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THERMODYNAMIC DATA OF THE AG-CU NANOALOYS PROCESSED BY MECHANICAL ALOYING ROUTE

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OUTLINE

- Objectives and motivations
- Experimental methods
- Selected experimental results
- Concluding remarks

Objectives

The aim of this study is the investigation of the correlation between the particle size (method of synthesis) and the thermodynamic data of the Ag-Cu nanoalloy with potential electrical/optoelectronic applications.

Ag- 28% Cu nano-sized powder particles have been synthesized by Mechanical Alloying (MA) using different processing parameters

The effect of the milling time and particle size on the thermal behavior and energetic parameters was highlighted by using a couple of methods: differential scanning calorimetry (DSC), thermal gravimetry (TG) and Drop Calorimetry in a large temperature range (from room temperature to 1000 ^{o}C)

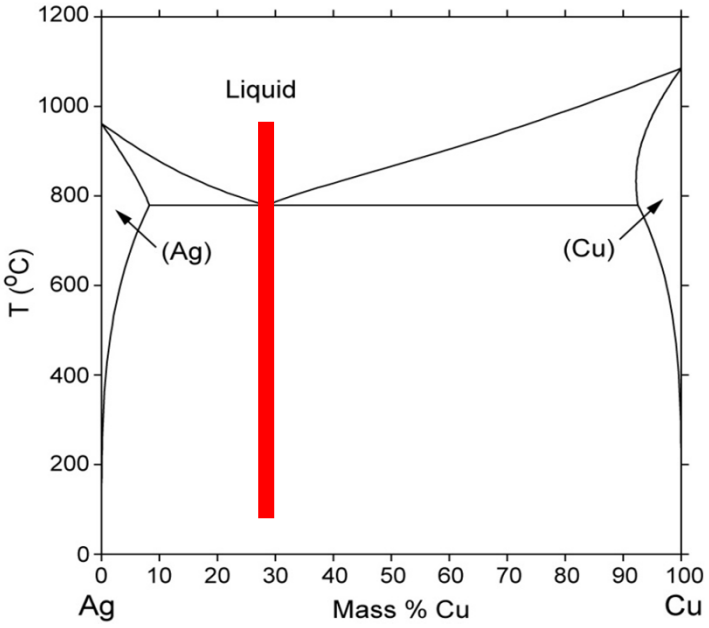
MOTIVATION

THE EUTECTIC AG-CU ALLOYS REPRESENT HIGH INTEREST MATERIALS FOR THE ELECTRICAL/OPTOELECTRONIC APPLICATIONS FOR THE FOLLOWING SCIENTIFICALLY REASONS:

- AVAILABILITY FOR ACCURATE SOLDERING TECHNIQUES EVEN AS LEAD-FREE ALLOYS;
- APPLICATIONS WHICH ARE DESIGNED TO FUNCTION AT TEMPERATURE VARIATIONS
- ACCESIBILITY FOR SOLDERING TECHNIQUE IMPROVEMENTS FROM THE POINT OF VIEW OF THE THERMOPHYSICAL PROPERTIES OF THE ALLOYS

MATERIALS

Ag flakes, 32.70.77 Sigma Aldrich code, 10 μm, 72% wt.
Cu powders, 20.77.80 Sigma Aldrich code, 75 μm, 28% wt



Ag-Cu NANOPOWDERS made by Mechanical Alloying process

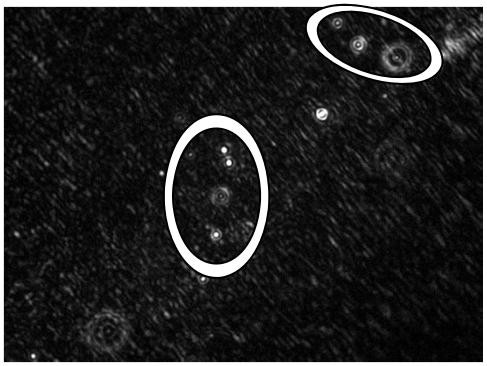
Milling time [h]	Sample code	Powder mixture Ag+28% wt.Cu
20	MA20	[350-470] nm
80	MA80	[60-80] nm

Equipment: Fritsch - Pulverisette 6; milling bowl and balls: agate

MA processing parameters
speed: 200 rpm
atmosphere: neutral (argon)
conditions: wet milling (water + ethylene glycol)
initial powders: Ag+Cu
milling balls: Φ5 – 10 – 20 mm
milling balls : powders ratio = 5
milling time: 20 and 80 h

PARTICLE SIZE DISTRIBUTION ANALYSIS EQUIPMENT: BROOKHAVEN 9PLUS/BI-MAS

Fig.1 MA80-1st dilution analysis:



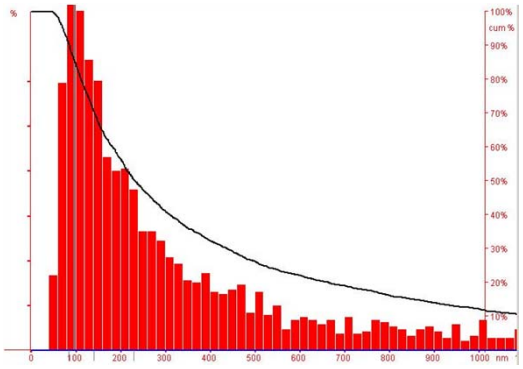
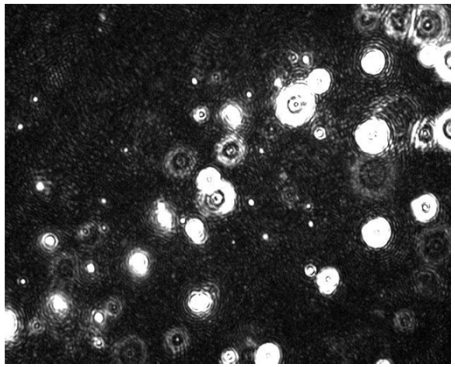


Fig.2 MA80-2nd dilution analysis:



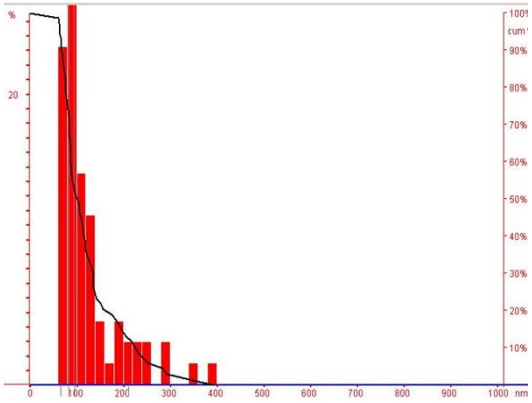
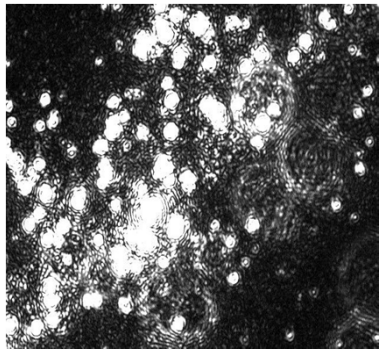
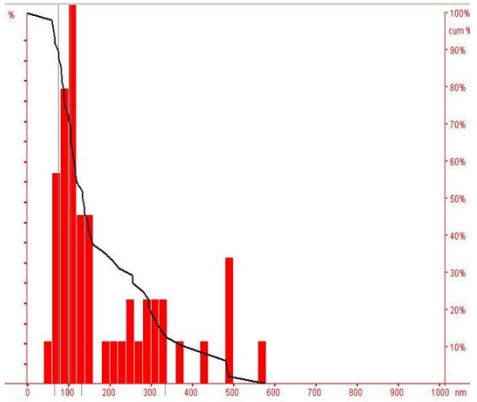


Fig.3 MA80-3rd dilution analysis:





(up) real time image of the MA80 powder particles; (down) particle size distribution

THERMODYNAMIC CHARACTERIZATION

➢**SetSys Evolution 18 (DSC-TG) *SETARAM***

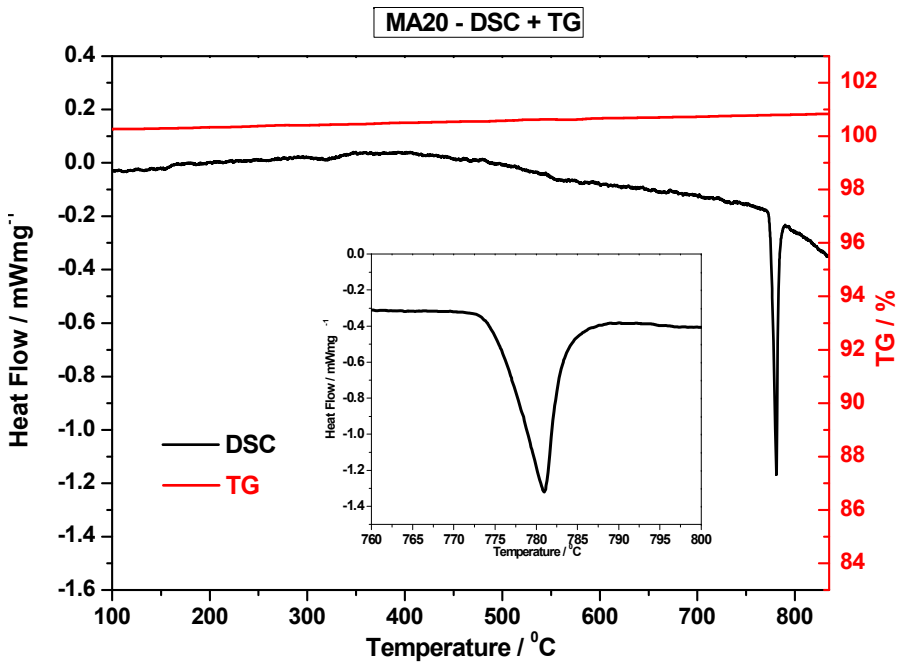
Thermal analysis measurements (TG and DSC) on the eutectic powder mixture Ag+28% wt. Cu, processed at different milling times.

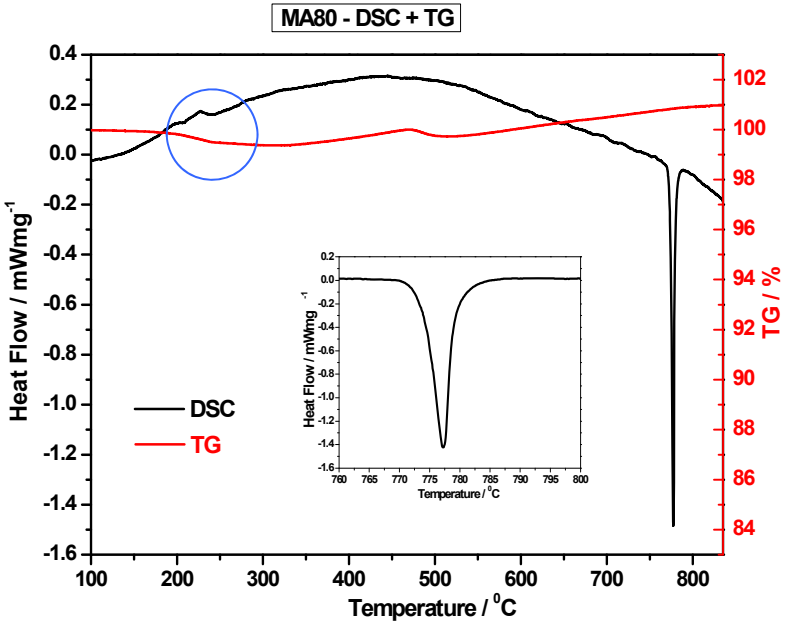
This analysis was carried out in dynamic argon atmosphere (16 ml/min) under non-isothermal linear regimes. Samples contained in alumina crucibles were heated in the temperature range of RT-835 ^{0}C, each time with the heating rate of 10 K min-1.

➢**Modular thermal analyzer based on Drop Calorimetry method (Model MHTC 96 drop - *SETARAM*)**

- The enthalpy increments ($H_T - H_{298}$) in the temperature range *ambient* - 1000 ^{0}C *in argon atmosphere (20 ml/min).*
- Determination of heat capacity C_p according to the continuous or incremental method.
- 3D Sensor Inside Technology, both the sample and the reference are completely surrounded by a flux meter, which means that the entire differential heat flux associated with the studied transformation or reaction can be measured.
- For a given temperature, 3 drops of sample were performed in order to get an average value. Before and after each sample drop, is intercalated a standard made by sapphire. The drops were made from 200^{0}C to 1000^{0}C with a 25^{0}C step into an alumina bed. The measuring error is 1-1.5 % for a minimal sample amount of less than 5 mg.

DSC AND TG RESULTS

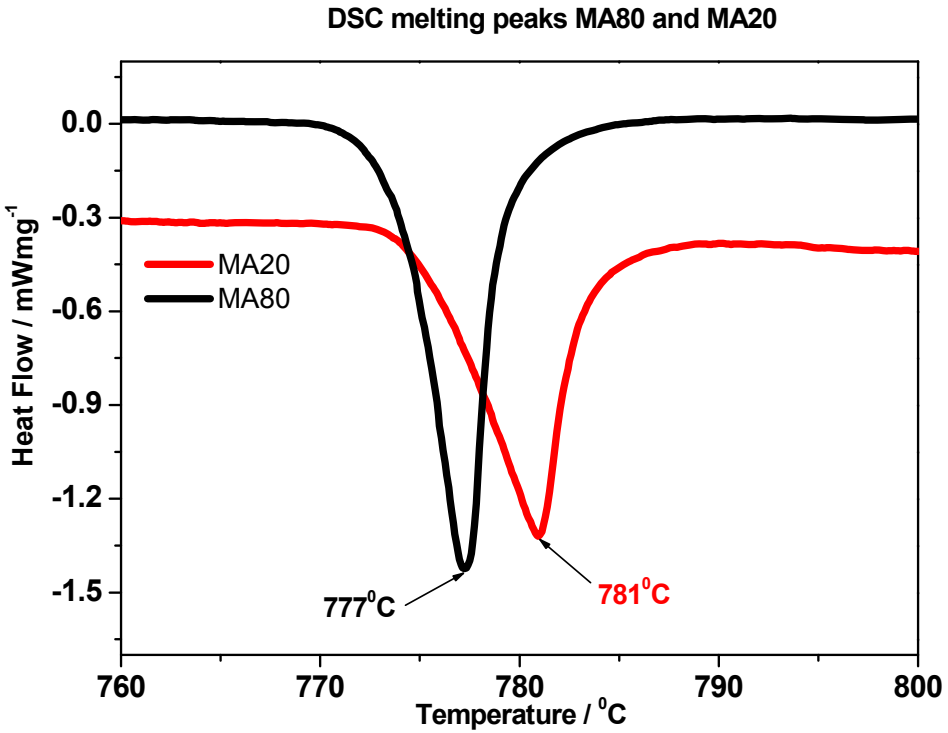




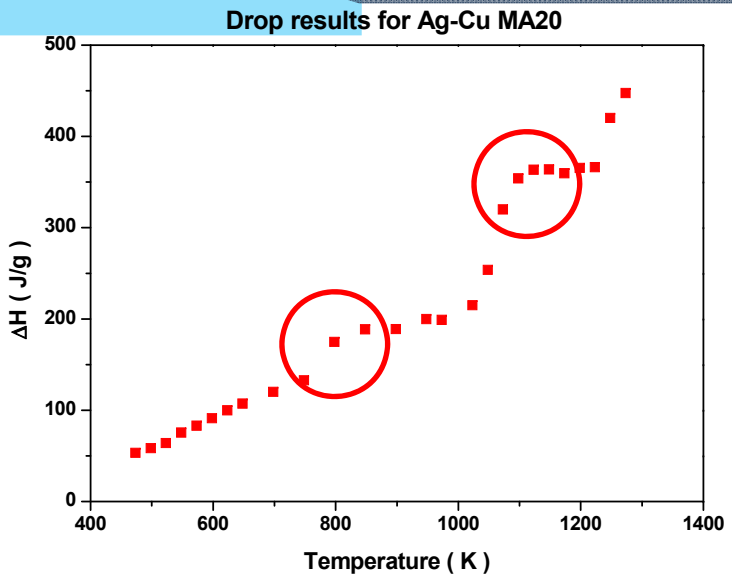
- Heat flow variation with temperature is not monotonous, some anomalies being observed at low and high temperature

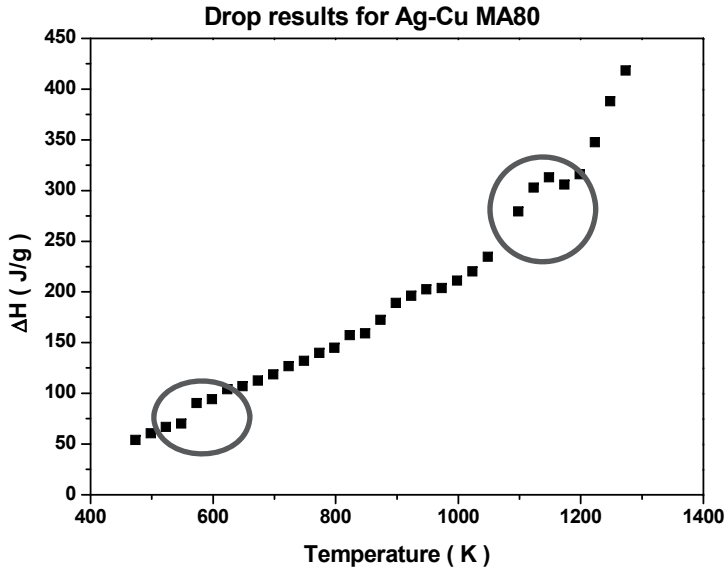
- In MA80 case we see around 280^{0}C an effect which could be assigned to the powders micro-relaxation effect during MA process. For MA20, this effect seems to be very weak.

- For both samples melting effect is well evidenced. The characteristique temperatures are shifted to lower temperatures in the case of nano-sized sample, as it is emphasized in the next slide.

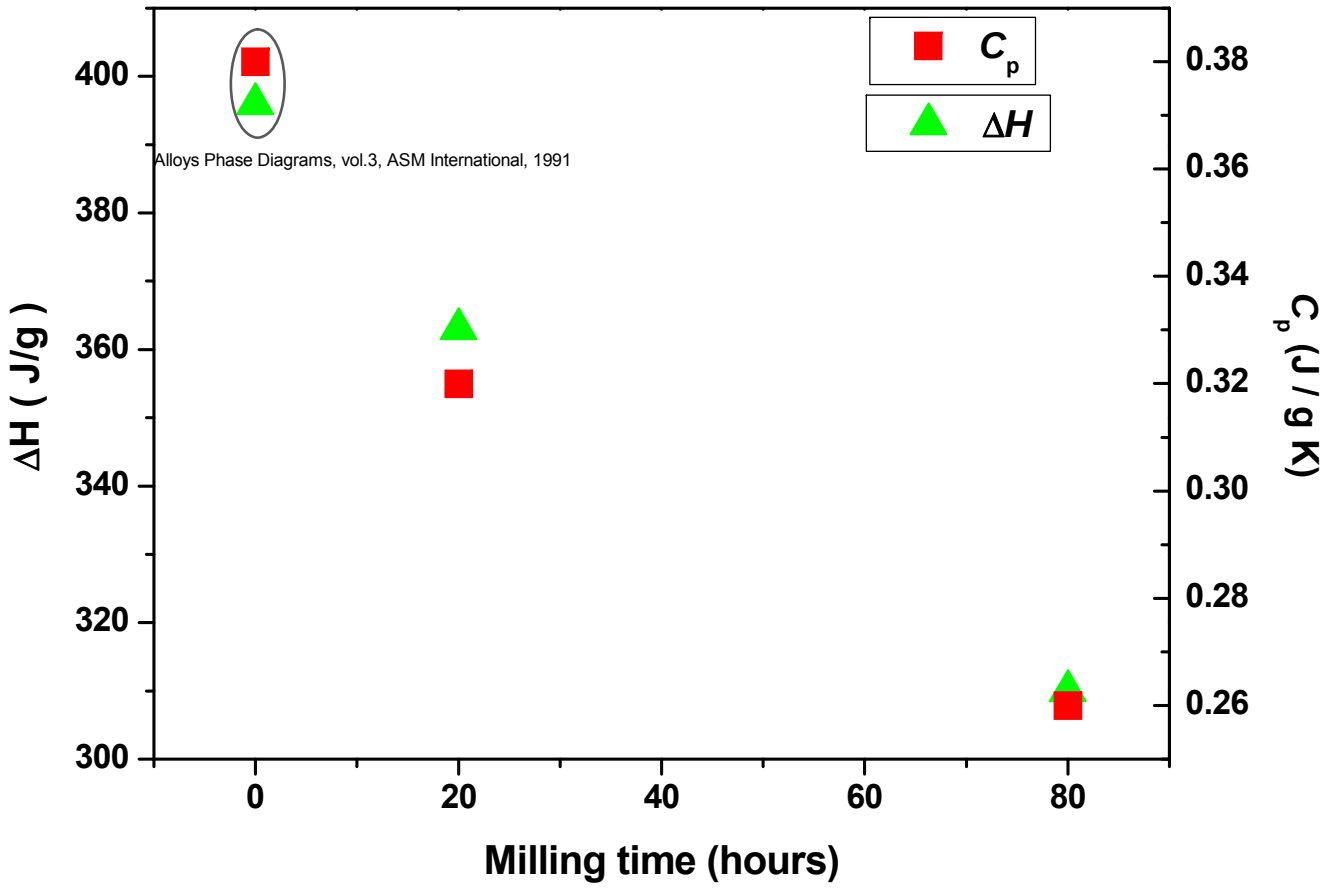


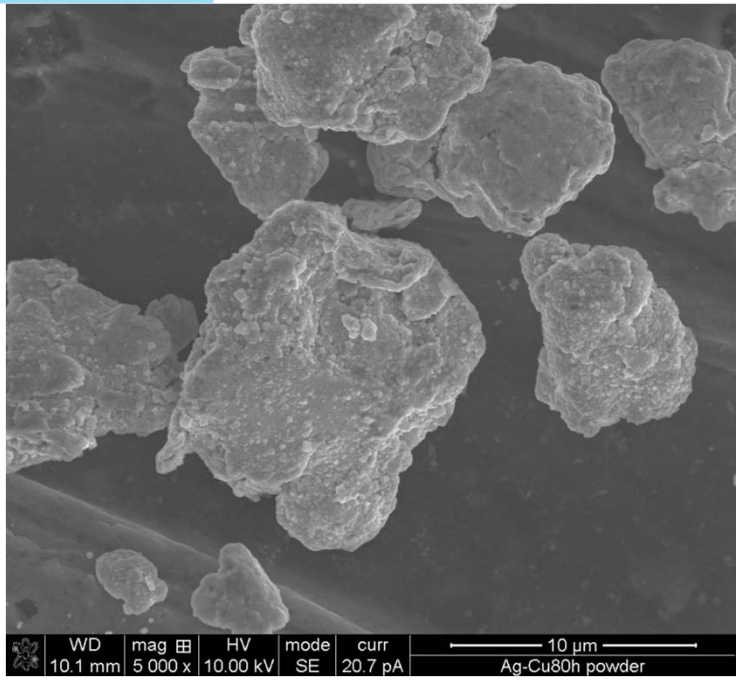
In order to further evaluate the thermal analysis data, the enthalpy of the samples was investigated by drop calorimetry using a multi-detector high temperature calorimeter (MHTC-96) of SETARAM. The thermal effects associated with the powder micro-relaxation, as well as with the melting are well evidenced by the enthalpy data. For the temperature ranges in which no transformations have been observed, the data were linear fitted and the heat capacities were determined.

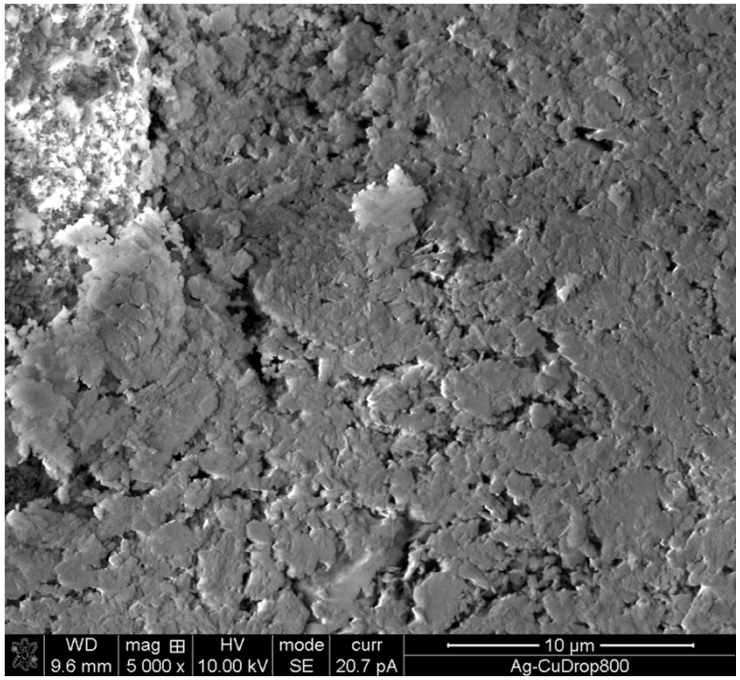




T, K	ΔH (J/g) MA20	ΔH(J/g) MA80	ΔG (MA20) (J/g)	ΔG (MA80) (J/g)
473	53.32	53.96	-1029.85	-396.03
498	58.48	60.7	-1081.94	-414.62
523	63.94	67.08	-1133.73	-432.91
548	75.56	70.3	-1179.36	-445.04
598	91.32	87.85	-1278.1	-1050.86
623	99.86	91.11	-1326.81	-1090.07
648	107.15	100.42	-1376.77	-1130.53
698	120.1	118.83	-1478.32	-1214.35
748	132.7	128.12	-1580.22	-1300.56
798	175	145.06	-165.42	-1379.12
848	188.75	159.24	-1753.17	-1460.44
898	189	189.3	-1867.42	-1525.88
948	199.76	202.62	-1971.16	-1608.06
973	199	202.01	-2021.17	-1656.42
1023	215	220.4	-2127.67	-1733.53
1098	353.92	279.4	-689.18	-1949.54
1123	363.57	303	-703.28	-1976.69
1148	363.9	314	-2276.5	49.96
1173	359.67	306	-2338.23	36.21
1198	365.52	316	-2389.88	40.46
1223	366.26	347.72	-2446.64	-8433.42
1248	420.32	388.1	-9339.04	-8572.54
1273	447.62	418.5	-9507.24	-8721.64


Alloys Phase Diagrams, vol.3, ASM International, 1991
C_p
ΔH
400
380
360
340
320
300
ΔH (J/g)
0.38
0.36
0.34
0.32
0.30
0.28
0.26
C_p (J / g K)
0
20
40
60
80
Milling time (hours)





SEM results for MA80 samples at 10 micrometers zoom

Conclusions

- The thermal behavior evidence: a) the powders micro-relaxation, b) alloy melting process
- Accurate enthalpy increment data as a function of temperature in the temperature range 200 -1000 ^{0}C could be measured by using Drop Calorimetry. The variation of enthalpy depends on both the temperature and the milling time used during the Mechanical Alloying (MA) route.
- For longer times of milling (which mean small particle size) the effect of the powder micro-relaxation is more evident. Instead, the melting point is shifted to lower temperature.
- Further studies are in progress in order to evidence correlation between the energetic parameters and the thermal expansion coefficients (measured in our laboratory by TMA method) as an useful parameter to evaluate the mechanical stability and deformability of the alloy as a function of temperature.
- The mechanical alloying is a promising method for the nanoalloys synthesis.
- Processing parameters can be changed in order to obtain different thermal effects. It is thus possible to find new routes to influence the behavior in terms of relaxation effects, melting point and deformation processes at low or elevated temperatures.

Acknowledgments

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THANK YOU !