International Journal of Current Engineering and Technology
E-ISSN 2277 – 4106, P-ISSN 2347 – 5161

Available at http://inpressco.com/category/ijcet

Research Article

Surface Treatment of NiTi Shape Memory Alloys used in Dentistry

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Accepted 12 Nov 2015, Available online 28 Nov 2015, **Vol.5, No.6 (Dec 2015)**

Abstract

*Ni/Ti shape memory alloys samples (**SMAs**) were prepared by powder metallurgy technique . A low power portable spot pulses unit was used for improving surface characteristics and (as an **attempt** to evaluate the feasibility of using it as an alternative for the conventional , huge , and costly laser equipment**) .** Its power was only **(1/3**) of the large unit . Several tests were conducted , such as , corrosion resistance , wear behaviour , Ni-ion release , hardness , and metallography . Significant improvements were observed in surface properties which may have substantial impact on numerous **dental** applications and probably secure important position in surface engineering of metal and alloys . The corrosion current , Ni-ion release , and volume of wear of the spot pulse Laser treated surface were (**4.5** % , **17** % , and **20** %) respectively with respect to the reference sample . An improvement of **481** % in Microhardness of the **532 nm** laser treated with respect to the reference . No **microcracks** were detected in any surface treated sample. The weight loss during wear test was almost **zero** within the test period.*

Keywords: *NiTi , Shape memory alloys , Spot pulse Laser , Surface treatment*

1. Introduction

NiTi shape memory alloys (SMAs) are widely used as implant materials in dental applications due to their superelasticity, superior biocompatibility, unique shape memory effect (SME), specific strength, corrosion resistance , and high damping capacity (R.E. Small man *et al* , 2007) . These alloys are widely used in technical and medical fields , such as , biomedical , aerospace , mechanical engineering and aeronautics . Various techniques were used to fabricate Ni/Ti alloys , such as, hot isostatic pressing , metal injection molding, spark plasma sintering , and combustion synthesis (T. Duerig *et al* , 1990) .

To obtain the best properties of these alloys, it is required to use the solid –state processing . Excellent finished performance can be achieved by these processes, because they produce homogeneous distribution of the reinforced articles and almost a near-net shape forming (K. otsuka *et al*, 1998). Extensive work was conducted for further improvements of Ni/Ti (SMAs) , including alloying and surface treatments (Forri J. , 2007) , heat treatment , and the addition of Nano-sized particles (David w. *et al*, 1999).

Recently, porous Ni/Ti (SMAs) of controlled porosity and characteristics pore size is produced (Tony Anson source, 1999). The fabrication process was done by multi-step sintering. Space - holder method was also employed. This process results in enhancing mechanical properties of the alloy.

In this work , a low power portable spot pulses unit was used for surface treatment and (as an attempt to evaluate the possibility of using it as an alternative for the conventional , huge , and costly laser equipment)**.** Its power was only (**1/3**) of the large unit. Several test were conducted, such as, corrosion resistance, wear behaviour, Ni-ion release, hardness, and metallography.

2. Experimental Work

Samples were prepared by powder technique where Ni, Ti were of particle sizes equal to 325 mesh and purity 99.9% . The specifications of the used low power spot pulses Laser unit are : Nd-Yag (Energy = 1000mj, frequency = 6HZ , number of pulses =10 , duration time = 3ms.

Compressive stress of 850 MPa was used for cold compacting (10mmx15 mm). Sintering was carried out at 850 C° for 6 hrs under vacuum of $\mathbf{10^{-3}}$ torr., table (1) show Specifications of the reference. Sintering cycle of the compacted samples are shown in Fig. (R.E. Small man *et al*, 2007). This cycle facilitates uniform distribution of heat and reduces thermal stresses.

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Table (1) Specifications of the alloys

Alloy	Composition	M_s Cº	M_f Cº	A_s Cº	A_f Cº
Ref.	57.56 Ni + 42.44 Ti	7	-10	10	33

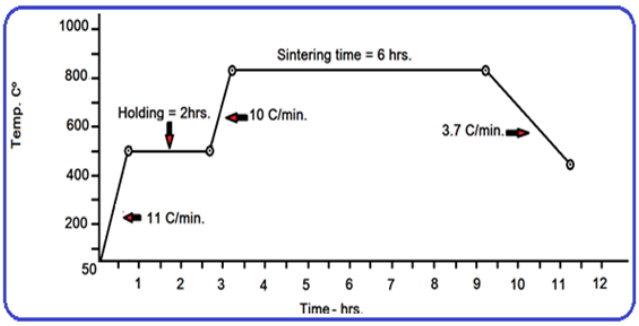

Fig (1) Sintering cycle of the prepared samples

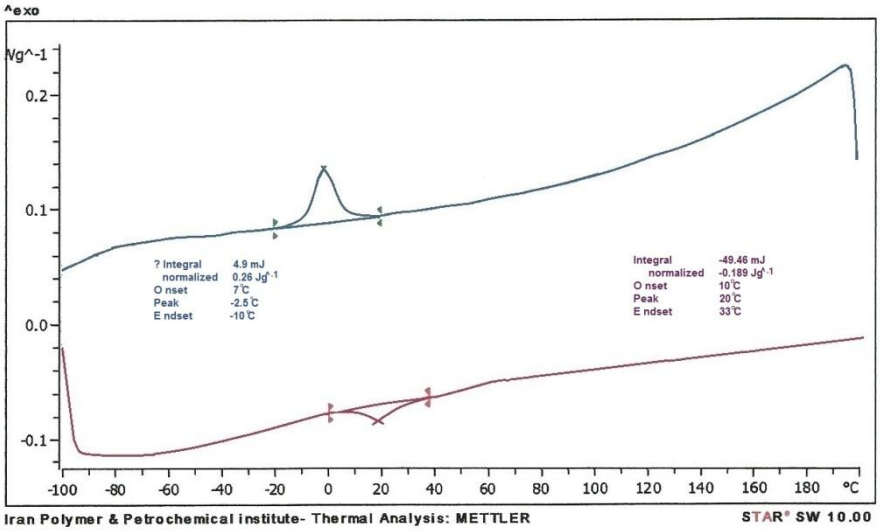

Fig (2) DSC test for the reference sample

Differential scanning calorimeter (**DSC**) was used t Fig (2) to determine the transformation temperatures of the reference sample.

Tafel extrapolation technique was adopted to evaluate the corrosion behavior of the prepared samples in artificial saliva at 37 Cº. Corrosion current was estimated by anodic polarization potentiodynamic .

Nickel-ion release was determined for both treated and untreated samples. Atomic absorption spectrometry was employed to measure Ni-ion release in artificial saliva at temperature 37C°. Test was conducted by immersion of individual samples for 15 days. Hardness and wear tests also conducted.

3. Results and Discussion

Metallography

The SEM micrograph of the reference sample is shown in Fig. 3. Results obtained from **XRD** indicate the presence of **TiNi** and **$TiNi_3$** phases. These results are **supported** by the expected phases found in the NiTi phase diagram.

Martensite (**B19**) is not expected since, the sample was not quenched. It was only furnace cooled.

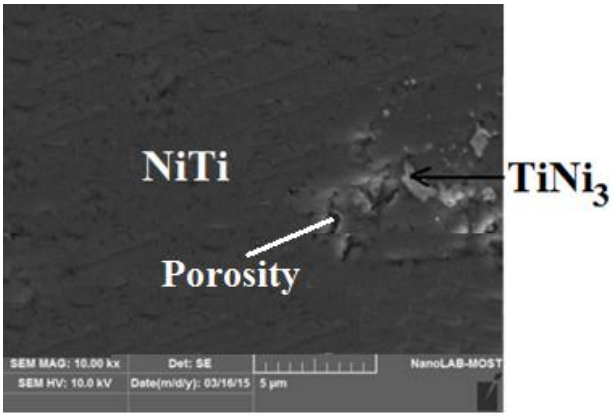

Fig (3) Microstructure of Reference sample sintered at **850** Cº

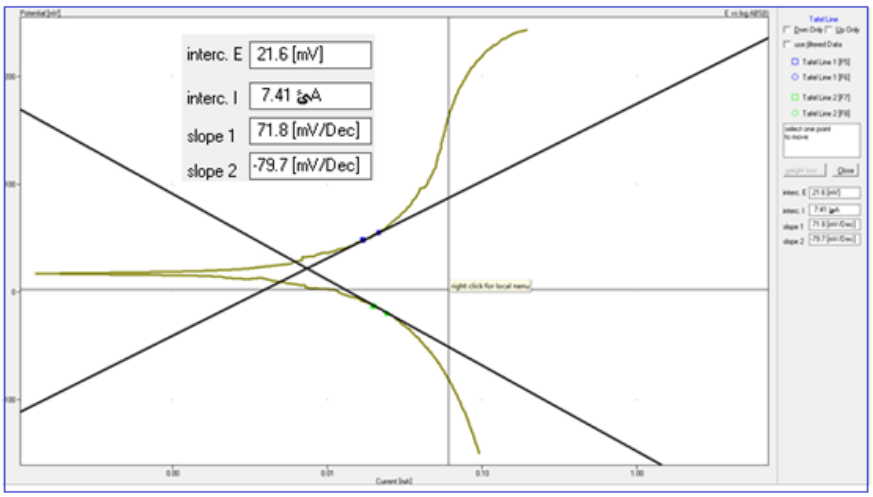

Fig (4) Polarization curve of Ref. Sample

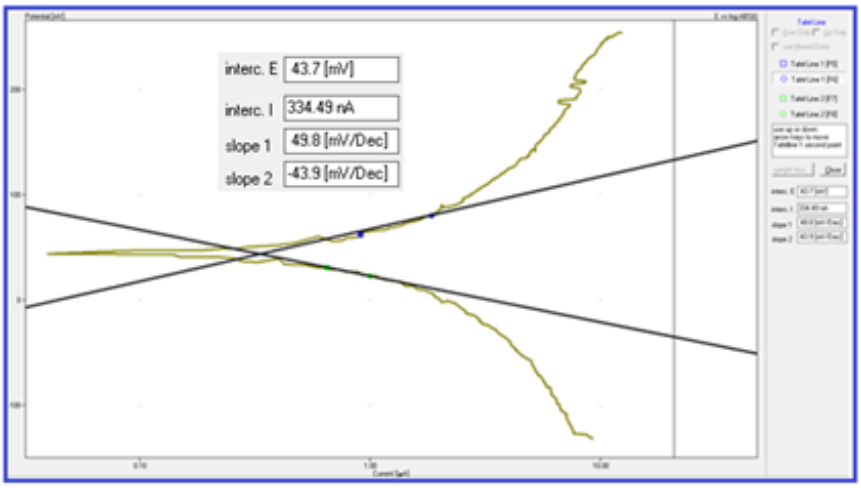

Fig (5) Polarization curve of laser (532 nm)

4. Corrosion behavior

Fig. (4) shows the polarization curve of the untreated reference (Ni/Ti) sample. The corrosion current is ($\boldsymbol{i_{corr.}}$ = **7.4 µA**).

Laser surface treatment (LST)

The used laser was a spot pulse of wave length (532 nm.). The duration time was (3ms). Tafel extrapolation method was adopted to determine the corrosion current**.** Corrosion behaviour of this group is show in Fig (5). The $\boldsymbol{i_{corr.}}$ = **334**nA, the corrosion current was only **(4.5%)** with respect to the corresponding value of the reference. Improvements observed in corrosion resistance produced by (**LST**), may be mainly attributed to the continuous, protective, adherent and compact passive ($\mathbf{TiO_2}$) titanium oxide which indicated by XRD.

According to electrochemical series, **Ti** is more noble (**less active**) than **Ni**. Therefore, Ni – **oxide is expected to be formed**. But that did not happened. This is attributed to formation of physical and chemical barriers which act as barriers to prevent oxidation of **Ni** (F. Viller Maux. *et al*, 1997). These barriers creates modifications in the diffusion process in such a way to prohibit the outward diffusion paths of **Ni**. Several factors affect this behaviour such as, residual stresses, surface finish , inhomogeneity and defects. As far as $\mathbf{TiO_2}$protectivity is concerned, the smooth surface is of more corrosion resistance.

However, it is well known that Ti is a highly reactive and of great affinity for oxygen (Weber, Marvin J., 1999). During the oxidation process of titanium, its state changes from Ti^{4+} (correspond to titanium oxide) in the uppermost layer of the surface treated oxide. It then changes to Ti^{2+} and Ti^{3+} (correspond to TiO and $\mathbf{Ti_2O_3}$.

As far as the bare **NiTi** is concerned, it is almost oxygen – free in the region below surface oxide, (Weber, Marvin J., 1999). As soon as sample surface is Laser irradiated, the reaction accelerates between the metallic ions and oxygen. This reaction is greatly enhanced by the high temperature generated by Laser application. The oxide film then grew and thickened

rapidly. Diffusion of oxygen will also be promote at such a high temperature to the heat affected zone (**HAZ**) below the surface oxide film

Removing Laser spot forces the sample to cool down rapidly. Hence, there is no enough time for oxygen to diffuse away so it remains in solid solution in the sample, (K. W. *et al*, 2011). Laser surface treatment is simply an energy injection in the sample, which is instantaneously absorbed by the lattice. Metal surface layer melts quickly. Removing Laser beam is then followed by rapid cooling (**quenching**) of the melted layer .

Cooling directly from the elevated temperatures is expected to produce great **refining** of grain size, microstructure of the surface, removal of inclusions and segregations, and causes substantial increase in hardness. It also reduces porosities and homogenize the surface layer chemically (Z. D. cui, *et al*, 2005).

The observed growing titanium oxide surface film was continuous, compact, **cracks-free**, adherent , and uniform. This is why it possesses such a high corrosion resistance.

The very active refining of grains represents an easy path for outward diffusion of titanium required for growing of oxide layer. This means an enrichment of the outer surface layer by **(TiO_2)** passive layer, which stands behind the observed resistance to corrosion. Fig (6) shows **SEM** micrograph of **TiO_2** formed on Laser surface treated sample (LST).

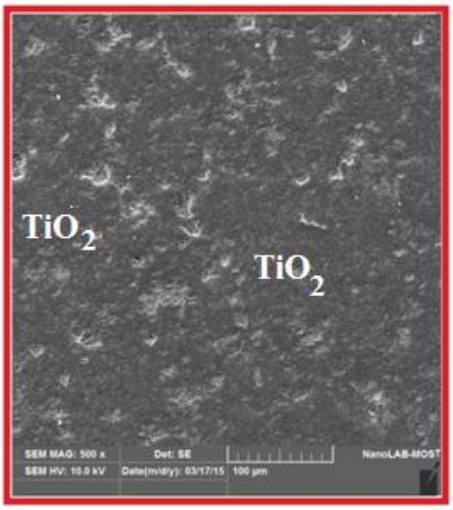

Fig (6) TiO_2 observed on (**LST**) sample

Ni-Release

In spite of the fact that nickel is necessary for human body, the presence of nickel at high level caused toxicity and allergenic, (H.C Man, *et al*, 2005). Ni-release was **0.2917** ppm for reference sample.

However, using spot pulse laser (532nm.) released very low value of nickel it was only (**0.0526**) ppm. This value represents **(17%)** of the reference. It is the high **refinements** of grains size, the redistribution of titanium at the sample surface, (H.C. Man, *et al*, 2001), the reduction in Ni/Ti ratio and the existence of **Ti_2Ni** which nucleates in **NiTi** matrix rich in Ti are all played crucial roles in this respect.

Laser spot pulses technique was deliberately adopted as an attempt to use it as an **alternative** for the conventail huge and costly Laser unit used by other researchers, (Amjed R. J., 2014). The spot pulses is of low power (**1/3**) of the large one, simple, economic and appears to be effective. The duration time was also shorter (**3**ms instead of **5**ms), table (2).

However, subjecting the sample surface by such a high power huge Laser unit beam and longer exposure time (**5**ms) generated sudden high temperature, which represents something like a **shock** or thermal impact on the samples surface. This caused very rapid inhomogeneous distribution in heating of the sample surface, i.e. this process generates non-uniform high **internal stress** which induced **microcracks,** can be roughly estimated from this relationship:

$\sigma = E\alpha\Delta T$, where :
σ = Stress induced in the metal, **N/m^2**.
α = coefficient of thermal expansion of the metal, C^{o-1}.
ΔT = Temperature change, C^o
α = $11x10^{-6}$ / Cº and E = 79 GP, then the induce stress are : **$\sigma = \alpha E \Delta T$**, then :
σ = $11\ x\ 10^{-6} x 79\ x\ 10^{9} x\ 1000$. **σ** = 869 MPa

These stresses are high enough to generate surface **micro-cracks** which deteriorate the mechanical and chemical properties [14] . However, such problem was avoided during using the portable spot pulses Laser, Fig. (7) shows a **crack – free** heat affected zone (**HAZ**). This is because, the energy of the Laser beam of such a unit was only (**1/3**) of the huge unit, and the duration time was only **(1/2)** one half.

This means the heating caused by Laser spot pulse was of **lower** heating rate and energy allow gradual distribution of heat. Hence, this is why the sample surface is **microcrack free**, Fig (7). On the contrary the Laser beam of the huge higher energy and rate, hits sample surface rapidly causing non-uniform distribution of heat. This results in the formation of high **residual stresses** which induced micro-cracks.

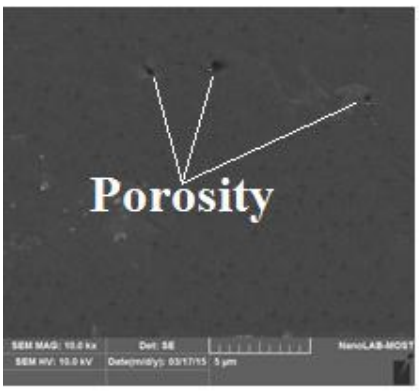

Fig (7) Micro **Crack-free** Laser treated (**HAZ**)

The situation is **aggravated** since, the thermal conductivity of treated surface is low (this permits the accumulation of heat). It is only **one half** of that of stainless steel. Similar conclusions for micro-cracks formation induced by the huge laser unit was observed by other workers, (A.K. Rajih, 1995).

Using the portable Laser unit facilitate the possibility of detailed examination of the heat affected zone (**HAZ**).

One of the disadvantages of the huge unit is that the decrease or probably the elimination of quenching ability of the remaining bulk metal. This may **prevent refining** the structure and even the formation of **martensite**. Hardness of the sample was measured from the center of the central spot to the edges of the sample. Laser surface treated sample, is shown in Fig. (8).

Mechanical Characterization

Measured hardness of the examined samples are shown in Table (2) and Fig. (8). It is obvious that, **Laser spot pulse** technique introduces a great increase in hardness.. It was in the range of **(4.5)** higher than the reference.

Hardness distribution across the diameter of the spot was measured,) Peak hardness was in the center and slightly decreased in the **HAZ**.

The sudden application of Laser beam represents a shock process Its similar to shot peening. This process induce residual compressive stress in the peened sample. Deformation and recovery in this case is more or less a thermomechanical treatment.

Increasing of hardness by the spot pulses may be enhanced by the encouragement of reaction within the irradiated surfaces between oxygen and ions of metal. This reaction is normally extended to the (**HAZ**) around and underneath the spot. Quenching directly from the melt however, is expected to produce great refining of grain size, microstructure of the surface, removal of inclusions and segregations, and causes substantial increase in hardness. It also reduces porosities and homogenize the surface layer chemically.

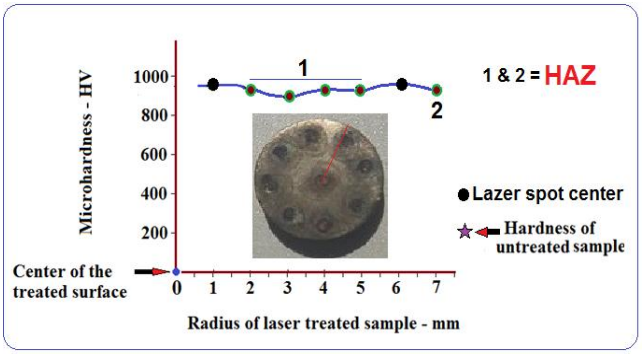

Fig (8) Hardness distribution across the radius of laser spot pulse

Wear behaviour

Evaluation of the tribological behaviour of Ni/Ti samples was carried out by pin-on –disc technique.

As shown in Fig. (9), it is obvious that, there is a general sharp decrease in weight loss with time. From tribological point of view, this behaviour is expected due to the process of asperity smoothing in the initial stages of contact associated with work hardening and eventually fatigue fractured.

It appears that, this is not the case for short laser spot pulse treated samples. Apparently, there is no measurable weight loss within this testing periods. This may be attributed to the great increase in surface smoothness and hardness (**970HV**) caused by spot pulses Laser treatment.

It is also well established that, wear rate mainly directly depends on the applied normal load and the sliding distance, and inversely on the value of either hardness or yield strength of the material. According to (Archard criterion), (J. F. Archard W. Hirst , 1956), wear resistance is inversely related to the hardness of the surface.

According to Archard question the overall wear rate (Q) can be estimated as follows:

$$\mathbf{Q = K \frac{WX}{H}},$$ Where :

Q = overall wear rate. **X** = sliding distance. **W** = applied load.
K = Archard constant (dimensionless) = 0.02. **H** = hardness.

The electrochemical, mechanical, and the treatment techniques become clear from the above.

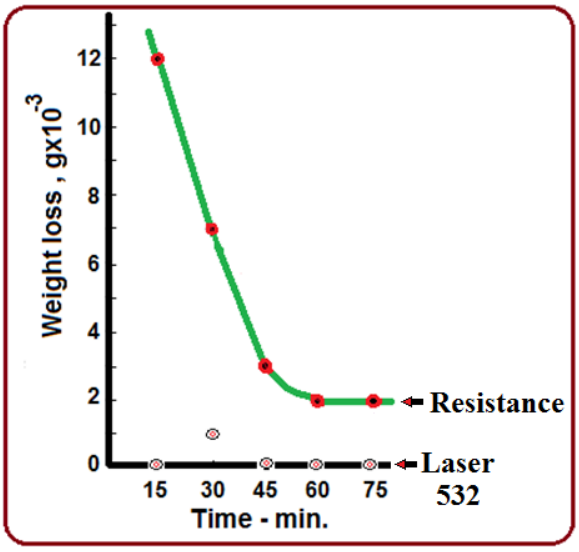

Fig (9) Comparison of wear behaviour

Table (2) Comparative of properties

Alloy	$\iota_{corr.}$	Ni-release ppm	Hardness HV	Wear rate	Weight loss	$\%\frac{\iota\, corr.}{\iota corr.\, Ref.}$	$\%\frac{Ni-relise}{Ni-release.\, Ref.}$	$\%\frac{hardness}{hardness_{Ref.}}$
Untreated	7.4 µA.	0.2917	200	6.26	$2x10^{-3}$	___	___	___
Laser 532 nm.	334 nA.	0.0526	970	1.3	$1x10^{-4}$	4.5 %	17 %	481 %
Ref. (Amjed R. J., (2014))	1.6 µA.	0.291	930	___	___	___	___	___

It may be worthwhile to withdraw an example to highlight the scientific, economical and design philosophy of the present work.

Important results were extracted from the simple portable spot pulse laser. For instance, the corrosion current and Ni-ion release were six **(6)** times, and three **(3)** times, respectively lower than the corresponding values of those obtained by the huge Laser equipment. Therefore, this alterative is effective. the wear rate was **1.3** for the **532**nm Laser treated with respect to **6.36** of the reference.

The adopted technique in this work facilitates the possibility of metallographic examinations of the **HAZ**, Fig.(8). While reference, (Amjed R. J., 2014). required accurate (spark machine) cutting of the sample.

Continuous Laser irradiation of sample surface in large Laser unit, however, reduces or completely eliminates the quenching ability of the surrounding metal. This is because the power generated and duration time are **(3**) times that of the portable one used in this work. Fig (9) shows the wear rate at the steady state.

Conclusions

1) The lowest value of corrosion current, of spot pulse (**532nm**) Laser treated samples was only (**334nA**). It was only (4.5%) of the reference current. while the best value obtained by the huge unit was (**1.6µA**).
2) Ni – ion release of the **(532nm)** spot Laser pulse was (**0.0526ppm**) compared to **(0.29ppm)** obtained by the huge Laser unit.
3) Laser treatment increased hardness from (200HV) to **(970HV)**, compared to the best value **(930HV)** of the large unit.
4) Wear rate of the Laser treated was practically zero within the test period.
5) Laser spot pulses facilitates the possibility of investigation of the **HAZ** without need to cut the sample accurately by a tedious spark machine.
6) No **microcracks** were detected in any of the Laser surface treated samples.

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