US 20090123329A1

(19) United States

(12) Patent Application Publication

(10) Pub. No.: US 2009/0123329 A1

(43) Pub. Date: May 14, 2009

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(54) **METAL MATRIX MATERIAL BASED ON SHAPE-MEMORY ALLOY POWDERS, PRODUCTION METHOD THEREOF AND USE OF SAME**

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(21) Appl. No.: **11/991,262**

(22) PCT Filed: **Aug. 30, 2006**

(86) PCT No.: **PCT/ES2006/000493**

§ 371 (c)(1), (2), (4) Date: **Nov. 4, 2008**

(30) **Foreign Application Priority Data**

Aug. 31, 2005 (ES) P200502129

Publication Classification

(51) **Int. Cl.**

C22C 9/04	(2006.01)
C22C 9/00	(2006.01)
C22C 30/02	(2006.01)
C22C 9/01	(2006.01)
C22C 9/06	(2006.01)
B22F 1/00	(2006.01)

(52) **U.S. Cl.** **420/478**; 420/469; 420/587; 419/62; 419/30; 420/486; 420/489

(57) **ABSTRACT**

The invention relates to a metal matrix material based on shape-memory alloy powders, to the production method thereof and to the use of same. More specifically, the invention relates to a metal matrix material which is characterised in that it is based on particles of shape-memory alloy powder, having a base of copper at a concentration of between 45 vol.-% and 70 vol.-% in relation to the total volume of the material, said powder particles being supported by a metal matrix. The invention also relates to a method of producing the aforementioned material and to the use of same for absorbing vibrations, particularly acoustic and mechanical vibrations.

METAL MATRIX MATERIAL BASED ON SHAPE-MEMORY ALLOY POWDERS, PRODUCTION METHOD THEREOF AND USE OF SAME

FIELD OF THE INVENTION

[0001] The invention relates to the area of Material Science and Technology as far as the design and production of the materials are concerned, and to the area of Physical Technology with regard to the properties of high damping.

The sectors of industrial activity in which the invention can apply are: domestic appliances and domotics, machine-tools and machinery in general, electronic packaging, transport including aeronautics, aerospace, construction.

STATE OF THE ART

[0002] The materials that have traditionally displayed the highest coefficient of damping have been polymers, owing to their visco-elastic behaviour. Nevertheless, in general, polymers have a low elastic modulus, which is a disadvantage for the design of materials with high damping for structural applications. In fact, the merit index for the design of structural damping is: the product of the elastic modulus (or rigidity modulus) E and the coefficient of damping tan(ϕ), so the aim is to optimise the relation tan(ϕ) E. For this reason, various types of high damping metal materials have been developed, also known as HIDAMETS (High Damping Metals), since metals have an elastic modulus very much higher than polymers.

[0003] Among metal materials, some of the ones with the greatest coefficient of damping are Shape Memory Alloys (SMA) [1]. These alloys undergo a thermoelastic martensitic transformation (reversible) between their high temperature phase, known as beta, and their low temperature phase, known as martensite, which can be induced by cooling or by the application of a mechanical stress. The interphases of martensite are mobile both during the transformation and in the martensite phase, and under the effect of a vibration or external mechanical stress they are liable to undergo movement, absorbing mechanical energy and giving rise to the powerful damping displayed by SMAs [2]. Copper-based SMAs are known to display a coefficient of damping higher than those of Ti—Ni which are the SMAs that are commercially used in practically all applications.

[0004] Nevertheless, given that massive SMAs still did not offer a sufficiently high coefficient of damping, a large number of Polymer Matrix Composite Materials have been developed containing rods, sheets, threads, etc., of SMA for various applications. In this field there are innumerable scientific publications and numerous patents.

[0005] In parallel, during the last decade the production technology for SMA powders has been developed by means of powder metallurgy, especially in copper-based alloys [3, 4]. In this field too, there are numerous scientific publications and patents, especially in Ti—Ni.

[0006] The most recent advance in the field of materials with powerful damping has been the development of Metal Matrix Composite Materials, where various concepts or types of material have been considered, which are described below:

a). —Composite materials formed directly by various sheets or pieces of SMA, whether this be of Ti—Ni or of copper base. In this case, as well as a great many publications, U.S. Pat. No. 4,808,246 can be highlighted.

b). —Composite materials with a soft metal matrix, responsible for the damping, and rigid particles (W, SiC) in a variable percentage, the sole aim of which is to increase the E modulus of the material [6].

c). —Composite materials with a soft metal matrix, responsible for the damping, and ceramic particles (VO_2) in a small proportion (1%) which contribute a narrow damping peak (of width 0.2° C.) owing to an anomaly in the rigidity of the particles when they undergo a phase transformation [7].

d). —Composite materials formed from particles of SMA with a rigid metal matrix (usually of aluminium or copper), with the aim of improving the structural or other properties of the matrix. In these, a small proportion of SMA particles are used since their aim is to improve the properties of the matrix. In this field, as well as scientific publications, there are also various patents [8-11].

e). —Porous materials (between 5% and 40% pores) formed from particles of SMA for damping. In this case, U.S. Pat. No. 5,687,958 can be highlighted.

[0007] The technical problem that is raised and which has led to the present invention is to achieve a material with a high coefficient of damping tan(ϕ), whose maximum can be adjusted to a particular temperature range, depending on the application it is intended for. Moreover, in the majority of applications, the elastic modulus E is required to be as high as possible in order to optimise the relation tan(ϕ)·E.

[0008] In view of the analysis presented on the state of the art, we consider that the materials forming the object of the present invention constitute an authentic novelty due to the combination of various aspects that are stated below:

*). —In the inventive materials, the SMA powder particles constitute the majority element with a percentage between 45% and 70%, being responsible for the powerful damping of the composite material.

*). —The powder particles are of copper base SMA and display the proper martensite transformation in an adjustable temperature range.

*). —The temperature range of the damping maximum of the composite material is very wide (>50° C.) and can be adjusted by controlling the composition of the SMA powder particles.

*). —The matrix has to be a low melting point metal matrix, and be ductile at the martensite transformation temperature of the SMA particles.

*). —The matrix contributes to the damping background and generates an amplifying effect of the damping of the particles, never described so far.

*). —The composite materials thus obtained can display a tan(ϕ)·E relation that can be optimised in a wide temperature range, better than any other material presently specified.

REFERENCES

[0009] [1] Shape Memory Materials. Edit. K. Otsuka, C. M. Wayman. Cambridge University Press, Cambridge (1998).

[0010] [2] Damping behaviour during martensitic transformation in Shape memory Alloys. J. San Juan, M. L. Nó. Journal of Alloys and Compounds 355 (2003) pp 65-71.

[0011] [3] Martensitic transformation in Cu—Al—Ni Shape Memory Alloys processed by Powder Metallurgy. J. San Juan, R. B. Pérez-Saez, V. Recarte, M. L. Nó, G. Caruana, M. Lieblich, O. Ruano. Journal de Physique IV (1995) pp C8-919.

[0012] [4] Advanced Shape Memory Alloys processed by Powder Metallurgy. R. B. Pérez-Saez, V. Recarte, M. L. Nó, O. Ruano, J. San Juan. Advanced Engineering Materials 2 (2000) pp 49-53.

[0013] [5] Composite material in rod, tube, strip, sheet or plate shape with reversible thermomechanical properties and process for its production. J. Albrech, T. Duerig. BBC Brow Boveri & Cie, U.S. Pat. No. 4,808,246 (1989).

[0014] [6] Damping and stiffness of particulate SiC—InSn composite. M. N. Ludwigson, R. S. Lakes, C. C. Swan. Journal of Composite Materials 36 (2002) pp 2245-54.

[0015] [7] Extreme damping composite materials with negative-stiffness inclusions. R. S. Lakes, T. Lee, A. Bersie, Y. C. Wang. Nature 410 (2001) pp 565-567.

[0016] [8] Metallic composite material having improved strength and vibration-damping property. Y. Furuya, T. Masumoto. Pat. JP6264161 (1994).

[0017] [9] Metal matrix composite material enhanced in strength, damping capacity, radiation resistance and corrosion resistance. Y. Furuya, Y. Nishi., T. Masumoto. Pat. JP7048637 (1995).

[0018] [10] Metal matrix composite reinforced with shape memory alloy. D. Barrett. US ARMY, U.S. Pat. No. 5,508, 116 (1996).

[0019] [11] Composite material and its production. J. Ninomiya, T. Suzuki, A. Hideno. FURUKAWA ELECTRIC CO Ltd. Pat. JP10017959 (1998).

[0020] [12] Metallic damping body. R. Renz, J. Kraemer. DAIMLER BENZ AG, U.S. Pat. No. 5,687,958 (1997).

DESCRIPTION OF THE INVENTION

[0021] The present invention relates to a metal matrix composite material characterised in that it is based on particles of shape-memory alloy powder, having a copper base with a concentration of between 45% and 70% by volume in relation to the total volume of the material, said powder particles being supported by a metal matrix.

[0022] According to a particular embodiment of the invention, the copper base is present in the material at a concentration of between 50% and 60% by volume in relation to the total volume of the composite material.

[0023] The inventive material displays a thermoelastic martensitic transformation at between −150° C. and +250° C.

[0024] According to a particular embodiment of the material, the copper base is selected from among Cu—Al—Ni, Cu—Zn—Al and Cu—Al—Mn.

[0025] Said metal matrix of metals or alloys surrounds the powder particles and acts as a binder for the composite material.

[0026] The metal matrix can, according to embodiments of the invention, comprise:

[0027] metals of melting point below 330° C. or

[0028] alloys of said metals with a solidifying point below 330° C.

[0029] Said metal, or metals (or their alloys), of low melting point, must be ductile at the temperature of the adjusted maximum damping. Among the low melting points metals that can constitute the metal matrix can be selected, among others, In, Sn, Pb, Cd, TI and their alloys.

[0030] According to additional embodiments of the inventive material, the metal matrix can be selected from among:

[0031] one or more metals of melting point above 330° C., or

[0032] alloys of said metals.

[0033] In this case, preferred metals are Zn or Mg.

[0034] In addition, according to particular embodiments of the material, the alloy powder particles will be able to have the same single concentration of copper base, or the composite material will be able to include particles of different concentrations of base copper. By means of heat treatments or other methods in the field of powder metallurgy, such as mechanical alloying for example, particles will be able to be included with a concentration gradient of copper base with the aim of the martensite transformation displaying a wider temperature range and thereby obtain a damping maximum that is widened in temperature.

[0035] In the event that the powder particles do not all have the same concentration of copper base, the percentage of particles with a different concentration of copper base can be equal to or less than 15% in relation to the entire composite material.

[0036] Other kinds of particles of different composition will also be able to be included in the composite material, being able to be rigid, metallic or ceramic, and having the sole purpose of increasing the modulus of the composite material.

[0037] Said powder particles of different composition can be present in the material in a percentage equal to or less than 15% of the composite material. Moreover, these particles can be chosen from among Rhenium, Tungsten, Molybdenum, Silicon Carbide and Boron Carbide.

[0038] The present invention furthermore relates to a method for obtaining a metal matrix composite material as defined above, which comprises:

[0039] preparing the shape-memory alloy powder particles, and

[0040] infiltrating the metal matrix.

[0041] The shape-memory alloy powder particles can be obtained by means of spraying with gas or by any other method permitting powder particles to be obtained which display the thermoelastic martensite transformation proper to shape-memory alloys.

[0042] Said method can furthermore comprise a stage of adjusting the temperature range of the damping maximum of the composite material via the direct or inverse martensite transformation temperatures of the powder particles, varying the composition of the constituent elements of the shape-memory alloy.

[0043] According to particular embodiments, said method can comprise the inclusion in the composite material of particles of different concentrations of copper base, which can be included in the composite material by means of heat treatment.

[0044] According to particular embodiments, said method can comprise the inclusion in the composite material of particles with a concentration gradient in the composite material by means of mechanical alloying.

[0045] According to particular embodiments of the method, when the metal matrix comprises metals with a melting point below 330° C., or alloys of said metals with a solidifying temperature of below 330° C., said method comprises:

[0046] preparing copper base powder particles,

[0047] introducing said particles into a mould,

[0048] degasifying in vacuo, preferably at a temperature of between 120° C. and 300° C., and

[0049] injecting the molten metal of the matrix by means of infiltration in vacuo.

[0050] The infiltration is carried out under pressure which can be achieved by means of centrifugation or by means of applying gas pressure to the melt.

[0051] According to particular embodiments of the method, when the metal matrix comprises one or more metals with a melting point above 330° C., or alloys of those metals, the properties of the martensite transformation of the shape-memory alloy powder particles will have to be preserved, due to which said method can be a powder metallurgy method, which comprises:

[0052] mixing the shape-memory alloy powder particles with powders of the metal or alloy of the matrix,

[0053] degasifying in vacuo,

[0054] and compacting.

[0055] In this case, the compaction can be carried out using sinterisation with uniaxial stressing at a temperature below 300° C. or the compaction can also be done by means of previous encapsulating in vacuo and subsequent isostatic compacting at high pressure at a temperature below 300° C.

[0056] This method can also possibly be used in the case of metal matrices with lower melting point, such as those mentioned above in the embodiment described in the method.

[0057] In the event that the matrix comprises metals with a melting point higher than 330° C. the method can alternatively be an infiltration method at high temperature, which can comprise:

[0058] preparing copper base powder particles,

[0059] introducing said particles into a mould,

[0060] degasifying in vacuo,

[0061] heating to above the temperature of the eutectoid of the corresponding SMA, such that the particles are in the high temperature phase, known as beta, proper to these alloys,

[0062] infiltrating the metal matrix at high temperature, and

[0063] tempering the composite material in a rapid cooling medium. Said rapid cooling medium can be water.

[0064] The choice of the metal matrix will serve to optimise the binder properties of the composite material, as will the relation $\tan(\phi)\cdot E$, and will be chosen according to the type of SMA used and the range of temperatures at which the composite material is going to find itself under service conditions in the various applications.

[0065] From the technical point of view, the shape-memory alloy powder particles contribute a high coefficient of damping for the composite material, owing to the movement of the martensite interphases, especially in the proximity of the martensite transformation temperature (direct or inverse). The matrix permits absorption of the deformation which the particles undergo when the martensite interphases move, whether this be in the martensite phase or when undergoing the transformation induced by temperature or stress. In this way, the matrix absorbs the deformation of the particles preventing the composite material from degrading. As well as serving as support for the particles in the composite material, the matrix also contributes to the continual damping background and generates an amplifying effect for the damping of the particles.

[0066] These materials incorporate a novel concept which solves the problem of obtaining a high coefficient of damping, adjustable in a specific temperature range. The temperature range of the damping maximum can be adjusted between −150° C. and +250° C., via the martensite transformation temperatures (direct or inverse) of the powder particles, which are in turn controlled by means of the composition of the elements constituting the alloy with shape-memory.

[0067] The advantages of the material lie in the fact that there does not currently exist any material permitting continual adjustment of the damping maximum peak in the desired range of temperatures. These materials display a coefficient of damping higher than other metallic materials and they optimise the relation $\tan(\phi)\times E$, which is used in the design of materials for damping, better than other alternative materials.

[0068] The optional addition of rigid, metallic or ceramic particles, along with particles of SMA, will have the aim of increasing the elastic modulus of the composite material.

[0069] The present invention also refers to the use of the composite material defined earlier for the absorption of vibrations. Said vibrations can be acoustic or mechanical.

[0070] The potential industrial applications of the present invention can be very numerous, and in general are all those in which a high damping of vibrations is required. Given below are some examples of applications which the materials of the present invention will be able to have:

[0071] In the domestic appliances sector, for absorption of vibrations and reduction of the ambient noise produced by them (washing machines, spin dryers, dishwashers, etc.)

[0072] In the Machine-Tools sector, for damping the vibrations of the machine and thereby be able to improve the precision of the machining and increase the machining speed. Moreover, it will also contribute to reducing ambient noise (acoustic pollution) in the workplace.

[0073] In the opto-electronic material industry, as a material for "electronic packing" with the aim of absorbing vibrations and protecting circuits and devices.

[0074] In the transport sector, for absorbing vibrations and increasing the comfort of the user, contributing to a "noise-clean" environment. Moreover, in the case of the Aeronautical sector, it can contribute to improving the fatigue life of certain structural elements, by reducing the amplitude of the vibrations that they are subjected to.

[0075] In the construction industry, for the manufacture of "anti-seismic" devices, based on high absorption of mechanical energy.

[0076] The solution contributed by the present invention to the problem raised is therefore a novel concept of composite material based on shape-memory alloy (SMA) powder particles with copper base, as the main damping elements with a percentage ≧40% embedded in a ductile metal matrix, of low melting point.

[0077] The concept in itself in innovative, since in traditional composite materials it is the matrix which acts as the damping element and the particles or fibres are added in order to increase the modulus.

[0078] The use of copper base SMA powders is in response to the fact that said alloys display a coefficient of damping higher than Titanium-Nickel base SMAs. Furthermore, via the control of the composition of these powder particles, the temperature of the damping maximum can be adjusted. The low melting point metal matrix, as well as providing support for the particles, also generates an amplifying effect on the damping, never before described.

EXAMPLES OF INVENTIVE EMBODIMENT

[0079] An example of embodiment of the composite materials that have been described is the following:

Alloy powders of Cu—Al—Ni have been used with a concentration by weight: 13.1% Al, 3.1% Ni, 83.8% Cu.

The powders were produced by means of spraying by gas. And powders have been used that were passed through a sieve of sizes between 25 and 50 microns.

The martensite transformation temperatures of the sprayed powders, measured by means of differential sweeping calorimetry (DSC), are: Ms=65° C., Mf=27° C., As =51° C., Af=95° C.

[0080] As matrix metal, in this case Indium of purity 99.99% was used.

[0081] The powders introduced into a teflon mould were degasified at 130° C. for 6 hours in a vacuum of 0.01 mbar.

[0082] The infiltration was performed at 190° C., by means of applying a helium gas pressure of 3 bars on the melt.

[0083] The composite material contained 60% by volume of Cu—Al—Ni particles and 40% indium.

[0084] The damping coefficient tan(ϕ) has been measured in torsion with a mechanical electroscopy equipment which permits one to work at different frequencies and according to temperature, since, as is well known, the coefficient of damping of a material depends on these two parameters.

[0085] The composite material displays two damping maxima at 65° C. and 100° C. corresponding to the direct and inverse martensite transformation respectively. Stated below are the values of the coefficient of damping for different frequencies:

[0086] at the frequency of 3 Hz, tan(ϕ)>0.01, between −100° C. and +125° C., with a maximum of tan(ϕ)≧0.05,

[0087] at the frequency of 1 Hz, tan(ϕ)>0.01, between −100° C. and +125° C., with a maximum of tan(ϕ)≧ 0.1,

[0088] at the frequency of 0.1 Hz, tan(ϕ)>0.035, between −100° C. and +125° C., with a maximum of tan(ϕ)≧0.3,

[0089] at the frequency of 0.03 Hz, tan(ϕ)>0.05, between −100° C. and +125° C., with a maximum of tan(ϕ)≧0.4,

[0090] at the frequency of 0.01 Hz, tan(ϕ)>0.09, between −100° C. and +125° C., with a maximum of tan(ϕ)≧0.6.

1. A metal matrix composite material which is based on particles of shape-memory alloy powder, having a copper base with a concentration of between 45% and 70% by volume in relation to the total volume of the material, said powder particles being supported by a metal matrix.

2. A metal matrix composite material according to claim **1**, which comprises a copper base with a concentration of between 50% and 60% by volume in relation to the total volume of the composite material.

3. A metal matrix composite material according to claim **1** which displays a thermoelastic martensitic transformation at between −150° C. and +250° C.

4. A metal matrix composite material according to claim **1** wherein the copper base is selected from among Cu—Al—Ni, Cu—Zn—Al and Cu—Al—Mn.

5. A metal matrix composite material according to claim **1**, wherein the metal matrix comprises:

metals of melting point below 330° C. or

alloys of said metals with a solidifying point below 330° C.

6. A metal matrix composite material according to claim **5**, wherein the metal comprises metals selected from In, Sn, Pb, Cd, Tl and their alloys.

7. A metal matrix composite material according to claim **1** wherein the metal matrix is selected from among:

one or more metals of melting point above 330° C.,

or

alloys of said metals.

8. A metal matrix composite material according to claim **7**, wherein said metals are Zn or Mg.

9. A metal matrix composite material according to claim **1**, wherein the shape-memory alloy powder particles all possess the same concentration of copper base.

10. A metal matrix composite material according to claim **1**, which comprises a percentage of particles of different concentrations of base copper.

11. A metal matrix composite material according to claim **1**, which comprises a percentage of particles of different composition.

12. A metal matrix composite material according to claim **11**, wherein said percentage of powder particles of a different nature is less than or equal to 15% in relation to the total volume of composite material.

13. A metal matrix composite material according to claim **11** wherein the powder particles of different composition are selected from rigid, metallic or ceramic particles.

14. A metal matrix composite material according to claim **13**, wherein said powder particles of different composition are selected from rhenium, tungsten, molybdenum, silicon carbide and boron carbide.

15. A metal matrix composite material according to claim **1**, which comprises:

60% of alloy powder particles of Cu—Al—Ni in relation to the weight of material, with a concentration by weight of 13.1% Al, 3.1% Ni, 83.8% Cu,

40% by weight of an indium matrix.

16. A method for obtaining a composite material defined in claim **1** which comprises:

preparing the shape-memory alloy powder particles, and

infiltrating the metal matrix.

17. A method for obtaining a composite material according to claim **16**, which comprises adjusting the temperature range of the damping maximum of the composite material via the direct or inverse martensite transformation temperatures of the powder particles, varying the composition of the constituent elements of the shape-memory alloy.

18. A method for obtaining a composite material according to claim **16**, which comprises including in the composite material particles of different concentrations of copper base.

19. A method for obtaining a composite material according to claim **18**, wherein the particles of different concentrations of copper base are included in the composite material by means of heat treatment.

20. A method for obtaining a composite material according to claim **18**, which comprises including particles with a concentration gradient of copper base in the composite material by means of mechanical alloying.

21. A method according to claim **16**, for obtaining a composite material defined in claim **5** which comprises:

preparing copper base powder particles,

introducing said particles into a mould,

degasifying in vacuo, preferably at a temperature of between 120° C. and 300° C., and

injecting the molten metal of the matrix by means of infiltration in vacuo.

22. A method according to claim **21**, wherein the infiltration is carried out under pressure which can be achieved by means of centrifugation or by means of applying gas pressure to the melt.

23. A method according to claim **16**, for obtaining a composite material defined in claim **7** which comprises:

mixing the shape-memory alloy powder particles with powders of the metal or alloy of the matrix,

degasifying in vacuo,

and compacting.

24. A method according to claim **23**, wherein the compaction is carried out by means of sinterisation with uniaxial stressing at a temperature below 300° C.

25. A method according to claim **23**, wherein the compaction is carried out by means of previous encapsulating in vacuo and subsequent isostatic compacting at high pressure at a temperature below 300° C.

26. A method according to claim **23**, which comprises:

preparing copper base powder particles,

introducing said particles into a mould,

degasifying in vacuo,

heating to above the temperature of the eutectoid of the corresponding SMA, such that the particles are in the high temperature phase, known as beta, proper to these alloys,

infiltrating the metal matrix at high temperature, and

tempering the composite material in a rapid cooling medium.

27. Method for absorption of vibrations which comprises use of the composite material defined in claim **1** therefor.

28. Method according to claim **27**, wherein the vibrations are selected from among acoustic and mechanical vibrations.

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