Li_2O-Al_2O_3-SiO_2$ mineral.

(2) A composite material having a low thermal expansivity according to Claim 1 wherein the matrix composition contains further up to 10 wt. % of one or more powdery substances selected from the group consisting of carbons, carbides, nitrides, oxides and borides.

(3) A composite material having a low thermal expansivity according to Claim 1 which comprises 70 to 99 vol. % of the matrix composition and 1 to 30 vol. % of one or more reinforcing fibers selected from the group consisting of glass fibers, ceramic fibers, metal fibers, metal-ceramic composite fibers and whiskers.

(4) A composite material having a low thermal expansivity according to Claim 3 wherein the aspect ratio of the reinforcing fibers is 20 to 100.

(5) A composite material having a low thermal ex-

pansivity according to Claim (4) wherein the reinforcing fibers have an average diameter of up to 100 μm.

(6) A composite material having a low thermal expansivity according to Claim (1), which is produced by heating, if desired under pressure, a homogeneous dispersion of one or more powdery substances selected from the group consisting of the above-mentioned metals and alloys thereof and said powdery $Li_2O-Al_2O_3-SiO_2$ mineral under vacuum or in a non-oxidizing atmosphere to sinter the same.

(7) A composite material having a low thermal expansivity according to Claim (2), which is produced by heating, if desired under pressure, a homogenous dispersion of one or more powdery substances selected from the group consisting of the above-mentioned metals and alloys thereof, one or more powdery substances selected from the group consisting of the above-mentioned carbons, carbides, nitrides, oxides and borides and said powdery $Li_2O-Al_2O_3-SiO_2$ mineral under vacuum or in a non-oxidizing atmosphere to sinter the same.

(8) A composite material having a low thermal expansivity according to Claim (3), which is produced by heating, if desired under pressure, a homogeneous

dispersion of one or more powdery substances selected from the group consisting of the above-mentioned metals and alloys thereof, one or more powdery substances selected from the group consisting of the above-mentioned carbons, carbides, nitrides, oxides and borides, the above-mentioned reinforcing fibers and said powdery Li_2O-Al_2O_3-SiO_2 mineral under vacuum or a non-oxidizing atmosphere to sinter the same.

(9) A composite material having a low thermal expansivity according to Claim 8 wherein the aspect ratio of the reinforcing fibers is 20 to 100.

(10) A composite material having a low thermal expansivity according to Claim 9 wherein the average diameter of the reinforcing fibers is up to 100 μm.

(11) A composite material having a low thermal expansivity according to Claim 6 wherein the average particle diameter of said powdery Li_2O-Al_2O_3-SiO_2 mineral is 2 to 10 times as large as that of one or more powdery substances selected from the group consisting of the metals and alloys thereof.

(12) A composite material having a low thermal expansivity according to Claim 7 wherein the average particle diameter of said powdery Li_2O-Al_2O_3-SiO_2 mineral is 2 to 10 times as large as that of one

or more powdery substances selected from the group consisting of the metals and alloys thereof.

(13) A composite material having a low thermal expansivity according to Claim 8 wherein the average particle diameter of said powdery Li_2O-Al_2O_3-SiO_2 mineral is 2 to 10 times as large as that of one or more powdery substances selected from the group consisting of the metals and alloys thereof.

(14) A composite material having a low thermal expansivity according to Claim 9 wherein the average particle diameter of said powdery Li_2O-Al_2O_3-SiO_2 mineral is 2 to 10 times as large as that of one or more powdery substances selected from the group consisting of the metals and alloys thereof.

(15) A composite material having a low thermal expansivity according to Claim 10 wherein the average particle diameter of said powdery Li_2O-Al_2O_3-Sio_2 is 2 to 10 times as large as that of one or more powdery substances selected from the group consisting of the metals and alloys thereof.

(16) A composite material having a low thermal expansivity according to Claim 11 wherein the average particle diameter of one or more powdery substances selected from the group consisting of said carbon,.

carbides, nitrides, oxides and borides is equal to or smaller than thta of one or more powdery substances selected from the group consisting of said metals and alloys thereof.

(17) A composite material having a low thermal expansivity according to Claim 12 wherein the average particle diameter of one or more powdery substances selected from the group consisting of said carbons, carbides, nitrides, oxides and borides is equal to or smaller than that of one or more powdery substances selected from the group consisting of said metals and alloys thereof.

(18) A composite material having a low thermal expansivity according to Claim 13 wherein the average particle diameter of one or more powdery substances selected from the group consisting of said carbons, carbides, nitrides, oxides and borides is equal to or smaller than that of one or more powdery substances selected from the group consisting of said metals and alloys thereof.

(19) A composite material having a low thermal expansivity according to Claim 14 wherein the average particle diameter of one or more powdery substances selected from the group consisting of said carbons, carbides, nitrides, oxides and borides is equal to

or smaller than that of one or more powdery substances selected from the group consisting of said metals and alloys thereof.

(20) A composite material having a low thermal expansivity according to Claim 15 wherein the average particle diameter of one or more powdery substances selected from the group consisting of said carbons, carbides, nitrides, oxides and borides is equal to or smaller than that of one or more powdery substances selected from the group consisting of said metals and alloys thereof.