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Electro-sinter-forged Ni–Ti alloy

Cristina Balagna [a, *], Alessandro Fais [b], Katya Brunelli [c], Luca Peruzzo [d], Miroslava Horynová [e], Ladislav Čelko [e], Silvia Spriano [a]

[a] Politecnico di Torino- DISAT Department, Corso Duca degli Abruzzi 24, 10129, Torino, Italy
[b] EPoS Srl, Strada delle Cacce 73, 10135, Torino, Italy
[c] Università d Padova- Dipartimento di Ingegneria Industriale, Via Marzolo 9, 35131, Padova, Italy
[d] CNR, Istituto di Geoscienze e Georisorse, Via Gradenigo 6, Padova, Italy
[e] Central European Institute of Technology, Brno University of Technology, Technická 10, 616 69, Brno, Czech Republic

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ABSTRACT

An innovative powder metallurgical process (Electro-Sinter-Forging – ESF) has been applied to a gas atomized Ni–Ti powder to avoid the typical drawbacks of the conventional industrial processing of this material: oxygen pick up, high processing temperature and slow cooling rate. At the same time, the ESF allows to overcome the low sintering activity of the Ni–Ti powders. Sintered materials, produced by using different processing conditions, are characterized and compared. Results concerning the thermal, structural, microstructural and mechanical analyses are reported and discussed. The density of the sintered samples increases by increasing the amount of applied energy and final pressure during the sintering process. The sample showing the highest density has a direct phase transformation on heating and cooling, with broad DSC peaks, and small thermal hysteresis; it is austenitic at room temperature, with a low amount of coarse (micrometric) precipitates, $Ti_4Ni_2O_x$ nanometric precipitates and high hardness. The ESF sintering at highest energies induces a "band-type" microstructure with a preferential crystallographic orientation; the crystallographic texture of the sintered samples has been investigated through Electron Back Scattering Diffraction (EBSD) analysis and a fiber texture <100> has been evidenced. The ion release from the sintered samples has been investigated: it is comparable to commercial Ni–Ti alloys currently used and it is correlated to the sample porosity. The biocompatibility has been demonstrated towards fibroblasts.

1. Introduction

Equiatomic nickel titanium (Ni–Ti or Nitinol) alloys are considered very attractive materials, due to their shape memory and superelastic effects, in addition to good fatigue and corrosion resistance [1,2]. The applications of Nitinol vary from the smart sensors and actuators, in the field of automotive and robotics, to the biomedical implants, for orthopaedics and cardiovascular surgery, or orthodontics wires [1,3,4]. Even if Ni is considered a hazardous and toxic element for human health, Ni–Ti alloys are characterized by biocompatible behavior, suitable for several biomedical applications. In fact, a Ni–Ti homogeneous surface, with very low roughness and without the presence of second phases, like Ni-rich particles or coarse carbides and nitrides, provides a very high corrosion resistance, due to the formation of a dense passive layer of TiO_2 on the surface. This feature limits and minimizes the Ni ion release, allowing the large use of Nitinol in the biomedical field [5–7].

The conventional industrial production of Ni–Ti alloys consists in casting, by induction or arc vacuum melting, followed by hot and/or cold plastic deformation [3,8]. High reactivity of the melt is a serious technical problem, due to its tendency to pick up oxygen and to react with the graphite crucibles [9], affecting the characteristic temperatures of the alloy [10,11]. The high temperature, reached during the casting processes, and the slow cooling rate usually produce relatively coarse grains, thereby reducing the mechanical performance of the cast material [8,10]. Further post-casting processes, as hot or cold working, heat treatments or machining, are usually required, in order to obtain suitable thermal and mechanical properties and to reach the final shape of the

* Corresponding author. Institute of Materials Engineering and Physics, Department of Applied Science and Technology, Politecnico di Torino, Torino 10129, Italy.
E-mail address: cristina.balagna@polito.it (C. Balagna).

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products (wires, tubes, ribbons, sheets and bars). These treatments affect the original characteristics of the cast material, by modifying the martensite/austenite ratio, transformation temperatures, microstructure and mechanical resistance [12].

Powder metallurgy is considered a potentially interesting way to produce semi-finished and near net-shape final components of Ni–Ti alloys, possibly reducing grain growth, inclusions of carbides and by minimizing the final machining procedures [8,13]. In addition, powder metallurgy generally allows the realization of products with lower cost and energy requirements, shorter time and higher production rate, with elevated reproducibility. On the other side, it must be considered that Ni–Ti powders show low sintering activity when processed by Metal Injection Molding (MIM) or Hot Isostatic Pressing (HIP), that is why alternative sintering processes are needed. Poor sintering ability of Ni–Ti powders is due to eventual contamination of TiC or oxide on the surface, acting as a sintering barrier, and/or low free surface energy of the powder particles to drive strong enough diffusion processes for the formation of stable sintering necks.

An innovative powder metallurgical process, called Electro-Sinter-Forging (ESF) [14], has been recently developed; it is an evolution of the previous capacitor discharge sintering method [15,16]. This technique is based on the sintering of an electrically conductive powder in a very limited time (less than 1 s), reaching a high final density. The process consists in the combination of a single short (10–100 ms) impulse of intense electric current (typical peak from 0.1 to 1 kA/mm^2), superimposed with a mechanical pulse in a properly designed mold. As reported in Ref. [14], the main parameters to be set, in order to achieve the optimization of the material sintering, are the Specific Energy Input (SEI), pre-applied pressure (before the rapid single pulse – P_{start}) and pressure at the end of the discharge (P_{end}). The applied pressure affects mainly the plastic deformation at the particles interfaces SEI is the Joule heat dissipated in the die set, normalized by the weight of the inserted powders, and it is a measure of the electromagnetic energy provided to the sample. The reached temperature during the process is not measured. Temperature can be modulated by changing the SEI and sintering can occur in the solid or liquid phase, according to the used parameters.

The aim of the present work is sintering of a gas atomized Ni–Ti powder by means of ESF and the characterization of the materials produced in different processing conditions. The characterization and comparison of the sintered specimens in terms of thermal, structural, microstructural and mechanical analyses are reported. Finally, the biocompatibility of the sintered samples was evaluated by means of *in vitro* ion release and cytotoxicity tests.

2. Materials and methods

Gas atomized Nitinol powder (51 at.% Ni and 49 at.% Ti, nominal Ap = 20 °C; particles size distribution: −80/+10 mesh, SAES-Smart Materials) was subjected to sintering by means of electro-sinter-forging process (ESF, EPoS Srl) with different values of SEI and pressure. The chemical LECO analysis demonstrates that the powder contains 0.007 ± 0.0001%wt. of C and 0.099 ± 0.0021%wt. of O whereas the Ni and Ti are 55.5 ± 0.02%wt. and 44.16 ± 0.02%wt, respectively. A small amount of N is registered (0.003 ± 0.0003% wt.). As mentioned into the introduction, the ESF technique is well described in Ref. [14]. The inner mold employed was a technical ceramic material, the plunger used to press and conduct electricitywas made of a tungsten alloy. Several cylindrically shaped samples with a diameter of 10 mm and height of 4 mm were prepared. Geometric density was evaluated during the sintering runs to find the best conditions for high density, whereas in a second moment, density was also evaluated through Archimedes' principle for comparison. The samples were labeled with an alphabetical sequence from A up to F, corresponding to increasing values of the process parameters. The sintered samples were cut and the cross-sections were mirror-polished with conventional metallurgical preparation methods for structural, microstructural analysis and micro-hardness testing.

2.1. Thermal analysis (DSC)

The characteristic transformation temperatures of the powder and sintered samples were detected through differential scanning calorimetry (DSC, Mettler DSC 30 Switzerland). The test was performed according to ASTM F2004-03 [17].

2.2. Structural and microstructural analysis (XRD, EBSD, Optical microscope, SEM, EDS, TEM)

The crystallographic structures of the powder and of the samples cross-sections were investigated using x-rays diffraction with a Bragg-Brentano type diffractometer (XRD, X'Pert Pro MRD, Panalytical) at room temperature.

The crystallographic texture was investigated with a scanning electron microscope (SEM CamScan MX2500) equipped with electron backscattered diffraction (EBSD) system constituted by CCD camera Nordif, image processor Argus 20 (Hamamatsu) and software CHANNEL 5 (HKL Technology). An accelerating voltage 30 kV was used during the experiments. Before carrying out the EBSD map, orientation contrast images were taken with the detector positioned in the forescatter position (FSE mode) [18]. The SEM-FSE image allowed to acquire qualitative information about the microstructure, different orientation of the grains and grain size.

Transmission electron microscopy (TEM) observation and microstructural analysis were conducted using Philips JEOL JEM-2100F with X-Max80 Oxford Instruments EDS detector for x-ray microanalysis. Lamellas for TEM observation were prepared from the cross-section of the sample parallel to the loading axis using focus ion beam (FIB, Tescan LYRA 3 XMU SEM/FIB/GIS).

Microstructures of the powder and samples were observed at the optical microscope, after polishing and surface etching. Etching was performed with a solution containing fluoridric acid (HF), nitric acid (HNO_3) and distilled water in the ratio 1:5:20.

The morphology of the starting powder and of the samples cross-sections were also observed by means of a scanning electron microscope (SEM, SEM-FEI, Quanta Inspect 200, FEI), equipped with the back scattering mode (BS-SEM) and with an EDS that was used to verify the elemental composition of the specimens.

The oxygen and carbon content of the sintered samples was evaluated by means LECO analysis.

2.3. Mechanical tests (Vickers microhardness)

Hardness of the samples cross-sections was evaluated through micro-indentation tests at room temperature. Five Vickers indentations were performed under an applied load of 10 g, 100 g and 200 g. The hardness values were measured in different areas from the external surface, close to the edge, to the center of the samples.

2.4. Biocompatibility in vitro analysis

2.4.1. Ion release test

Some samples (cut as half of the original ones) were subjected to Ni ion release test. The samples (three for each type) were dipped into 15 ml of simulated body fluid (SBF, [19]) solution at 37 °C, with a total refresh of the liquid after 3 h, 24 h, 3, 7, 14 and 28 days. The