From Ni-P metastable alloy nanoparticles to bulk nanostructured MMC with tunable mechanical and magnetic properties.

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Highlights

- Ni-P alloy nanoparticles with 50-200 nm in diameter were prepared by polyol process
- Reactive SPS process leads to Nanostructured MMC with Ni as matrix and Ni_3P as reinforcement phase
- Grain size of Ni matrix can be varied in a wide range 150-600 nm
- MMC mechanical behavior evolves from brittle to ductile

1. Introduction

Spark Plasma Sintering has emerged as a promising non-conventional consolidation process. Indeed SPS is characterized by specific heat treatment in comparison with powder metallurgy methods: high sintering rate, local high temperature generated by spark discharges leading to a very low consolidation time. This allows achieving fully dense consolidation without an excessive grain growth. Thus, when the starting material is in form of nanopowder, the as-obtained bulk material is nanostructured and show structural and physical properties closely governed by its fine microstructure [1, 2].
Besides these advantages, several recent works have shown that Spark Plasma Sintering can also be used as a reactive process to elaborate nanostructured materials starting from raw reactants[3,4].
In this context, we report in this work on a Metal Matrix Composite (MMC) based on nickel elaborated by a bottom – up strategy combining chimie douce and reactive Spark Plasma sintering. The chimie douce (polyol process) allows the synthesis of metastable Ni-P alloys in form of nanoparticles which are in a second step consolidated by R-SPS. Microstructural, mechanical and magnetic characteristics of the as-obtained MMC based on Nickel as matrix and Ni_3P as reinforcement phase will be discussed in function of the main experimental parameters of the R-SPS process.

2. Methods

The experimental protocol adopted to elaborate the Ni-P powders can be summarized as follows: the concentration of nickel salt (nickel acetate hydrate) was taken equal to 0.08 M and the concentration of sodium hydroxide equal to 0.262 M. The reducing effect of polyol is amplified by adding sodium hypophosphite a strong reducing agent with the ratio R = $[NaH_2PO_2]/[Ni(OAc)_2\ 4.H_2O]$ = 3. The precursors were mixed together, stirred at room temperature until complete dissolution in ethyleneglycol (EG), and then heated to the boiling temperature of the polyol (196 °C) under continuous mechanical agitation for 2h.

The SPS sintering of the Ni-P nanopowders has been realized according to the following process: 2 g of the powder was versed in a cylindrical graphite matrix (internal diameter of 10 mm). After establishing a primary vacuum in the apparatus, an uniaxial pressure was firstly applied on the graphite die containing the powder. Its value was increased up to 53 MPa in 1 min and then the heating starts while maintaining this

pressure. All samples were held, at a final sintering temperature set between 598 and 600°C for 10 min and then rapidly cooled down. Under these conditions, the as-obtained specimens present height of about 3 mm.

3. Results and discussion

Metastable Ni-P alloys in form of nanoparticles were elaborated by the polyol process. These particles have the fcc nickel structure with phosphorus inserted inside and size varying in the range of 50-200 nm. Then, the reactive SPS process transformed these metastable alloys into bulk nanostructured MMC where the matrix is constituted of nickel and Ni_3P is the reinforcement phase formed during sintering with a weight percentage between 9 and 12%. The mechanism of this phase apparition assumed the diffusion of phosphorus from the inside of the initial nanoparticles to the grain boundaries, where occur nucleation and growth of Ni_3P nanoparticles. These nanoparticles have a spherical shape with a size not exceeding 225 nm, while the nickel grains have a polygonal shape whose size range from 179 to 560 nm.

We have studied the influence of two sintering parameters namely temperature and heating time on the microstructural, mechanical and magnetic properties of nanostructured MMC.

Vickers hardness depends on the size ratio D_{Ni}/D_{Ni3P}. It reaches a value of 600 Hv when both sizes are small and the ratio is close to 2.5. The other mechanical characteristics seem to depend only on the size of the nickel matrix grains. The yield strength and mechanical strength increase as the grain size decreases and the rupture in these materials varies between brittle and ductile fracture (Figure1).

The bottom-up strategy developed in this work enabled us to elaborate materials having both ferromagnetism characteristics along with enhanced mechanical performances in comparison with Ni bulk. Indeed, it is found that the materials developed in this work, present a weak ferromagnetic with low coercivity not exceeding 7 Oe accompanied with relatively high hardness up to 6 GPa a high value in comparison with that of Ni bulk (2 GPa). Furthermore one of the elaborated materials namely Np25-600 meets the characteristics required for a soft ferromagnetism with a coercivity lower than 1.25 Oe.

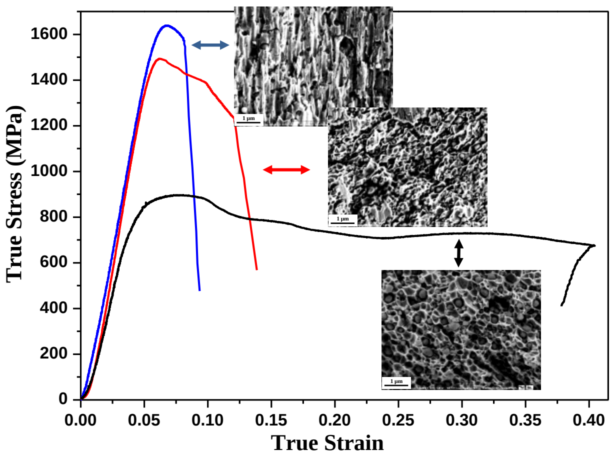

Figure1. True stress vs. true strain curves and fracture facies for MMC obtained from nanoparticles of 50, 100 and 200 nm in diameter

4. Conclusions

A bottom-up strategy combining polyol process and reactive SPS process enabled us to elaborate MMC with based on Ni as metal matrix and Ni_3P as reinforcement phase. The as-obtained materials show mechanical behavior varying from brittle to ductile depending mainly from the Ni grain size which varies in a wide range 150-600 nm. In comparison with nickel bulk behavior, the as obtained MMC exhibit both ferromagnetism characteristics along with enhanced mechanical performances.

References

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Keywords
Polyol, SPS, Metastable Ni-P alloy, Metal Matrix Composite,