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Ni-Ti MULTIFUNCTIONAL MATERIALS SINTERED VIA CONCENTRATED SOLAR ENERGY

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Abstract: *This paper presents a study on the solar sintering of Ni-Ti alloys using concentrated solar energy. The sintering process was conducted in a vertical solar furnace, resulting in excellent fusion and controlled microstructures. The evaluation of wetting characteristics and electrochemical behavior provided insights into their performance in aqueous environments. The samples present hydrophilic character and good corrosion resistance, ranging from* $2.46 \cdot 10^{-6}$ *to* $3.50 \cdot 10^{-2}$ *mm/year. The utilization of concentrated solar energy offers sustainable and energy-saving advantages for large-scale production. These findings highlight the potential of solar sintering for tailoring Ni-Ti alloys with desired properties for various applications, including medical devices, energy absorbers, or mechanical couplings.*

Key words: *concentrated solar energy, sintering, corrosion resistance, surface properties, alloys.*

1. INTRODUCTION

Nickel-Titanium (Ni-Ti) alloys possess remarkable properties, including a distinctive shape memory effect (SME), good superelasticity, favorable biocompatibility, and exceptional energy absorption capabilities [1-5]. These characteristics have garnered significant interest across diverse fields such as medical devices, energy absorbers, actuators, and mechanical couplings [6, 7].

Powder metallurgy (PM) serves as a straightforward, energy-efficient, and extensively employed method for manufacturing Ni-Ti alloys [8-10]. Moreover, powder sintering emerges as a highly effective technique for generating diverse porous structures, facilitating bone tissue ingrowth, and offering an efficient means of reducing implant stiffness for example [7, 11].

The utilization of concentrated solar energy (CSE) presents a compelling approach for sintering multifunctional alloys, offering unique advantages in terms of rapid heating and cooling rates that can impact the microstructure and phase transformation behavior of the materials, as compared to traditional powder metallurgy sintering in conventional electric power furnaces [12-16].

The ability to achieve precise control over heating and cooling rates enables the manipulation of the alloy's microstructure, or bulk (solid material or foam), leading to enhanced material properties and the customization of Ni-Ti alloys for specific functionalities [15].

The application of CSE for sintering alloys is still in its early stages, and research in this area is ongoing to find the optimal parameters for achieving the best possible balance between homogeneity and useful properties (mechanical strength, wear resistance, corrosion resistance, etc.) [16, 17]. So far, several studies have exhibited promising outcomes for various types of alloys, demonstrating the potential of CSE in their sintering process. These alloys encompass a range of compositions, including:

1. Iron-based alloys: Notable examples include Fe-Cr and Fe-Al alloys, which are employed for corrosion-resistant applications [18, 19].
2. Aluminium-based alloys: Al-Cu alloys, particularly in thermally aged conditions, have

shown favourable results when sintered using CSE [19].

3. Copper-based alloys: Alloys such as Cu-W, designed for high-temperature applications, have exhibited promising sintering behavior with CSE [20, 21].

4. Wear-resistant special alloys: Special attention has been given to superalloys, which consist of a matrix predominantly composed of titanium or nickel. These alloys possess excellent wear-resistant properties and have shown potential for successful sintering using CSE [22-25].

Additionally, the application of CSE in sintering has shown promising outcomes for metallic-ceramic composites. These composites typically comprise a metal matrix (such as ferrous or Ni-Cr-based) combined with ceramic reinforcements, including carbides, borides, silicides, and other similar materials [16, 25].

Collectively, these findings emphasize the versatility of CSE in sintering a variety of alloy types, paving the way for advancements in materials science and the development of high-performance alloys for diverse applications. Continued research in this field holds great potential for exploring new alloy compositions and further optimizing the sintering process using CSE. A more thorough understanding of alloy systems and sintering mechanisms, will help overcome these issues and unlock the full potential of CSE for sintered alloys.

This paper presents the methodology employed for obtaining bulk alloys through the sintering of pre-pressed powders comprising different Ni and Ti ratios. The sintering process was carried out utilizing a concentrated solar energy source, specifically a vertical solar furnace situated at PROMES-CNRS in Font-Romeu Odeillo, France.

The primary focus of this paper is to evaluate the electrochemical behaviour and wetting characteristics of the sintered materials, which are crucial aspects in the design of multifunctional materials. The electrochemical behaviour was assessed through various characterization techniques such as linear polarization and electrochemical impedance spectroscopy, shedding light on the corrosion resistance and stability of the sintered alloys in relevant environments.

Additionally, the wetting characteristics of the materials were investigated using contact angle measurements, providing insights into their hydrophobic or hydrophilic properties.

2. EXPERIMENTAL PART

2.1 Materials

The titanium and nickel powders used in this study (spherical powders, 50~100 μm) were purchased from SkySpring Nanomaterials, Inc. (Houston, TX, USA) and were of 99.9% purity.

Different Ni-Ti powder mixture ratios were prepared by weighing the powders, according to Table 1.

Table 1

Powder mixtures used for the sintered samples obtaining and their encoding.

Sample code	Powder amount (% wt.)	
	Ni	Ti
Ni	100	0
Ni50	50	50
Ti	0	100

The powders and powder mixtures were mechanically blended in a ball mill for 1 hour and then pressed in pellet form with the help of a hydraulical press (~100 MPa). For each composition, ten different pressed materials were considered.

The pressed pellets were sintered using a concentrated solar energy vertical furnace (PROMES-CNRS in Font-Romeu Odeillo, France, Figure 1) under argon (3.5 L/min flow rate) at a sintering temperature of 1000°C and heat treatment duration of 10 minutes. This equipment is a medium-power solar furnace (MSSF) with a maximum deliverable power of 1.5 kW at the focal point.

Fig.1. Vertical CSE furnace from PROMES-CNRS

The inert gas flow rate, sintering temperature and sintering duration were chosen prior to onsite trial-and-error experimenting.

2.2 Methods of analysis

The electrochemical behavior of the pressed and sintered alloys was investigated in a 3.5% wt. aqueous NaCl solution using a PalmSens EmStat 4LR potentiostat-galvanostat, which was coupled to a Faraday-isolated three-electrode standard electrochemical cell (Figure 2). The electrochemical cell consisted of a reference electrode (Ag/AgCl, saturated KCl), a counter electrode (Pt), and a working electrode (sample).

To assess the corrosion rate, linear polarization (LP) measurements were performed, providing insights into the alloys' corrosion resistance. Additionally, electrochemical impedance spectroscopy (EIS) was conducted to obtain detailed information about the impedance response of the alloys in the electrolyte.

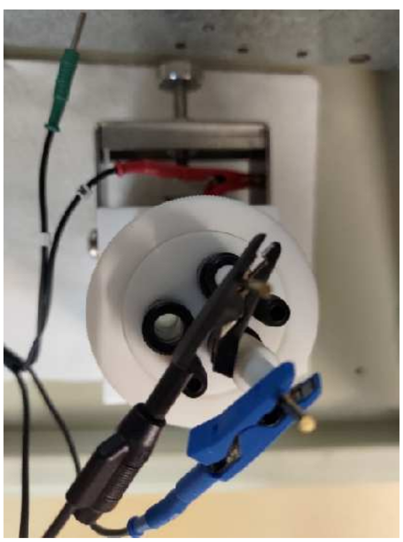


Fig.2. Standard cell used for the electrochemical tests

In LP analysis, a potential sweep of ±150 mV vs. the open circuit potential (OCP) was considered, at a scanning rate of 10 mVs^{-1}.

For EIS, an AC current amplitude of 10 mV was applied vs. OCP in a frequency interval between 100 mHz and 100 kHz.

All the electrochemical measurements were performed after a period of equilibrating (i.e., maintaining without applying any current) the samples in the NaCl electrolyte for at least 600s.

The wetting behavior, specifically the hydrophilicity or hydrophobicity, of the samples was assessed using an L2004A1 Contact Angle goniometer (Ossila Inc., UK, Figure 3). The contact angle of distilled water and glycerol (sessile drops with a volume of 5 μL) on the surface of each tested sample was measured.

To evaluate the surface energy of the samples, the contact angle values were input into the instrument's software, which utilizes the Owens-Wendt-Rabel & Kaelble (OWRK) model [26]. This model allows for the calculation of surface energy based on the contact angle measurements, providing valuable information on the interfacial properties of the samples.

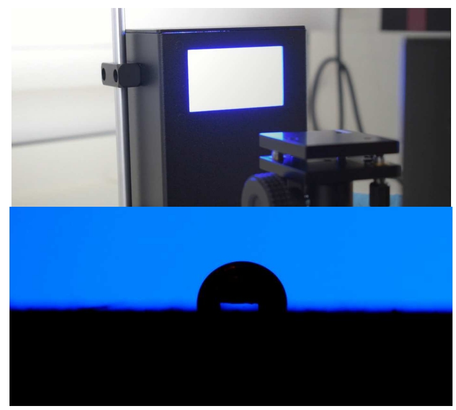


Fig.3. Setup used for the wetting behavior analysis

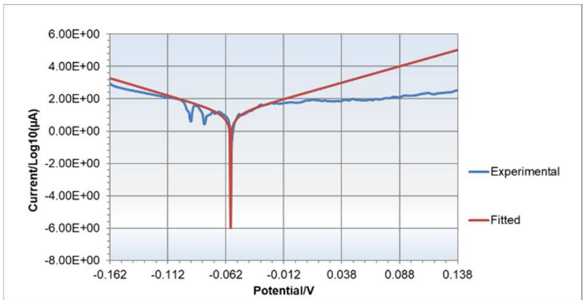
The contact angle of water on the sample surface and the measurement of surface energies provides valuable insights into the behavior of the sample in aqueous environments and contribute to a deeper understanding of electrochemical corrosion mechanisms. By correlating these parameters, significant knowledge regarding the samples response to corrosive conditions and underlying electrochemical processes involved in corrosion understanding can be achieved.

3. RESULTS AND DISCUSSION

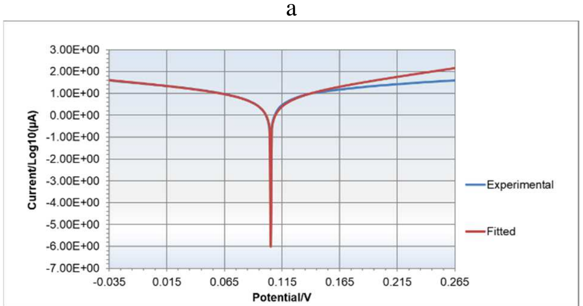
3.1 Electrochemical behavior

The electrochemical measurements were performed both on pressed and non-sintered powders (Ni and Ti non-sintered samples are presented herein) as well as on the solar-sintered samples (Ni, Ni50 and Ti).

The LP analysis results for the unsintered Ni and Ti samples are presented in Figure 4a and b.



a



b

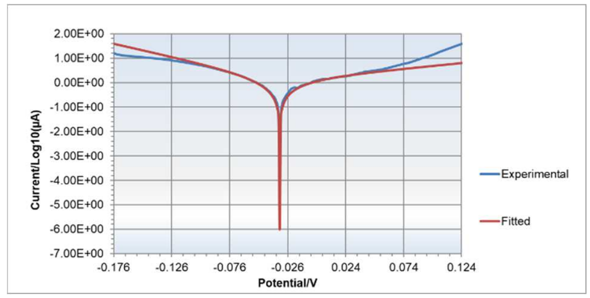
Fig.4. Linear polarization curves with fitted Butler-Volmer model for the unsintered samples: (a): Ni, (b): Ti

It can be seen from Figures 4a and 4b that the equilibrium OCP for the unsintered Ni samples is -60 mV, respectively + 112 mV for the unsintered Ti samples, clearly indicating a more pronounced corrosion resistance for the later (an increased tendency to be passivated with a protective layer of oxides).

The sintered Ni samples exhibit higher OCP values, suggesting that the sintering process promotes the formation of surface oxides, resulting in a more cathodic potential, as depicted in Figures 5a-c. It can be observed that nickel experiences a slight reduction in OCP, leaning towards anodic values, indicating a tendency to oxidize and release Ni^{2+} ions when exposed to the saline aqueous environment.

Specifically, the Ni50 sample demonstrates an OCP of -6 mV, implying a neutral tendency towards both oxidation and passivation, suggesting that these two processes are in equilibrium.

The corrosion current value (I_{corr}) is estimated by fitting the Butler-Volmer equation to the experimental linear polarization curves.



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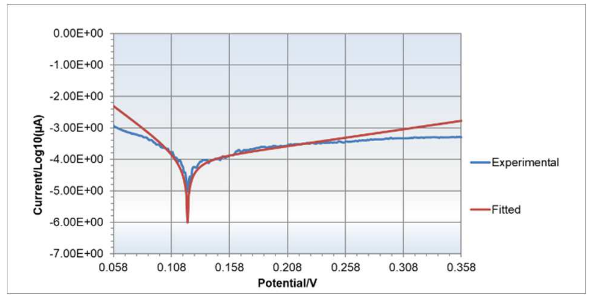

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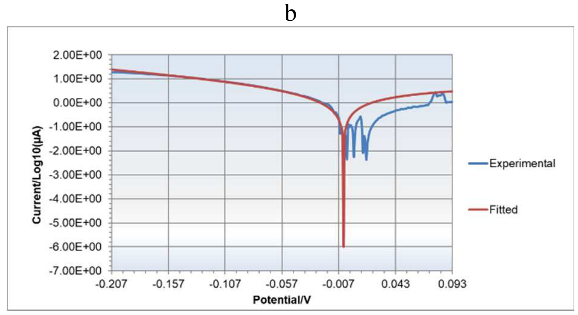

c

Fig.5. Linear polarization curves with fitted Butler-Volmer model for the sintered samples: (a): Ni, (b): Ti, (c): Ni50

The corrosion rate (CR, mm/year) of the samples is calculated with Equation 1 [22]:

$$CR = \frac{I_{corr} \cdot K \cdot EW}{A \cdot d}. \qquad (1)$$

Where: K is a constant (K= 3272 mm/A·year·cm), EW is the equivalent electrochemical weight (calculated based on the composition of each sample), A is the area of the sample exposed to the electrolyte (1cm^2) and d is the density of the sample.

Table 2

Parameters of the Butler-Volmer fit for the sintered samples and their corrosion rates.

Sample / Parameter	**Ni**	**Ni50**	**Ti**
Rp (kΩ)	22.68	2390	$1.38 \cdot 10^5$
I_{corr} (µA)	2.96	$8.8 \cdot 10^{-2}$	$2.10 \cdot 10^{-4}$
CR (mm/year)	$3.50 \cdot 10^{-2}$	10^{-3}	$2.46 \cdot 10^{-6}$

In Table 2, the Butler-Volmer fit parameters are provided, including the polarization resistance (Rp), which reflects the specimen's resistance to oxidation under the influence of an external potential. The Rp values are given alongside the corrosion current and corrosion rate for each sample.

The titanium sintered samples and, consequently, the Ni50 sample, which contains equal weight proportions of Ni and Ti, exhibit the lowest corrosion rates among the tested samples. This indicates their superior corrosion resistance compared to the other samples.

The results obtained from electrochemical impedance spectroscopy (EIS) for the unsintered Ni and Ti samples, as well as the sintered Ni, Ti, and Ni50 samples, offer further insights into the corrosion mechanisms at play.

Nyquist plots, depicting the imaginary impedance (-Z'') versus the real impedance (Z'), are presented in Figures 6 and 7 for the unsintered Ni and Ti samples, and in Figure 8 for the Ni50 sintered sample, which is representative for all the sintered samples.

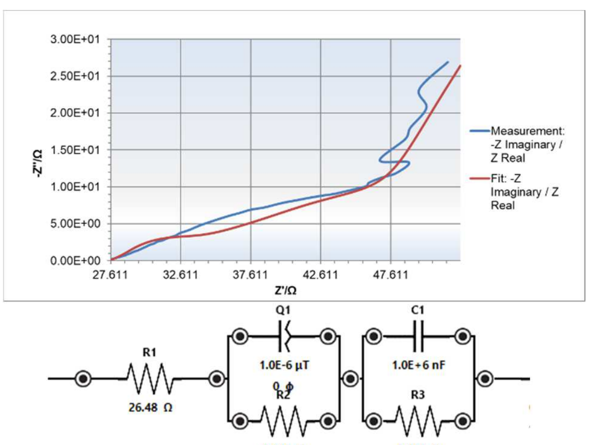

Fig.6. EIS data as Nyquist plots and model equivalent electrical circuit for the Ni unsintered samples

All these plots from Figures 6 and 7 are accompanied by fitted data based on appropriate equivalent electrical circuits [22].

The impedance values observed for the unsintered samples are in the range of kΩ, suggesting a relatively lower resistance to the aqueous environment.

Moreover, the presence of multiple capacitive elements in the equivalent circuits fitted to the electrochemical impedance spectroscopy (EIS) data indicates a dissipative-capacitive behavior in the unsintered samples.

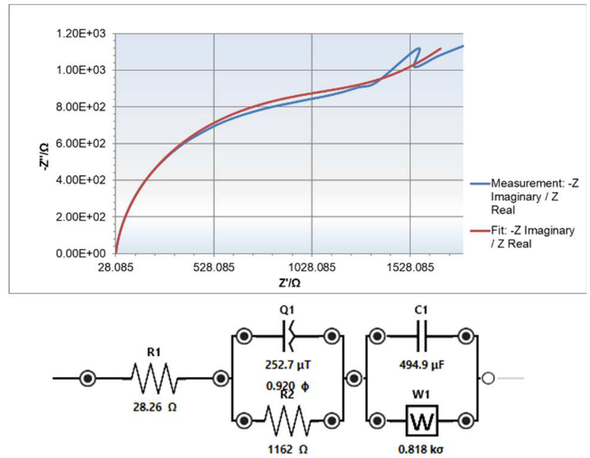

Fig.7. EIS data as Nyquist plots and model equivalent electrical circuit for the Ti unsintered samples

This behavior implies a strong tendency for pitting corrosion, which is characterized by localized corrosion attack in the form of pits or cavities on the sample surface.

The Nyquist plot is also shown in Figure 8 for the Ni50 sample.

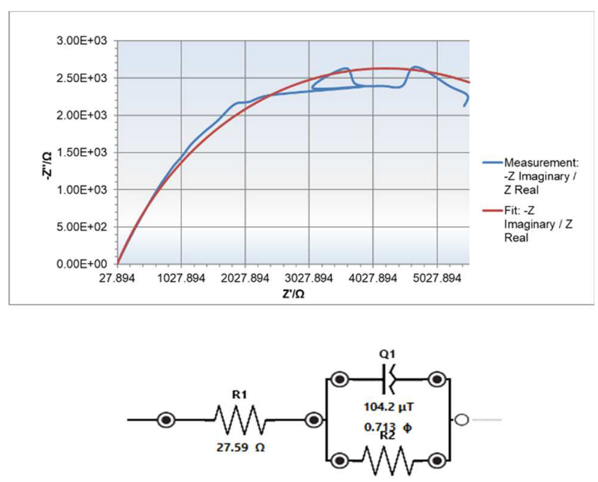

Fig.8. EIS data as Nyquist plots and model equivalent electrical circuit for the Ni50 sintered sample

It is evident that the sintering process brings about a transformative effect on the material, resulting in a distinct behavior that closely resembles that of an organic coating with minimal signs of corrosion initiation. The observed changes in behavior highlight the significant influence of sintering on the material's performance and corrosion resistance.

This finding underscores the potential of sintering as a means to impart unique characteristics and enhance the protective properties of the material, offering new possibilities for its application in various fields.

3.2 Wetting behavior

Figures 9a, b, and c present the initial contact angles measured for the Ni, Ti, and Ni50 samples during the wetting process using distilled water. The left and right contact angles are recorded for each sample.

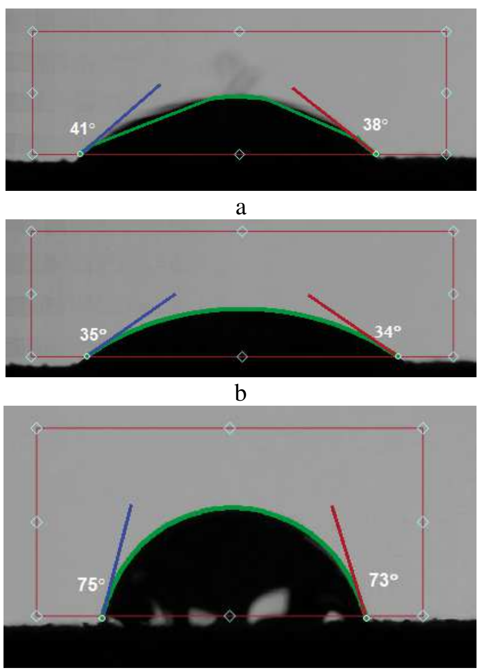

Fig.9. Water contact angles for the sintered samples: (a): Ni, (b): Ti, (c): Ni50.

As it can be seen from Figure 9a and 9b, the sintered Ni and Ti samples both present a markedly hydrophilic character (i.e., the initial contact angles are lower than 90°). This owes for a high spreading ability of water on the surface, especially on prolonged exposure to humid environments. The Ni50 sample presents a less markedly increased hydrophilic character (Figure 9c), probably due to its favorable surface chemistry (the presence of non-stoichiometric oxides on the surface). The surface energies of the samples γ (mN/m) determined as per the OWRK approach are presented in Table 3.

The surface energy of each sample can be decomposed into a polar term (γ^p, taking into account all hydrophilic and polar interactions of the surface in question) and a dispersive (γ^d, van der Waals contributions-dominated) term.

Table 3

Surface energies of the sintered samples.

Sample code	γ (mN/m)	γ^p (mN/m)	γ^d (mN/m)
Ni	45	38.2	6.8
Ni50	37	18	19
Ti	49.5	24.6	24.9

The surface energy values presented in Table 3 indicate that the dominating contribution to the surface energy is the polar one (for Ni), while for Ni50 and Ti samples, the dominating contribution is dispersive (their hydrophilic character is not directly linked to their metallic character) in this case.

4. CONCLUSION

The results of this research on solar sintered Ni-Ti alloys could open avenues for potential applications and further research:

Tailored Material Properties: The solar sintering process has demonstrated its capability to engineer the microstructure of Ni-Ti alloys, leading to controlled modifications of their mechanical and chemical properties. This breakthrough has far-reaching implications for industries that rely on materials with specific attributes, such as aerospace, medical devices, and automotive, where performance customization is pivotal.

Advancing Corrosion Resistance: The enhanced corrosion resistance observed in solar-sintered Ni and Ti samples showcases their potential for enduring harsh environmental conditions. This characteristic is of great importance in numerous fields, from marine engineering to renewable energy applications, where materials' durability is paramount.

Promising Applications: The hydrophilic nature of the sintered samples opens up new possibilities for their use in environments where water interactions are pivotal. The potential applications span from biomedical devices that need to interact seamlessly with body fluids to advanced coatings and environmental technologies, including water purification and catalysis.

Paving the Way for Future Studies: Future studies could delve deeper into optimizing the sintering process, exploring the potential of different alloy compositions, and novel applications across diverse industries.

5. ACKNOWLEDGEMENTS

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Materiale multifuncționale pe bază de Ni-Ti sinterizate folosind energie solară concentrată

În acest studiu au fost obținute aliaje prin sintetizarea pulberilor pre-compactate pe bază de Ni și Ti, amestecate în diferite rapoarte de masă. Procesul de sintetizare a fost efectuat folosind o sursă ESC, mai exact un cuptor solar vertical situat la PROMES-CNRS în Font-Romeu Odeillo, Franța. Materialele sintetizate au prezentat o bună fuzionare în condițiile specifice de lucru utilizate în cuptorul solar, care au implicat o temperatură de sintetizare de 1000°C și o durată de tratament termic de 10 minute. O observație interesantă a fost natura hidrofilă a materialelor sintetizate, atribuită prezenței de oxizi pe suprafața acestora. Pentru a evalua performanța aliajelor, s-au efectuat teste de coroziune electrochimică într-un mediu de soluție apoasă de NaCl cu o concentrație de 3.5% în greutate, utilizând tehnici precum polarizarea liniară și spectroscopia de impedanță electrochimică.

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