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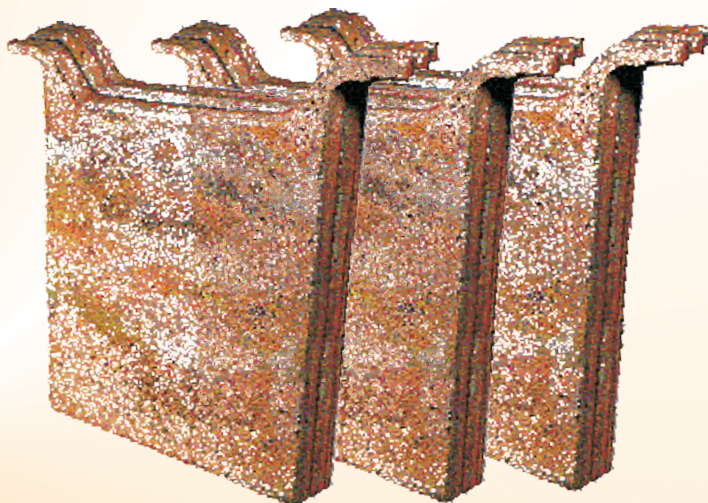
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BAKAR COPPER

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CROSS
BORDER
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Romania-Serbia

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REVIEW PAPER

Field: Materials

PROJECT POCAL - POLE OF COLLABORATION IN THE NEW FUNCTIONAL ALLOYS

Abstract

The basic information about the Romania-Republic of Serbia IPA Cross-border Cooperation Programme under the Project "Pole of Collaboration in the New Functional Alloys - POCAL", MIS ETC no. 1328 are given in this paper. The main activities and tasks in the project, as well as participants are presented, too.

Keywords: *IPA Cross-Border Cooperation Programme Romania-Republic Serbia, POCAL Project, Functional Alloys, Shape Memory Alloys*

1 INTRODUCTION

The project with the title "Pole of Collaboration in the New Functional Alloys", the acronym POCAL and MIS ETC no. 1328 is the project within the Romania-Republic of Serbia IPA Cross-Border Cooperation Programme approved by the European Commission on the 27th of March 2008 by Decision C (2008)107 and approved by the Programme Joint Monitoring Committee of the "Romania - Republic of Serbia IPA Cross-Border Cooperation Programme" on 22nd May 2015 in Timisoara.

The project is obtained during the Call for proposal no. 2, within the Priority axis 1: "Economic and Social Development" and Measure 1.4: "Support increased levels of research and development and innovation in the border region".

The implementation period of the project is one year, i.e. from 23.09.2015 to 22.09.2016.

The project POCAL has realized by the Universitatea Politehnica Timisoara (Politehnica University of Timisoara), Ro-

mania - as a lead partner and Institut za rudarstvo i metalurgiju Bor (Mining and Metallurgy Institute Bor), Serbia - as partner 2.

The Politehnica University of Timisoara was founded in 1920, short time after the union in one state of all the Romanian territories supervened in the context of the political redefinitions in Europe. At present, Politehnica University of Timisoara has 10 faculties and 4 independent departments. 15 000 students, 850 teaching staff and 900 administrative and auxiliary staff study, respectively, work within their framework.

The Politehnica University of Timisoara is one of the biggest and most well-known technical universities from Central and Eastern Europe. During its 95 years of existence, Politehnica University of Timisoara produced over 100 000 engineers, very appreciated both in Romania and abroad, for their competence and seriousness. The portfolio of specializations, the curricula and the syllabi of the Politehnica University of Timisoara are well attuned to the needs of the society, the university cultivating close relationships with it.

Beyond its good name in education, the Politehnica University of Timisoara has also the recognition of a first class actor on Romanian scientific research scene, with remarkable results both on the national and international level. The Politehnica University of Timisoara possesses an educational and research infrastructure both buildings and equipments comparable with the one of the most prestigious European universities.

The Copper Institute Bor was founded in 1962. In the year 2007, its name was changed into the Mining and Metallurgy Institute Bor. Throughout the years, the Institute has acquired numerous references in the field of mining and metallurgy of copper and precious metals in India, Burma, Iran, Sierra Leone, Armenia, Turkey, Zambia, Pakistan, Kazakhstan, Bosnia and Macedonia.

The Mining and Metallurgy Institute Bor with more than 54 years of working experience has managed to join high quality and reliability in scientific and research work, engineering and

consulting, experimental and specialized production, material and equipment testing, control of product quality, materials and production processes, and control of the quality of environment.

The Institute is active at the domestic and foreign market in the fields of geology, mining, mineral processing, metallurgy, technology, chemical control, ecology, information technology, industrial IT, engineering, mechanical engineering and publishing.

Among its activities, the ones that should not be forgotten are various kinds of expertise and studies, investment programmes, investment-technical documentation, documentations for tenders and alike. Also, research and development activities include prefeasibility and feasibility studies, basic design, process design, detail design, supervision commissioning, start up, and staff training.

2 PROJECT POCAL CONSISTENCY WITH PROGRAMME STRATEGY

The project POCAL possesses a consistency with the IPA Cross-Border Romania-Republic Serbia Programme, which has two main objectives:

- Increasing the overall competitiveness of the economy in the border area, and
- Improvement the quality of life for the communities of the border area

The main priority axis objectives are:

- Support for research and development events - conferences, meetings, workshops
- Creation of and access to research and development co-operation networks
- Support for research, development and innovation centers
- Joint initiatives of cooperation between economy and research

Nowadays, research and development activities as one of the major pillars of progress is in continuous need for collaboration between people with similar interests, and complex challenges may be answered by taking advantage of the experience of various groups who have already approached part of the problems.

In the Romania-Republic of Serbia cross-border region, issues related to development are similar, since typical activities are similar. In fact, the mining and metallurgical activities in the regions in questions in Serbia and Romania are challenged by current scientific development and are in need for a serious restructuration.

For achieving its goals, the project will develop a cross-border network for research and development in the new functional materials engineering, adapted to the specific areas of interest, such as metallurgy, and novel developments, such as functional, multifunctional and intelligent materials as well as micro and nanoengineering in the field.

The project can have an important impact on the way future specific activities will shape the cross border regions by supporting through research and transfer of knowledge the orientation toward novel materials and technologies that is eco-friendly, compared to classic and existing less value-incorporating and affecting the environment.

Although, the border can be perceived as divisive, this project will link the partners and the beneficiaries in a joint project, where partners have exquisite complementary expertise. This way, the beneficiaries can take advantage of collaboration with best skilled researchers in the region, share and develop knowledge, initiate high-level research and support new fields of collaboration.

The project POCAL objectives will be achieved by focusing on:

- Excellence in innovation and transfer of knowledge through the creation of a cross-border partnership for re-

search and development, which aiming to develop of novel functional materials.

- Development of laboratories equipped for addressing the new challenges related to the novel materials exploration with open access for future partners interested in developing industrial products.
- Spreading knowledge in the border regions by organizing the research and development events.
- Preparing the transfer of knowledge from research and development activities toward practical applications in the benefit of the cross-border area.

Also, the project POCAL will have an educational component via the training activities that will be offered and the activities that will imply a cross-border exchange of information and researchers. The dissemination activities will also be opened to people looking to gain information about the field of activity of POCAL network.

3 PROJECT POCAL OBJECTIVES

This project takes advantage of the unique qualities of the participants on both side of the border in the field of advanced materials, with the aim to initiate a network of collaboration in research and development that is going to address the subject of smart materials with focus on the shape memory alloys. These materials will be fabricated using the most advanced techniques and characterized with state of the art equipments that will become part of the network.

The POCAL partnership expects to address the issue of fabrication the shape memory alloys by sintering and nanoengineering, techniques for which scarce information exists, especially on fabrication the materials with functional gradient.

These goals of the project POCAL will be realized within the following objectives:

Creation of the POCAL Cross-Border Network, which will become the main center for innovation in functional materials in the cross border area, providing support for innovation and involving the most important universities and research institutes from the area favoring to transfer the innovation from laboratories to the pre-implementation phase of new materials focused on the shape memory alloys.

Development of Interconnected Innovation Clusters, based on the experience accumulated a continuous optimization of the structures and methods that will be considered by joint participation in international calls for projects and promotions on both sides of the border.

Joint Research in Advanced Functional Materials, aims to develop the new generations of smart materials based on functional alloys like the shape memory alloys.

Design of the Transfer of Knowledge Mechanisms, the results developed within the framework of project POCAL will be opened to the companies interested in using these results of research or looking to use the existing facilities in order to explore the possibilities to develop innovative products.

Promotion, the project POCAL is going to promote awareness of the need to restructure through researching and development as well as education the traditional fields, based on recent developments that could lead to a sustainable economy.

Development, the project POCAL will become a pole of excellence of both intraregional and neighboring regions aiming to connect itself to the similar networks for improving its activities based on the new needs in sustainable development or social inclusion of people needing to shift from traditional qualifications in order to find a better position on the regional job market.

Preparation for self-support, is related to real regional needs both in Serbia and Romania, and it is connected to the international efforts to provide a sustainable development via advanced materials and technologies and answers the traditional activities needs.

4 PROJECT POCAL ACTIVITIES

The project POCAL has realized per 17 activities and is going to tackle the problem of functional materials for actuating applications by fabricating the shape memory alloys with improved properties via sintering and severe plastic deformation. This will be done by developing the new fabrication and characterization capacities in both partner's institutions and by taking advantage of the proven experience in the field, considering that both partners have proven excellence record on one side by innovating in the field of novel functional materials belonging to the shape memory alloy families, on the other hand in fabricating and developing nonferrous materials for industrial applications.

Both partners are major players in the research and development activities in their countries and have been involved in numerous research contracts at national and international level. The partners will look for every possible opportunity to continue the collaboration due to the mutual interest in developing the research on subjects proposed in the partnership.

The project is going to develop a demonstrator based on properties of the shape memory alloys and will open a transfer of knowledge center to facilitate the collaboration with industrial sector.

The partners will try to develop viable products to be offered for market commercialization and requiring further collaboration from the partners. Such multiplicative effects are a further source of credibility for the proposal submitted and are ex-

pected to encourage a lasting collaboration between the partners beyond the funding period.

5 PROJECT POCAL EXPECTED RESULTS

The project POCAL has a few expected results such as:

Network of collaboration - The network of collaboration will be the main asset of the project. It will be a continuous source for research and development innovation in the field of materials in the cross border region.

Web portal - The POCAL web portal will be the main gate to the internal and collaborations between the partners and with external partners such as companies, research and development groups in the cross border region or in the world, interested in developing the field.

State of the art fabrication lab - The need to develop new functional materials belonging to the shape memory alloy families is related to the advanced equipment for fabrication and estimation the phase transformation characteristics.

State of the art characterization lab - The partnership needs a well equipped laboratory for characterization the materials fabricated and investigated in the partnership.

Demonstrator - The demonstrator based on the shape memory alloy properties will be the proof of the partnership capacity to address the applicative issues.

Dissemination activities - The dissemination via the activities proposed, in addition to the web portal will favor and strengthen and expand the cross border collaborations.

Transfer of knowledge center - The transfer of knowledge center will be the main element for collaboration with industrial partners that will find the results of collaboration interested enough to be applied in their companies.

Joint applications - Joint application that will jointly be developed by the partners based on experience achieved in the project.

Self support plan - The plan will outline the activities to be carried out after the completion of the project by the partners, they way the results of collaboration to be jointly exploited in the benefit of the partners and people in the cross border region.

The project POCAL contribution to the programme and priority axes result indicators are as follows:

- Increased importance of research and development and innovation in the border area.
- Increased competences for personnel to develop re the search-related activities.
- Activities strengthening the scientific collaboration.
- Dissemination the scientific results.
- Increased capacity to develop high level research.
- Results of collaboration to be protected.
- Transfer of knowledge initiated activities.

6 PROJECT POCAL TEAM

The members of the project POCAL team from the Politehnica University Timisoara are:

- Prof. Dr. Corneliu M. Craciunescu, Joint Project Manager
- Ms. Adriana Szakallas, Joint Financial Manager
- Dr. Ing. Iosif Hulka, Joint Marketing Manager
- Prof. Dr. Ing. Ion Mitelea, Researcher 1

- Prof. Dr. Ing. Victor Budau, Researcher 2
- S. L. Dr. Ing. Dragos Utu, Researcher 3
- M. Sc. Ing. Lazar Soveja, Researcher 4

The members of the project POCAL team from Mining and Metallurgy Institute Bor are:

- Dr. Eng. Ana Kostov, Joint Scientific Advisor
- Dr. Eng. Aleksandra Milosavljević, Joint Research Coordinator
- B. Sc. Eng. Radiša Todorović, Researcher 1
- M. Sc. Eng. Zdenka Stanojević Šimšić, Researcher 2
- Dr. Eng. Mile Bugarin, Researcher 3
- Dr. Eng. Milenko Ljubojev, Researcher 4
- B. Sc. Ec. Borivoje Stojadinović, Researcher 5
- B. Sc. Ec. Slađan Milenović, Researcher 6
- B. Sc. Ec. Vesna Florić, Internal Audit Coordinator

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ORIGINAL SCIENTIFIC PAPER

Field: Materials

ALUMINUM-COPPER BINARY SYSTEM

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Abstract

The importance of Al-Cu alloys is reflected in a wide range of their applications but that's not the only reason for Al-Cu binary system investigation. The complexity and occurrence of various phenomenon regarding this system make it an interesting for considerable investigating. This study was done in order to give a complete view of conducted investigations regarding phase equilibria, thermodynamics and thermodynamic optimization of Al-Cu binary system from early beginnings till now days.

Keywords: *Al-Cu binary system, phase equilibria, thermodynamics, optimization*

INTRODUCTION

Al-Cu alloys have a wide range of technological applications due to their good properties such as high strength, hardness, good electrical and thermal conductivities, machinability, etc. One more convenience about these materials is the fact that their fabrication is not complicated.

Al-Cu system is not interesting for investigation only because of its alloys, but also because of a considerable theoretical interest for this system, too [1]. The complexity of Al-Cu system and occurrence of various phenomenon make it an interesting subject for exploring from the early twentieth century [2-4] till now, and a significant number of studies based on calculations or

experimental work regarding this system are presented in literature.

J.L. Murray [5] in his assessment, done in the middle of eighties of the last century, critically reviewed all literature data regarding phase equilibria, transformations, crystal structures thermodynamics and metastable phases up to 1983.

Since 1983, this system has been investigated very intensively either experimentally or theoretically.

PHASE EQUILIBRIA

D.A. Bennett and D.H. Kirkwood [6], determined experimentally the phase equilibria between solid alloys and liquid in the Al-rich region at maximum solid solubility of Cu in Al of 2.87 at% Cu while H. Liang et al. [7] found that solubility of Cu in Al is 2.7 at% Cu.

Using differential thermal analysis (DTA), Z. Bojarski et al. [8] investigated the phase transformations in several Cu-12.4% Al alloys.

In the frame of phase equilibria re-determination in the composition range between 31 and 37.5 at% Cu, T. Gödecke and F. Sommer [9] proposed a new solubility range for Al_2Cu (θ) phase, which is formed by a peritectic reaction at 592°C, from 32.05 to 32.6 at% Cu at 549°C and from 32.4 to 32.8 at% Cu at 250°C [10]. They also studied the metastable form of Al_2Cu phase with composition of 32.75 at% Cu and metastable phase equilibria [8,9]. All their investigations were done experimentally by DTA, magneto-thermal analysis, magnetic susceptibility measurements versus temperature (MTA), and optical microscopy. At the same time S. W. Chen, and C. C. Huang [11], determined the solidification curves of the metastable Al_2Cu phase.

Investigating the phase equilibria in the temperature range 500-1000°C and in the composition range 40-85 at% Cu of Al-Cu system, by different structural and thermal methods, Liu et al. [1], found that in the composition range 60-75 at% Cu β_0 the phase does not exist at 1000°C. Also, they found that the phase

transformation between γ_{D83} and γ_H observed in the temperature range 800-900°C in the composition range 62-68 at% Cu is not a first-order reaction but a kind of second-order ordering reaction; the temperature of the eutectoid reaction $\beta \rightarrow \alpha + \gamma_{D83}$ is $559 \pm 1^\circ\text{C}$ and the invariant reactions $\gamma_H \rightarrow \beta + \gamma_{D83}$ and $\gamma_H + \varepsilon_1 \rightarrow \gamma_{D83}$ were not confirmed.

Phase diagrams of Al-Cu binary system, obtained as a result of all these investigations, were amended and improved by the subsequent studies regarding this system. J.L. Murray [5] gave his version of Al-Cu phase diagram which was re-published a few years later [12]. T.B. Massalski et al. [13], redrawn the Murray's phase diagram [4] in their compilation of phase diagrams. A complete Al-Cu phase diagram based on ref. [8,11] was proposed by P. Riani et al. [14].

Recently, N. Ponweiser et al. [15], have constructed the phase diagram of Al-Cu system shown in Fig. 1, where part above the temperature of 450°C is based on their own experimental work (optical microscopy, DTA, SEM, and XRD), and the range below 450°C was added based on ref. [13] in order to indicate the existence of the α_2 phase.

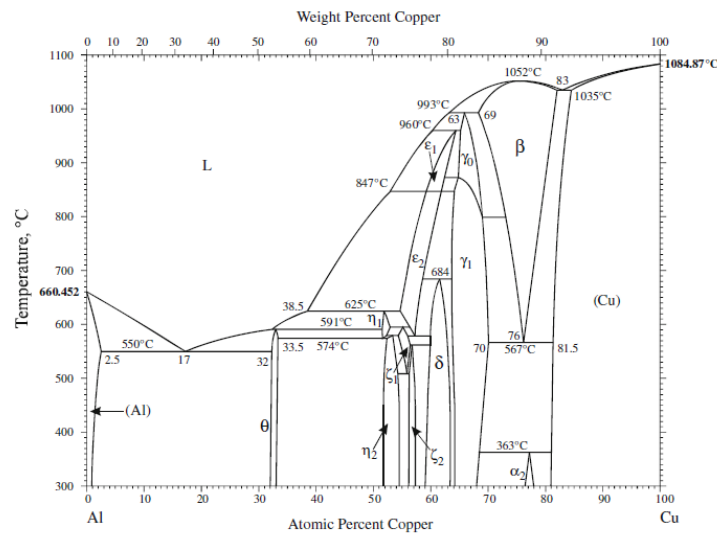


Fig. 1. Phase diagram of the Al-Cu binary system [15]

L. Kaufman and H. Nesor [16] have done the first calculated Al-Cu phase diagram by the CALPHAD method but considering only four of the eleven intermetallic phases [14]. Later, S. W. Chen et al. [17] obtained and improved phase diagram including six intermetallic phases [14].

THERMODYNAMIC INVESTIGATION

Partial and integral mixing enthalpies of liquid phases of this system were experimentally determined using the calorimetric methods by M. Kawakami [18], W. Oelsen and W. Middel [19], R. Hultgren et al. [20], B. Predel [21], A. Yazawa and K. Itagaki [22], V.T. Witusiewicz et al. [23], as well as H. Flandorfer et al. [24].

The first available published works regarding thermodynamic properties of Al-Cu system were done by M. Kawakami [18], and W. Oelsen and W. Middel [19], in which they have obtained the exothermic values of enthalpies at 1473 K and 1373 K.

K. Itagaki and A. Yazawa [22] measured integral enthalpy of mixing of liquid alloys by direct mixing calorimetry in the range of Cu composition from 11 at% Cu to 90 at% Cu, at 1375 K. The minimum of enthalpy was reported to be 10,200 J/mol at 62 at% Cu [22,24].

V.T. Witusiewicz et al. [23] have done a thermodynamic evaluation of the Al-Cu binary system consisted of literature data from different sources [25-29], and their own experimental results. They determined the thermodynamic parameters of the liquid alloys and γ D83 phase by calorimetric measurements.

Thermodynamic properties of this binary system were investigated by H. Flandorfer et al. [24], too. These authors determined the partial and integral enthalpies of mixing the liquid alloys performing high temperature drop calorimetric measurements. All investigations were done up to 40 at% Cu at 973K.

Based on the first-principles calculations in terms of the 16-atom special quasi-random structures (SQSs), Gao et al. [30], investigated the enthalpy of mixing at 0 K as well as the Gibbs energy of mixing, enthalpy of mixing, and entropy of mixing of the solid solutions (BCC, FCC and HCP type), regarding the Al-Cu binary system.

Recently, S. M. Liang and R. Schmid-Fetzer [31] reassessed all thermodynamic parameters of Al-Cu system in which the available experimental data have been comprehensively compared with calculated results for the first time. The η_1/η_2 phase transition and the α_2 phase have been introduced in their study for the first time. Also, a new model of crystal structure for γ_H and γ_{D83} phases has been proposed, too [31].

OPTIMIZATION

The first calculated Al-Cu phase diagram by CALPHAD approach was done by L. Kaufman and H. Nesor [16] taking into account only four intermetallic phases in calculation while S. W. Chen et al. [17] improved it considering six intermetallic phases.

V.T. Witusiewicz et al. [23] carried out the optimization of the Al-Cu system by modelling the Gibbs energy of all individual phases using the CALPHAD method.

Not so long ago, Gao et al. [30] have done the optimization of thermodynamic properties for solid solutions of BCC, FCC and HCP crystal structures of the Al-Cu system.

Recently, S. M. Liang and R. Schmid-Fetzer [31] have calculated the Al-Cu phase diagram by the CALPHAD method using the optimized thermodynamic parameters in calculations.

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ORIGINAL SCIENTIFIC PAPER

Field: Materials

SHAPE MEMORY ALLOYS AS A PART OF SMART MATERIALS GROUP

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Abstract

Smart materials are functional in comparison with conventional materials, and their classification is based on the relationship between stimulus and response. From this large group of materials, specific type is shape memory alloys (SMA). These types of smart materials have a lot of applications in various fields of engineering. The most effective and widely used SMA alloys are nickel-titanium, copper-based alloys with addition of zinc, aluminum and nickel, and iron-based alloys with manganese and silicon.

Considering all material characteristic, including price, copper-based alloys are the most commercial from the group of SMA.

Keywords: *smart materials, shape memory alloys (SMA), copper*

INTRODUCTION

Advanced materials for various purposes are widely used in the whole world, and among them are so-called smart materials. Smart materials respond to the environmental influences, changing some of its characteristics. Depending on the change in external conditions, there is a change of material properties (mechanical, electrical, structural). Smart materials are generally incorporated in the systems whose main characteristics may change drastically depending on the need for certain properties. Depending on which properties are changed, different multiple types of smart materials are observed. All of them are functional materials, but the difference is in the degree of smartness de-

pending on the initiation of the environment and the response of the material. So there are materials whose properties change under the influence of electrical, magnetic, thermal or optical environment influence, and in accordance with that and with different types of response or change features.

From a wide range of smart materials, the shape memory alloys (SMA) are a separate group. These materials react to a thermal stimulus, i.e. change in temperature, and have a mechanical response, i.e. there is a change of their mechanical properties. So, after deformation at a certain temperature, the material returns to its original shape. The change in crystal structure above the transformation temperature leads to a return to its original shape. There are a large group of these materials: SMA based on nickel and titanium, SMA based on copper, and on the basis of iron.

The most used alloys are so-called nitinol alloys [1], i.e. SMA based on nickel and titanium. These alloys have a wide application area because of the high deformation degree (up to 8%), as well as thermal stability and corrosion resistivity. Despite that, the production is limited with certain conditions because of titanium reactivity, so melting must be done in vacuum, and the transformation temperature will be from -100 up to $+100^{\circ}\text{C}$.

Most commercial alloys compared to nitinol are certainly copper-based alloys, due to the fact that they are less expensive and that the melt does not have to be performed in a protective atmosphere. They are mostly a combination of copper with zinc and aluminum or aluminum and nickel [2]. The degree of elongation for these alloys is slightly lower (4-5%) while the transformation temperature are -180 to $+200^{\circ}\text{C}$ for Cu-Zn-Al and -140 to $+100^{\circ}\text{C}$ for the Cu-Al-Ni alloys.

In contrast to the above mentioned, the shape-memory alloys based on iron have a deformation capacity of only up to 4%. These are the Fe-Mn-Si alloy, which after only small deformations can return to its original shape.

Shape memory alloys have a wide application as shown in

Figure 1.

The application of shape memory alloys can be seen in large systems (industrial systems, aeronautics) and in home use (air conditioners, various safety valves, etc.) as well as in medicine. The greatest application which these alloys have achieved is in the mechanical and electromechanical control systems due to the sensitivity of the small and repeated temperature changes. Now, the industrial applications appear in a wide spectrum of commerce. Eyeglass frames were an early example of a new use of super-elasticity which has grown to be a world - wide product.

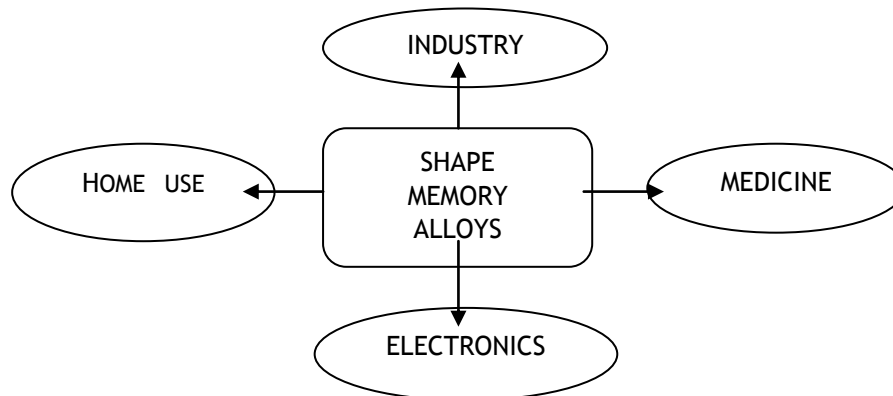


Figure 1 *Shape memory alloys applications area*

THE SHAPE MEMORY EFFECT

Shape memory effect means the ability of metals and alloys which are plastically deformed in the martensitic state or in a temperature range of martensitic transformation, to establish the original shape during the heating. Heating leads to recovery of high temperature initial phase crystals and removing the plastic deformation. At the same time, all the physical and mechanical properties are returned. Martensitic crystal structure is the basis for achieving the effect of shape memory. This effect can be achieved in two ways: exposing the alloy to a pressure at certain temperature, or rapid quenching alloy at certain critical

temperature. The more used methodology is quenching, due to the fact that the martensitic structure occurs spontaneously, with shearing of atoms in the alloy or by nucleation. So, change is characterized by a diffusion-free transformation characterized by the coordinated movement of large atomic groups.

In the shape-memory alloys two phases are observed: martensite and austenite. Martensite is a relatively soft phase which is easily deformed and exists at lower temperatures as opposed to the austenite. In high-alloyed carbon-free iron alloys, as well as some non-ferrous alloys, during the heating after quenching the diffusion-free transformation of austenite into martensite, or another starting phase is possible. Such a transformation is called a reverse martensitic transformation. It is possible thanks to a large number of alloying elements, which lowers the temperature of phase equilibria and there is no decomposition of austenite phase during the transformation of martensite-austenite.

Although there is a wide range of shape memory alloys the most of practical interest are those alloys which have a reverse effect, those one that can restore a significant part of deformation. One-way shape memory alloys are the alloys which have martensite deformation after heating, so there is a shape-memory effect in one direction (one-way shape memory), while the ones that can change shape in both directions, after cooling again and return to its original shape are so-called the two-way shape-memory alloys.

SHAPE MEMORY ALLOYS BASED ON COPPER

Copper-based alloy with shape memory effect are very commercial and they are mainly alloys with zinc, aluminum and nickel. Figure 2 shows the liquidus projection in Cu-Zn-Al system, while the Table 1 gives a review of the possible invariant reaction in the same system [3].

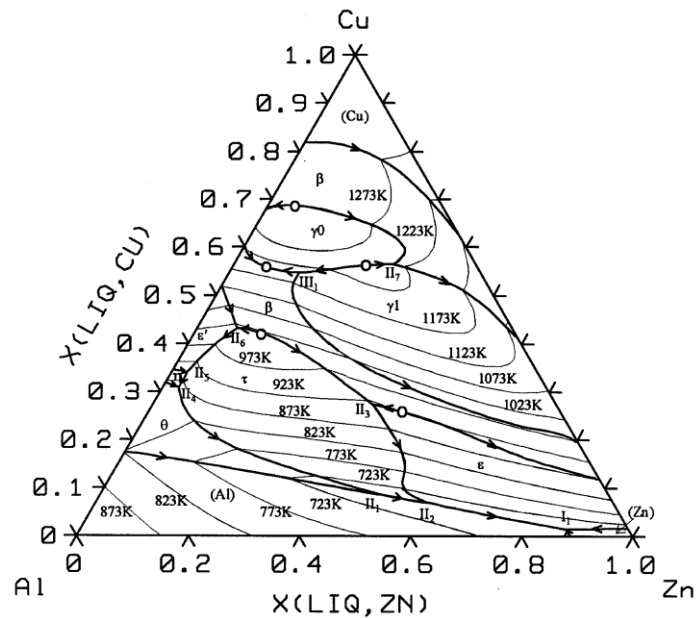


Figure 2 Calculated liquidus projection in Cu-Zn-Al system [3]

Table 1 Calculated invariant reactions in Cu-Zn-Al system [3]

Reaction	Temperature, K	Composition of liquid phase
$L + \theta - (Al) + \tau$	698	Cu _{8,6} Zn _{50,5} Al _{40,9}
$L + \tau - (Al) + \varepsilon$	694	Cu _{6,8} Zn _{60,1} Al _{33,1}
$L - (Al) + (Zn) + \varepsilon$	654	Cu _{1,6} Zn _{87,2} Al _{11,2}
$L + \beta - \varepsilon + \tau$	917	Cu _{27,4} Zn _{39,5} Al _{33,1}
$L + \eta - \varepsilon + \theta$	853	Cu _{31,2} Zn ₂ Al _{66,8}
$L + \varepsilon' - \varepsilon + \eta$	893	Cu _{34,3} Zn ₂ Al _{62,8}
$L + \beta - \varepsilon + \varepsilon'$	1010	Cu _{43,5} Zn _{6,9} Al _{49,6}
$L + \gamma^\circ - \beta + \gamma$	1226	Cu _{56,4} Zn _{28,6} Al ₁₅
$L + \gamma + \gamma^\circ - \beta$	1197	Cu _{54,6} Zn _{12,6} Al _{32,8}

The possibility of shape memory effect depends upon the alloy ability to undergo the thermo-elastic martensite deformation. The alloy is first cooled and transferred to the martensitic phase, when there is possibility of mechanical deformation. As long as the lower temperature, the alloy is deformed or if heated, martensite again deformed into the austenite and the alloy returns to its original shape.

Martensitic transformation does not occur at a certain temperature, yet there is whole temperature range which is different for each monitored system.

Various deformation temperatures, and the corresponding voltage curves for Cu-Zn-Al alloys are shown in Figure 3.

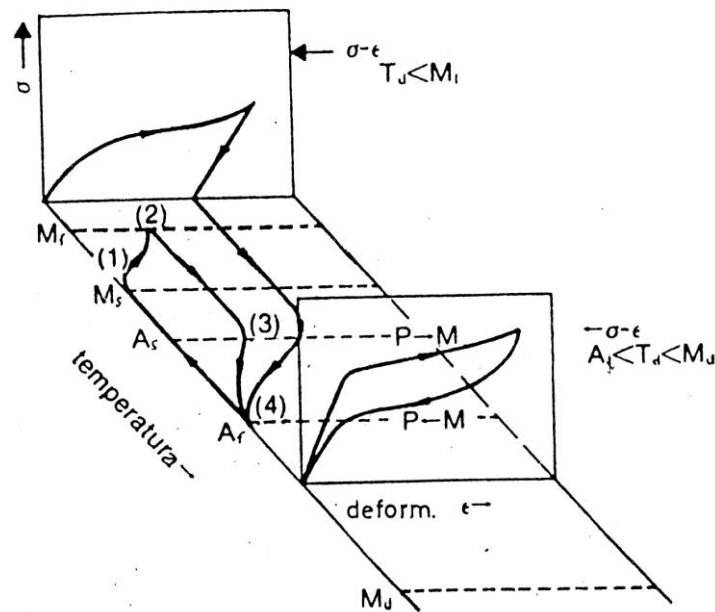


Figure 3 Schematic overview of the voltage curves depending on deformation temperature (M_s -temperature of beginning martensite formation at cooling; M_f -temperature of the martensitic transformation ending; A_s -starting temperature of high temperature phase formation; A_f -ending temperature of high temperature phase formation at heating; M_d -below this temperature martensite can be reversed into the original phase)

In the upper left corner in Figure 3, the alloy deformation below the M_f temperature is shown, while alloy is fully in martensitic condition. For a relatively low stress there is a possibility when the deformation can be deposited in the martensite structure at certain stress. When unloading once, the elastic distance can be observed in any metal. Heating to A_f temperature, martensite with added deformation disappears and the original structure returns.

In contrast, in the lower right corner in Figure 3, the curve corresponding to the alloy deformed between the temperatures the A_f and M_d is shown, while the alloy is in the initial phase at high temperature. Here is a tensile martensite before the applied deformation ($P \rightarrow M$). After release, martensitic structure is unstable and is converted to the original phase ($P \leftarrow M$). During this reversible process each deformation which was incorporated into the tensile-martensite disappears and the material returns to its original shape. This behavior of materials was called the pseudo-elasticity.

Cu-Zn-Al alloys are widely used in the industry (thermostats, control equipment, connectors, etc.). The most obvious examples are the various types of springs with different systems for remote regulation and control.

CONCLUSION

The shape memory alloys based on copper, e.g. Cu-Zn-Al, are part of the wide smart materials family, and have wide applications in industry as well as home use as constitutive elements of various assemblies. Their great advantage over the other types of SMA is low price, as well as the role of environmental friendly materials.

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ORIGINAL SCIENTIFIC PAPER

Field: Materials

INTERNAL FRICTION CHARACTERIZATION THE PHASE TRANSFORMATION IN THE Cu-Zn-Al SHAPE MEMORY ALLOY

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Abstract

The use of internal friction for characterization the phase transformation in a the Cu-Zn-Al shape memory alloy was exemplified for a cantilever type sample, using flexural oscillations. The main martensitic phase transformation zones were well individualized on the internal friction vs. temperature spectrum for the Cu-Zn-Al sample, indicating - as expected - a damping maxima in the phase transformation region where the number of interfaces (i.e. in martensite and between martensite and austenite) is the highest.

Keywords: *shape memory alloys, damping, internal friction, Cu-based alloys*

1 INTRODUCTION

Shape memory alloys are multifunctional materials [1] that possess in addition to the shape memory properties a set of associated properties, among which the most important are the superelastic behaviour [2], the ferromagnetic behaviour [3] or biocompatibility (in certain compositional ranges) [4]. Their damping capacity is one of the highest that can be found in metals and is extremely dependent on the microstructural particularities [5]. Thus the analysis of this property as a function of temperature can provide the important information for practical

use of shape memory alloys in various applications aiming to improve the damping of mechanical system.

The absorption spectra of the mechanical energy in metals [6] can be used to characterize the martensitic phase transformation in the shape memory alloys, whether as internal friction, ultrasound absorption or energy dissipation [7]. The internal friction characterizes the interaction between neighbouring areas of material as a result of viscous deformation that leads to heat generation. The heat dissipation occurs during dynamic processes that arise as a result of external stresses that lead to displacements of atoms and ions. This dissipation is also discernable on the corresponding damping curves.

A typical damping curve is exemplified in Figure 1 for the case of free oscillation, showing the main elements like the amplitude (A), the attenuation over time (t) and the oscillation period (T).

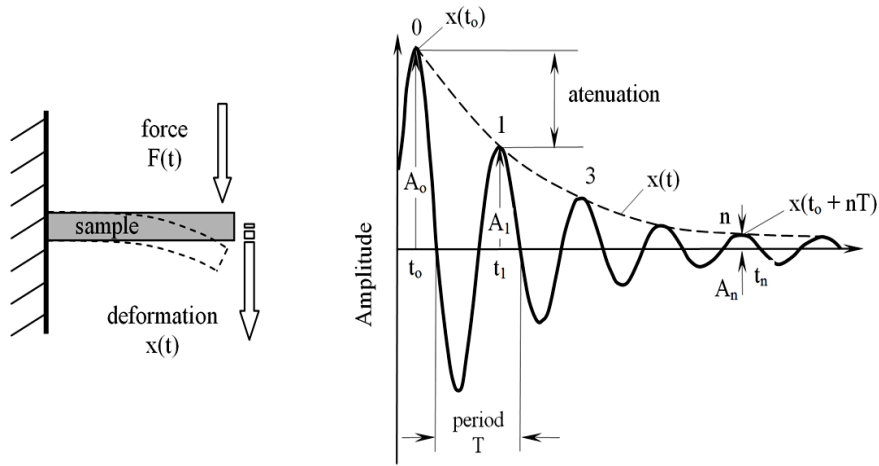


Fig. 1 Basic elements of an attenuation curve used for calculation the internal friction

The A_0 amplitude associated with the initially induced deformation is attenuated over time until the oscillation finally it gets annulated. The internal friction can be further on calculated taking into account the initial and final amplitude as well as the number of oscillation, as follows:

$$Q^{-1} = (1/\pi n) \ln (A_1/A_n)$$

Depending on frequency, several mechanisms are considered to lead to the changes in the internal friction among which: changes in the orientation of defect pairs, grain boundary viscosities, twin boundary viscosity, displacement of interstitial atoms, thermoelastic phenomena or exchange of thermal energy between the grains.

The martensitic phase transition in the shape memory alloys is a thermoelastic transformation that develops between a low temperature phase - martensite (M) and a high temperature phase - austenite (A). Since the phase transformation is thermoelastic, developing between austenite starts (A_s) and finishes (A_f) temperatures on heating and between martensite starts (M_s) and finishes (M_f) temperatures on cooling, the internal friction can be used as a tool for its investigation.

This work shows the experimental results obtained on investigation the internal friction of a Cu-Zn-Al alloys, using the forced oscillation method.

2 EXPERIMENTAL DETAILS

A Cu-Zn-Al shape memory alloy was manufactured after the elemental components were inserted in a quartz ampoule and melted in an induction furnace. Following melting, the resulting ingot was homogenized at 800°C for 24 hours and subsequently deformed during successive passes through a rolling device, with prior heating at 800°C.

The resulting strip, thickness of 0.5 mm, was solution annealed at 850°C and ice-water quenched, with typical martensitic structure observed by optical and electron microscopy. A one hour stabilization treatment was applied at 150°C, to reduce the the excess vacancies resulting from the quenching.

The internal friction was analyzed on heating and cooling using an AE 102 Acoustic Elastometer (Vibran inc.) that allows simultaneous determination of elastic modulus, internal friction and actuation of a cantilever-type sample. This is made in an RLC circuit by analyzing the change in distance of the free end of cantilever to an electrode, as shown in Fig. 1.

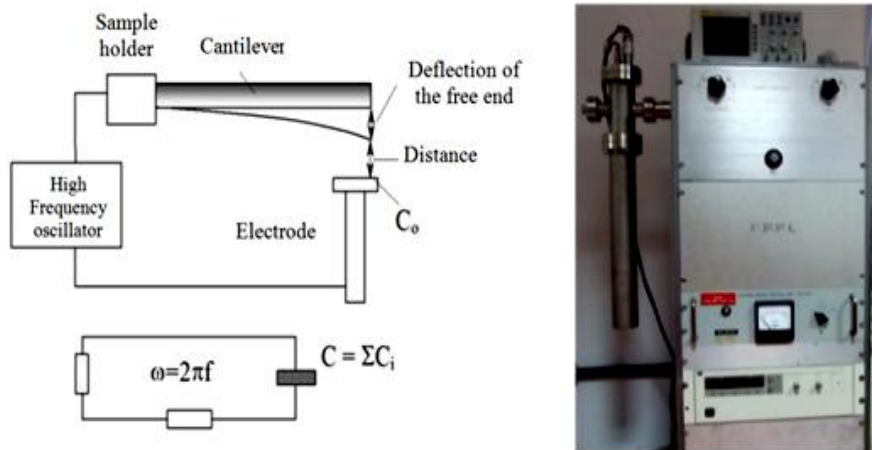


Fig. 2 The AE 102 Acoustic Elastometer principle and the equipment used in the experiments

The internal friction measurement system is composed of an oscillator, a sample holder, the cantilever to be measured and an electrode. The oscillation frequency (f) of the LC circuit can be expressed as a function of the total capacity C and inductance L :

$$f = \sqrt{\frac{1}{4\pi LC}}$$

The inductance of the circuit can be kept constant during measurement. Assuming that the change in the total capacity of circuit is only the result of change in the C_o capacitance (due to the change in the distance between the electrode and cantilever), it follows that the frequency “f” is a measure of the cantilever’s displacement.

The AE102 acoustic elastometer measurement system allows the automatic determination of resonance frequency of a cantilever type sample in the 80-93 MHz range. The deviation from the set values i.e. a lower frequency than 80 MHz means that the sample is too close to the electrode and, conversely, a frequency higher than 93 MHz means that the cantilever free end is too far from the electrode. The internal friction measurement systems allows the possibility to control the excitation power of the cantilever, of the oscillation phase and the frequency filters to be used in the experiments while continuously monitoring the vibration signal.

Using the sinusoidal forced oscillations applied to the cantilever, sample is forced to oscillate with the same frequency as the imposed one, however, due to the dynamical process a phase difference Δt is recorded between the applied and resulting signal. The internal friction is given by the $\tan \delta$ in fig., with the following relationship between the parameters that characterize the phase shift δ and logarithmic decrement Δ : $Q^{-1} = \Delta/\pi = \tan \delta$

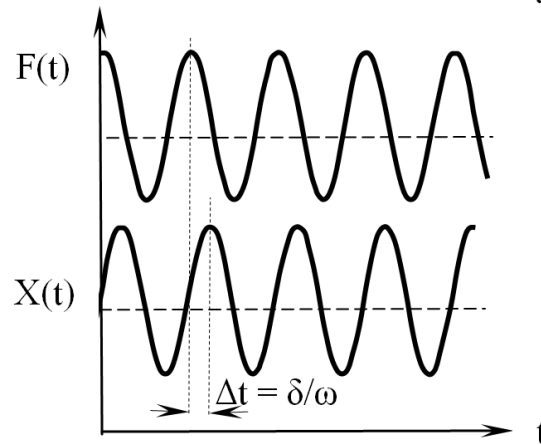


Fig. 3 Details of the forced oscillation elements to determine the internal friction

The system allows the heating and cooling in high vacuum, with the internal friction values for a given temperature (T) determined automatically, as a function $Q^{-1} = f(T)$. Thus the changes of the internal friction vs. temperature can be analyzed to identify the changes in the slopes that would reflect the martensitic transformation occurring in the cantilever.

3 EXPERIMENTAL RESULTS AND DISCUSSIONS

The chemical composition of the Cu-Zn-Al alloy, determined by energy dispersive X-ray spectroscopy is detailed in Table 1.

Table 1 Chemical Composition of the sample analyzed in this study

Cu-Zn-Al Alloy	Cu	Zn	Al
[wt%]	69.03	27.82	3.15

The composition is located in the range of the shape memory alloys in the Cu-Al-Zn system []. The room temperature

microstructure of the Cu-Zn-Al alloys is shown in Fig. 4 and emphasizes typical martensitic variants at the grain boundary.



Fig. 4 Typical microstructure observed for the Cu-Zn-Al alloy
The internal friction (Q^{-1}) as a function of temperature of the Cu-Zn-Al cantilever type sample is shown in Fig. 5.

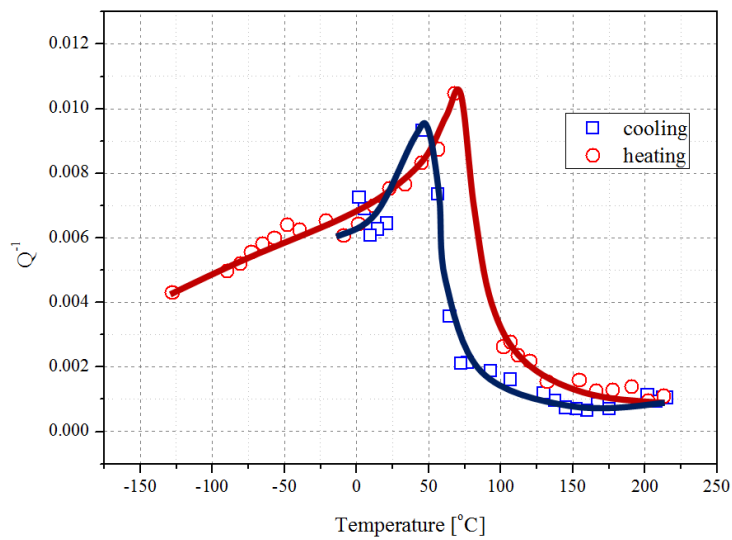


Fig. 5 Internal friction vs. temperature spectra of the Cu-Zn-Al cantilever-type sample

In terms of damping behaviour the shape memory alloys three distinct regions can be observed on damping vs. temperature curve, i.e.:

- The parent phase temperature range ($T > A_f$), characterized by low internal friction values and consequently a low damping behaviour with limited potential for practical applications
- The martensitic phase range ($T < M_f$) is characterized by higher damping, related to the mobility of interfaces between the martensite variants.
- The martensitic transformation range ($M_s > T > M_f$ and $A_s < T < A_f$) is characterized by an increase of up to 10 times compared with the values observed in the martensitic state. The presence of the two phases, i.e. martensite and parent phase add to the number of interfaces to be counted since martensite/austenite interface also plays a role. On heating, first the the internal friction increases as the austenite phase forms, thus increasing the number of interfaces in the microstructure that are capable of dissipating energy. On further heating following reach of the internal friction peak, the number of interfaces is decreasing as less martensite is available for transformation and less martensitic variants are present in the microstructure. While the transformation of martensite into austenite is closer to its completion, the lack of interfaces in austenite as well as the disparition of martenite and its variants lead to the decrease in the internal friction.

The $Q^{-1}(t)$ spectra is typical, with the main elements present as they have been identified by Van Humbeeck [5], i.e. the intrinsic component Q^{-1}_{int} that reflects the contribution of each

phase, the phase transformation component Q_{PF}^{-1} associated with the transformation mechanisms and the phase transformation kinetic component Q_{KPT}^{-1} influenced by the temperature variation rate.

4 CONCLUSIONS

The analysis of the internal friction allows gathering of useful information concerning the damping capacity of noises and vibrations and conditions for the optimal properties, but also as a valuable tool for characterization the martensitic transformation in the shape memory alloys.

The use of internal friction for characterization the phase transformation in the Cu-Zn-Al shape memory alloy was exemplified for the cantilever type sample, using flexural oscillations. The main martensitic phase transformation zones were well individualized on the internal friction vs. temperature spectrum for the Cu-Zn-Al sample, indicating - as expected - a damping maxima in the phase transformation region where the number of interfaces (i.e. in martensite and between martensite and austenite) is the highest.

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ORIGINAL SCIENTIFIC PAPER

Field: Materials

PHYSICO-MECHANICAL CHARACTERISATION OF Cu-Zn-Al SHAPE MEMORY ALLOY

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Abstract

Results of physico-mechanical and metallography investigation of Cu-Zn-Al shape memory alloy with room temperature of martensitic transformation are shown in this paper.

Keywords: Cu-Zn-Al alloy, shape memory effect, martensitic transformation

1 INTRODUCTION

The effect of a shape memory is ability of some metals and alloys deformed in martensite state or at temperature interval of martensitic transformation to regain their original shape during the heating process due to a complete or almost complete absence of deformation [1,2].

The heating process causes restoration of crystals in the high-temperature phase called beta or parent phase and the removal of plastic deformation. At the same time, all physical and mechanical properties are restored.

During the shape recovering process, the alloys can produce a displacement or a force, or combination of the two, as a function of temperature. The starting force of recovering shape process is difference between free energies of parent and martensitic phases during the reverse transformation. The complete

shape recovering is only notice if the martensitic transformation is crystallography reverses and if the deformation process is done without plane shearing [2,3].

Shape memory effect has been studied for many binary and ternary alloys, as well as for some pure metals. However, wide application can be found only for the nitinol (Ni-Ti alloys) and copper-based alloys that show the shape memory effect.

Copper-based alloys, compared to the nitinol alloys, possess somewhat lower mechanical properties due to their larger grain size and elastic anisotropy [4]. But, they can be improve, considerably without deterioration of a shape memory effect, by small grain, method of rapid solidification, sinter metallurgy or by adding the elements such as Zr, V, B, Ti, Cr, etc. [5].

In this paper, the results of the physico-mechanical and metallography characterisation of Cu-Zn-Al shape memory alloy with room temperature of martensitic transformation, as well as investigation of hysteresis of the alloy are shown.

2 EXPERIMENTAL

The Cu-Zn-Al shape memory alloys are usually obtained by classical method of melting, casting and manufacturing. Generally, all alloys with martensite structure have heavy plastically deformation, which consists of a few cycles of rolling at hot and drawing at cold with series of intermediate annealing treatments, from ingots to rods and wires of small cross-section. However, it is necessary to keep the chosen composition of alloy during the production process, which is difficult by zinc evaporation during casting process. Also, plastically deformation of these alloys is heavy, with a lot of operations of rolling, drawing and intermediate annealing treatments.

Because of that, the Cu-Zn-Al shape memory alloy is obtained using the technology of continuous casting of wire and profiles of small diameters, which is developed in the Mining and Metallurgy Institute Bor for some pure metals [6].

The principle of this method of continuous casting is used the procedure of crystallization above the melt for directly ob-

taining of the copper-based shape memory 8 mm wire. The principle of technology is as follows [6]: The cooler for copper-based shape memory wire casting is dipped into the melt. The protection shell made of heat-resistant material, which does not react with molten alloy and layer of heat-insulation material, protect the cooler from the influence of melt and high temperatures. Hydrostatic pressure of surrounding melt drives the molten alloy into graphite crucible. The molten alloy hardens in the crucible by heating exchange through the primary part of crystallizer, which is water-cooled. Hardened wire leaves graphite crucible at high temperature. Vacuum is used to prevent the oxidation of cast wire caused by high temperature on its surface.

Apart from the above mentioned role, vacuum serves also for provision the required differential pressure inside cooler, which enables penetration of molten alloy into graphite crucible. For prevention of oxidation of cast wire after leaving the cooler, temperature on its surface should be below 60°C.

3 RESULTS AND DISCUSSION

After obtaining of 8 mm wire with chemical composition for Cu-Zn-Al alloy: Cu-69.7%, Zn-26.3% and Al-4%, the samples of wires are treated in the aim to obtain the wire of 1.8 mm with the shape memory effect as follows: 2h of homogenization at 800°C in low oxidation atmosphere, then drawing to the dimension 4x4, with thermal treatment: 15 min of annealing at 400°C, quenching in water, 120 min annealing at 550°C, cooling in furnace to 450°C and air cooling and drawing to the dimension 1.8 mm.

In the aim to reach the martensite structure, the samples are heating 5 min in nitrogen atmosphere at 800°C and quenched in cold water and the alloy was memorized in the martensite state.

In the aim to determine the characteristics of obtained Cu-Zn-Al shape memory alloy, investigations of mechanical properties and metallography are done. The obtained results are shown in Table 1 and Figs 1-6.

Table 1 - Results of physic-mechanical properties

N ^o	Condition of materials	Toughness	Hardness
		J/cm ²	HV
0	As-cast condition	20	314
1	Hot-rolled at 850 ^o C	40	354
2	Annealing at 850 ^o C (10 min), quenched in water	34	379
3	Annealing at 900 ^o C (10 min), quenched in water	33	368
4	Annealing at 850 ^o C (10 min), quenched in water + ageing at 400 ^o C (1h) + air cooling	22	492
5	Annealing at 850 ^o C (10 min), quenched in water + ageing at 450 ^o C (1h) + air cooling	16	475
6	Annealing at 850 ^o C (10 min), quenched in water + ageing at 500 ^o C (1h) + air cooling	26	448
7	Annealing at 850 ^o C (10 min), quenched in water + ageing at 450 ^o C (1h) + cooling in furnace	21	454
8	Annealing at 900 ^o C (10 min), quenched in water + ageing at 400 ^o C (1h) + air cooling	20	504
9	Annealing at 900 ^o C (10 min), quenched in water + ageing at 450 ^o C (1h) + air cooling	19	478
10	Annealing at 900 ^o C (10 min), quenched in water + ageing at 500 ^o C (1h) + air cooling	18	464
11	Annealing at 900 ^o C (10 min), quenched in water + ageing at 450 ^o C (1h) + cooling in furnace	23	479

According to the results of mechanical investigation shown in Table 1, it is noticed that the optimal characteristics of alloy are obtained for the following state of materials: annealing, quenched in water, ageing at 400^oC 1 hour, and then air cooling.

This conclusion is verified by metallography, Figs. 1-6.

Microstructure of cast alloy consists of a lot of big bright crystal α -solid solution in the dark basically β -crystals (Fig. 1). In appearance, this structure corresponds with the martensite structure with notable locality Widmanstatten structure. This structure is not favourable for cold plastic deformation, because the present struc-

ture is very brittle, and therefore the only possible deformation is at elevated temperatures.



Figure 1 *Microstructure of as-cast alloy, (x960)*



Figure 2 *Microstructure of alloy, hot deformed (x960)*



Figure 3 *Microstructure of alloy, annealed at 850°C for 10 min and water quenched (x960)*

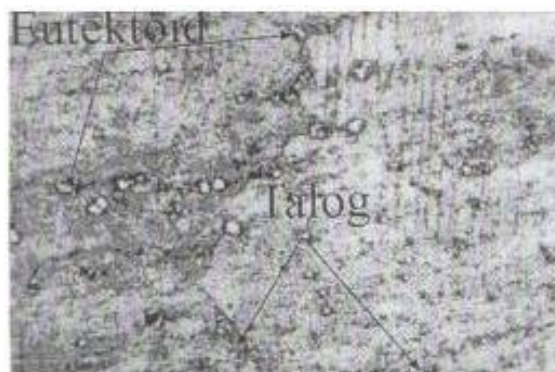


Figure 4 Microstructure of alloy, annealed at 900°C for 10 min and water quenched (x960)



Figure 5 Microstructure of alloy quenched from 850°C and aged at 400°C for 1h (x960)



Figure 6 Microstructure of alloy quenched from 900°C and aged at 400°C for 1h (x960)

Hot-processed alloy sample consists of bright crystals of α -solid solution surrounding the crystals of dark β -phase. Between the crystals of α -solid solution in the dark based β -phase particles extracted notice precipitate, but in a very small volume shares (Fig. 2). Compared to the as-cast structure, the microstructure is somewhat finer, because the α -solid solution is better deployed in the β -base as a result of deformations in hot condition.

The microstructure of annealed state of alloy is given in Figures 3 and 4. It is noted that the large polygonal grains formed with the present of eutectoid and precipitate deposited on the grain boundaries. Due to higher temperatures (Fig. 4), there was a complete transformation of martensite structure.

Microstructure of the alloy aging state consists of the large polygonal grains with separate participate and eutectoid on the grain boundaries. In the sample of alloy that is quenched in water from 850°C, the appearance of residual martensite structure with a fine needle was observed (Fig. 5), while the sample quenched from 900°C and subsequently ageing at 400°C, the presence of residual martensite and eutectoid was noted, but there has been a phenomenon of thermal deposition on the grain boundaries and within each grain (Fig. 6). In this sample, martensite structure with Widmanstätten schedule was observed, since the α -solid solution was separated in the form of martensitic needles.

4 CONCLUSION

Establishing a correlation between the state of the material, microstructure and mechanical properties it can be concluded that the combination of thermo-mechanical processing regime, can achieve such a state of the material that provides the good mechanical properties.

By reducing the particle size α -solid solution of hot processing increases the hardness and impact toughness compared to the as-cast state.

Heat treatment of hot-processed alloy increases the hardness, while the impact toughness gradually decreases as the microstructure can be explained by the appearance of brittle phases, as a result of thermal deposition.

Optimal properties are obtained for the condition of material that was subjected to the heat treatment according to the following scheme: annealing at 850 °C and 900 °C (10 min) + quenched in water + aging at 400 °C (1 hour) + air cooling.

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ORIGINAL SCIENTIFIC PAPER

Field: Materials

RESISTANCE TO CAVITATION EROSION OF AMPCO 45 (CuAl10Ni5Fe2.5Mn1) DEFORMABLE BRONZES

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Abstract

This paper analyzes the behavior of cavitation erosion of a special bronze used for manufacturing of marine and fluvial ships propellers. Cavitation tests were conducted on a vibrating device with piezoceramic crystals in accordance with ASTM G32 - 2010. The cavitation erosion behavior was carried out based on the variation curves of MDE cavitation parameters (mean depth of erosion) and MDER (mean depth of erosion rate) with test duration. After cavitation the surface topography and structural changes occurred at the marginal layers were investigated using the optical and scanning electron microscopy, thus justifying the mechanism through which the surface degrades under the impact of microjets generated by the implosion of the cavitation bubbles.

Keywords: *cavitation erosion, special bronze, microstructure*

1 INTRODUCTION

It is known that the sail speed presents a great interest for the manufacturers of marine and fluvial ships. The cavitation phenomena occurred on surface of propellers cause local material loss leading to reduced operating performance and even to failures. Therefore, most research laboratory aim to study the hydrodynamic cavitation, thus the formation and development of cavitation on the propeller blade [1-4]. Since most propellers of

large sea and river ships, used for goods transportation and leisure trips, are made of stainless steel and special bronzes [5-8], it is important to know the degradation mechanisms and ways to improve cavitation erosion behavior to increase their lifetime. AMPCO 45 bronze is a material widely used in systems working with liquids and hydraulic machines, possessing high mechanical characteristics both at high and low temperature, good refractory and high corrosion and wear resistance.

This paper aims to analyze the cavitation erosion behavior of AMPCO 45 bronze by highlighting the surface degradation mechanism influenced by the microjets impact which occurs after the implosion of cavitation bubbles.

2 MATERIALS, EXPERIMENTAL PROCEDURES AND DATA PROCESSING

The material studied in the present work has the chemical composition presented in Table 1, its mechanical characteristics at ambient temperature are shown in Table 2.

Table 1. Nominal chemical composition

Symbol	Al [%]	Ni [%]	Fe [%]	Mn [%]	Other [%]	Cu [%]
AMPCO 45 (CuAl10Ni5Fe2.5Mn1)	10.0	5.0	2.5	1.0	Max. 0.5	Balance

Table 2. Average values of mechanical characteristics, in delivery state

Symbol	Hardness HB	Yield strength $R_{p0.2}$ (N/mm ²)	Tensile strength, R_m (N/mm ²)	Breaking elongation A_5 (%), Longitudinal
AMPCO 45 (CuAl10Ni5Fe2.5Mn1)	226	512	811	14,8

Using the above presented material, specimens for structural analysis and cavitation erosion tests were prepared. The investigation of the cavitation erosion was conducted on a standard apparatus with piezoelectric crystals (Figure 1) which belongs to the Cavitation Laboratory of University Politehnica Timisoara respecting fully the ASTM G32-2010 provisions [12]. The apparatus allows an automatic control of the cavitation hydrodynamic process [9-11].

The functional parameters of the apparatus with piezoelectric crystals are: the power of electronic generator of ultrasounds: 500W; vibration frequency: $20000 \pm 2\%$ Hz; double vibration amplitude: 50 μm ; sample diameter: 15.8 mm; power supply: 220 V/50 Hz; temperature of working liquid: $22 \pm 1^\circ\text{C}$; Prior testing, the specimens surface (frontal) was polished to a roughness of $R_z = 0.063 \mu\text{m}$.



Fig. 1 *Vibration apparatus with piezoelectric crystals*

The test method involves mounting the specimen on the sonotrode and their immersion to a depth of 5-10 mm, in potable or distilled water (depending on the requirements imposed for

the testing liquid [11], which is at 20-22°C) thereupon the cavitation attack starts with a total period of time of 165 min, divided into 12 intermediary periods: one of 5 and 10 minutes and 10 periods of 15 minutes each. At the end of each intermediary period, after the end of scheduled testing time for cavitation, the specimen is washed in bi-distilled water and acetone, dried and gravimetric measured using an analytical balance in order to determine the mass loss resulted after cavitation erosion. Also, after each intermediate attack the damaged surfaces are investigated by the optical and scanning electron microscopy to reveal the evolution in time of material structure degradation. At the end of 165 minutes of cavitation attack, the samples are cut longitudinally into two halves, mounted in resin and polished in order to study the structural changes after the impact of micro-jets and shock waves generated by the implosion of cavitation bubbles.

In addition, surface roughness measurements were carried out after testing each set of specimens.

3 EXPERIMENTAL RESULTS

In order to analyse the cavitation erosion behaviour by drawing the experimental values approximation curves, obtained for three specimens, the average value of mass loss was calculated for each mediate period during the test. By means of mean mass loss the experimental values of mean depth erosion (MDE) were determined and also the medium depth of erosion ratio (MDER). Figure 3 presents the two specific curves representing the bronze behaviour exposed to the erosion produced by vibrating cavitation.

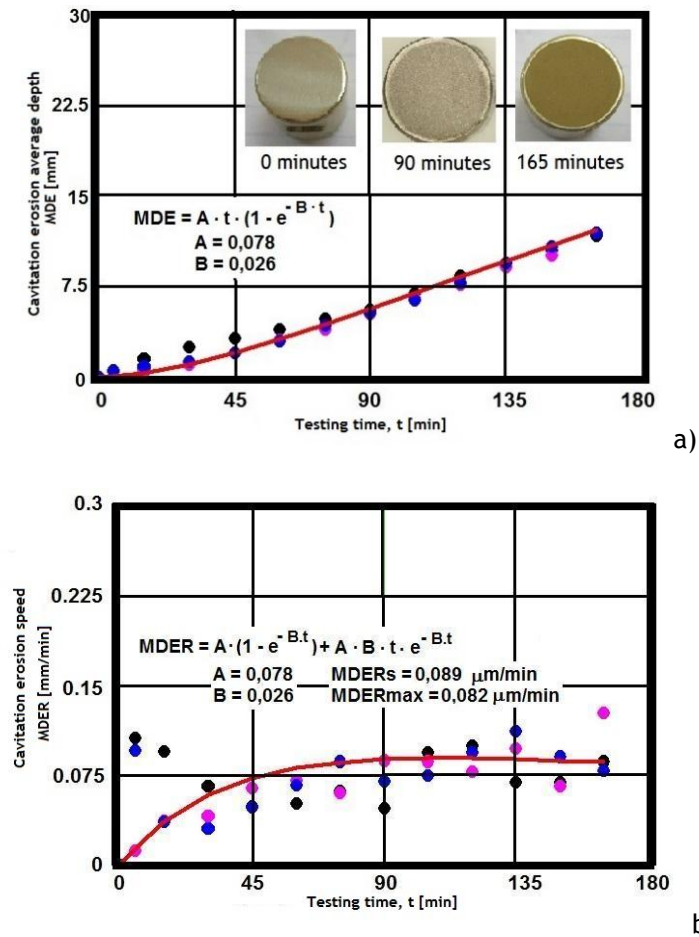


Fig. 2 Specific curves of cavitation resistance a) evolution of cavitation erosion average depth function of time and b) evolution of cavitation erosion speed function of time

Analysing the two graphs it might be observed a good approximation of experimental points by the analytical constructed curves. In order to highlight the evolution of erosion in the exposed surface to cavitation attack, Figure 3 presents the surface images of one of three samples at three characteristic times (0, 90 and 165 minutes).

The dispersion of experimental points, in both diagrams from Figure 3, shows that the cavitation erosion is a phenomenon with

a non-uniform nature; each of three samples, obtained from the same bar, behaves slightly differently than the other two samples. The evolution of mean depth erosion curve (MDE) presented in Figure 3a, shows that since the 45th minute the shape tends to a linear one, which means, practically, that from this moment the behaviour of bronze is the same until the end of cavitation test. In fact, the same phenomenon is observed for all three samples in Figure 3b. Differences between the experimental values, whether we refer to the mean depth erosion (MDE) whether we refer to the erosion average penetration speed (MDER), are small, proving structural homogeneity and uniform distribution of the mechanical characteristics on surface and material core. This dispersion mode is specific to materials with high resistance to cavitation erosion. Also, the small differences between the maximum value of MDER parameter (0,089 $\mu\text{m}/\text{min}$) and the one towards it tends to stabilize (0,082 $\mu\text{m}/\text{min}$) shows that the studied bronze is part of materials with very good resistance to cavitation erosion and it might be used in the manufacture of highly stressed parts at cavitation, such as ship propellers.

Higher differences between the experimental points and those from the approximation curve, until the 15th minute (Figure 3b), it is caused also due to abrasive dust and roughness of the surface, expelled during the test, which is why this cavitation attack interval, usually [3, 9] it is not analyzed from the point of view of material behaviour, being heavily dependent by the washing degree and cleaning of the specimen, before the cavitation test start.

The images shown in Figures 4 and 5 highlight the particularities of the mechanical degradation of the surface after the test for material state processed by hot plastic deformation. The microstructure of the base material consists essentially of a solid solution α and a reduced proportion of eutectoid $\alpha + \gamma'$. Since the solid solution imprints a good plasticity, and the eutectic increases the mechanical strength characteristics, it is expected that the initiation of cavitation phenomena will start at the interface of two structural constituents and continue with structural

plunging grains of solid solution. This fact is clearly seen from the images presented in Figure 4. In addition, scanning electron microscopy (Figure 5) highlights the formation of annealing twins and cavitation in the first place of solid solution grains.

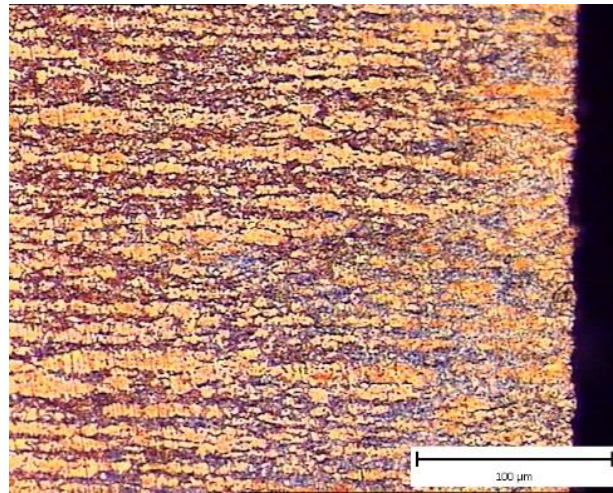


Fig. 4 Optical micrograph of a longitudinal section exposed to cavitation 165 min (x 200)

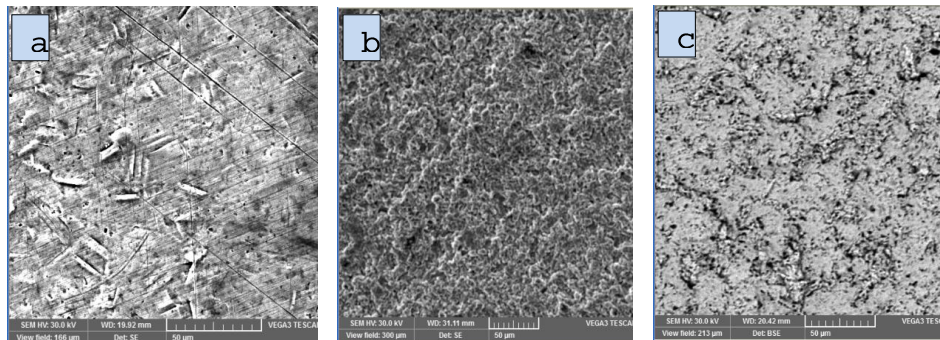
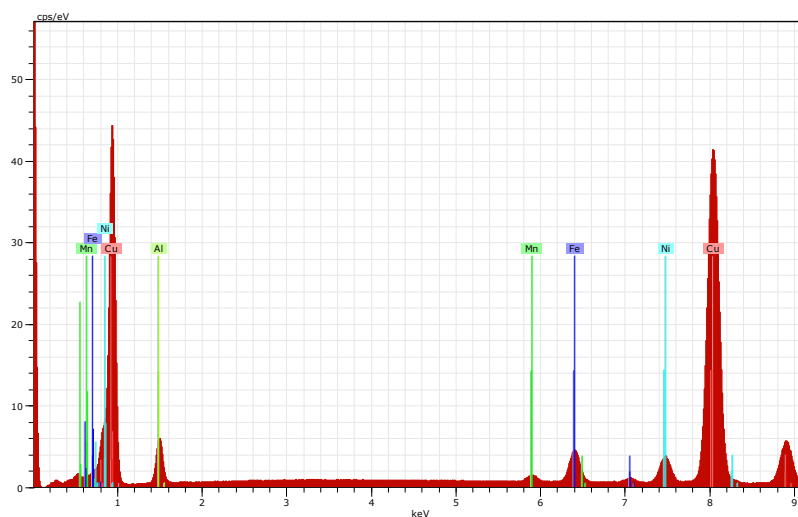


Fig. 5 Scanning electron micrographs of specific areas

EDX analyses, conducted on specimen surface (Figure 6) beside the scanning electron microscopy confirms that the degradation phenomenon of cavitation is uniform and does not cause changes in the chemical composition of material.



Spectrum: Acquisition

Element	Series	unn. [wt.%]	C norm. [wt.%]	Atom. [at.%]	Error (1 Sigma) [wt.%]
Aluminium K-series		8.96	8.68	18.12	0.48
Copper K-series		84.33	81.74	72.45	2.09
Manganese K-series		0.82	0.80	0.82	0.05
Iron K-series		3.89	3.77	3.80	0.12
Nickel K-series		5.17	5.01	4.81	0.15
Total: 103.17 100.00 100.00					

Fig. 6 EDX spectra and quantification at the surface of the tested specimen after 165 min

Typical surface topographies of specimens subjected to cavitation tests after 165 minutes (Figure 7) shows that the cavity depths are very fine and uniformly distributed ($<10\ \mu\text{m}$). They are determined by α solid solution ex-grains which possess a lower microhardness and of the grains boundaries, which contain a high density of crystal lattice defects. Colonies of mechanical eutectic mixtures with higher microhardness appear in relief.

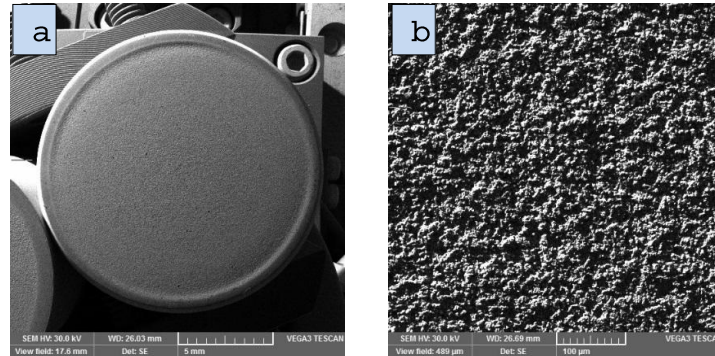


Fig. 7 Images of surface exposed to cavitation after 165 min; a) x8; b) x 300

4 CONCLUSIONS

The low standard deviation, obtained from statistical analysis, show that the AMPCO 45 bronze behaved almost evenly throughout the cavitation attack.

The evolution of approximation curves of experimental data points and reduced dispersion, from the corresponding points of the three samples, suggests that the analysed bronze is homogenous from structural point of view with similar behaviour and resistance compared to the materials with very good resistance to cavitation.

The microstructure of plastic deformation is mainly made of a solid α solution and a low amount of eutectoid $\alpha + \gamma'$. Since the solid solution α imparts a very good plasticity and the eutectoid increases the mechanical strength characteristics, the cavitation phenomenon starts at the interface between two structural constituents and continues by plunking the grains from solid solution.

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- [12] *** Standard Test Method for Cavitation Erosion Using Vibratory Apparatus ASTM G32-2010

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