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ORIGINAL SCIENTIFIC PAPER

Field: Materials Science

CRITICAL ISSUES IN ASSESSMENT THE CORROSION AND BIOCOMPATIBILITY OF SHAPE MEMORY ALLOYS IN VIEW OF THEIR USE IN MEDICAL APPLICATIONS

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Abstract

Shape memory alloys are materials with unique properties and some of their compositions can be used in biomedical applications. An analysis of corrosion and biocompatibility in view of materials selection for biointegration is made on the basis of assessment the most important issues related to the implant materials. The study of several alloys families, including the recent Ni-free shape memory alloys is presented.

Keywords: shape memory alloys, biocompatibility, corrosion, application

1 INTRODUCTION

Biocompatibility is an important property of several materials used in the medical sector. According to Williams, biocompatibility is "the ability of a material to perform with an appropriate host response in a specific application" [1].

On the other hand, the use of materials in biomedical applications also related to the type of device and its position in or outside the human body. Classification that differentiates between the main types of contacts between the materials and human body is detailed in Fig. 1 (adapted after K. R. St. John [2]):



Fig. 1 Biocompatibility classification based on the Body-type contact [2]

Metals are used for many years for medical treatments implying contact with or insertion in the human body. They have been considered as a natural solution even before the biocompatibility became a concern, with corrosion affecting the integrity of the implant and hampering its role. Over time, corrosion-resistant steels were developed and are still extensively used in biomedical applications, although CoCrMo show better wear resistance, while Ti based alloys, with lower density are nowadays metals of choice for many implants. In dentistry, the need to easily manufacture the complex shapes, with peculiar properties (e.g. amalgams). An overview the metallic materials used in various medical applications, exemplified in Table 1, was presented by Hermkwan et al. [3]. CRITICAL ISSUES IN ASSESSMENT THE CORROSION AND BIOCOMPATIBILITY OF SHAPE MEMORY ALLOYS IN VIEW OOF THEIR USE IN MEDICAL APPLICATIONS

	•	
Division	Example of implants	Type of metal
Cardiovaccular	Stent	316L SS; CoCrMo; Ti
Cardiovascular	Artificial valve	Ti6Al4V
Orthonadic	Bone fixation (plate, screw, pin)	316L SS; Ti; Ti6Al4V
Orthopaedic	Artificial joints	CoCrMo; Ti6Al4V; Ti6Al7Nb
Dontista	Orthodontic wire	316L SS; CoCrMo; TiNi; TiMo
Dentistry	Filling	AgSn(Cu) amalgam, Au
Craniofacial	Plate and screw	316L SS; CoCrMo;Ti; Ti6Al4V
Otorhinology	Artificial eardrum	316L SS

 Table 1 Overview of metallic materials used in biomedical applications [3]

A special category of metallic materials for biomedical applications are the shape memory alloys. Shape memory alloys are multifunctional materials with extraordinary properties that are not commonly observed together in other materials, like: one way and two way shape memory effects, superelasticity, damping capacity, ferromagnetism. Some alloy families even show the biocompatibility and they are currently used in increasing number for applications inside and near the human body.

2 METALLIC MATERIALS FOR BIOMEDICAL APPLICATIONS

An analysis of the main classes of materials with respect to their biological compatibility is shown in Table 2. It identifies the main metals and alloys, used in biomedical applications.

DIDIOgical		Class of materials	
compatibility N	letals	Ceramics	Polymers
Gold			Polyethylene
Cobalt-chro	omium alloys		Polyamide
Biotolorant Stainless st	eels		Polymethylmetacrylate
Zirconium			Polytetrafuorethylene
Niobium			Polyurethane
Tantalum			
Bioinert Commercia	lly pure Ti	Aluminium oxide	
Ti alloys (T	i-6Al-4V)	Zirconium oxide	
		Hydroxyapatite	
		Tricalcium phosphate	
		Calcium	
Bioactivo		pyrophosphate	
bloactive		Fluorapatite	
		Carbon: vitreous,	
		pyrolitic	
		Bioglass	

Table 2 Biological compatibility of main classes on materials

In terms of properties needed for medical applications that can be used for the preliminary selection (not involving direct interaction with the human body), the main ones that need to be considered are:

- Mechanical properties (strength, stiffness, fatigue) depending on the specific application and can be adjusted within certain limits through thermal and thermomechanical treatments. Pure metals are not often used because their mechanical properties are significantly weaker than the ones of the alloys they are part of. The use of metallic materials is the primary choice for applications that need high mechanical properties.

In terms of mechanical properties, an example of metallic materials that are used in biomedical applications, is shown in Table 2 [4].

Atribute	Stainless Steel	Cobalt- Chrome	Titanium	Nitinol
Strength	Medium	High	High	High
	(300/560MPa)	(600/1140MPa)	(880/950MPa)	(500/1400MPa)
Stiffness	High	High	Moderate	Very low
	(200 GPa)	(200 GPa)	(90 GPa)	(~20 GPa)
Fatigue	Good in load	Good in load	Good in load	Good in load
	control	control	control	control
Corrosion	Good - Cr ₂ O ₃	Good - Cr ₂ O ₃	Excellent - TiO ₂	Excellent - TiO ₂
	(500 mV)	(500 mV)	(800mV)	(800mV)
Other	MRI artifacts	L-605 is radiopaque	Can be radiopaque	Shape Memory

 Table 3 Selection table for the main metallic materials used in biomedical applications [4]

- Wear resistance for application implying contact with the other materials and body parts is a property that can be improved through the surface treatments, application of protective coatings to adjust the tribological properties in conjunction with the wear properties of the other parts the components gets into contact.
- Corrosion resistance is an extremely important property that can lead to release of corrosion products and can also be influenced

by the surface treatments, with the preliminary assessment that can be made based on galvanic series chart (Fig. 2 [5]). Corrosion is especially important because the corrosion products can affect the surrounding physiological environment and generate the additional corrosion-related issues. Some metals form (in natural or stimulated conditions) continuous passive films that prevent a direct interaction between metal and physiological environment, unless the protecting film is damaged. In addition, the pH of different environments of the human body is of high importance, for example the average pH of blood is 7/5-7.6; bones 5.5-7.5; saliva 5.5-7.5; in the mouth between 4.5 - 7.5 (depending on decays, 5-6.3 in the case of no decays).

- Radioopacity is influenced by the density and atomic number. For thinner or radiotransparent structures markers made out of gold, platinum, or tantalum are integrated in current implants to increase the radioopacity [6].



Fig. 2 Corrosion potential of several materials in seawater (redrawn after [6])

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One of the main characteristics of metals used in biological environments is release of metal ions. The toxicity of metal ions is reportedly analyzed based on the standard electrode potential ($E(\theta)$) and can be for assessment the potential of metals to be used in biocompatible applications, as shown in Fig. 3 [7].



Fig. 3 Evaluation of toxicity based on electrode potential [7]

Another important issue is related to the alergenic reactions that can affect people with a hypersensitivity to certain metal ions. Nickel, chromate, manganese, and molybdenum eluted from stainless steel stents are known to induce the allergic contact dermatitis, but also copper, zinc, palladium, cobalt, tin and even gold have been reported as leading to the allergic reactions in case of dental implants and prosthetis [8].

In summary, for being used in medical application, a metallic material should be at least chemically inert, not leading to the allergenic or carcinogenic reactions, to be sterilizable, radioopaque, easy to handle and cost effective. Examples of metallic materials and their properties, used in manufacturing implantable medical devices, are shown in Table 3 [9]. CRITICAL ISSUES IN ASSESSMENT THE CORROSION AND BIOCOMPATIBILITY OF SHAPE MEMORY ALLOYS IN VIEW OOF THEIR USE IN MEDICAL APPLICATIONS

AU C 11		
Alloy family	Reason for medical use	Some typical uses
Stainless	Fatigue strength, corrosion	Fracture fixation, stents, hip stems,
steels	resistance	spinal implants, cables
Cobalt base	Fatigue strength, corrosion	Joint replacement, stents, pacemaker
	resistance, wear	conductor wires, spinal disc
alloys	resistance	replacements, dental bridgework
Titanium	Fatigue strength, corrosion	Joint replacement, dental implants,
alloys	resistance, ability to bond	fracture fixation, spinal fusion
	to bone (osseointegration)	implants, spinal disc replacements
Nitinol	Shape memory	Stents
Tantalum	Corrosion resistance,	Porous structures for bone ingrowth, X-
Idildium	radiopacity	ray markers
Zirconium	Wear resistance of	loint ronlacomont
LIICOITIUITI	oxidized zirconium	Joint replacement
Distinum	Radiopacity, electrical	Bacomakor electrodos, guido wire
	properties, corrosion	marker bands, anounter soils
alloys	resistance	marker banus, aneurysm colls
	Corrosion resistance,	Crowns, inlays, guide wire marker
Gold alloys	radiopacity	bands

 Table 3 Metallic materials for use in biomedical implants [9]

3 ANALYSIS OF THE SHAPE MEMORY ALLOY FAMILIES IN VIEW OF THEIR BIOINTEGRATION

Among the shape memory alloy families, NiTi (Nitinol) is the most widely used one, both inside and in contact with the human body. A large number of application based on superelastic and shape memory effect have been developed and are currently successfully used.

A typical NiTi composition is shown in Table 4

Table 4 Typical Nitinol composition

Element	Weight %	
Nikel	55.79	
Titanium	43.98	
Oxygen	0.05 max	
Carbon	0.05 max	
Mn, Si, Cr, Co, Mo, W, V	<0.01	
Nb, Al, Zr, Cu, Ta, Hf	<0.01	
Ag, Pb, Bi, Ca, Mg, Sn, Cd	<0.01	
Zn, Sb, Sr,Na, As, Be, Ba	<0.01	
Fe	<0.5	
В	<0.001	

The presence of Ti in Nitinol favours the formation of TiO_2 on surface and provides the good corrosion and bicompatibility properties. The corrosion behavior of NiTi shape memory alloys is influenced by the surface condition that could influence the surface composition. According to SAES Smart Materials Inc., heat treatments and wire drawing may contaminate the surface and increase the pitting corrosion susceptibility, while mechanically polished or electropolished and then passivated parts, are highly corrosion resistant and have the ability to repassivate in the event of a small local destruction the passive film. In addition, galvanic effects may also influence the corrosion resistance if the Nitinol parts get in contact with materials that have strong galvanic effect (e.g. Au, Pt), in contracts with the case in which they are in contact with stainless steels, Ti or Ta.

In terms of biocompatibility Nitinol is considered to have similar biocompatibility properties as stainless steels. However, in spite of the fact that TiO_2 inhibits the release of additional components (especially Ni) as well as the electron exchange at the tissue-implant interface [10], Nitinol is still under suspicion for being potentially toxic or producing the allergic reactions due to the Ni content. Various studies have shown that formation of TiO_2 on surface of Ni-Ti reduces the exchange of Ni ions with biological medium, but the simple presence of Ni still raises serious concerns, especially since Ni release appears to be very high in the first stage of e implantation and the fact that an improperly prepared surface may further favour this release.

NiTi-based alloys are developed with the intention to modify the properties (corrosion resistance, transformation temperatures, hysteresis, radioopacity, etc.) through the addition of alloying elements like Cu, Zr, Hf, Pd, Ta. In some instances surface treatments are applied to modify the Ni content.

The addition of Cu is effective in shaping the hysteresis of transformation, however, at higher Cu content the release of copper may occur as well as cytotoxic effects can be observed. Zr and Ta improve the corrosion resistance, while Pd and Ta significantly improve the radioopacity.

In order to eliminate the concerns related to the presence and release of Ni from Nitinol implants, Ni-free shape memory alloys have been developed. Biocompatible shape memory alloys can form in Ti-based alloys and these observations could lead to a major turning point in the use of shape memory materials for biocompatible applications. Most of the current research has been focused on the alloy systems that are based on the metastable β -Ti alloys prepared as bulk materials and influence of the composition on occurrence the shape memory and related properties has been studied based on particular experiments.

Two main properties are sought in biocompatible shape memory alloys: the actual memory effect[s] and "superelasticity" and NiTi have these unique properties. Exploration of the new Ni-free biocompatible systems capable of replacing the NiTi shape memory alloys is important in enlarging the use of smart materials in biomedical applications.

It has been observed that several Ti-based alloy systems show favourable conditions for occurrence the stabilized β phase, such as Ti-X-Y (X= Mo, Nb, V, Ta, Sc; Y=Al, Si, Ge, Ga, In, Ag, Sn, Mo) biocompatible shape memory alloys, based and the influence of additional elements in ternary systems using combinations of α and β stabilizing components is of current interest. Baker reported the shape memory effect in a Ti-35 wt.% Nb (Ti-21.7 at.%Nb) alloy [11]. In fact, it has been shown that the martensitic transformation in β -type Ti alloys can lead to a disordered BCC- orthorhombic transition above a critical alloying content. In addition, the transformation temperature (often related to the body temperature) is an important factor for biocompatible phase transition materials, and alloying elements can be used in order to adjust the temperatures and preserve at the same time optimal properties. In addition, it has been shown that the texture can play an important role in increasing the apparent transformation strain [e.g. Fukui 2004 in Ti-Nb-Al alloys], and heat treatments can be effective in increasing the alloys properties.

Several Ti-based alloy families have shown the potential to become the next generation of biocompatible shape memory alloys. Among them the following systems have been considered in recent years:

- Ti-Mo-X (Ag, Sc, Sn, Ga, Nb). In Ti-Mo based alloys, it has been shown that the martensitic transformation temperature decreases with increasing Mo and Ga content [16] and composition and annealing parameters play an important role in increasing the critical stress for slip. The shape memory effect is related to the stress induced martensitic transformation and Sc addition (5-7%) significantly improves the shape recovery [12]. Recoverable strains as high as 3.5% have been achieved in Ti-9.7Mo-4Nb-2V-3Al suggesting a high potential for superelastic applications [13].

In addition, Ti-Mo-Nb-V-Al are claimed to have a good biocompatibility (assessed through cytotoxicity, acute irritation, systemic toxicity, rabbit pyrogen, indirect and direct contact hemolysis and short-term implantation) [14].

- Ti-Nb-X (Sn, Mo, Zr, Ta, Al, Ga). It has been shown that Ti-(22-27)at.%Nb alloys shape memory effect and/or superelasticity. Several additional elements as Zr, Ta, Al and O can be added to stabilize these properties. The stress and strain induced martensitic transformation is affected by the low critical stress for slip deformation resulted in only a small superelastic strain. The heat treatment condition also affects the shape memory and superelastic properties (up to 3% recoverable strain has been obtained in solution treated alloys, and aging at low temperatures can lead to an increase in the critical stress for permanent deformation). Texture is another element that has to be considered in Ti-Nb alloys (in Ti-22Nb-6Ta (at.%) alloy - the Young's modulus is lowest along the <100> and is highest along the <111> [15]; texture also play an important role in Ti-Nb-Al alloys in increasing the apparent transformation strain [16]).

Results on Ti-Nb-Zr showed the positive contribution of Zr on the typical shape memory and superelastic behaviour (fig. 5), with Zr contributing to the increase in maximum recovery strain, decrease of (*M*s) temperature (by 38K with 1 at.% increase of Zr content), while high Zr contents lead to disappearance the shape memory effect [17].

Tantalum can be also used to control the transformation temperature in Ti-Nb alloys, as well as the critical stress for permanent deformation. The use of alloying element is of high importance for decrease the transformation temperatures so that the transition range is in a suitable range for biocompatible applications. For example, Ta addition leads to 30K decrease in Ms temperature for every 1 at.% increase of Ta content in the Ti-22Nb alloy [18].

Ti-Ta-X based alloys. Ti-Ta with a composition range about 50% Ta show a shape memory effect with transition temperatures ranging in the 400-200°C. In order to be used in biocompatible applications, the transformation temperatures need to be reduced. Recent research showed that Ti replacement by Sn and especially Zr may lower the transformation temperatures [19].

Beside the set of properties especially sought in the Ti-based alloys, the additional properties to be used in additional applications can be identified. For example the <<multifunctional titanium alloy "GUM METAL" >> (Ti-36%Nb-2%Ta-3%Zr-0.35%O (mass%)) developed at Toyota Central R&D Labs., Inc.) shows an amazing set of properties achieved by cold working, such as: ultralow elastic modulus with high strength, super-elastic like nature, super-plastic nature permitting cold plastic working to 99.9% or more with no work hardening at room temperature, ultra-high strength of more than 2000 MPa near-zero linear expansion coefficient (Invar pro-perty) and constant elastic modulus (Elinvar property) over a wide temperature range from -200 C to +250 C (see also Fig. 7 for details) [20-23].

Concerning the biocompatibility of ferromagnetic shape memory alloys, so far only a few results are reported and - due to the different compositions - the results are different. Ni-Mn-Ga fe-rromagnetic shape memory alloys appear to show accelerated pi-tting when exposed for 12 hours to a 7.4 pH at 37°C. By contrast, the FePd ferromagnetic shape memory alloys appear to be biocompatible and even bioactive, when deposited as thin films [24].

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STUDY THE SUPERELASTICITY IN A BIOCOMPATIBLE ROOT CANAL NEEDLE MADE OUT OF NITI SHAPE MEMORY ALLOY

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Abstract

The NiTi shape memory alloys are usually used in biomedical applications. One of the most used properties is superelasticity, which allows large deformation with small changes of force and recovery the initial form after removing the applied force. The superelastic properties of a root canal needle are analyzed based on a compression test that leads to the buckling of the shape memory alloy needle.

Keywords: shape memory alloys, superelasticity, root canal needle

1 INTRODUCTION

Shape memory alloys based on Ti are materials with significant potential for use in biomedical applications, since they are capable of shape recovering following a plastic deformation and - in addition they show superelastic properties that associate large displacements with only a small change in the force exercised on the shape memory alloy component [1, 2]. In terms of biocompatibility, the NiTi shape memory alloys show biocompatibility [3] and a large number of applications have been developed overtime [4].

Beside the shape memory effects, these alloys also possess a number of associated properties, among which the most important in terms of the number of applications is a pseudoelastic behavior with the commercial name superelasticity [5]. This behavior is associated with the presence of a plateau on the stress-strain curve, thus in the superelastic range small changes of the applied force/stress are associated with large elongations/strains.

Medical applications of the shape memory alloys belonging to the NiTi family is increasing and such materials are used in complex applications - like endovascular surgery or in dentofacial orthopedics [5].

The aim of this work is to analyze the mechanical properties of a root canal needle when it is subjected to compression and to analyze its pseudoelastic region.

2 EXPERIMENTAL DETAILS

A commercial root canal needle was used for the experiments, with the scanning electron microscope image observed in a TESCAN Vega 3LM electron microscope. The Energy Dispersive X-ray Spectroscopy (EDX) analysis of composition was performed on the edge of root canal needle with a Bruker Quantax 200 system equipped with Peltier-cooled XFlash 410M silicon drift detector.

The needle was mounted in a fixture placed in a HZ-1004C Computer Servo Material Testing Machine (Fig. 1) that allowed us to study the effect of applied force with respect to the axial buckling of the root canal needle.



Fig. 1 Mounting of the root canal needle in testing machine

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The results are analyzed and in terms of the supereleastic behavior of the needle during its buckling when subjected to the axial compression.

3 RESULTS AND DISCUSSIONS

The low magnification scanning electron microscope image of the root canal needle is shown in Fig. 2, revealing its particular shape.



Fig. 2 Image of the root canal needle

Fig. 3 Localization of the area for EDX compositional analysis

The Energy Dispersive X-ray *Spectroscopy (EDX)* analysis of composition was carried out on the edge of the root canal needle, in the marked region in Fig. 3. The result of compositional analysis is shown in Fig. 4, with the corresponding Ni and Ti percentages.



	Total	99.82	100.00	100.00	
Titanium	K series	49.37	49.46	54.54	1.38
Nickel	K series	50.45	50.54	45.46	1.27
	Series	unn. C [wt.%]	nor. C [wt.%]	Atom C [at.%]	Error (1 Sigma) [wt.%]

Fig. 4 Details of the EDX analysis

The force - vertical displacement curve recorded as a result of compression and corresponding buckling of the root canal needle test is shown in Fig. 5.



Fig. 5 Result of the root canal needle test

The loading-unloading curve shows the characteristics typical for superelastic behaviour, with the presence hysteresis. On loading, the wire is in austenite state and it starts buckling when the pressing force exceeds 11N. Once the austenite-martensite phase transition in the needle develops, and the wire further buckles showing evidence of a plateau around 8.5 N on loading. and corresponding one around 5 N during unloading.

4 CONCLUSIONS

The analysis of a root canal needle showed a typical superelastic behaviour observed when compressive force was axially applied. A buckling occurred on a tip of the root canal needle, where diameter is also smaller.

The superelasticity occurred for a load of about 9 N and the corresponding loadin-unloading curve showed a hysteresis of about 4 N.

The results lead to the conclusion that such a root canal needle can have properties suited for the treatment of issues associated with root canals that are with significant sinusoids, due to a fact that they can be easily bent in the superelastic range to complicated shapes with minimum effort.

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ORIGINAL SCIENTIFIC PAPER

Field: Materials Science

MICROSTRUCTURAL CHARACTERIZATION OF MARTENSITE IN THE Cu-Zn-AI SHAPE MEMORY ALLOY

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Abstract

The Cu-Zn-Al shape memory alloy was manufactured, plastically deformed, heat treated and characterized in terms of structural and microstructural aspects.

Quenching in water, following heating at 850°C, lead to the observation of a typical martensitic microstructure, with twins revealed by optical and electron microscopy. The presence of martensite in the structure was further confirmed through the X-ray diffraction.

Severe plastic deformation lead to an increase of hardness compared to the undeformed samples, a more pronounced increase was observed for the quenched sample.

Keywords: shape memory alloys, Cu-based, CuZnAl, martensitic transformation microstructure

1 INTRODUCTION

The use of shape memory alloys (SMA) in practical applications is already recognized via a number of products used especially in medical field [1]. Several shape memory alloy families have been developed over time, with the most important one being the Nitinol (Nickel Titanium-Naval Ordnance Laboratory), a material with excellent properties but also with a very high manufacturing cost [2]. Over time, many other shape memory alloys have been developed in order to identify the new properties (e.g. ferromagnetism, improved biocompatibility, etc.) or reduced manufacturing costs (e.g. FeMnSi, Cu- based, Ni-Mn-Ga) [3-6].

The Cu-based shape memory alloys are represented by two main families: Cu-Zn-based, used in several applications, and Cu-Al-based that also shows the promising perspectives [7]. The transformation temperature range of CuZnAl SMA, is between -100 and 120°C, for compositions of 15-30% Zn and 3-7% Al, with copper as balance, while for Cu-Al-based SMAs the transformation temperature range is significantly higher.

The Cu-Zn-Al shape memory alloys are easy to manufacture by induction melting, with the melting temperature in the range of 950- 1020° C. The Young modulus is comparable for both states (72 GPa for austenite and 70 GPa for martensite), but the yield strength is about 80 MPa in martensitic and 350 MPa in austenitic state, respectively. The recoverable strain can reach up to 4-5% and transformation hysteresis is in the range of 15-25°C.

The main disadvantage of the Cu-Zn-Al alloys is due to the aging phenomena governed by diffusion that can occur in both austenitic and martensitic stage as well as fatigue.

This work reflects the joint results in developing and characterizing the copper-based shape memory alloys of the Mining and Metallurgy Institute in Bor and Politehnica University Timisoara.

2 EXPERIMENTAL DETAILS

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.

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Due to 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.

The principle of this method of continuous casting uses the procedure of crystallization above the melt for directly obtaining of the copper-based shape memory 8 mm wire. The principle of technology is as follows: 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 protecting the cooler from the influence of melt and high temperatures. Hydrostatic pressure of surrounding melt drives the molten alloy into a 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.

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 at 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 a furnace to 450°C and air cooling and drawing to the dimension of 1.8 mm.

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

Plate samples have been prepared for microstructural characterization. The equipment used for this purpose consisted of:

- Optical microscope Olympus BX 20, under polarized light;
- Scanning electron microscope TESCAN Vega 3LM;
- Energy Dispersive X-ray Spectroscopy (EDX) with a Bruker Quantax 200 system equipped with Peltier-cooled XFlash 410M silicon drift detector;

- X ray diffraction unit Panalytical X'Pert³;
- Rolling equipment for plastic deformation;
- Vickers Hardness Tester

The as-deformed samples were first heated up to 850° C, and then cooled in a combination of water and salt. A stabilization treatment was also applied by immersing the samples in boiling water.

The microstructure was analyzed to observe the martensitic structure both in polarized light as well as in the scanning electron microscope, where the composition of the Cu-Zn-Al alloy was also determined.

Samples were subsequently subjected to the plastic deformation with high deformation rates in the received and quenched states and the resulting samples were tested to observe the hardness variation in relationship to the deformation degree.

3 RESULTS AND DISCUSSIONS

The optical microstructure of the quenched samples is shown in Fig. 1, with a typical martensitic structure observed on the edge of sample.



Fig. 1 Optical microscopy microstructure obtained in polarized light for the quenched Cu-Zn-Al samples

The typical martensite twins were also observed on scanning electron microscope image (Fig. 2), while the elemental analysis detailed in Fig. 3 locates the manufactured alloy in the compositional range for the shape memory alloys in the Cu-Zn-Al system. The X-ray diffraction data collected for the quenched sample, showed in Fig. 4, indicates a predominantly martensitic structure, with the relevant peaks in the 40° to 45° 20 range.



Fig. 2 Scanning electron microstructure of the quenched Cu-Zn-Al alloy



Fig. 3 Details of the elemental analysis of the Cu-Zn-Al alloy, with: a. actual composition, b. EDX spectra recorded for the Cu-Zn-Al alloy



Fig. 4 X-ray diffract gram of the quenched Cu-Zn-Al sample

A severe plastic deformation with a 50% deformation rate of samples in the unquenched and quenched state lead to an increase in the HV0.3 hardness, both in the received and quenched state, with significantly higher augmentation in quenched state compared to the unquenched one (Fig. 5).



Fig. 5 HV0.3 hardness results of samples deformed by 50% in the quenched and unquenched states, respectively

For both states, the high rate deformation leads to significant deterioarations of thye samples integrity and further solutions are sough

(e.g equal channel angular pressure) to explore the effect of severe plastic deformation on thye structure and properties.

4 CONCLUSIONS

A Cu-Zn-Al shape memory alloy was manufactured, plastically deformed, heat treated and characterized in terms of structural and microstructural aspects.

Quenching in water, following heating at 850°C, lead to the observation a typical martensitic microstructure, with twins revealed by optical and electron microscopy. The presence of martensite in the structure was further confirmed through X-ray diffraction.

Severe plastic deformation lead to an increase of hardness compared to the undeformed samples, a more pronounced increase was observed for the quenched sample.

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ORIGINAL SCIENTIFIC PAPER

Field: Materials Science

SEVERE PLASTIC DEFORMATION OF COPPER VIA ACCUMULATIVE ROLL BONDING AND EQUAL CHANNEL ANGULAR PRESSURE

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Abstract

Experiments on severe plastic deformation of copper using the accumulative roll bonding and equal channel angular pressure are discussed. The influence of the applied deformation rate is highlighted, respectively the number of passes on microhardness and microstructure of deformed material. It is appreciated that there is a good relationship between the microhardness and microstructure obtained after deformation and that the increase of mechanical characteristics is a consequence of refinement the granulation because of following a severe plastic deformation.

Keywords: copper, microhardness, severe plastic deformation, accumulative roll bonding, equal channel angular pressing

1 INTRODUCTION

Severe plastic deformation (SPD) is a technique that is done with great efforts, without significant changes in overall dimensions of the workpiece [1-2]. Severe plastic deformation mechanisms leads to a nano-structuration of grain size of less than 30 nm and can be explained by the evolution of dislocations lines and grain boundaries [3-5]. Severe plastic deformation methods are capable of producing each one individual nano-structures [6-8]. Plastic deformation processes have reached the tech-

nologies border top-down (transforming the material) and bottom-up (material sintering), meaning nanotechnologies. Using the plastic deformation processes, one can get finished or semifinished parts which possess an ultrafine granulation (ultrafine grained metals), a structure that cannot be obtained by conventional methods.

In the Equal Channel Angular Pressing (ECAP) process, the severe plastic deformations are introduced into a material by forcing a sample (billet) with a piston through a die consisting of two channels of equal cross-section, which intersect at an angle between 90° and 120° [9].

Accumulative roll bonding (ARB) is a <u>severe plastic deformation</u> process. It is a method of rolling a stack of metal sheets, which is repeatedly rolled to a severe reduction ratio, sectioned into two halves, piled again and rolled. It has been often proposed as a method for production themetal materials with ultrafine grain <u>microstructure</u> [10].

2 MATERIAL, EXPERIMENTAL PROCEDURES AND DATA PROCESSING

The experiments were performed on cooper samples, with chemical composition presented in Table1.

 Table 1 Chemical composition of copper used in experiments:

Element	Cu	Fe	Si	Al	Zn	Mn
Content, wt.%	98.75	0.11	0.13	0.34	0.66	0.01

ARB and ECAP were utilised as the SPD methodes. Figure 1 presents 1 the ARB equipment, and Figure 2 the one used for the ECAP method. To specify that the equipment used for ECAP method, it was designed and realiyed and presented in Figure 3.



Fig. 1 The equipment used for severe plastic deformation via ARB

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SEVERE PLASTIC DEFORMATION OF COPPER VIA ACCUMULATIVE ROLL BONDING AND EQUAL CHANNEL ANGULAR PRESSURE







Fig.3 ECAP Device

The macroscopic image of the metallographically prepared samples after deformation is presented in Figure 4 (ARB method), and in Figure 5 the ECAP method.



Fig. 4 Metalographic samples ARB (L, l and S symbols are explained later)



Fig. 5 Metallographic sample ECAP

3 EXPERIMENTAL RESULTS

The resulting samples after SPD were subjected to the hardness HV0.3 tests and optical and electronic metallographic analysis. Table 2 and Figure 6 present the hardness variation as a fun-ction of the deformation rate applied (40, 60, 80, 90%) ARB met-hod, and Table 3 and Figure 7 present the hardness variation depending on the number of passes (ECAP method).

Commission to ma	Microhardness HV0.3					
Sample type	٨	Average				
Initial state						
S	114	116	122	117.33		
L	115	125	130	123.33		
l	126	120	122	122.67		
40% deformation grade						
S	115	127	123	121.67		
L	133	127	132	130.67		
l	139	142	138	139.67		
60% deformation grade						
S	139	135	137	137.00		
L	137	145	133	138.33		
l	140	153	141	144.67		
80% deformation grade						
S	146	147	140	144.33		
L	148	153	151	150.67		
l	143	150	156	149.67		
90% deformation grade						
S	150	142	146	146.00		
L	151	156	153	153.33		
l	156	156	150	154.00		

Table 2 Measured microhardness values



Fig. 6 Hardness variation as a function of the deformation rate for samples taken out of S L and l surfaces

 Table 3 Hardness variation following the ECAP passes

	Microhardness Cu HV0,3				
Sample type	Measured Values Average				
Initial state	119	121	122	121.33	
1 pass	139	143	141	141	
2 passes	160	168	163	163.66	
3 passes	174	181	176	177	
4 passes	185	187	184	185.3	



Fig. 7 Hardness variation following the ECAP passes

With increase of the applied deformation degree, namely the number of passes, the hardness increases.

In the case of ARB method, the microstructure evolution observed through optical microscopy, as a function of the apllied deformation degree, is shown in Figures 8, 9, 10, 11 and by SEM microscopy in Figures 12, 13, 14, 15.



Fig. 8 Microscopic images of samples before deformation (Samples S, L, l)



Fig. 9 Microscopic images of samples with 40 % deformation grade (Samples S, L, l)



Fig. 10 Microscopic images of samples with 60 % deformation grade (Samples S, L, l)



Fig. 11 Microscopic images of samples with 80 % deformation grade (Samples S, L, l)



Fig. 12 SEM images of samples before deformation (Samples S, L, l)



Fig. 13 SEM images of samples with 40 % deformation grade (Samples S, L, l)



Fig. 14 SEM images of samples with 60 % deformation grade (Samples S, L, l)



Fig. 15 SEM images of samples with 80 % deformation grade (Samples S, L, l)

Figures 16, 17, 18, 19 show the microstructures obtained depending on the number of passes (ECAP method).



Fig. 16 Microscopic images of the sample before deformation (a) curved zone (b) and exit (c) after the first pass



Fig. 17 2 passes Fig. 18 3 passes Fig. 19 4 passes

From presented images results occurs that with increasing the deformation degree (ARB method), and the number of passes (ECAP method) grain finishing occurs.

4 CONCLUSIONS

From the experimental results it can be observed that the SPD leads to the improvement of mechanical properties and structure modification. Microstructural analysis revealed that with increasing the degree of deformation (ARB method), respective the number of passes (ECAP method) increases the degree of refinement of the microstructure of analyzed material and improvement of mechanical characteristics. There is a good agreement between the measurement results of hardness and microstructures obtained in the case of copper using the ARB and ECAP methods of SPD. There are undergoing researches by the ECAP method with angle of 90 degrees and further microstructural characterizations.

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ORIGINAL SCIENTIFIC PAPER

Field: Materials Science

DETERMINATION OF THE ACTIVATION ENERGY IN THE SHAPE MEMORY ALLOY CuZnAl

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Abstract

Determination of the activation energy of a copper-based shape memory alloy is shown in this paper. Simultaneous TD-DTD method is used to determine the temperature of martensitic and reverse transformation at various rates of heating and cooling, and to determine the process kinetic parameters related to the shape memory effect in the investigated ternary alloy. The obtained high value of activation energy is shown that the processes of martensitic and reverse transformations are surface controlled and they are in the kinetic region.

Keywords: activation energy, copper-based shape memory alloy, martensitic and reverse transformation, shape memory effect, heating and cooling rates

1 INTRODUCTION

Shape memory effect is ability of certain plastic deformed metals and alloys 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 high-temperature phase, which is called beta or parent phase, and the removal of plastic deformation. Concurrently, all physic-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 [3]. Martensitic transformation is achieved by formation of martensite and grows continuously with decrease of temperature and increase of stress, and decreases continuously, becoming smaller according to the same curve with increase of temperature or decrease of stress.

The martensitic transformation is characterized by the following temperatures [1-3]:

- *Ms* the temperature at which martensite starts to transform into the parent (high-temperature) phase,
- *Mf* the temperature at which martensite finishes to transform into the high-temperature (parent) phase,
- *As* the temperature at which the parent (high-temperature) phase starts to transform into the martensite, and
- *Af* the temperature at which the high-temperature (parent) phase finishes to transform into the martensite.

The main goal of this paper is to define the temperatures of martensitic and reverse transformation, which are significant for the shape memory effect, as well as the kinetic parameters related to the shape memory process in the investigated CuZnAl alloy, which have been determined by the methods of Kissinger and Ozawa.

2 EXPERIMENTAL

The CuZnAl alloy was obtained by melting the charge that was prepared of oxygen-free copper, pre-alloy CuZn and pre-alloy of CuAl. The charge melting was carried out in a vacuum furnace with a charcoal cover. Alloy was cast into molds. The obtained chemical composition was: Cu=68.9%, Zn=27.6%, Al=3.5%.

After preparation of external surfaces, laths of dimensions $5x50 \text{ mm}^2$ were cut. The obtained laths were heated at 850° C for 10 min and then quenched in water. In this way, it was formed the martensite structure in the investigated alloy because the cooling process is carried out from the high-temperature beta phase region. The prepared samples of laths of the investigated alloy were used for TD-DTD investigations.

Simultaneous TD-DTD investigations were carried out on the electronic dilatometer 402E at high temperatures (Netzsch, Germany) with molybdenum pipe furnace and protective gas atmosphere of hydrogen.

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Experiments were carried out at various heating and cooling rates of 3, 5, 10, 15 and 20° C/min.

The obtained phases of the copper-based shape memory alloys are determined by X-ray diffraction (XRD) model Explorer, GNR with X-ray tube Cu-Ka (1.541874A). Operated condition is 40kV voltage and 30mA current. Configuration is θ - θ geometry.

3 RESULTS AND DISCUSSION

Chemical composition of the obtained alloy is shown in Fig. 1.

The obtained copper-based alloys with shape memory effect are developed from the binary systems of alloys: CuZn and CuAl. The CuZnAl shape memory alloys contain from 68% to 80% copper and from 20% to 32% zinc and aluminum in different portions.

Martensitic transformation of these alloys depends on tempe-rature and varies a lot of composition. Namely, only small change of composition causes a large variation of temperature of thermoelastic martensitic transformation, because it is necessary to keep the selected composition of alloy during the production process.

Although, the temperature of martensitic transformation of Cu-Zn-Al alloys with the shape memory effect can be regulated in wide interval, the practical upper limit is about 120° C, due to transformation became unstable above this temperature because of rapid ageing. All the obtained alloys possess the temperature of martensitic transformation to 120° C.

In the aim to determine the characteristics phases, the XRD analysis is done and results shown that the investigated samples of the shape memory copper-based alloys obtained by method of crystallization above melt possess 3 phases: α , β and α + β and those structures are applicable for further mechanical deformations and material processing.

Simultaneous TD-DTD method is used for determination the temperatures of martensitic and reverse transformation, at various rates of heating and cooling. This method is also used for determination the process kinetic parameters related to the shape memory effect in the investigated Cu-Zn-Al alloy.



Fig.1 XRD of CuZnAl alloy

Temperatures of the start, finish and maximum transformation of martensite into parent phase at various heating rates (reverse transformation) and temperatures of the start, finish and maximum transformation parent phase into martensite at various cooling rates (martensitic transformation) obtained by TD-DTD curves are given in Table 1 and Table 2, respectively.

Heating rate, ⁰C/min	Ms, ⁰C	Mf, ⁰C	Mm, ⁰C
3	341	241	290
5	360	259	316
10	387	281	356
15	415	305	392
20	436	315	407

Table 1 Start, finish and	maximum temperatures of	^r martensitic transf	ormation
---------------------------	-------------------------	---------------------------------	----------

Cooling rate, ⁰C/min	As, ^o C	Af, ⁰C	Am, ⁰C
3	263	400	315
5	280	426	335
10	295	452	355
15	314	475	373
20	331	495	381

The obtained curves and temperatures serve as a basis for determination the kinetic parameters and activation energy of the process of martensitic and reverse transformation.

Since various heating and cooling rate were used, the methods of Kissinger and Ozawa are used for determination the activation energy:

- By the Kissinger method:

$$\ln(\varphi/T_m^2) = C - E/RT_m$$
(1)

By the Ozawa method:

 $ln\phi = C_1 - E/RT_m$

(2)

where: ϕ is heating/cooling rate, T_m the maximum on the TD-DTD curve, E the activation energy, R the universal gas constant, C and C₁ the integration constant.

The obtained values of activation energy for the investigated shape memory alloy CuZnAl at different heating and cooling rates determined by theKissinger and Ozawa methods are given in Table 3.

Table 3 Activation energy for CuZn27.6Al3.5 shape memory alloys

E(kJ/mol)	Kissinger method	Ozawa method
Heating	82	92
Cooling	40	50

According to the obtained results, the following observation may be made:

The transformation in CuZnAl shape memory alloy is characterized by temperature hysteresis because there is a difference between temperature of the finish martensitic transformation into parent phase and temperature of the start of parent phase transformation into martensite.

The value of temperature hysteresis of transformation is related to the activation energy for transformation. That is a specific quantity of non-chemical free energy for the investigated shape memory alloy, i.e. the surface energy and plastic deformation energy.

The As temperature for reverse transformation is lower than the Ms temperature, and it could be concluded that the martensitic transformation is transformation of the second order for the investigated alloy, because Af>Ms>As>Mf.

The high values of activation energy over 40 kJ/mol shows that the processes of the martensitic and reverse transformation are surfaced controlled, and it is in the kinetic region.

4 CONCLUSION

The formation of martensite from the parent phase is possible even if the Gibbs free energy of martensite is lower than Gibbs free energy of the parent phase. Thus, the Gibbs free energy is the activation energy for transformation of the parent phase into martensite.

In order to achieve sufficient activation force for transformation the parent phase into martensite, it is necessary that the Gibbs free energy, in absolute value, should be larger than the non-chemical energy. Therefore, Ms is the maximum temperature at which martensitic transformation can occur.

The reverse transformation occurs prematurely, since the accumulated elastic energy promotes chemical activation energy provided by heating, in which the As temperature for reverse transformation will be lower than the Ms temperature.

The obtained high values of activation energy over 40 kJ/mol shows that the processes of the martensitic and reverse transformation are surfaced controlled, and it is in the kinetic region.

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ORIGINAL SCIENTIFIC PAPER

Field: Materials Science

GOLD-COPPER BINARY SYSTEM

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Abstract

The Au-Cu binary system is one of the earliest investigated systems for which several order-disorder type transformations were determined.Good properties of the alloys of this binary system enable their application in electronics, dentistry, medicine, communications, chemistry, but mainly in jewelry manufacturing.This study represents an overview of conducted investigations concerning the phase equilibria, thermodynamics and thermodynamic optimization of Au-Cu binary system.

Keywords: Au-Cu binary system, phase equilibria, thermodynamics, optimization

INTRODUCTION

The Au-Cu binary system is one of the earliest investigated systems for which several order-disorder type transformations were determined [1]. Such interest for this system derives in good properties of its alloys and their applicability in electronics, dentistry, medicine, communications, chemistry, but mainly in jewelry manufacturing. Jewelry produced of gold and copper occurs in different shades of red color depending on copper content. All investigations and fundamental discoveries relating Au-Cu binary system were conducted during the twentieth century. There are numerous references on the phase equilibria, thermodynamics and crystal structures in this binary system, and H. Okamoto at al. [1], gave a comprehensive literature review with data obtained till 1987. Later, during the nineties of the last century, Sundman et al. [89] have done a thermodynamic optimization of this binary system.

PHASE EQUILIBRIA

Liquidus and solidus in Cu-Au system have been investigated and determined byRoberts-Austen and Hose [2], Kurnakov and Zemczuzny [3], Bronievski and Wesolowski [4], Bennett [5], as well as Zaitseva and Priselkov [6].

Boundary between solid solution based on gold, (Au) and Au₃Cu phase, which was formed as a result of peritectoid rection [7,9,41,42], has been investigated by Grube et al. [7], LeBanc and Wehner [8], Rhines et al. [9], Batterman [10], Hirabayashi [11], Korevaar [12], Wright and Goddard [13], Luthy et al. [14], Kozlov and Strenchenko [15], etc. The results of these investigations defer more or less from each other in accordance with the fact that it is difficult to accomplish the state of phase equilibrium at low temperatures, (for Au₃Cu the phase under 240°C), [1]. Determination of the Au₃Cu boundary in the above mentioned investigations has been done using the different experimental methods. It has been established, using thermal analysis, that the field of existence of Au₃Cu phase goes till 9 at.% Cu in gold - rich area and till 38.5 at.% Cu in copper - rich area [16,17].

The occurrence of the AuCu and AuCu₃phases was first observed by Kurnakov et al., [18] by thermal analysis, hardness and X-ray measurements [1]. Bain [19-21], and Johansson and Linde [22-24], confirmed the existence of these two phases in their work. Primordial opinion was that the ordered AuCu phase, designated as AuCu(I), transforms directly into the FCC type of disordered form designated as AuCu (D) at high temperatures. Johansson and Linde extended this theory discovering the exis-tence of the AuCu(II) form of this phase at high temperatures [1,24]. Actually, at high temperatures ordered tetragonal AuCu (I) phase transforms to ordered orthorombyc AuCu(II) form [1]. There are numerous references concerning mentioned transformations, AuCu(II) \leftrightarrows AuCu(I) andAuCu(II) \leftrightarrows AuCu(D), carried out using the various experimental techniques like thermal analysis [25-32], electrical resistivity [7-9,27,28,33-38], X-ray analysis [31,39-43], dilatometry [7,34,37,], electromotive force [44,45], calorimetry [28,29,33,37,46-50], differential thermal analysis - DTA [14,51], etc. It was found that the transformation temperature of AuCu(II) \leftrightarrows AuCu(D), is 410±2°C [9,14,33,38,43,52,53], and transformation temperature of AuCu(II) \leftrightarrows AuCu(I) is 385 ±2°C [52,54].

Rhinesat al. [9] and Newkirk [41,42], have done Au-Cu phase diagram with defined boundaries of all phases in this binary system based on experimental results of electric resistivity, and X-ray analysis. They confirmed a congruent formation of AuCu and AuCu₃ phases through their investigations, too.

A detailed and precise phase diagram of the Au-Cu system between 40 and 60 at.% of Au was obtained and published bz Pianelli [43,55]. According to Grube et al. [7], between AuCu₃ and AuCu (I), the two-phase field exists from 34 to 37 at.%Au as a result of the eutectoid decomposition of the solid solution based on gold (Au) and copper (Cu). Studying the Au-Cu system, Rhines [9] confirmed the eutectoid transformation and precisely determined position of the eutectoid point at 36 at.%Au and temperature $284^{\circ}C$.

The area of the AuCu₃ (I) phase was investigated and determined by Rhinesat et al. [9], based on the electric resistivity measurements and X-ray analysis. Analyzing date of Jaumot and Sutcliffe[56], obtained by X-ray analysis, Newkirk confirmed the existence of the twophase field around AuCu₃ (I) phase, not only from the Au-rich side, but also from the Cu-rich side [1,42]. The AuCu₃ (I) phase were formed from the disordered phase by congruent transformation and by eutectoid transformation at the Au-rich area. According to literature, temperature of congruent transformation is 390°C, and 284°C of the eutectoid transformation at concentration of 36 at.% Au [9]. Airoidiat al. [57], as well as Hertz [58], also studied these two transformations and determined that temperature of the congruent transformation is 390°C.

There are considerable number of investigators who explore different parts of $AuCu_3$ (I) phase boundaries using thermal analysis [5, 33, 59], electric resistivity measurements [7-9, 27, 28, 33-37, 60, 61], X-ray analysis [22, 23, 56, 62-64], differential thermal ana-lysis - DTA [51],

dilatometry [7, 34, 37, 65], electromotive force [44,45], modulus of elasticity [66-70], electron microscopy [71-73], etc.

According to Scott [74], the $AuCu_3$ (II) phase occures in the Au-rich area as narrow single-phase field which lies inside two-phase area of gold and copper based solid solutions, (Au,Cu), and AuCu₃ (I) phase. Boundaries of this phase were explored by Yakel[64], Scott [74], as well as Van der Perreat et al. [75].

A huge number of studies, presented in literature, which refer to $AuCu_3$ (II) phase are focused on crystal structure of this phase and its influence on order-order and order-disorder transformations [55, 56, 64, 72, 76-80].

Detailed systematization of data regarding phase equilibria, thermodynamics and crystallography of Au-Cu binary system was done byOkamoto at al. [1], and based on these data they have constructed a phase diagram of this system, represented in Figure 1.



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

THERMODYNAMIC INVESTIGATIONS

The enthalpy of mixing for liquid has been determined by Edwards and Brodsky [81], Oriani [82], Neckel and Wagner [83], Itagaki and

Yazawa [84], Hager et al. [85].During the eighties of the last century, Topor and Kleppa [92], have systemized the existing thermodynamic parameters including the enthalpy of mixing the liquid phase.

The enthalpy of mixing for the disordered alloys has been determined by Orr [86], at 720 Ka s a function of composition. The same author also determined the enthalpies of formation for the stoichiometric ordered compounds.

Hirabayashi [29], and Sima [87] measured a heat capacity for the AuCu phase at high temperatures (T = 600 to 720K).

The heat capacity for AuCu₃phase was determined by Kuczynski et al. [88] in temperature interval of T= 473 to 1173K.

Tissotat et al. [51], investigated and determined the enthalpy of order-disorder transformations for Au₃Cu phase.

Oriani [45, 82], has investigated a thermodynamic activity of copper and gold. He assessed all date regarding Cu activity including his own experimental results at 773K and plotted it [45]. Oriani determined the activities of Cu and Au in the liquid phase in the whole range of compositions at 985°C [82, 89].

THERMODYNAMIC OPTIMIZATION

Thermodynamic optimization of the Cu-Au binary system was carried out by Sundman et al. [89]. They used a fcc Bravais lattice [90], for the liquid disordered and ordered phases, and for the so-lid phases the Borelius-Gorski-Bragg-Williams [91], approximation in their calculations. The model is developed in the frame of the Compound Energy Formalism (CEF), [89].

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[1] B.A. Willis, Mineral Processing Technology, Oxford, Perganom Press, 1979, p. 35. (for the chapter in a book)

[2] H. Ernst, Research Policy, 30 (2001) 143-157. (for the article in a journal)

[3] http://www.vanguard.edu/psychology/apa.pdf (for web document)

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