



Full length article

## Low Young's modulus Ti-based porous bulk glassy alloy without cytotoxic elements



M. Nicoara<sup>a</sup>, A. Raduta<sup>a</sup>, R. Parthiban<sup>b</sup>, C. Locovei<sup>a</sup>, J. Eckert<sup>b,1</sup>, M. Stoica<sup>a,b,\*</sup>

<sup>a</sup> Politehnica University Timisoara, P-ta Victoriei 2, 300006 Timisoara, Romania

<sup>b</sup> IFW Dresden, Institute for Complex Materials, Helmholtzstr. 20, 01069 Dresden, Germany

### ARTICLE INFO

#### Article history:

Received 30 November 2015

Received in revised form 12 February 2016

Accepted 11 March 2016

Available online 12 March 2016

#### Keywords:

Bulk glassy alloy

Porous Ti-based alloy

Biocompatibility

Mechanical properties

### ABSTRACT

A new a biocompatible  $\text{Ti}_{42}\text{Zr}_{40}\text{Ta}_3\text{Si}_{15}$  (atomic %) porous bulk glassy alloy was produced by combination of rapid solidification and powder metallurgy techniques. Amorphous alloy ribbons were fabricated by melt spinning, i.e. extremely fast quenching the molten alloy with  $10^6$  K/s from  $T = 1973$  K down to room temperature. The ribbons were then cryo-milled at liquid nitrogen temperature in order to produce powder, which was subsequently hot pressed. The resulting thick pellets have a porosity of about 14 vol%, a high compression strength of 337 MPa and a Young's modulus of about  $E = 52$  GPa, values very close to those characteristic of cortical bone. Moreover, the morphology of the samples is very similar to that of cortical bone. The biocompatibility, which is due to the absence of any toxic element in the chemical composition, together with the suitable mechanical behavior, make these samples promising for orthopedic and dentistry applications.

### Statement of Significance

Ti-based alloys are nowadays the standard solution for biomedical implants. However, both the conventional crystalline and amorphous alloys have higher rigidity as the human bone, leading to the damage of the bone at the interface, and contains harmful elements like vanadium, aluminum, nickel or beryllium. The hierarchical porous structures based on glassy alloys with biocompatible elements is a much better alternative. This work presents for the first time the manufacturing of such porous bodies starting from Ti-based amorphous alloy ribbons, which contains only non-harmful elements. The morphology and the compressive mechanical properties of these new products are analyzed in regard with those characteristic to the cortical bone.

© 2016 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

## 1. Introduction

Titanium alloys have become for many decades a standard solution for biomedical implants used in orthopedics and dentistry, since they combine good mechanical properties with biocompatibility [1–3]. However, some problems connected with the use of titanium alloys still persist. The implants have to meet several requirements that could be antagonistic for some metallic alloys: enhanced mechanical resistance, appropriate load bearing capacity – simultaneously with low rigidity, similar to human bone – and


they must prevent the stress shielding effect as well as the reduction of bone density (osteopenia). Conventionally, implants have a modulus of elasticity considerable higher than cortical bone. For example, commercially pure titanium has a rigidity of approximately 100 GPa, while stainless steel, tantalum and cast Co-Cr alloys have more than 200 GPa [2,4]. The Ti-6Al-4V alloy, which has become over the years the most popular alloy for fabrication of implants because of its high mechanical strength and moderate price, has a Young's modulus around 112 GPa, which is several times higher than the values of 4–30 GPa characteristic for the human bone [4]. Attempts to improve the mechanical properties eventually led to development of new titanium based alloys [4,5]. For example, both  $\beta$ -Ti alloys and Ti-based bulk metallic glasses (BMGs) have received considerable attention in recent decades [6–9]. While alloying with  $\beta$ -stabilizing systems, containing Nb, Zr, Ta, Fe, Cr, Mo, etc. may reduce the modulus to below

\* Corresponding author at: IFW Dresden, Helmholtzstr. 20, 01069 Dresden, Germany.

E-mail address: [m.stoica@ifw-dresden.de](mailto:m.stoica@ifw-dresden.de) (M. Stoica).

<sup>1</sup> Present address: Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, and Department Materials Physics, Mountanuniversität Leoben, Jahnstrasse 12, A-8700 Leoben, Austria.

# Optimizing the parameters for in situ fabrication of hybrid Al-Al<sub>2</sub>O<sub>3</sub> composites

Mircea Nicoara<sup>1</sup>  · Cosmin Locovei<sup>1</sup> · Carmen Opris<sup>1</sup> · Daniel Ursu<sup>2</sup> · Radu Vasii<sup>3</sup> · Mihai Stoica<sup>1,4</sup>

Received: 6 December 2015 / Accepted: 26 May 2016  
© Akadémiai Kiadó, Budapest, Hungary 2016

**Abstract** A new powder metallurgy technique was developed in order to increase the reinforcement proportion of aluminum with two different fractions of Al<sub>2</sub>O<sub>3</sub>. Aluminum powders were mixed with 20 % vol of alumina particles as primarily reinforcement, and additional alumina was produced in situ as a result of reaction between Al and additional 7.5 % vol of Fe<sub>2</sub>O<sub>3</sub> powder. The three grades of powders were milled and hot-pressed into small preforms, and differential scanning analysis (DSC) was performed to determine the kinetics of microstructural transformations produced on heating. DSC curves were mathematically processed to separate the superposing effects of thermal reactions. Transformation points on resulting theoretical curves evidenced two distinct exothermal reaction peaks close to the melting point of aluminum that were correlated with formation of Fe–Al compounds and oxidation of aluminum. Microstructural investigations by means of SEM-EDX and XRD suggested that these exothermal reactions produced complete decomposition of iron (III) oxide and formation of Fe–Al compounds during sintering at 700 °C, and therefore, heating at higher temperatures would not be necessary. These results, along with calculation of activation energies,

based on Kissinger's method, could be used to optimize the fabrication of Al-Al<sub>2</sub>O<sub>3</sub> composites by means of reactive sintering at moderate temperatures.

**Keywords** Aluminum-based composites · Alumina particle reinforcement · Reactive sintering · Kissinger's method · Mathematical modeling

## Introduction

Aluminum-based composites are considered feasible for many engineering applications, because they combine low specific mass with enhanced mechanical properties [1, 2]. It is well known that reinforcing aluminum with ceramic particles such as Al<sub>2</sub>O<sub>3</sub>, SiC, BN could improve stiffness and mechanical strength, as well as fatigue and wear behavior. The coefficient of thermal expansion for the resulting material is also significantly reduced [3–5]. Powder metallurgy tends to impose itself as the main fabrication method for aluminum matrix composites, because of its flexibility and potential for higher microstructural quality of materials, but some technological problems still persist, which impede large-scale applications [6].

The main difficulty consists in providing higher particle reinforcement. Ceramic and metallic powders are difficult to mix uniformly, because metallic particles usually have larger diameters [7]. Therefore, ceramic particles tend to agglomerate, especially for more than 15–20 % vol of reinforcement, and final microstructure is characterized by clusters, or even networks of ceramic particles, which could produce extreme fragility. Rearrangement of ceramic particles is difficult to achieve, requiring additional hot deformations. Some ceramic reinforcements could also

✉ Mircea Nicoara  
mircea.nicoara@upt.ro


<sup>1</sup> Politehnica University Timisoara, Bd. M. Viteazul 1, 300222 Timisoara, Romania

<sup>2</sup> Nat. Inst. for R. D. in Electrochemistry and Condensed Matter, Str. P. Andronescu 1, 300224 Timisoara, Romania

<sup>3</sup> TEHNOMAG CUG, Bd. Muncii 18, 400641 Cluj-Napoca, Romania

<sup>4</sup> Institute for Complex Materials, IFW Dresden, Helmholtzstraße 20, 01069 Dresden, Germany

# About thermostability of biocompatible Ti–Zr–Ta–Si amorphous alloys

Mircea Nicoara<sup>1</sup>  · Aurel Raduta<sup>1</sup> · Cosmin Locovei<sup>1</sup> · Dragos Buzdugan<sup>1</sup> · Mihai Stoica<sup>1,2</sup>

Received: 6 December 2015 / Accepted: 11 May 2016  
© Akadémiai Kiadó, Budapest, Hungary 2016

**Abstract** Ti-based amorphous alloys produced by ultra-rapid melt cooling represent an excellent option as biomaterials because of their mechanical properties and corrosion resistance. However, complete elimination of toxic elements is affecting the glass-forming ability and amorphous structure could be obtained only for thin ribbons or powders that are subsequently processed by powder metallurgy. Amorphous ribbons of special  $Ti_{42}Zr_{40}Ta_3Si_{15}$  alloy, which is completely free of any toxic element, were produced by melt spinning, and the thermostability of resulting material was investigated in order to estimate its ability for further heat processing. Isochronal differential scanning calorimetry (DSC) was used to determine transformation points such as glass transition temperature  $T_g$  or crystallization temperature  $T_x$ . The activation energy for crystallization of amorphous phase was calculated based on Kissinger method, using heating rates ranging between 5 and 20 °C min<sup>-1</sup>. Amorphous structure of resulting ribbon was evidenced by means of X-rays diffraction (XRD) and high-resolution transmission electron microscopy (HR-TEM). It was determined that amorphous  $Ti_{42}Zr_{40}Ta_3Si_{15}$  alloy has a high activation energy for crystallization, similar to other Ti-based amorphous alloys, which provides good thermal stability for subsequent processing, especially by means of powder metallurgy techniques.

**Keywords** Amorphous alloys · Melt spinning · Kissinger's method · Thermostability · Biocompatible materials

✉ Mircea Nicoara  
mircea.nicoara@upt.ro

<sup>1</sup> Politehnica University Timisoara, 300222 Timisoara, Romania

<sup>2</sup> Institute for Complex Materials, 01069 Dresden, Germany

## Introduction

Titanium alloys represent the most used biomaterials in orthopedics and dentistry, because they combine excellent mechanical properties and corrosion resistance. In spite of extensive use, some important inconveniences still persist. Titanium alloys have high mechanical resistance and suitable ductility, which provide very good loading capacity for orthopedic and dental implants, but they have rigidities higher than human bone. This fact is responsible for the stress shielding effect, which consists in progressive reduction in bone density, culminating sometimes with implant failure. For example, Ti-6Al-4V, which is the most popular titanium alloy for fabrication of orthopedic implants, has Young's modulus around 112 GPa, while cortical bone has rigidity values ranging between 4 and 30 GPa [1–4].

Another important problem related to the use of titanium alloys is biological safety of alloying elements, which are responsible for releasing metallic ions. For example, Ni, which is extensively used as amorphization element for newly developed bulk metallic glasses (BMGs) with titanium base, has been proved to be allergenic, and possible cause for other harmful effect to human body, such as genotoxicity, carcinogenicity, and mutagenicity. Some extensively used amorphization elements with proven cytotoxic effect are Cu, Ag, Zn, and Be. Others such as Co, Cr, Fe, Mo, V, Al, and Mn are responsible for adverse tissue reactions. The large number of alloying elements that are harmful to human body is considerably limiting the development of new titanium-based biomaterials. The design of new compositions is based on a list of alloying additions considered non-problematic, which are eligible for future researches. This list includes Nb, Ta, Zr, Si, Mo, Sn, Pd, In, Sr, B, Ca, and Mg [5–12].

Article

# New Cu-Free Ti-Based Composites with Residual Amorphous Matrix

Mircea Nicoara <sup>1</sup>, Cosmin Locovei <sup>1</sup>, Viorel Aurel Șerban <sup>1</sup>, R. Parthiban <sup>2</sup>, Mariana Calin <sup>2</sup> and Mihai Stoica <sup>1,2,\*</sup>

<sup>1</sup> Materials and Manufacturing Engineering Department, Politehnica University Timisoara, P-ta Victoriei 2, Timisoara RO-300006, Romania; mnicoara@gmail.com (M.N.); cosmin.locovei@gmail.com (C.L.); viorel.serban@upt.ro (V.A.Ș.)

<sup>2</sup> Institute for Complex Materials, IFW Dresden, Helmholtzstr. 20, Dresden D-01069, Germany; p.ramasamy@ifw-dresden.de (R.P.); m.calin@ifw-dresden.de (M.C.)

\* Correspondence: m.stoica@ifw-dresden.de; Tel.: +49-351-4659-644

Academic Editor: Jordi Sort

Received: 14 March 2016; Accepted: 26 April 2016; Published: 30 April 2016

**Abstract:** Titanium-based bulk metallic glasses (BMGs) are considered to have potential for biomedical applications because they combine favorable mechanical properties and good biocompatibility. Copper represents the most common alloying element, which provides high amorphization capacity, but reports emphasizing cytotoxic effects of this element have risen concerns about possible effects on human health. A new copper-free alloy with atomic composition  $Ti_{42}Zr_{10}Pd_{14}Ag_{26}Sn_8$ , in which Cu is completely replaced by Ag, was formulated based on Morinaga's d-electron alloy design theory. Following this theory, the actual amount of alloying elements, which defines the values of covalent bond strength  $B_0$  and d-orbital energy  $M_d$ , situates the newly designed alloy inside the BMG domain. By mean of centrifugal casting, cylindrical rods with diameters between 2 and 5 mm were fabricated from this new alloy. Differential scanning calorimetry (DSC) and X-rays diffraction (XRD), as well as microstructural analyses using optical and scanning electron microscopy (OM/SEM) revealed an interesting structure characterized by liquid phase-separated formation of crystalline Ag, as well as metastable intermetallic phases embedded in residual amorphous phases.

**Keywords:** Ti-based composites; phase separation; Cu-free alloy

## 1. Introduction

Titanium alloys still raise the highest research interest among biomaterials for orthopedic and dental applications since they possess the most favorable combination of properties [1,2]. In terms of mechanical properties, titanium alloys have good mechanical strength and ductility [3], as well as acceptable wear resistance [4]. They also have excellent resistance to bio-corrosion [4], they stimulate the proliferation of new cells and tissues [1], and reported incidence of adverse toxic, irritating, inflammatory, or allergic reactions produced by released elements is relatively moderate [1]. Therefore, over the years, some titanium alloys like Ti-6Al-4V and Ti-6Al-7Nb became standard solution for medical implants [1]. In spite of undeniable advantages, classical crystalline alloys based on titanium still present some inadequate properties: certain alloying elements such as vanadium, aluminum, nickel, *etc.* could release harmful metallic ions inside human body, having well established allergenic or cytotoxic effects [5,6]. They also have considerable higher rigidity than cortical bone, which is responsible for stress shielding effects of orthopedic implants and degradation of mineral density in patients' bones (osteopenia) and still present relatively low bioactivity in relation with human tissues [1,3,4,6,7].



# Ti-based bulk glassy composites obtained by replacement of Ni with Ga



A. Raduta<sup>a</sup>, M. Nicoara<sup>a</sup>, C. Locovei<sup>a</sup>, J. Eckert<sup>b, c, 1</sup>, M. Stoica<sup>a, b, \*</sup>

<sup>a</sup> Politehnica University Timisoara, P-ta Victoriei 2, 300006 Timisoara, Romania

<sup>b</sup> IFW Dresden, Institute for Complex Materials, Helmholtzstr. 20, 01069 Dresden, Germany

<sup>c</sup> University of Technology Dresden, Institute of Materials Science, 01062 Dresden, Germany

## ARTICLE INFO

### Article history:

Received 28 August 2015

Received in revised form

12 October 2015

Accepted 17 October 2015

Available online xxx

### Keywords:

Amorphous metals

Alloy design

Biocompatibility

Rapid solidification

Microstructure

Microscopy

## ABSTRACT

This article evaluates the possibility to replace nickel by gallium, which is considered non-toxic for biomedical use, in a Ti-based bulk metallic glass. A new alloy with the atomic composition  $Ti_{41.5}Zr_{2.5}Hf_5Cu_{37.5}Ga_{7.5}Si_1Sn_5$  free of Ni and other toxic elements was designed and manufactured by means of suction casting the molten alloy into copper molds. Cylindrical rods with diameters up to 3 mm and a length of 50 mm were successfully produced. Further investigations by differential scanning calorimetry and X-ray diffraction in Bragg-Brentano configuration, as well as in transmission using synchrotron radiation, evidenced the main crystalline phases in the new alloy, together with a small content of amorphous matrix. Further in-depth analyses using scanning electron microscopy coupled with elemental mapping, high-resolution transmission electron microscopy and high-angle annular dark-field imaging, revealed a fine microcrystalline structure consisting of  $\gamma$ -CuTi and complex GaTi/CuGaTi intermetallics, together with a remnant amorphous matrix. Such kind of composite samples may open the door for new biomedical devices.

© 2015 Published by Elsevier Ltd.

## 1. Introduction

Due to major challenges for specific properties, the development of biocompatible materials for orthopedic and dental applications has attracted considerable interest among researchers. Titanium-based materials have been considered for many decades as most promising solutions for biomedical applications but they suffer from several inadequate properties: some alloying elements have allergenic or cytotoxic effects on the human body, they have considerable higher rigidity than cortical bone and also have a relatively low bioactivity in contact with human tissues [1]. The development of Ti-based glassy alloys based on rapid cooling techniques revealed some considerable improvements in comparison with the already classical Ti–6Al–4V and Ti–6Al–7Nb crystalline compounds [2]. It has been proved that the absence of grain

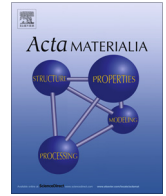
boundaries, as well as segregations and other structural heterogeneities, enhances the corrosion resistance and improves mechanical properties such as tensile strength and wear resistance [3]. At the same time metallic glasses have a lower Young's modulus than their crystalline counterparts, together with a high elastic strain limit of approximately 2%, which is almost double than for similar crystalline metallic alloys [4].

The first Ti-based amorphous alloys produced by rapid cooling were based on the Ti–Zr system with various additions of harmful transition metals [5]. They were reported in 1993 and in 1994 the first Ti–Zr–Ni–Be BMG was patented [6]. Many investigations with respect to alloy design of Ti-based BMGs were done from 1998 onward, and have led to the development of several alloy families such as Ti–Ni–Cu–(Zr, Be) [7], Ti–Ni–Cu–(Sn, Si) [8–10], Ti–Zr–Be–(Cr, Al, Ni, Fe) [11–13] etc. The research has been constantly focused on larger critical dimensions for amorphous samples, enhanced mechanical properties and improved biocompatibility. One of the largest rod diameters that has been achieved so far for Ti-based glasses (i.e. 14 mm) was found for the  $Ti_{40}Zr_{25}Cu_{12}Ni_3Be_{20}$  alloy fabricated in 2005 [7]. More recently (in 2010), a new  $(Ti_{41}Zr_{25}Be_{28}Fe_6)_{91}Cu_9$  alloy with an exceptionally critical size larger than 32 mm was synthesized [14]. In spite of their

\* Corresponding author. IFW Dresden, Institute for Complex Materials, Helmholtzstr. 20, 01069 Dresden, Germany.

E-mail address: [m.stoica@ifw-dresden.de](mailto:m.stoica@ifw-dresden.de) (M. Stoica).

<sup>1</sup> Present address: Erich Schmid Institute of Materials Science, Austrian Academy of Sciences (ÖAW) and Department Materials Physics, Montanuniversität Leoben, Jahnstraße 12, A-8700 Leoben, Austria.



## Structure evolution of soft magnetic $(\text{Fe}_{36}\text{Co}_{36}\text{B}_{19.2}\text{Si}_{4.8}\text{Nb}_4)_{100-x}\text{Cu}_x$ ( $x = 0$ and $0.5$ ) bulk glassy alloys



Mihai Stoica<sup>a,b,\*</sup>, Parthiban Ramasamy<sup>a</sup>, Ivan Kaban<sup>a</sup>, Sergio Scudino<sup>a</sup>, Mircea Nicoara<sup>b</sup>, Gavin B.M. Vaughan<sup>c</sup>, Jonathan Wright<sup>c</sup>, Ravi Kumar<sup>d</sup>, Jürgen Eckert<sup>a,e</sup>

<sup>a</sup>IFW Dresden, Institute for Complex Materials, Helmholtzstr. 20, D-01069 Dresden, Germany

<sup>b</sup>POLITEHNICA University Timisoara, P-ta Victoriei 2, RO-300006 Timisoara, Romania

<sup>c</sup>European Synchrotron Radiation Facility (ESRF), F-38042 Grenoble, France

<sup>d</sup>Department of Metallurgical and Materials Engineering, Indian Institute of Technology Madras, 600036 Chennai, India

<sup>e</sup>TU Dresden, Institute of Materials Science, D-01062 Dresden, Germany

### ARTICLE INFO

#### Article history:

Received 18 February 2015

Revised 21 May 2015

Accepted 27 May 2015

#### Keywords:

Bulk metallic glasses  
Synchrotron radiation  
Thermal analysis  
Phase transformation  
Magnetic properties

### ABSTRACT

Fully amorphous rods with diameters up to 2 mm diameter were obtained upon 0.5 at.% Cu addition to the  $\text{Fe}_{36}\text{Co}_{36}\text{B}_{19.2}\text{Si}_{4.8}\text{Nb}_4$  bulk metallic glass. The Cu-added glass shows a very good thermal stability but, in comparison with the Cu-free base alloy, the entire crystallization behavior is drastically changed. Upon heating, the glassy  $(\text{Fe}_{36}\text{Co}_{36}\text{B}_{19.2}\text{Si}_{4.8}\text{Nb}_4)_{99.5}\text{Cu}_{0.5}$  samples show two glass transitions-like events, separated by an interval of more than 100 K, in between which a bcc-(Fe,Co) solid solution is formed. The soft magnetic properties are preserved upon Cu-addition and the samples show a saturation magnetization of 1.1 T combined with less than 2 A/m coercivity. The relaxation behavior prior to crystallization, as well as the crystallization behavior, were studied by time-resolved X-ray diffraction using synchrotron radiation. It was found that both glassy alloys behave similar at temperatures below the glass transition. Irreversible structural transformations take place when approaching the glass transition and in the supercooled liquid region.

© 2015 Acta Materialia Inc. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

### 1. Introduction

Ferromagnetic metallic glasses and the resulting nanocrystalline alloys, produced through crystallization of the corresponding glassy precursors, are the softest magnetic materials known so far [1]. Based on their unique magnetic properties, many products consisting of ferromagnetic metallic glasses such as for example anti-theft labels or highly efficient magnetic transformers are widely used [2,3]. Since the first ferromagnetic metallic glass Fe-C-P was found in 1967 [4], Fe- and (Fe,Co)-based alloys are regarded as attractive industrial alloys due to a relatively low price and simple routes for fabrication. In general, multi-component alloys require lower critical cooling rates for glass formation and promote the formation of bulk metallic glasses (BMGs). Together with their high strength and good corrosion resistance [5–8], ferromagnetic metallic glasses may have a good potential for application as advanced functional and structural materials. Within several new BMG families developed in the last decade, (Fe–Co)–

Si–B–Nb glassy alloys play an important role because they combine high glass-forming ability (GFA) with good magnetic and mechanical properties [9]. It was shown that the best composition in this alloy family is the  $\text{Fe}_{36}\text{Co}_{36}\text{B}_{19.2}\text{Si}_{4.8}\text{Nb}_4$  alloy, which may be cast as amorphous rods with a diameter up to 7 mm [10]. These BMGs can reach a compressive strength of 4000 MPa [11] and show a DC magnetization of 1.13 T [10]. It was demonstrated that at least in the case of Fe-based glassy ribbons with small contents of Nb, minor addition of Cu might be a good way to trigger nanocrystallization of Fe(Si), averaging out the magnetic anisotropy and therefore increasing the soft magnetic properties, similar as in case of FINEMET alloys [12]. However, the nanocrystallization provokes a serious embrittlement of the ribbons, which makes their handling difficult.

In the (Fe–Co)–B–Si–Nb bulk amorphous alloy system, several groups have tried to elucidate the influence of a minor addition of Cu on GFA, mechanical and magnetic properties of the resulting alloys. Jia et al. reported on the GFA of  $(\text{Fe}_{36}\text{Co}_{36}\text{B}_{19.2}\text{Si}_{4.8}\text{Nb}_4)_{100-x}\text{Cu}_x$  ( $x = 0, 0.5, 0.6, 0.7$  and  $1.0$ ) alloys [13]. It was found that upon 0.6 at.% Cu addition 1 cm long fully glassy rods with 4 mm diameter can be cast. Shen et al. established that *in situ* formation of (Fe,Co) and  $(\text{Fe,Co})_{23}\text{B}_6$  microcrystalline grains

\* Corresponding author at: IFW Dresden, Institute for Complex Materials, Helmholtzstr. 20, D-01069 Dresden, Germany.

E-mail address: [m.stoica@ifw-dresden.de](mailto:m.stoica@ifw-dresden.de) (M. Stoica).



# Partikelverstärkte Verbundwerkstoffe

M. Nicoar\_\*, R. L. Cucuruz\*\*, I. Car\_i\_\*\*\*

Eine Kategorie der Strukturwerkstoffe, denen in den letzten Jahren viel Aufmerksamkeit geschenkt wurde, sind Verbundwerkstoffe mit metallischer Matrix, die mit keramischen Partikeln verfestigt ist. Zu den vielversprechenden Eigenschaften dieser Kategorie von Werkstoffen gehören die Zugfestigkeit, Fließgrenze, parallel mit einem hohen Elastizitätsmodul, gepaart mit einem geringem spezifischem Gewicht, bei geschätzten Produktionskosten, die geringer sind als bei anderen fortschrittlichen Werkstoffen. Das Einfügen keramischer Partikel in die metallische Matrix führt zu einer Erhöhung der Verschleiß- und Dauerschwingfestigkeit, sowie zu einem verbessertem Verhalten bei hohen Temperaturen, die Werte der Zeitstandfestigkeit, erlauben, in einigen Anwendungen, die Ersetzung von Superlegierungen. Die wichtigsten Nachteile, die bei den zur Zeit gefertigten, mit harten Partikeln verstärkten Verbundwerkstoffen auftreten, sind eine verminderte Zähigkeit und Duktilität, welche die Anwendungsperspektiven dieser Werkstoffgruppe im Maschinenbau einengen.

Beim aktuellem technologischen Stand sind die Verbundwerkstoffe mit polymerischer Matrix im allgemeinen gut bekannt und sind auch in verschiedenen Bereichen verwendet, hauptsächlich in elektrotechnischen Erzeugnissen, elektrischen Haushaltsgeräten, Sport- und Freizeitgeräten usw., während die Verbundwerkstoffe auf Keramikbasis noch am Anfang stehen und nur in wenigen spitzentechnologischen Anwendungen zu finden sind. Die Verbundwerkstoffe mit metallischer Matrix sind das Objekt intensiver Forschungen um aus der experimentellen Phase und dem Stadium der Pilotproduktion zur industriellen Anwendung überzugehen.

Die Verwendung von Metallen als Matrix der Verbundwerkstoffe bietet eine Serie von kennzeichnenden Vorteilen, hauptsächlich im Vergleich zu den Verbundwerkstoffen mit polymerer Matrix:

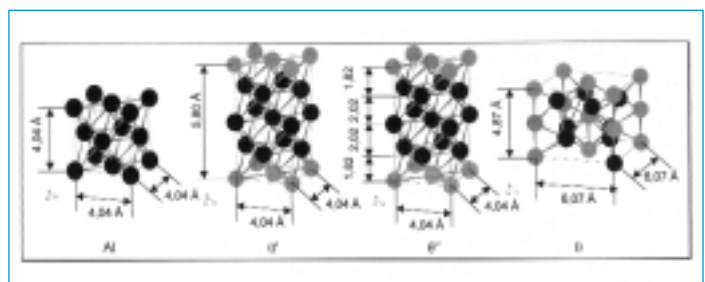
- gute Leistung bei relativ hohen Temperaturen;
- hohe Korrosionsfestigkeit, erhöhte physikalische und chemische Stabilität;
- gutes Verhalten bei Scherbelastung, selbst bei stark anisotropen Werkstoffen;
- die Möglichkeit effiziente und sehr produktive Herstellverfahren anzuwenden, wie z.B. Gießen, Verformen, Spanen, Schweißen usw.;
- verschiedene Möglichkeiten Umwandlungen durch Wärme- oder thermomechanische Behandlungen hervorzurufen.

Als metallische Matrix werden am häufigsten Aluminium, Magnesium, Titan, Kupfer, Zink, Nickel, Eisen und ihre Legierungen verwendet. Die Aluminiumle-

gierungen, die bisher die Mehrzahl der metallischen Matrizen der hergestellten Verbundwerkstoffe darstellen, haben außergewöhnliche Anwendungsperspektiven, sowohl aus technisch – wirtschaftlichen Gründen, wie auch aus ökologischen. Man vermutet, dass sie möglicherweise die dominierenden Werkstoffe der Zukunft sein könnten, hauptsächlich in der Automobilindustrie, Aeronautik, Sportwaren, Maschinenbau, Bauwesen u.a. Die Verfestigung mit harten Partikeln gehört zum Trend der Perfektionierung und Diversifikation der Aluminiumlegierungen, der Vergrößerung des Spektrums ihrer physischen und mechanischen Eigenschaften, zu Werten, die es erlauben, klassische Werkstoffe, vor allem Stähle und Gusseisen, zu ersetzen.

Entgegen einiger spektakulärer Anfangsergebnissen, die den Enthusiasmus vieler Forscher genährt hatten, haben die partikelverstärkten Verbundwerkstoffe mit metallischer Matrix die ersten Vorhersagen nicht bestätigt und ihre Anwendung ist zur Zeit gering. Der Skeptizismus den viele potentielle Anwender diesen Werkstoffen entgegenbringen, wird auch vom Mangel an technologischen Kenntnissen, an Entwurfsspezifikationen genährt, sowie von der Tatsache, dass die bisher unternommenen Forschungen sich auf grundlegende, theoretische Aspekte bezogen haben. Aus diesen Gründen sind die Forschungen in diesem Bereich, in den letzten Jahren, in ein Reifestadium getreten, mit einer deutlichen Orientierung zu applikativen Aspekten. Es werden neue, einfachere und preiswertere Technologien gesucht, die gleichzeitig attraktiver für den Anwender sind.

Abb. 1: Die Gitterzellen der Phasen aus dem Legierungssystem Al – Cu



\* D.-Ing. Mirvea Nicoar\_, Oberassistent Universität „Politehnica“ Timi\_oara, Rumänien

\*\* Dr.-Ing. Roland L. Cucuruz, Professor Universität „Politehnica“ Timi\_oara, Rumänien

\*\*\* Dr.-Ing. Ioan Car\_i\_, Professor Universität „Politehnica“ Timi\_oara, Rumänien



ELSEVIER

Journal of Magnetism and Magnetic Materials 201 (1999) 49–52

**M** Journal of  
**M** magnetism  
**M** and  
magnetic  
materials

www.elsevier.com/locate/jmmm

# The use of amorphous and quasi-amorphous Fe–Cr–P powders for fabrication of magneto-rheological suspensions

Marin Liță, Mircea Nicoară\*

*Faculty of Mechanical Engineering, Department for Materials Science and Heat Treatments, Politehnica University of Timișoara, Bd. M. Viteazul nr. 1, 1900 Timisoara, Romania*

---

## Abstract

Magneto-rheological suspensions (MRS) have been obtained by mean of ultrasonic dispersion of Fe–Cr–P amorphous and quasi-amorphous ferromagnetic powders in a polymeric solution. Ferromagnetic powders have more than 80% amorphous phase and the average dimension smaller than 1  $\mu\text{m}$ . The resulting suspensions present interesting magnetic and magneto-rheological properties, as well as good structural stability of powder over time and temperature. The suspension has also a good gravitational stability for periods of time longer than one week. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Amorphous powder; Magneto-rheological suspension; Magnetic properties

---

## 1. Introduction

Magneto-rheological suspensions (MRS) are relatively a new class of materials, obtained from ferromagnetic particles, with a diameter below 1.0  $\mu\text{m}$ , dispersed into a liquid. Under the action of a magnetic field, magneto-rheological suspensions become quite rigid and their viscosity may increase significantly, which make them interesting for applications in system control and vibrations damping [1, 2]. In order to be attractive on a larger scale, these materials should have an answer time up to milliseconds under the action of a magnetic field of

about 0.5 T, and must be structurally stable in time and within a range of temperature between  $-40$  and  $+150^\circ\text{C}$ . An acceptable gravitational stability must be also achieved, therefore a period of one week will be considered suitable for some applications.

The quality of MRS depends mainly on particle size and magnetic properties, linking forces between particles, as well as the macromolecular structure of the dispersion liquid [3].

## 2. Experimental procedure

One amorphous powder sort denoted by (1) has been obtained by mechanical milling of  $\text{Fe}_{82}\text{Cr}_6\text{P}_{12}$  rapidly solidified ribbons. Three

---

\* Corresponding author. Fax: (40)-56-130336.

E-mail address: nicoara@mec.utt.ro (M. Nicoară)



## Computerized Image Processing for Evaluation of Microstructure in Metallic Matrix Composites

NICOARĂ Mircea<sup>1, a</sup>, RĂDUȚĂ Aurel<sup>1, b</sup> and LOCOVEI Cosmin<sup>1, c</sup>

<sup>1</sup>Universitatea "Politehnica" of Timișoara, Facultatea de Mecanică

Bd. Mihai Viteazul Nr.1 Timișoara, Timiș, RO-300222, Romania

<sup>a</sup>mircea.nicoara@mec.upt.ro, <sup>b</sup>aurel.raduta@mec.upt.ro, <sup>c</sup>cosmin.locovei@mec.upt.ro

**Keywords:** particle - reinforced aluminum, hot extrusion, particle distribution, powder metallurgy, image analysis.

**Abstract.** Fabrication of aluminum matrix composites reinforced with ceramic particles via powder metallurgy techniques present considerable advantages, especially large flexibility of reinforcement volume content. However since metal particles are considerably larger than ceramic reinforcement, ceramic clustering become more and more frequent as the reinforcement proportion increases, and high ratio plastic deformations are mandatory. An experimental program has been developed to determine particle redistribution of ceramic reinforcement by mean of large-ratio extrusion of aluminum composites, containing up to 20% vol. of reinforcement. Evaluation of particle redistribution by extrusion has been determined using a computer-based technique of image analysis for resulting optical micrographies. The image processing has included particle detection, particle measurement and classification.

### Introduction

Particle reinforcement is unanimously considered a most promising method to improve mechanical properties of lightweight alloys, based mostly on aluminum, magnesium or titanium. As consequence, significant increase of strength, stiffness, wear resistance and fatigue limit may be achieved. Among the fabrication techniques powder metallurgy has a special role, based on some major advantages such as structural homogeneity or possibility to embed even very small particles at reinforcement proportions up to 60%. Since fabrication costs seem to be critical for applications, some general tendencies have been observed:

- Fabrication techniques should be based on standard P/M technologies, usually a blending-pressing-sintering route similar to classic materials, that are easy to reproduce and could be implemented with minor technological modifications;

- Both metallic particles and ceramic reinforcements have to be cheap and produced in large quantities, preferably already available on the market;

This last requirement usually produces large difference in particle size between metallic and ceramic powder that could affect material homogeneity, especially when ceramic reinforcements are added in higher proportion. Therefore conventional PM techniques will determine formation of clusters and pores, where ceramic particles are agglomerated inside metallic matrix, as seen in Fig. 1. Reinforcement clustering is responsible for dramatic loss of material toughness and ductility, and for this reason secondary processing by mean of high-ratio plastic deformation; becomes necessary for improvement of particle distribution.

So far both clustering of ceramic particles during PM processing and redistribution of reinforcement have been evaluated mostly qualitative. This paper is proposing a more objective tool that could better evaluate microstructural effects of plastic deformation as secondary processing, based on image processing. The computerized processing of the images assumes that a number of mathematical operations have to be followed and logical decisions have to be made in a precise and organized manner.

## Sample preparation and HR-TEM investigation techniques of Ti based, Ga containing, amorphous alloys

LOCOVEI Cosmin<sup>1, a\*</sup>, NICOARA Mircea<sup>1, b</sup> and RADUTA Aurel<sup>1, c</sup>

<sup>1</sup>POLTEHNICA University of Timisoara, Bd. M. Viteazul 1, 300222 Timisoara, Romania

<sup>a</sup>cosmin.locovei@upt.ro, <sup>b</sup>mircea.nicoara@upt.ro, <sup>c</sup>aurel.raduta@upt.ro

**Keywords:** Ti-Zr-Cu-Ga alloys, biocompatible alloys, TEM sample preparation, FIB sample preparation, HR-TEM investigation, SAED investigation, CBED investigation.

**Abstract.** Titanium based bulk metallic glasses (BMGs) are characterized by properties such as high corrosion resistance, Young's modulus, hardness, fracture strength and wear resistance that recommend them as performant biomaterials for orthopedics and dentistry. Present researches have been focused on some Ti-Zr-Cu-Ga-Si-Sn alloy which could be feasible alternative to almost classical nickel containing BMGs. has been casted by vacuum suction in a copper mold. Suction casting has been used to produce by mean of ultra-rapid cooling experimental samples as 2mm cylinders, and complex investigation program based on optical microscopy, SEM, and HR-TEM techniques has been performed to characterize resulting microstructure. Although presence of gallium produces considerable difficulties in sample preparation, investigations based on high resolution transmission electron microscopy (HR-TEM) have evidenced simultaneous presence of amorphous, crystalline and partially crystalline structures.

### Introduction

Development of metallic biomaterials has been focused for decades on improvement of some critical qualities that are important for fabrication of implants. In relations with human body they should be biocompatible, which could signify that material is relatively inert in contact with biological environments, bioactive in order to promote tissue ingrowths and vascularization and even biodegradable at controlled rates to act as temporary implants. In this respect titanium alloys imposed themselves as the first choice in comparison with stainless other steels and Co-Cr alloys for their exceptional resistance to corrosion.

Biocompatibility of titanium alloys should be completed with suitable mechanical properties, considering the functioning conditions as permanent implant in orthopedics and dentistry, where high loading stresses usually occur, so both mechanical strength and acceptable toughness are required. High mechanical properties of titanium alloys are most favorably completed with low density, which only enhance the ability to use them as first class permanent implants [1].

However practical use of titanium alloys evidenced some important drawbacks, the most important being mechanical compatibility with the human bone. They are much stiffer then bone, so higher Young's Modulus is producing the „stress shielding“ effect and reduction in bone density (osteopenia). If mechanical functionality of biomaterials could be defined as ratio between mechanical strength and Young's Modulus ( $BF = \sigma/E$ ), it means that 2 ways may be considered to improve behavior: increasing mechanical strength and reducing stiffness.

Improvement of mechanical strength has been achieved so far by mean of complex alloying, which eventually produced titanium grades that are characterized by both exceptional loading capacity and good toughness. Nevertheless complex alloying leads to the presence of additions that are now known as cytotoxic and allergic elements such as V, Al, Ni, Co, Cu etc. Therefore recent researches are focused on replacement with non-toxic elements, that should be exclusively used in titanium alloys, such as Nb, Ta, Zr, Pt, Sn, Si, In etc [2-5].

Bulk metallic glasses (BMGs) on titanium base could represent an interesting choice in development of titanium-based implants for both mechanical and environmental reasons. High