MULTIFUNCTIONAL MATERIALS OF ULTRA-PERFORMANCE FOR SPECIAL APPLICATIONS

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ABSTRACT

After 11th September 2001, the global security environment has changed radically, passing from symmetrical to asymmetrical risks and threats. This is especially based on using different forms at rapid reaction based on using advanced technologies in the field of communications sensors and ammunitions. The researches in the military field are working on identifying those solutions which will allow counter acting those asymmetric actions through using conventional military means, and through increasing their efficiency and reducing the collateral damages. Nowadays, in medium and long range military actions are used 8360 tones of conventional ammunition per 5 days of action (implying large quantities of materials with negative impact on the environment), which have efficiency of max 50% from their real potential. From the data obtained so far, in Iraq 300,000 tones of ammunition with different purposes were used, from which more than 60% were used in urban areas with recognized implications on the environment and the social and economical activities in the area. Through using other technologies to create ammunition (intelligent and nonpolluting) it is considered that at a reduction of 30% of their quantity, their efficiency will raise to over 70%. The aims of this paper consists in the development of complex multifunction materials with nanometric structure and controlled characteristics for special use (civil and or military) with the aid of integrated and flexible technologies for industrial, sectorial and inter-sectorial [1].
Hard alloys based on tungsten (AGW) are this category of metallic materials that have as main compound the tungsten, alloyed with one or many transition metals, like Ni, Cu, Fe, Co etc. Tungsten base hard alloys, composite type have a characteristic embedding structure, biphasic, where the major phase is formed by spheroidal tungsten grains, crystallized in cubic system with centered volume (ccv), embedded in a more ductile matrix, formed by a solid solution soft alloying metal or metals (as a rule from iron group) saturated in tungsten, crystallized in cubic system with centered sides (ccs). This type of alloys have an unique configuration of remarkable properties consisting of: high density, superior mechanical resistance, high ductility, good corrosion resistance, high capacity of radiation absorption, good processing properties, remarkable toughness. The levels of these properties can be modified in very large limits by the help of composition and microstructure, determined in turns by the elaboration technological parameters, depending on the applications of AGW.

Some of the potential applications of the system of materials above-mentioned realised by integrated technologies type mechanical alloying – plastic state forming procedures – sintered in micro-wave field, can be:

* application in army field: Different parts devoted to equip systems of weapons like: non-toxic missiles (that do not contain uranium, lead, etc), missiles with controlled behavior at impact, anti-tank ammunition, guiding devices for cruise rockets, etc;

* other fields: Different products for air industry (counterweights to statical and dynamical balance the ailerons for planes and helicopters, mechanisms of control for direction of low rudders, of rotor pallets, devices for radiation barriers allowing attenuation of X rays, disks for computers, magnetic strips, constant magnets, sensors and convectors for solar energy, heads for digital reading, substitutes for diamond powder, inductive compounds, high temperatures resistors, etc.

**KEY WORDS**
Conventional ammunition, complex multifunction materials, heavy alloys.

1. INTRODUCTION

Hard alloys based on tungsten (AGW) are this category of metallic materials that have as main compound the tungsten, alloyed with one or many transition metals, like Ni, Cu, Fe, Co etc. Tungsten base hard alloys, composite type have a characteristic embedding structure, biphasic, where the major phase is formed by spheroidal tungsten grains, crystallized in cubic system with centered volume (ccv), embedded in a more ductile matrix, formed by a solid solution soft alloying metal or metals (as a rule from iron group) saturated in tungsten, crystallized in cubic system with centered sides (ccs). This type of alloys have an unique configuration of remarkable properties consisting of: high density, superior mechanical resistance,
high ductility, good corrosion resistance, high capacity of radiation absorption, good processing properties, remarkable toughness [2].

The firing of small arms ammunition is a significant environmental and health problem. The ammunition’s projectile which is traditionally composed of lead and copper, is the principal source of pollution. Rifle, pistol, and shotgun projectiles composed of materials which are not significant environmental or health hazards, and that are economically recyclable are being developed. The primary objective is to develop high density, non-toxic bullets. The projectiles must meet all performance specifications of current bullets, but must significantly reduce or eliminate exposure of the shooter to hazardous materials and reduce environmental contamination.

Controlled impact behavior and penetration are additional considerations for the use of a fragile projectile that disintegrates upon impact, reduces damage to training facilities, lowers the risk of ricochet and thus personal injury, and permits the use of a broader range of weapons in situations where overpenetration is a problem (e.g. inside a nuclear reactor facility or a hazardous waste storage area).[3]

Mechanical alloying is a versatile method for producing advanced materials by solid state powder processing and has already received numerous industrial applications.

At a qualitative level, the phenomena occurring during mechanical alloying have been understood and consist, essentially in a continuous process of deformation, fracturing, local heating, solid state welding and re-fracturing of powder particles under the effect of the transferred energy from the milling balls /1/. Submicron or nanocrystalline powders, amorphous phases or intermetallic compounds may be thus obtained at room temperature. Mechanical alloying has a wide range of materials such as: alloys (Al-Fe, Al-Ni, W-Cu, W-Ni-Cu, W-Ni-Fe); intermetallics (Si-Cu, Ti-C, Ti-Si, Ti-Br); magnetics (Fe-Si, Fe-Be-N, Ba-Fe-O); hard materials (W-C, V-C, Ti-C, Si-N, Fe-C) and many others[4] are suitable to be processed nowadays by mechanical alloying.

In recent years the group of tungsten – based materials known as heavy alloys by virtue of their high density (16 to 18.5 x 10^3 kg m^-3) have found an increasing number of applications in mass balancing and inertial gyroscopes and vibration dampeners, and also in, radioactive shielding and heavy duty electrical contacts. Processing such materials by mechanical alloying is very attractive, but through investigation is still required to keep under control the resulting material characteristics, mainly its microstructure (very fine structure, high dispersion grade, amorphous phases etc.))[5].

2. EXPERIMENTAL CONDITION

A flow sheet for obtaining W-Ni-Cu sintered products that includes mechanical alloying was proposed and investigated. This purpose have been performed in the following sequence: • experimental materials systems choose; • powder characterization in accordance with actual international standards; • gravimetric
dosage of component powders; • filling in planetary mill with W-Ni-Cu powders and balls followed by milling during 195 h period; • dosing the W-Ni-Cu powders mixture after the mechanical alloying, by homogenization of this mixture during 35 h; • binding the obtaining powder mixture; • pressing; • debinding - presintering; • sintering; • characterizing the products resulted; • mechanical processing.

As raw materials is has been used pure W, Ni, and Cu powders with the following weight ratio: W:Ni:Cu = 95:3.5:1.5. The characteristics were determined according to International Standards: ISO 3923/1 – Apparent density; ISO 4490 – Flowing rate.

The particle size was measured with a Fisher apparatus (powder permeability to water). A mixture of tungsten, nickel and copper powders were ground in an attritor, without protective atmosphere or lubricant.

<table>
<thead>
<tr>
<th>Material</th>
<th>Flowing rate (g_{50g})</th>
<th>Apparent density (g/cm^3)</th>
<th>Particle size FSSS ((\mu m))</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>not flowing</td>
<td>3.40 ± 0.01</td>
<td>1.62 ± 0.01</td>
</tr>
<tr>
<td>Ni</td>
<td>not flowing</td>
<td>2.46 ± 0.01</td>
<td>4.86 ± 0.01</td>
</tr>
<tr>
<td>Cu</td>
<td>not flowing</td>
<td>1.34 ± 0.01</td>
<td>5.81 ± 0.01</td>
</tr>
</tbody>
</table>

For milling an attritor with the following parameters: • milling speed = 100 rot/min; • milling time = 195 hours; • ball / powder weigh ratio = 3:1; • filling grade = 25 % has been used.

As shown in Fig. 2 previously the copper powder used was reduced in Siemens Plania furnance, in hydrogen atmosphere at the 270°C.

As shown SEM scanning electron micrograph in Fig. 1 reduced copper powder before mechanical alloying consisted of micronics particles of irregular shapes (dendritic structure).

As shown in Fig. 3 tungsten powder was of a spherical particle shape with an average size of 1 \(\mu m\); micronics particles of irregular shapes with surface roughness, were also put in evidence nickel particles were of spherical shape with a powerful tendency of agglomeration.

The powders were mechanically alloyed together with the copper reduced powder, then they were homogenized during 35 h, in a taper closed having a 75 mm diameter and 95 mm length, fixed on a rotating device, the rotation \(n= 60\) rot/ min.

The mechanically alloyed powder was taken out of the container periodically to follow the progress of alloying every 20 hours. The total grinding time was 195 hours. After 30 hours milling we have observed the sticking of the powder to steel balls and tank of attritor. After a longer time the powder started to agglomerate.
3. RESULTS AND DISCUSSION

The effect of mechanical alloying on the powder mixture characteristics are presented in Table 2.

Table 2. The characteristics of processed powders after 195 hours ball milling

<table>
<thead>
<tr>
<th>Powder type</th>
<th>Main diameter FSSS (μm)</th>
<th>Flow rate s/50 g</th>
<th>Free descharged apparent density g/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-Ni-Cu</td>
<td>0.20 ±0.01</td>
<td>No flow</td>
<td>4.88 ±0.01</td>
</tr>
</tbody>
</table>

The data in Table 2 show that increasing the milling time has resulted in an increased apparent density and a decreased particle size. Increasing of the apparent density could be explained by particle shape changes during milling. So, by increasing the milling time, the sharp edges of the particles become rounded. It means that particles packing amount increases and, also mechanical interlocking are reduced.[4]

The morphology of the W-Ni-Cu composite powder mixture at the end of the applied ball milling process is revealed in Fig. 4, a homogenous distribution of very fine grains and uniform repartition of components is clearly seen.

Also are seen conglomerates with irregular shapes formed by welding of many particles. As a result, after 195 hours grinding, the shape of particles submitted to mechanical alloying was not yet stabilized.

The series of SEM micrographs in Fig. 5 (a, b, c, d) were recorded in order to put in evidence the way by which the mechanical alloying process influences the morphology of powder particles: it can be seen that the powder particles, due to the repeated impacts, start to agglomerate (Fig. 5a), to repeatedly break (Fig. 5b), following a complex process of fragmentation, deformation, cold welding and diffusion on a small scale (Fig. 5c and 5d).

The mechanically alloyed powder mixtures were, then, binded to paraffin (2%), sieved in a semidry state by a sieve with 0,1 mm mesh size and dried, finally obtaining a mixture “ready to be pressed”.

The pressing was performed bilaterally on a steel die with a circular section, showing the following characteristics: \( \phi_{ext}=47 \text{ mm} \), \( \phi_{int}=14,3 \text{ mm} \); \( S=(\phi_{ext}^2-\phi_{int}^2)=15,73 \text{ cm}^2 \), for a specific pressure, the green compacts were debinded in the Siemens Plania furnace, in a hydrogen atmosphere, by using as packing agent - alumina, which was
calcined in advance at 1450 °C, during 5 h, in order to provide heat resistance (endurance).

The parameters of the debinding presintering process were:

• $\text{H}_2$ atmosphere;
• heating rate up to 500°C: 0.8 °C/min;
• heating rate between 500-800°C: 3.5 °C/min;
• presintering temperature: 800°C;
• 30 min exposure time to presintering temperature;
• total duration of the debinding – presintering cycle: 8h 30 min;

The sintering operation was performed in heating evacuated induction furnace, with intermediate frequency currents, of Balzers type. The sintering operation parameters were:

• sintering temperature: 1250°C;
• 60 minute exposure time to sintering temperature;
• total duration of the cycle: 8 hours.

Further investigation was carried on the sintered product. The sintered material was characterised by the physical – mechanical and structural properties all along the stage. In Table 3 are indicated the physical and mechanical characteristics of the sintered markers obtained from mechanically alloyed powder mixtures.

**Table 3. Physical and mechanical characteristics of sintered markers**

<table>
<thead>
<tr>
<th>Material type</th>
<th>Density (g/cm³)</th>
<th>Brinell Hardness HB</th>
<th>Stretch resistance (N/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sintered markers 1250°C</td>
<td>16.99</td>
<td>220</td>
<td>790</td>
</tr>
</tbody>
</table>

The sintered grades were prepared for metallographic examination with the aim to:

• determine the presence, type and repartition of pores;
• determine the microstructure.

The SEM micrographs in Fig. 6.a, b emphasize the uniform repartition of the two phases present in the material: the Ni-Cu metallic binder phase and the tungsten (W) phase.

Also put in evidence in Fig. 6. a,b is the lack of porosity which has as a result the obtaining of a particular density of the material, very close to the theoretical density.

The experimental results from Table 3 and Fig. 6 give us reasons to consider the technological flow-sheet we have investigated in this paper (including mechanical alloying) as a valuable route for manufacturing a series of products which are representative for the W-Ni-Cu system.

Fig. 7 shows the representative product from W-Ni-Cu system – small and medium ammunition projectile[3].
4. CONCLUSIONS

The experiments lead to the following conclusions:

• During the milling process, the powder particles are trapped between the milling balls and then plastically deformed, thus rupturing the layers of surface contaminants on individual particles and exposing a clean metal surface;

• By the mechanical alloying technique we have succeeded to obtain a powder composed of W-Ni-Cu with a very fine granulation, a uniform repartition;

• The higher homogeneity of the W-Ni-Cu powder mixture obtained through the mechanical alloying process appears to have had a significant effect on the densification of the particular powders, perhaps by allowing both of the liquid-phase-driven sintering mechanisms to proceed more effectively;

• The emphasized technological flow-sheet which includes mechanical alloying will allow the manufacturing of products which are representative for the W-Ni-Cu system – small and medium ammunition projectile, which comply with the users requirements.

REFERENCES

[1] Irina Carceanu, Georgeta Cosmeleata, Ion Roceanu - Multifunction complex materials with nanometric structure and controlled characteristics for special use / NANOSTRUCT, Program of Excellence Research, Project 143/2006


Fig. 1. Morphologic aspect of reduced copper powder-particles of dendritic shapes
(SEM micrograph 3000X)

Fig. 2. Morphologic aspect of Ni powder
(SEM micrograph 2480X)

Fig. 3. Morphologic aspect of W powder
(SEM micrograph 2480X)
Fig. 4. SEM micrograph of the WNiCu powder mixture after 195 hours ball milling 4780X

Fig. 5. SEM micrographs revealing the morphological changes of the composite WNiCu powder mixture during the mechanical alloying process
a. after 45 hours of milling; b. after 80 hours of milling;
c. after 80 hours of milling; d. after 120 hours of milling

Fig. 6. SEM microstructure of the mechanically alloyed $W_{95}\text{Ni}_{3.5}\text{Cu}_{1.5}$ powder mixture after sintering for 1 h at 1250°C
a. 2000 X magnification; Murakami etchant;
b. 10000X magnification; Murakami etchant

Fig. 7. Raw powders – Final products sintered from the mechanically alloyed $W_{95}\text{Ni}_{3.5}\text{Cu}_{1.5}$ powder mixture