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Dense Nanostructured Materials Obtained by Spark Plasma Sintering and Field Activated Pressure Assisted Synthesis Starting from Mechanically Activated Powder Mixtures

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Abstract:

The preparation of highly dense bulk materials with a grain size in the range of a few to a few hundreds nanometers is currently the objective of numerous studies. In our research we have achieved a measure of success in this regard by using the methods of mechanically-Activated, Field-Activated,Pressure- Assisted Synthesis, MAFAPAS, which has been patented, and Mechanically- Activated SparkPplasma Sintering, MASPS. Both methods, which consist of the combination of a mechanical activation step followed by a consolidation step under the simultaneous influence of an electric field and mechanical pressure, have led to the formation of dense nanostructured ceramics, intermetallics, and composites, such as, $MoSi_2$, FeAl, $NbAl_3$, and TiN-TiB_2. In this report, both one-step synthesis-consolidation and sintering of different nanostructured materials by SPS and FAPAS were investigated.

Keywords: *Spark plasma sintering, Mechanical activation, Field activation, Pressure assisted synthesis*

1. Introduction

The relative dearth of experimental data on mechanical properties of nanomaterials has been attributed to the difficulty in preparing dense bodies [1]. The recent success has been the results of combining mechanical activation with field activation. Four decades ago, high energy ball milling and mechanical alloying of powder mixtures were reported to be efficient techniques for the preparation of nanocrystalline metals and alloys. However, in such a case, it is necessary to add a consolidation step to obtain a fully dense material. In fact, to elaborate, from nanopowders, nanostructured dense materials having the desired form, one or several steps of compaction before or during the sintering are necessary. However, during this operation along with densification grain growth also takes place and can dramatically change the nanostructure to microstructure [2]. Consequently, to obtain materials that are dense and nanostructured, it is necessary often to use non-conventional sintering techniques. One promising technique was the combination of mechanical and field activation. A few years ago, the simultaneous effect of an electrical field combined with an applied pressure during

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the combustion, using the Field-Activated Pressure-Assisted Synthesis (FAPAS) process was found to be suitable to produce good quality dense intermetallic compounds in a one step process [3,4]. Consequently, the application of this technique on mechanically activated powders was undertaken in order to investigate a new route hereafter called the MAFAPAS process [5,6].

Success in forming dense bulk nanostructures stems from the use of two forms of activation sequentially: mechanical activation (MA) by high-energy ball milling and field activation by the use of high-density currents. In field-activated pressure-assisted synthesis (FAPAS) activation is accomplished by an AC current (60 Hz), the sample is subjected to a uniaxial pressure during the passage of the current. With this approach, several dense nanostructured materials have been fabricated, including intermetallics (e.g., FeAl [6] and $NbAl_3$ [7]), ceramics (e.g., $MoSi_2$ [8]) and composites (e. g., TiN-TiB_2 [9]). In a recent paper [10], the optimal conditions for producing dense (99% relative density), nanostructured (≈ 80 nm crystallite size) FeAl were determined.

A process that also relies on field activation, called Spark Plasma Sintering (SPS), has been also developed and has received increased attention [11]. The combination of mechanical activation and the SPS, hereafter called the MASPS process, has been shown to be suitable for the production of materials having nanostructure and a controlled consolidation level. In fact, the SPS process is a newly developed synthesis and sintering process that, it is claimed uses microscopic electric discharges between the particles under pressure [12]. This has been acknowledged to reduce significantly the synthesis and densification temperatures limiting the grain growth. This process is similar to conventional hot pressing, in that the precursors are loaded in a die (typically graphite) and a uniaxial pressure is applied during the synthesis or the sintering. However, instead of using external heating source, a pulsed DC current is allowed to pass through the sample and also through the electrically conducting pressure die.

Consequently, in order to control such processes (i.e. to produce materials with a perfectly controlled degree of densification and microstructure), it is vital that an understanding of the mechanisms involved in the processes is at hand. In particular, it will be essential to compare these two sintering processes (reactive or non-reactive) with different conducting materials (e.g. intermetallics) or insulating (e.g., ceramics). In fact, in the framework of this work, a comparative study between the FAPAS (field activation by an AC current) and SPS (field activation by pulsed DC current) processes was initiated. Such a study should allow us to understand the role of the electric stimulation on the sintering conditions and on the microstructure of the end products.

In this paper, we present results on the sequential use of mechanical and field activations to (a) synthesize and simultaneously densify nanostructured materials, and (b) to microalloy a refractory silicide for enhanced mechanical properties. The objective of this part was to demonstrate the effectiveness of this approach in forming a variety of highly dense nanostructured materials. The objective of the second part was to incorporate Mg atoms onto the Si sub-lattice of $MoSi_2$, a goal that has not been previously accomplished and whose practical implications are quite important [13]. Theoretical calculations have shown that the undesirably high ductile-brittle transition temperature (DBT) of $MoSi_2$ can be substantially lowered if Mg can be substituted for Si on the latter's sub-lattice [14]. Previous efforts at accomplishing this goal were not successful primarily due the high vapor pressure of Mg.

2. Experimental methods and materials

2.1. Simultaneous Synthesis and Consolidation of Nanostructured Materials

The MAFAPAS and MASPS used in this work to produce dense nanostructured FeAl

from a powder mixture of elementary reactants are based on the combination of two principal steps:

(i) **Mechanical Activation (MA)**: a mechanical activation step performed in a high-energy planetary ball mill. Mixtures of pure elemental powders of Al (Cerac, 15-20 μm particle size, and 99.5% purity) and Fe (Prolabo, 10-15 μm particle size, and 99.5% purity) in a stoichiometric ratio of 53 at% Fe (and 47 at % Al) were co-milled in a Fritsch planetary ball mill (the vario - mill P4 Pulverisette). The mill is based on the G5 planetary prototype developed by Gaffet [15,16]. This planetary mill allows for shock frequency (ω) and shock energy (Ω) to be independently selected. Based on previous work [17] a specific ball-milling condition was selected for this work. The rotation speeds of the platform (Ω) and the vials (ω) were set at 150 and 200 rpm, respectively, and the milling time was chosen to be 4 h uninterrupted. The aim was to avoid the formation of any aluminide phases during milling. The charge ratio C_R (ball to powder mass ratio) was 7.

(ii) **Field Activation**: The mechanically activated (MA) powder mixtures were first cold compacted into cylindrical graphite dies lined with graphite foil using a uniaxial pressure of 80 MPa for 2 minutes.

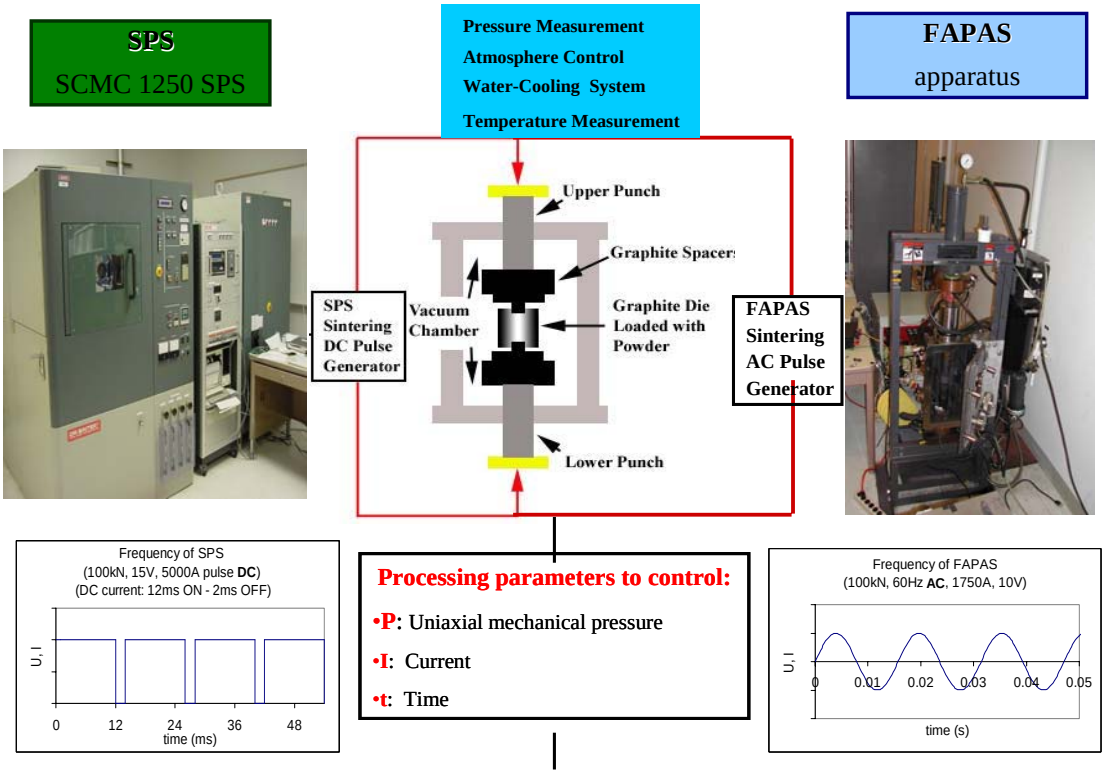
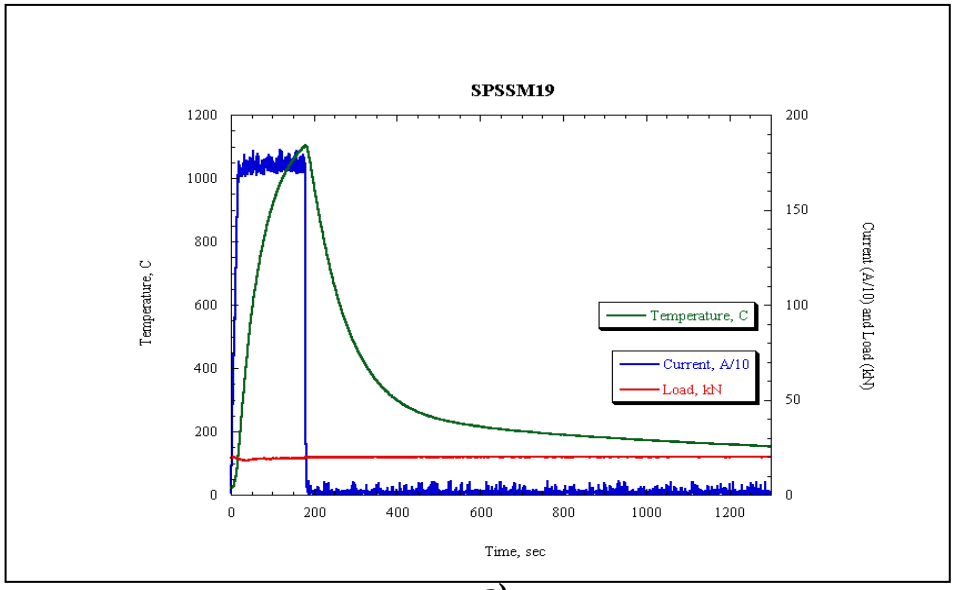


Fig. 1 General description of SPS (on the left) and FAPAS (on the right) machines and their characteristics.

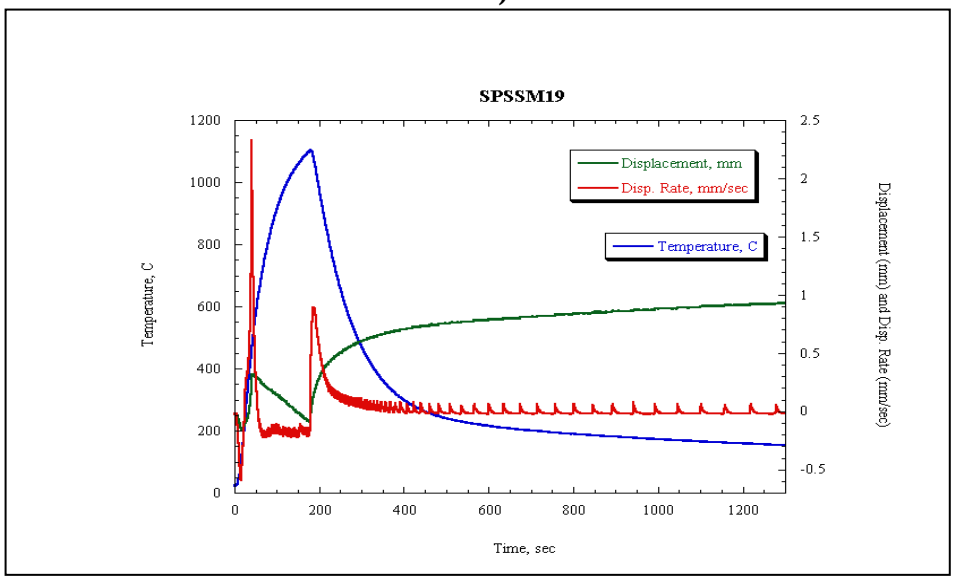
The relative density of the green sample resulting from this process was about 70%. The graphite die containing the cold-compacted samples was placed inside the SPS (Fig.1a) or FAPAS (Fig.1b) reaction chambers. The chambers were then evacuated and back-filled with argon (industrial argon, 99.995% pure) to minimize oxidation.

(a) FAPAS: Once inside the FAPAS, the samples were then subjected to a high AC current (1750A; 60Hz) and a pressure (70 MPa). Under these conditions, a reaction is initiated and is completed within a short period of time (2-5min) after which the current is turned off and the samples were allowed to cool. Temperatures were measured by an optical pyrometer focused on the surface of the die.

(b) SPS: The apparatus used is the 1050 SPS machine made by the Sumitomo Coal Mining Company [11]. This machine consists of a uniaxial 100 kN press combined with a 15V, 5000A pulsed DC power supply. The pulse cycle in this work was 12 on and 2 off. This means that there were 12 pulses of 3.2 ms each followed by a 6.4 ms (2x3.2 ms) off. A uniaxial pressure of 70 MPa was applied during the reaction and maintained during cooling. A high DC current was applied, increasing from 0 to 1750 A in 20 s then held at the maximum value for 220 s. Temperatures were measured on the external surface of the die by means of a type-K thermocouple and/or a pyrometer. As an example, the changes of the SPS parameters during the synthesis of the intermetallics are shown in Fig. 2. The temperature, current, and shrinkage depicted in this figure are the same for all samples and compositions.



a)



b)

Fig. 2 a) Evolution of temperature, current and load versus the time and b) Evolution of temperature, and shrinkage versus the time for producing dense nanostructured FeAl using SPS technology

The end products were typically disks of 18.8 mm in diameter and 2.2 mm in height. The samples were first polished with SiC paper to remove surface contamination from the

graphite die and foil. Phase analyses were made by X-ray diffraction (XRD) using a D5000 Siemens high-resolution diffractometer with a monochromatic Cu-K_β beam (λ=0.1392 nm) focused with a secondary curved graphite monochromator. The microstructure of the end products was studied by scanning electron microscopy (SEM) and the local phase composition was determined by energy dispersive X-ray spectrometry (EDXS). In order to show the composition distribution, the samples were cut along the axial direction and were embedded in carbon charged resin (Konductomet®). A back-scattered electron (BSE) SEM technique was also used to determine the elemental distribution. The density of the end products was evaluated by the Archimedes method.

2.2. Microalloying of $MoSi_2$

The starting materials were pure elemental powders of silicon, molybdenum, and magnesium (Alfa Aesar Ward Hill, Massachusetts). All powders had a sieve classification of –325 mesh. The Si and Mo powders were 99.999% pure and the Mg powders were 99.8% pure. The powders were mixed to give a nominal Mo/Si ratio of 1/2 but adjusted by the addition of Mg which is to be substitutionally incorporated into the Si sub-lattice. The level of addition was varied but a typical value is 5.00 at% based on Si. Thus 5 at % means the product would be Mo ($Si_{1.9}Mg_{0.1}$).

The mixed powders were milled in a Fritsch planetary mill (Pulversette 4). A charge ratio, C_R, of 14 and a rotational speed of 250 rpm were utilized in this work. The milling cycle adopted was 24 h total time, with the cycle being 5 min on 10 min off, providing a total actual milling time of 8 h. The starting nonmilled and post-milled powders were analyzed in a Scintag XDS-2000 diffractometer using CuKα radiation (λ=1.5405 Å). The powders (nonmilled and milled) were then densified (and or reacted) in a Spark Plasma Sintering (SPS) apparatus (Sumitomo, model 1050). The dense samples were analyzed for evidence of Mg incorporation using X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), TEM, EELS, and HRTEM.

3. Experimental Results

3.1. Dense Nanostructured Materials

Mechanical Activation (MA): The structure of the mechanically activated powders is seen as aggregates (0.2 to 200 μm, Fig. 3) composed of Al and Fe nanocrystallites. Mechanical activation leads to the formation of a large contact area between reactants.

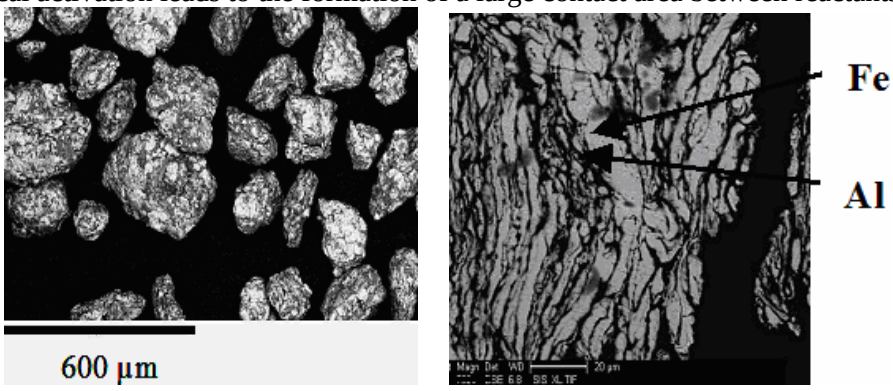


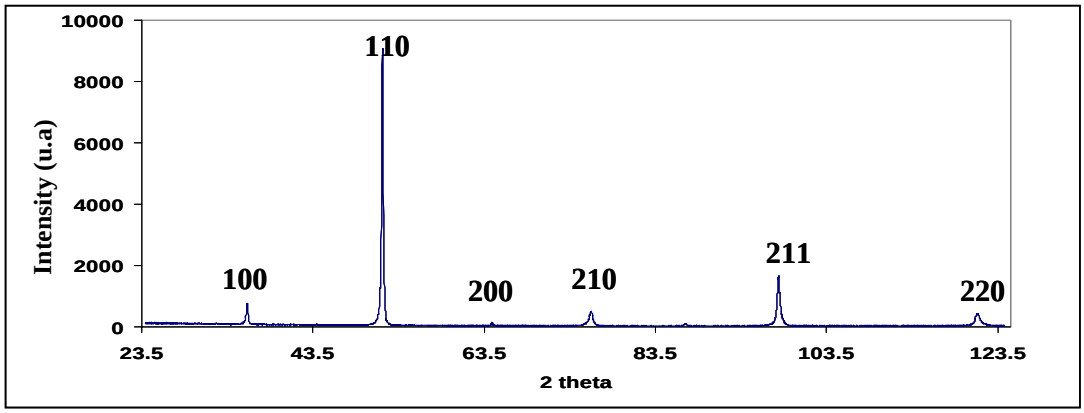
Fig. 3 SEM observations of MA powders (G5(150/-200/4h)) in the case of FeAl system.

Conventional interpretative methods (i.e. XRD line-broadening peak profile analysis) showed that the Fe and Al particles exhibit average crystallite sizes of 70 nm and 50 nm,

respectively. As a consequence, repeated fractures and welding during the short duration ball milling create polyinterfaces at a nanometric scale and destroy the oxide surface layers which may exist on the Fe and Al powders.

Field activation (case of reactive sintering): XRD patterns of the products of both processes (MASPS and MAFAPAS) are presented in Fig. 4. The XRD patterns confirm the presence of the FeAl phase only. However, despite the polishing step, graphite contamination is still possible, as indicated by the presence of small graphite peaks. Identical XRD patterns were obtained from different samples showing the reproducibility of these processes.

a) SPS



b) FAPAS

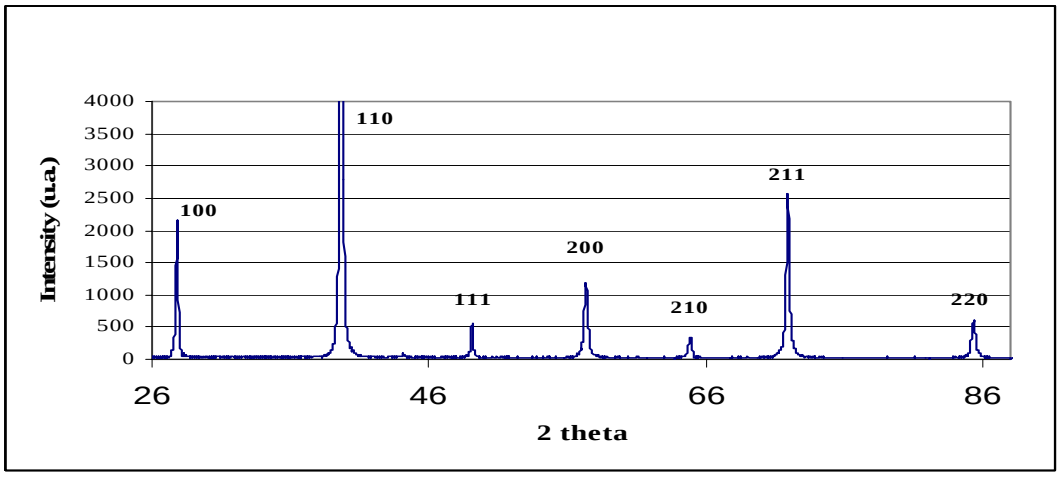


Fig. 4 XRD patterns of FeAl produced respectively by a) SPS and b) FAPAS techniques.

The XRD profile line analysis described by Langford [18] for the (h00) and (hh0) harmonics was used to determine the mean apparent crystallite size and microstrain level. Results of such an analysis are summarized in Table I.

Tab. I Characteristics of end-products produced by FAPAS and SPS process respectively.

Process	Density	Phase	Crystallite sizes	I_{100}/I_{110}
MAFAPAS	98 – 99%	$Fe_{53}Al_{47}$	30 – 90 nm	14 – 16 %
MASPS	93 – 99%	$Fe_{53}Al_{47}$	30 – 60 nm	10 – 16 %

Using our current method, the synthesized FeAl exhibits a crystallite size ranging from ~30 to ~100 nm. Global and local phase analysis (EDXS) on several areas revealed that

the composition of samples is close to the expected compositions based on the initial stoichiometry. Explanations of the small difference in composition (i.e. scatter) can be attributed to the difference in composition in each mechanically activated grain or by the possible presence of Al_2O_3 in the grain boundaries or the possible distribution between A2 and B2 phases. Relative density measurements by the Archimedes method provided values of 93.5% and 98.5% for each sample made by the FAPAS and SPS methods, respectively.

3.2. Microalloyed $MoSi_2$

XRD patterns of nonmilled powders that had been reacted in the SPS showed the presence of free magnesium, indicating that it was not incorporated into the $MoSi_2$ phase [**14**]. In contrast, the XDR patterns of the powder that was milled and subsequently treated in the SPS showed that no free magnesium is present. Subsequent TEM and EDS analyses showed that Mg was indeed incorporated. HRTEM analyses were made on milled and reacted samples containing Mg.

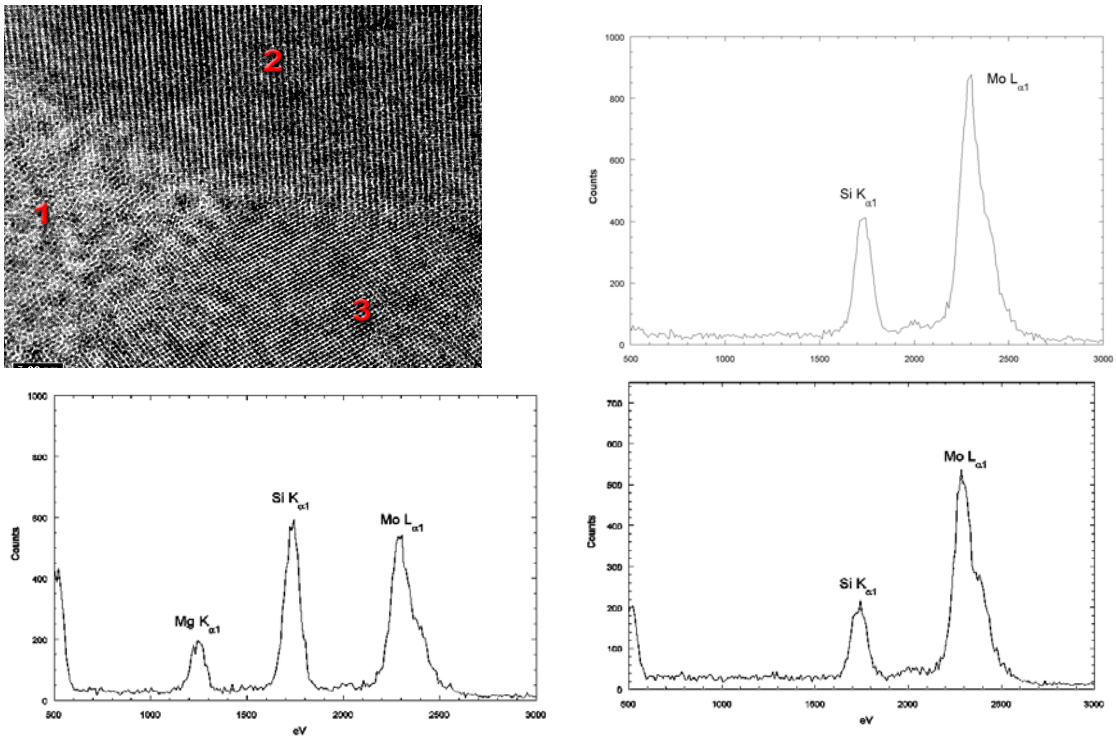


Fig. 5 HRTEM analysis of 3 grains. 1. $MoSi_2$ with Mg incorporation (spectrum below the photograh). 2 and 3 Mo_5Si_3 without Mg incorporation (spectra on the right)

Fig. 5 shows three grains with boundaries exhibiting no discernable impurity phases. EDS analyses on the three grains (numbered in Fig. 5) showed that grain 1 is $MoSi_2$ while grains 2 and 3 are Mo_5Si_3. Furthermore, the analysis shows that there is no detectable magnesium within the Mo_5Si_3 grains. More important, however, is the evidence of the presence of Mg within the α-$MoSi_2$ grain.

4. Discussion

While the experimental evidence of the benefit of the current is overwhelming, the nature and the actual role played by the current are not well understood. The current can

influence these processes contributing one or more of the following: (i) Joule heating (the rapid rate of Joule heating is a significant outcome), (ii) mass transport enhancement due to electromigration or defect generation [19], and (iii) creation of an electrical discharge (or/and plasma) which is created surrounding the particles and that such a condition is the reason for the clean grain boundaries reported in materials sintered in the SPS [20]. The difficulty remains in the experimentally demanding requirements to isolate the thermal effect from the mass transport effect and to directly verify the occurrence of plasma under actual SPS conditions.

For the case of reactive sintering (n(A+B)➔ nAB, where n means nanostructure), it was shown that high-energy ball milling treatment allows the control of the formation of pure and nanometric compounds by fixing the reactant powder microstructure. Mechanical activation (MA) can increase the combustion front velocity by a factor of three compared to the value obtained under the same condition on nonmilled reactants [21]. Indeed, MA would promote the number of potential nucleation sites and produce finer crystallites. In addition, the presence of mechanically alloyed phases has been found to have a positive effect on the final microstructure because these later act as a heterogeneous nucleation site with a good distribution inside the grains and hence decrease the combustion temperature [21]. Then, the full benefit of such nanostructured materials may be preserved only if the consolidation process can eliminate extensive grain growth. Spark Plasma Sintering processing is a consolidation method, which has demonstrated the capability of retaining the fine-grained size of starting powders (FeAl nanophase prepared by a 20 hours mechanical alloying processing, [22]). Indeed, the SPS process is a very interesting route that allows compaction and simultaneous synthesis-consolidation of ceramics and powdered metals at low temperature with short holding time, the mechanisms for densification and grain growth behind this process have not yet been explored [23].

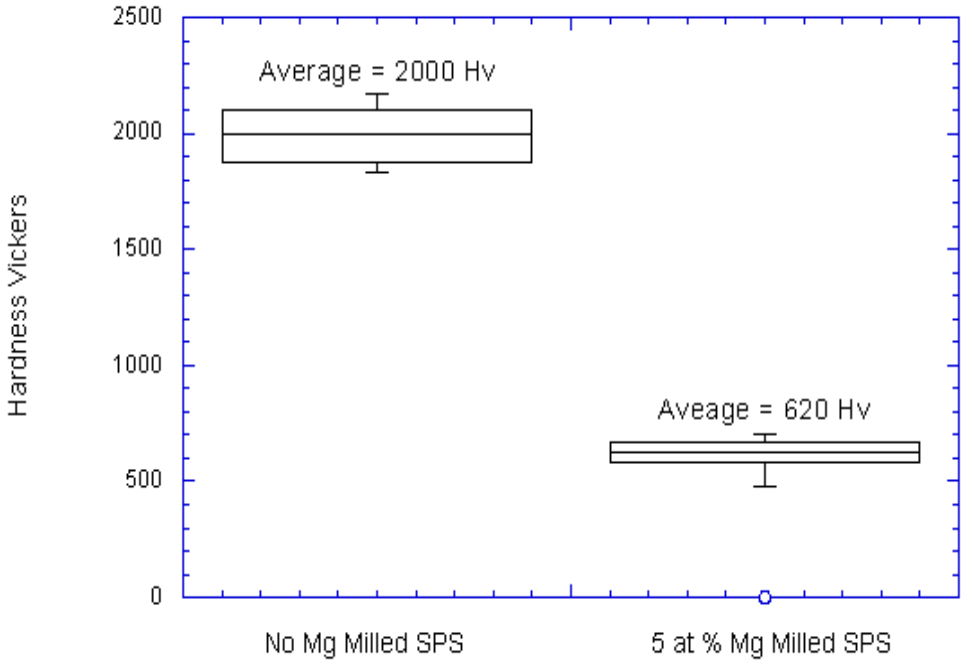


Fig. 6 Effect of Mg (5 at.%, Si based) incorporation on hardness of $MoSi_2$

However, it has been demonstrated [24, 25] that it was possible to control the microstructure of end products by controlling the SPS parameters of temperature, the heating rate, and pressure. Indeed, it was shown [26], that the critical temperature at which the grain

growth rate is appreciable depends on the characteristics of the precursor powders such as particle size, degree of agglomeration, etc., and also on the applied pressure and the heating rate. In our work, the use of a very fast heating rate is an important requisite for maintaining the nanostructure. Indeed, the benefit effect of using a high heating rate which is reported elsewhere [27, 28] is to enhance the final density of the product in metal-Al systems. This effect was attributed to the extent of liquid phase formation during the combustion reaction. According to these authors, a higher heating rate decreases the amount of pre-combustion phases formed to slow heating rate interdiffusion.

The results on the microalloying of $MoSi_2$ showed that Mg was successfully incorporated into this silicide. The important consideration with respect to this accomplishment is whether the incorporation of Mg has an influence on the mechanical properties of $MoSi_2$. Hardness measurements were made on microalloyed and "pure" $MoSi_2$ prepared by the same method. The results, presented in Fig. 6, show that the incorporation of 5 at.% Mg on the Si sub-lattice (3.3 At mg overall) resulted in a dramatic decrease in the hardness, about 70% reduction. These results give clear verification of the theoretical calculations [14] and demonstrate the advantage of the processing method combining mechanical and field activations.

5. Conclusion

The sequential application of mechanical and field activation was shown to be an effective method for the fabrication of dense bulk nanostructured materials. Mechanical activation was accomplished by high-energy planetary milling and filed activation was made through the use of the SPS or FAPASA methods. Dense nanostructured ceramics, intermetallics and composites have been prepared by this approach. However, complementary experiments between SPS and FAPAS processes should be performed in order to understand the role of the current stimulation. Such experiments are in progress. In addition, the approach was also shown to be effective in the hereto fire unachieved goal of microalloying $MoSi_2$ with Mg. The resulting properties of the microalloyed silicide confirmed previously published theoretical predictions.

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***Резюме**: Получение образцов большой плотности, размер зерен которых от нескольких нанометров до нескольких сотых нанометров – в нынешнее время являются объектом исследования во многих работах. В наших исследованиях мы успешно использовали методы механической активации, активирование полем, синтез при помощи давления (запатентированный метод) и механически активированное плазменное спекание. Оба метода, состоящиеся из одноступенчатой механической активации и одноступенчатой консолидации под одновременным влиянием электрического поля и механического давления привели к образованию плотной наноструктурной керамаики интерметаллов и композитов типа $MoSi_2$, FeAl, $NbAl_3$, и TiN-TiB_2. В данной работе изучен одноступенчатый синтез консолидации и спекание различных наноструктурных материалов методами плазмы и активирование полем и синтезом при помощи давления.*

***Ключевые слова**: плазменное спекание, механическая активация, активирование полем, синтез под давлением.*

***Садржај**: Припрема узорака велике густине са величином зрна од неколико нанометара па до неколико стотина нанометара, тренутно је тема великог броја радова. У нашем истраживању постигли смо успех применом метода: механичке-активације, активирање пољем, синтеза помоћу притиска (која је патентирана), и механички-активирано синтеровање плазма варницом. Обе методе, које се састоје од комбинације једностепене механичке активације и једностепене консолидације под истовременим утицајем електричног поља и механичког притиска, довеле су до образовања густе наноструктурне керамике, интерметала и композита, као што су $MoSi_2$, FeAl, $NbAl_3$, и TiN-TiB_2. У овом раду проучена је једностепена синтеза консолидације и синтеровање различитих наноструктурних материјала методама плазма варницом и активираним пољем, као и синтезом помоћу притиска.*

***Кључне речи**: Синтеровање у плазми, механичка активација, активирање пољем, синтеза под притиском.*