ROMANIAN ACADEMY

„Ilie Murgulescu” Institute of Physical Chemistry

DOCTORAL THESIS

ABSTRACT

STUDY OF PHASE EQUILIBRIA IN NANOALLOY SYSTEMS

Scientific advisor,

CS I Dr. Tănăsescu Speranţa Valeria

PhD Student,

Milea Ion Alexandru

BUCHAREST

2015

TABLE OF CONTENTS

Keywords: Nanoalloys, Drop calorimetry, Phase equilibria

INTRODUCTION

The reduction of particle size and the possibility to obtain alloys at nanometric scale has lead to a remarcable enhancement of alloy properties, new opportunities arising for technological applications in various domains: electronics, catalysis, magnetic devices, optoelectronics etc. These new properties due to the unique effect of the nanostructure raise new questions important for both, basic research and applications – regarding the relation between composition, structure and properties.

One of the key factors responsible for understanding the physical and chemical modified properties associated with the rise of the surface/volume ratio at a nanometer scale is the change of the energetic parameters. However, the literature is rather scarce as concerns the thermodynamic properties of these alloy systems, the majority of information being based largely on theoretical calculations.

Ag-Cu is one of the reference systems for classical alloy systems. It is well known that Ag and Cu are mutually immiscible in solid state and the heat of mixing is positive. But using non-equillibrium techniques such as rapid quenching, vapor deposition, plasma processing or mechanical alloying, one can obtain metastable phases of this nanoalloy, yet each of these methods will leave the own mark on the properties of the resulting nanosystem. For the Ag-Cu system there is no experimental data regarding thermodynamic functions relevant for the thermodynamic evaluation of the processes accompanying the formation of nanoalloy phases associated with a specific synthesis method. Current studies regarding thermal stability refer to limited domains of compositions and temperature.

In order to bring original contributions to the proposed subject, within the present thesis was realized a systematic thermodynamic study of micro and nanostructured phase equillibria in Ag-Cu systems synthesized by mechanical alloying in different conditions of processing (different milling times). For this study, two compositions situated in distinct areas of the phase diagram of Ag-Cu system have been selected: 72% Ag - 28% Cu corresponding to eutectic composition, and 50% Ag – 50% Cu. This study has been carried out on the basis of a compex thermodynamic approach, taking into consideration the following aspects: the influence of the synthesis parameters on the thermodynamic properties; the correlation of thermodynamic parameters with structure, composition (Ag/Cu ratio), thermal expansion and electrical properties in large domains of temperature; the identification of energetic parameters which favour the stability of nanostructure phases.

The objectives of the current study are:

1. **Structural and morphological characterization of powders obtained by mechanical alloying.** In order to determine the alloying degree of Ag and Cu, as well as particle and crystallite size, a couple of measurements have been performed: X-ray diffraction measurements (XRD), electronic microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). XRD analysis was carried out at room temperature, as well as by *in situ* heating of sample in order to determine the constituent phases and the phase transformations during heating.
2. **Thermodynamic and thermochemical study of phase equillibrium in 72% Ag – 28% Cu and 50% Ag – 50% Cu systems obtained by mechanical alloying.** Thermodynamic properties (relative

enthalpy, specific heat, relative entropy and Gibbs free energy) in isothermal regime have been obtained by drop calorimetry using a multi-detector high temperature calorimeter SETARAM MHTC-96 operating in the drop mode. The thermochemical behaviour to heating was analyzed using the DSC technique. These measurements allowed to evidence the influence of particle size and synthesis parameters on the thermodynamic and thermochemical behaviour of the studied nanomaterials.

3. **Thermal expansion and electrical properties study of 72% Ag - 28% Cu and 50% Ag – 50% Cu obtained by mechanical alloying.** Depending on the temperature, the following characteristics of the materials have been determined: thermal expansion coefficient, conductivity and electrical resistivity.
4. **Study of the corelations between composition-structure-properties and the highlighting of the role of energetic parameters in the control of the material stability on a nanometric scale**

Thesis structure:

The PhD thesis is structured in 6 chapters included in 3 distinct parts:

Part I: Current level of research (chapters 1 and 2)

Part II: Experimental part (chapter 3)

Part III: Original contributions (chapters 4, 5 and 6)

The thesis concludes with bibliographic references, followed by the list of ISI published papers, as well as communications at national/international scientific events.

In **Chapter 1, Introduction**, after a short presentation of the importance of the approached domain, the scope, specific objectives and thesis structure are presented.

Chapter 2 contains a description of the current level of research in the nanoalloy field, insisting on the possibility of obtaining metastable phases in non-equillibrium conditions. Based on bibliographic research, the main theoretical and experimental aspects regarding the role of the energetic parameters in the understanding and the control of the nanostructured material's stability, especially in the case of nanoalloys are critically discussed. At the same time the need for contributions in this domain is identified.

Chapter 3 contains the presentation of the studied materials together with the description of the synthesis method and the methodology and experimental techniques used for ~~of~~ physico-chemical—characterization(XRD, XPS, SEM, DSC, TMA, drop calorimetry), insisting on the thermodynamic and thermochemical methods.

Chapter 4 contains the original contributions regarding the experimental results obtained from the study carried out on the system with the eutectic composition **72% Ag – 28% Cu**. The powders were structurally and morphologically characterized, the thermodynamic stability of micro and nanostructured phases was studied, thermal expansion and electrical properties.

Chapter 5 contains original contributions regarding experimental results obtained from the study that was carried out on the system with the composition of **50% Ag – 50% Cu**. The structure, thermodynamic stability, thermal expansion and electrical properties of micro and nanostructurate phases were analyzed.

Chapter 6 contains the final conclusions resulting from the present study.

STRUCTURAL CHARACTERIZATION OF NANOMETRIC POWDER SYSTEMS Ag - 28%Cu AND Ag - 50%Cu

Using Brookhaven 9Plus/BI-MAS technique it was determined that only samples milled for 80 hrs presented nanometric particle size distribution.

XPS spectroscopy measurements registered the photoelectrons high frequency spectra of the most prominent transitions for C1s, O1s, Cu2p and CuLMM. The binding energies in case of Ag3d and Cu2p are assigned to the formation of the Ag-Cu alloy.

Using X-ray diffraction (XRD) measurements, the structures of the Ag-Cu alloys milled for 80 hrs having atomic ratio Ag/Cu = 1 and eutectic composition were analyzed. In both cases, the most intense diffraction line associated with Ag-Cu alloys is shifted compared to the position of the pure Ag line, showing the formation of a solid solution $AgCu_{ss}$. The medium crystallite size at room temperature and during heating until 973 K was calculated. The crystallite size variation with temperature is not monotonous. Until 503 K the crystallite size is stable. After this temperature, crystallite size rises with the temperature. Also using XRD analysis, it was observed experimentally that the lattice parameter tend to higher values for compositions with a higher concentration in Cu.

THERMODYNAMIC STUDY OF MICRO AND NANOSTRUCTURED PHASE EQULIBRIA IN METASTABLE POWDER SYSTEMS OF Ag-Cu OBTAINED BY MECHANICAL ALLOYING

Ag - 28%Cu system

For the thermodynamic study were used differential scanning calorimetry in dynamic regime of temperature (DSC) and drop calorimetry in isothermal conditions.

1. DSC diagrams of powders processed at different times of milling revealed the following:

- The effect associated with the relaxation of microstresses observed at low temperatures, around 450-480 K, process specific only to samples obtained through mechanical alloying. This effect is more obvious for the sample milled for 80 hrs.
- Large exothermic signals around 480-973 K specific to the phase separation and grain growth processes. For the first time in this thesis we made a distinction between the domains of temperature in which these processes evolve, using DSC and XRD results.
- For the first time it was observed the shifting of melting temperature point to lower values with the reduction in grain size.

2. Thermal effects from DSC diagrams were evaluated using drop calorimetry and the following aspects were observed:

- The relative enthalpy variation with temperature is not monotonous, thermal effects revealed by DSC curves were also obtained using drop calorimetry. For the first time in the literature we reported the Ag-28%Cu enthalpy increments for samples obtained in different processing conditions (different milling times) (Fig. 1).

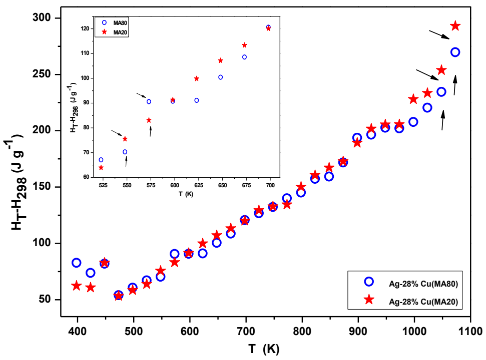


Fig.1 Relative enthalpy variation with temperature for a microstructured sample Ag-28%Cu(MA20) and for a nanostructured sample Ag-28%Cu(MA80)

- We determined thermodynamic functions: specific heat, relative entropy, Gibbs free energy function. The enthalpy of formation of an alloy Ag-28%Cu by using direct synthesis method (in calorimeter) has been also determined. The obtained value of -48.14 J/g shows that the process of formation of an nanoalloy in mechanical alloying conditions is possible.
- The higher values for enthalpy and specific heat at low temperatures, around 400-450 K, are explained by the nanocrystalline structure generated by processing using ball milling technique. High values of entropy around 473-548 K are characteristic for the high degree of disorder present at the grain boundaries (Fig.2).

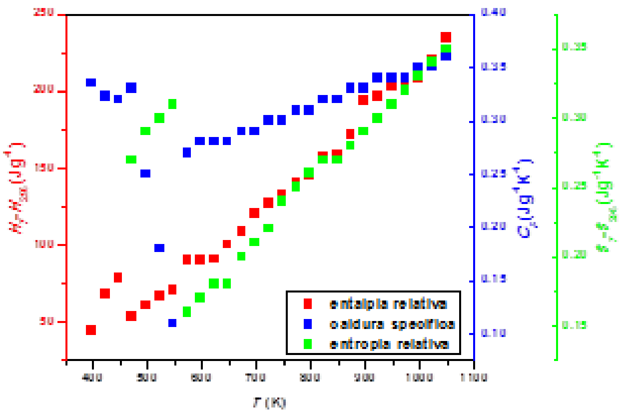


Fig.2 Temperature dependence of enthalpy increments, specific heat and relative entropy for Ag-28%Cu(MA80) sample

- In the temperature domain related to the grain growth process (573-1048 K), specific heat of nanometric powders, milled for 80 hrs, has a different behavior compared to micrometer samples (Fig.3). A first observation is that until 673 K, specific heat of nanostructured sample has a higher value compared to the microstructured samples. A second observation is that the specific heat of nanostructured sample has a weak dependence on the temperature compared to micrometer sized samples. This behavior can be explained by the particularities of grain growth process in nanocrystalline samples; an important role in the stabilization of the nanostructure is played by the decrease in interfacial energy and the presence of stress in the crystalline structure.

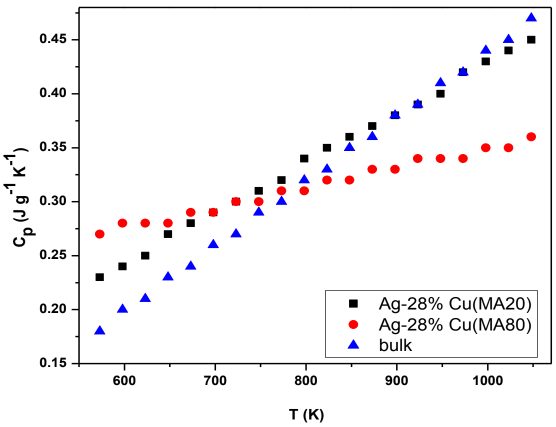
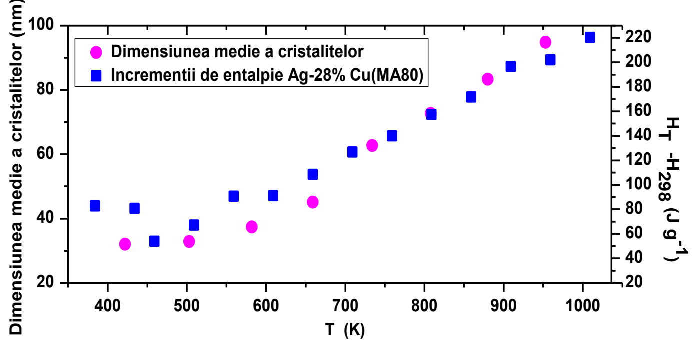


Fig.3 The temperature dependence of specific heat in the temperature domain of the grain growth process. Comparison between nanometer and micrometer sized powders.

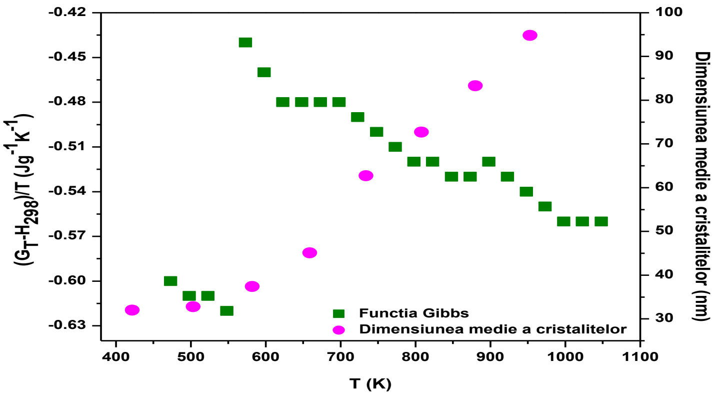
- The smaller values of free energy over 548 K shows the tendency of the structure to become thermodynamically stable after the elimination of structure microstress and the phase separation processes.

CRYSTALLITE SIZE INFLUENCE ON THE EVOLUTION OF THE THERMODYNAMIC PROPERTIES

Results obtained using drop calorimetry were correlated with the results obtained from XRD. It was observed an unusual variation of crystallite size during heating. Until temperatures around 500-550 K, crystallite size has a weak dependence of temperature. Meanwhile, relative enthalpy and Gibbs function have minimum values at these temperatures, values correlated with the medium crystallite size values (Fig 4a and 4b). This study shows that nanocrystalline materials can exhibit the stabilization of crystallite size phenomenon until higher temperatures. The onset temperature for grain growth process and the energy of activation for this process have higher values compared to the conventional materials.



(a)



(b)

Fig.4 Crystallite size and relative enthalpy variation with temperature (a), and free energy variation with temperature for a nanostructured sample Ag-28%Cu(MA80) (b)

Ag-50%Cu system

DSC measurements showed also that in the case of a Ag-Cu system with a higher concentration of Cu the thermal effects associated with the relaxation of microstress, phase separation and grain growth are also present with the specification that phase separation process occurs at lower temperatures in case of a system richer in Cu.

As in the case of the eutectic composition sample, thermodynamic parameters represented by relative enthalpy, specific heat, relative entropy and Gibbs free energy function were also determined.

During a comparison with the eutectic system the following aspects were observed:

- The sample with a higher concentration of Cu has a higher enthalpy on the whole temperature domain (Fig. 5).
- The relative enthalpy and specific heat also present higher values at low temperatures, result explained by the nanostructure characteristic disorder (Fig. 5 and Fig. 6).
- Higher values of entropy in the case of both concentrations are seen for nanostructured samples compared to microstructured samples on the whole temperature domain.
- The free energy minimum is shifted to lower temperatures for the samples with a high Cu content. In the temperature domain associated with the grain growth process the free energy values are approximately the same (Fig.7).

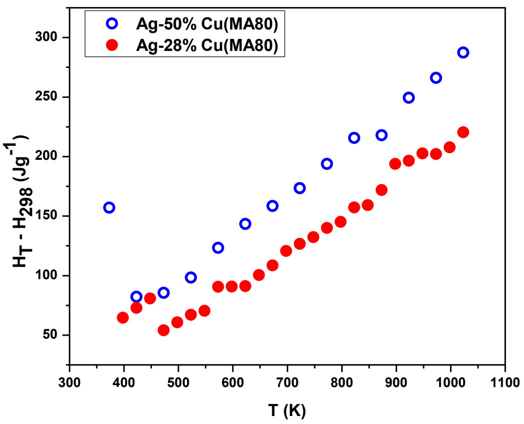


Fig. 5 The relative enthalpy of two samples milled for 80 hrs, but having different composition: Ag-50%Cu(MA80) and Ag-28%Cu(MA80)

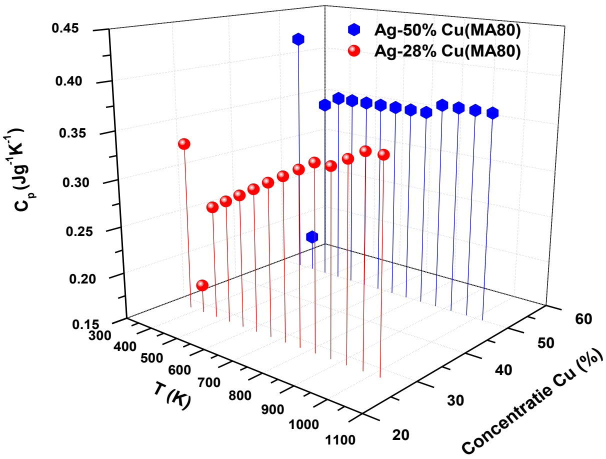


Fig. 6 Specific heat variation with temperature for samples with different compositions: Ag-50%Cu(MA80) and Ag-28%Cu(MA80)

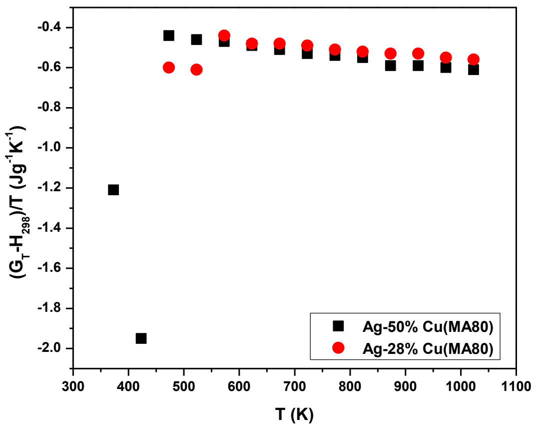


Fig. 7 Gibbs free energy evolution of Ag-50%Cu(MA80) and Ag-28%Cu(MA80) samples

The results obtained in the comparative study of thermodynamic properties of nanostructured samples of different compositions show that the effect of composition on thermodynamic parameters is more important at low temperatures, before the beginning of grain growth process. The conclusion is important for the selection and optimization of materials in the view of applications.

CORRELATION BETWEEN THERMODYNAMIC PROPERTIES, THERMAL EXPANSION AND ELECTRICAL PROPERTIES

- For the first time there were made thermal expansion measurements for Ag-Cu alloys and have been determined the coefficients of thermal expansion on the temperature range associated with the thermodynamic stability and the crystallite size stabilization domains. The coefficient of thermal expansion of nanometer samples Ag-28%Cu(MA80) and Ag-50%Cu(MA80) are 44×10^{-6} K^{-1} and 39×10^{-6} K^{-1}, respectively. These values are approximately 2.5 times higher than those of micrometric samples (18×10^{-6} K^{-1}), confirming theoretical data, as well as some literature results regarding the thermal expansion coefficient of some metallic materials and alloys with nanometer structures.

- Electrical resistivity measurements revealed that the variation of relative resistivity with the temperature is dependent of crystallite size and Cu concentration. Until temperatures close to 600 K, the relative resistivity of the two samples decrease. At 560 K, nanometric sample Ag-50%Cu(MA80) shows a relative resistivity minimum, after that it begins to increase, having a similar behavior with that of thin films Cu(Ag) copper rich and of micrometer Cu. Relative resistivity of nanometric sample Ag-28%Cu continues to decrease until around 800 K, after which it remains at a constant value until 1000 K.
- In Fig. 8 and Fig. 9 the correlation between the average crystallite size, thermal expansion, electrical properties and the free energy has been presented. The temperature range where the minimum energy values were observed is indicative for the temperature domain of the crystallite size stabilization and where the grain growth process is inhibited.

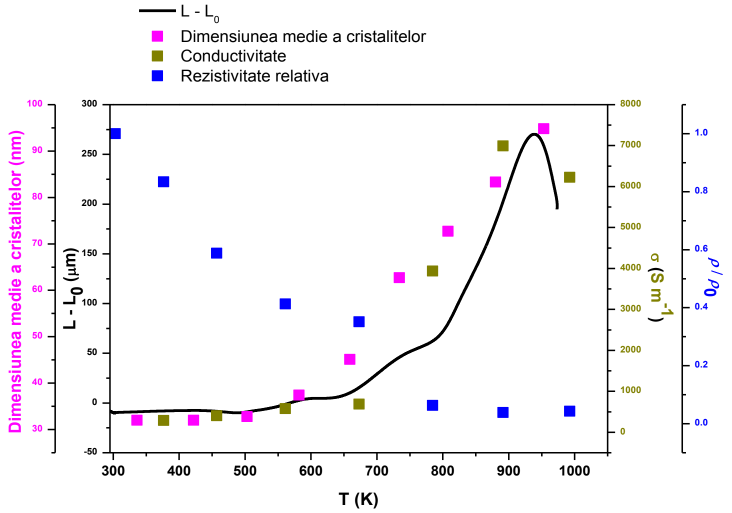


Fig. 8 Correlation between average crystallite size, thermal expansion, conductivity and relative resistivity for Ag-28%Cu(MA80) sample

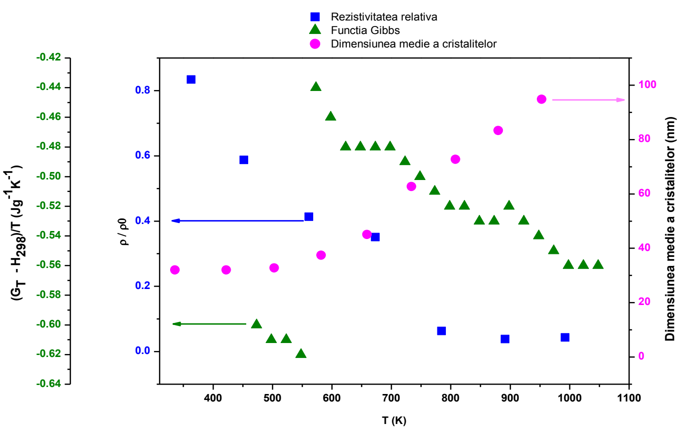


Fig. 9 Correlation between free energy, relative resistivity and average crystallite size in Ag-28%Cu(MA80) sample

It was shown that in mechanically alloyed nanosized samples, the thermodynamic properties there are not only the driving force for grain growth process, but also may be used to explain the experimentally observed stability and the change of properties in a large domain of temperature.

CONCLUSIONS

The study has lead to the following conclusions and original contributions:

- For the first time the thermodynamic behavior of the micro and nanostructured phases for the Ag-28%Cu(MA80) corresponding to the eutectic composition has been studied in a large domain of temperature by coupling calorimetric measurements in both dynamic (DSC) and isothermal regimes(drop calorimetry).
- For the first time have been determined the thermodynamic functions (relative enthalpy, specific heat, relative entropy and Gibbs energy function) relevant for the thermodynamic evaluations of processes accompanying the formation and transformation of phases in nanoalloys.
- Correlations existent between composition, structure and the thermodynamic behavior have been determined. Transformations related to microrelaxation, phase separation and grain growth processes have been determined.
- For the first time measurements of thermal expansion for Ag-Cu nanoalloys have been performed and the coefficients of thermal expansion on the temperature domain corresponding to the stabilization of crystallite size have been obtained.
- For the first time has been studied the correlation between energetic parameters that controls the grain growth process in nanoalloys samples, the electrical properties and the thermal expansion.
- The results obtained in the present study give for the first time evidence that, the concept of thermodynamic nanostructure stabilization is a real phenomenon for the mechanically alloyed Ag-Cu nanopowders.

The results are important for both fundamental and practical reasons:

- The study highlighted new aspects related to thermodynamic stability of investigated materials, thermodynamic behavior being explained not only by structural changes due to the synthesis method, but also by the fact that energetic parameters are extremely sensible to the variation of particle size.
- It’s essential to understand the role of energetic parameters in the control of nanostructured materials stability from a fundamental standpoint, but also from the perspective of finding new ways to control the enhanced properties.
- A major importance is the identification of thermodynamic stability conditions with consequences over the grain growth process for applications in which the maintenance of nanocrystalline structure until higher temperatures is essential.
- The understanding of the structure-properties correlations allows the exploration of new opportunities to obtain nanocrystalline materials using non-equlibrium processes – such as mechanical alloying.

List of ISI published works in the thesis research field

1. A. Milea, O. Gîngu, S. Preda, G. Sima, C. Nicolicescu, S. Tănăsescu, *Thermodynamic measurements on Ag-28% Cu nanopowders processed by mechanical alloying route*, J. Alloy. Compd., 629, 2015, 214-220; I.F. 2.726
2. O. Gîngu, P. Rotaru, A. Milea, A. Marin, C. Nicolicescu, G. Sima, S. Tănăsescu, *In-situ synthesis of AgCu/Cu2O nanocomposite by mechanical alloying: The effect of the processing on the thermal behavior*, Thermochim. Acta, 606, 2015, 1-11; I.F. 2.105
3. S. Tănăsescu, A. Milea, O. Gîngu, F. Maxim, C. Hornoiu, S. Preda, G. Sima, *Correlation between thermodynamic properties, thermal expansion and electrical resistivity of Ag-28% Cu nanopowders processed by the mechanical alloying route*, Phys. Chem. Chem. Phys., 2015, **DOI:** 10.1039/C5CP01390A; I.F. 4.198

List of oral/poster communications presented at national/international scientific events

Oral communications:

- **Alexandru Milea**, Oana Gîngu, Petre Rotaru, Speranța Tănăsescu, *Thermodynamic data of the Ag-Cu nanoalloys processed by mechanical alloying route*, 22th Symposium of Thermal Analysis and Calorimetry, 12 February 2013, Bucharest.
- **Alexandru Milea**, Oana Gingu, Anca Sofronia, Florentina Maxim, Speranta Tanasescu, *Thermodynamics of nanoalloys synthesized by the mechanical alloying method*, 12th Edition of National Seminar–of Nanoscience and Nanotechnology, Romanian Academy, 16 May 2013, Bucharest.

Poster communications:

- Speranța Tănăsescu, Oana Gîngu, Petre Rotaru, **Alexandru Milea**, Andreea Neacșu, *Thermodynamic data of the Ag-Cu nanoalloys processed by mechanical alloying route,* COST Action MP0903 NANOALLOY, 19-21 November, 2012, Antalya, Turkey.
- Speranța Tănăsescu, Oana Gîngu, Petre Rotaru, **Alexandru Milea**, *Thermodynamic and thermomechanical measurements on Ag-Cu nanopowders processed by mechanical alloying route*, COST Action MP0903 NANOALLOY, Final Conference, 5-9 April, 2014, Santa Marguerita Ligure, Spain.
- **Alexandru Milea**, Oana Gîngu, Petre Rotaru, Speranța Tănăsescu, *Thermodynamic data of the Ag-Cu nanoalloys processed by mechanical alloying route,* International Conference of Physical Chemistry ROMPHYSCHEM15, 11-13 September, 2013, Bucharest, Romania.