

Effects of High-Energy Ball Milling on High Entropy Alloys synthesis by Spark Plasma Sintering.

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# Highlights

- High Entropy Alloys (HEAs) are a new class of promising materials.
- The solid-state synthesis (powder metallurgy) of HEAs is unusual and encouraging.
- Two sets of high-energy ball milling parameters were studied for the synthesis.
- An AlCoCrFeNi HEA was synthesized and consolidated. It exhibits a dual microstructure.

#### 1. Introduction

High entropy alloys (HEAs) contain five or more principal elements with each elemental concentration between 5 at% and 35 at% [1]. They offer a wide range of properties and are a very promising field of study [2]. The equimolar AlCoCrFeNi composition has been much studied because it can easily be compared to conventional structural materials composed of similar constituents (e.g., steels and M-Cr-Al alloys). HEAs are typically produced by arc-melting. However, this type of elaboration leads to the formation of dendrites that induce the deterioration of mechanical properties. Other processes, such as Powder Metallurgy, have been studied and seem advantageous [3]. Indeed, a solid-state route enables industrial manufacturing and nano-crystalline materials with enhanced properties. Concerning the AlCoCrFeNi composition, Ji et al. reported the formation of a bcc phase and a fcc phase with the combination of Mechanical Alloying (in a High-Energy Ball Miller HEBM) and Spark Plasma Sintering [4] whereas other groups such as Mohanty et al. found a more complex microstructure with tetragonal precipitates [5]. Most of the works concerning the elaboration of HEAs by HEBM report the use of Mechanical Alloying (or Mechanosynthesis) that implies a complete chemical reaction with the total consumption of the initial constituents (e.g. monitored by the disappearance of the elemental peaks with XRD) followed by a consolidation step. In this work, we propose to evaluate the role of Mechanical Activation (i.e. an incomplete mechanosynthesis) followed by a reactive sintering step.. In this case, the particle reactivity is greatly enhanced because of an increase in the number of interfaces between reactants and the creation of defects. The sintering step is critical and much more complex to handle since diffusion plays the major role.

# 2. Methods

Elemental powders of Al, Co, Cr, Fe and Ni with high purity (all > 99.2 %, Alfa Aesar) were processed by high-energy ball milling (Fritsch Pulverisette P4). The ratio K=w/W between the rotating speed of the sun wheel W and the rotating speed of the grinding chamber w was set at 0,2 (milling mode A) and 1 (milling mode B). The powders were then consolidated by Spark Plasma Sintering (FCT Systeme GmbH HPD 10) at 80MPa and between 900 and 1100°C with a heating rate of 50°C/min. The final sintered samples are less than 1 cm tall cylinder with a radius of 1 cm. The powder distribution size was measured by laser granulometry (Malvern 2000). The powders and the sintered samples were analyzed by XRD (Siemens D5000), SEM and EBSD (JEOL JSM 7600F).



# 3. Results and discussion

After the low energy ball milling (milling A), the agglomerates exhibit a granular microstructure composed of almost pure elemental particles (Fig 1. a). When the energy is increased, the microstructure of the agglomerates becomes lamellar (thinner than 100 nm) (Fig 1. b). In terms of agglomerates size, the highest energy mode (B) leads to the smallest ones (Dn50=2,3  $\mu$ m, half the size of those obtained by the milling A). The sintering of A-activated powders does not allow us to attain chemical homogeneity: large particles remain almost pure.

The milling B followed by sintering leads to a microstructure mainly composed of a Fe-Cr rich fcc phase (5% Al, 25% Co, 25% Cr, 27% Fe, 18% Ni) and a Ni-Al rich bcc phase (19% Al, 22% Co, 12% Cr, 15% Fe, 32% Ni). Both phases are composed of grains smaller than 1  $\mu$ m.



Figure 1. Cross-section of milled powders with milling mode A (a) and B (b).

# 4. Conclusions

Small grains (< 1  $\mu$ m) with a rather good chemical homogeneity were produced with an adequate set of milling conditions and sintering parameters. However nano-sized precipitates not yet identified are formed. They could be oxides (due to the impurities of the initial powders) or carbides (due to the use of graphite dyes for the SPS). Thus, it remains to determine the nature of these precipitates and find a way to hinder their formation.

#### References

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#### Keywords

High entropy alloys; High-energy ball milling; Microstructure; Synthesis