T.2 Modification of metallic surfaces with high power CO_2 laser

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Introduction

Many of the life-limiting mechanisms of engineering components originate from associated surfaces. These include corrosion, wear, stress-corrosion cracking, fatigue, corrosion-fatigue etc.. Material's susceptibility to these degradation mechanisms is strongly influenced by surface characteristics including chemical composition, microstructure, hardness, state of stress, roughness, nature of previous processing etc. A suitable modification of the character of the surface, without changing bulk of the material, provides an effective way to modify material's response to these unwanted effects. Surface modification can be in terms of change in composition, microstructure, topography, hardness, state of stress, cleanliness etc. The broad area of surface modification, now popularly known "Surface Engineering", has vast potential for providing cost-effective solution to enhance/extend life of engineering components operating under susceptible conditions. Laser, with its wide range of characteristics (e.g. wavelength and mode of operation - continuous wave/pulsed) and associated flexibility to manipulate with the help of optics, has emerged as a powerful tool to precisely control desired surface effects. Lasers are capable of inducing different kinds of surface effects including thinfilm deposition, solid-state transformation hardening, melting, alloying, cladding, surface cleaning/decontamination, shock peening etc. Compact lasers with the flexibility of transportation through fine optical fibers (e.g. diode, fiber and Nd:YAG lasers) are attractive industrial tools for processing in hostile environments or in the regions with limited access. With the integration of highly automated workstations with lasers, which are cost effective, powerful, reliable and compact, laser material processing (LMP) is set to become tomorrow's processing technology.

Realizing the important role that lasers can play in shaping Indian industry, CO_2 laser program was initiated at RRCAT, with the objective of developing high power industrial CO_2 lasers. Subsequent years witnessed development of high power lasers, ranging from 10 kW to 20 kW. During late-90s, activities were initiated towards material processing with in-house developed CO_2 lasers. For material processing applications, 3.5 kW and 10 kW transverse flow CO_2 lasers were integrated with beam delivery systems and computer numerically controlled 3-axis workstations. Recently, a 5-axes CNC workstation has also been integrated with 3.5 kW laser system for laser rapid manufacturing (LRM). During last couple of years, a variety of laser processing studies have been carried out and forthcoming part of the paper describes a few important laser surface treatment studies performed at Laser Material Processing Division of RRCAT.

1. Laser hardfacing to suppress dilution in Colmonoy deposit on austenitic stainless steel

Nickel-base alloys, "Colmonoy", have been selected as hardfacing material for many austenitic stainless steel (SS) components in 500 MWe Prototype Fast Breeder Reactor (PFBR) at Kalpakkam [1]. Hardfacing is intended to impart enhanced galling resistance to the mating surfaces and to avoid self-welding in the flowing sodium environment at a temperature of about 823 K. A major problem associated with Colmonoy hardfacing of SS components is extensive dilution from the base metal. Due to large difference in the melting temperatures of Colmonoy and SS, Colmonoy deposits pick up significant amount of dilution from SS base metal. C. R. Das et al [2] reported that Colmonoy 6 deposits on type 316LN SS, made by Gas Tungsten Arc Welding (GTAW), carry extensive dilution from the base metal, which significantly influences their microstructure and hardness up to a deposit thickness of 2.5 mm.[2] For overcoming adverse effects of dilution, it is essential to increase thickness of post-machined Colmonoy deposit, which not only adds to the cost of fabrication but also causes greater distortion of the component.

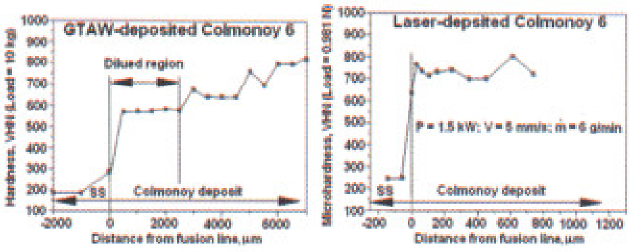


Fig.T.2.1: Comparison of hardness profiles across transverse cross-sections of Colmonoy deposits made by GTAW and laser.

Low heat input characteristics of laser cladding process has been exploited to suppress dilution in Colmonoy 6 deposits on type 316L SS base metal. Very low degree of dilution was achieved in laser-deposited Colmonoy by carefully controlling process parameters. Fig.T.2.1 compares hardness profiles across the cross-sections of Colmonoy 6 hard-faced SS specimens made by GTAW and laser. Crack-free Colmonoy 6 deposits were obtained by keeping the specimens undergoing hardfacing in a specially made sand bath maintained at 673 K and leaving the hard-faced specimens buried under sand for about 15 minutes [3]

2. Laser-assisted graded hard facing of Stellite 6

Co-based alloys "Stellite" are extensively employed as hardfacing material for many engineering applications for enhanced resistance against high temperature wear, oxidation and corrosion. In Fast Breeder Test Reactor (FBTR), there are many applications of Stellite overlay on austenitic SS to obtain enhanced galling resistance at elevated temperatures of about 823 K[4,5]. Large difference in the coefficients of thermal expansion between austenitic SS and Stellite often causes cracking of Stellite hardfaced SS components. Cracking resistance of Stellite 6 clad SS components can be effectively enhanced by providing smooth transition in chemical composition across substrate/clad interface. Present work describes laser-assisted graded deposition of Stellite 6 overlays on type 304 SS.

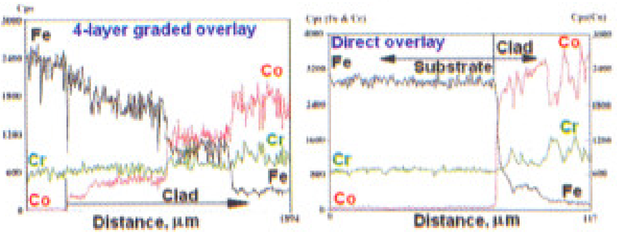


Fig.T.2.2: Comparison of concentrations profiles of Fe, Co and Cr across transverse cross-sections of graded and direct Stellite6 deposited austenitic SS specimens.

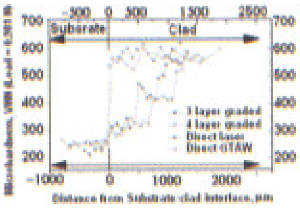


Fig.T.2.3: Comparison of micro-hardness profiles across transverse cross-sections of graded and direct Stellite6 deposited austenitic SS specimens.

The process of laser cladding has been employed to deposit 3 and 4-layered graded Stellite 6 overlays on SS. Multiple clad layers of graded composition were deposited by laser cladding with pre-mixed alloy powders of different compositions. In contrast to abrupt transition in chemical composition and micro-hardness across substrate /clad interface of directly hardfaced SS specimens, graded hardfaced specimens exhibited gradual transition in chemical composition and micro-hardness across substrate/clad interface. Both, the composition and micro-hardness measurements on graded hardfaced specimens exhibited stepped profiles, with each step coinciding with the interface between successive graded layers, as shown in Fig.T.2.2 and T.2.3. Graded overlaid specimen demonstrated higher cracking resistance under thermal cycling conditions than that of directly overlaid specimen [6].

3. Laser surface alloying with Cr, Ni and Mo to enhance pitting resistance of austenitic SS

Austenitic stainless steels are susceptible to localized corrosion in chloride bearing environment [7]. Super austenitic SS, with high concentrations of Cr (≈25%) and Mo (≈6.5 %), exhibits superior corrosion resistance than the popular 18/8 variety of SS. Surface alloying of SS with Cr and Mo, therefore, offers an economical means of enhancing corrosion resistance of relatively cheaper type 18/8 SS. The method of laser surface alloying, achieved by melting of powder-coated substrate, does not result in uniform chemical composition of the modified surface [8,9] In the present study, desired surface alloying was effected by laser cladding type 304L SS substrate with pre-mixed powders of type 316L SS and Cr. For controlling ferrite content in the weld metal, arising out as a result of addition of ferrite stabilizers like Cr and Mo, laser cladding was also performed with pre-mixed powders of type 316L SS, Cr and Ni. The average chemical compositions of resultant (Cr+Mo) and (Cr+Ni+Mo) alloyed surfaces, as found out by Quantitative Energy Dispersive X-ray Fluorescence (EDXRF) (in wt%) were: 24.2 Cr; 9 Ni; 2 Mo; 0.6 Mn and 24.4 Cr; 21.7 Ni; 1.4 Mo; 0.3 Mn, respectively. Potentio-dynamic polarization studies performed in 0.5 M NaCl solution demonstrated that the combined effect of Cr, Mo and Ni alloying in raising pitting resistance was more pronounced than that produced by alloying with Cr and Mo, as shown in Fig.T.2.4. Laser surface alloying with Cr, Mo and Ni brought about more than 3-fold increase in pitting potential over that of the untreated substrate (from 310 mV to 980 mV) whereas pitting potential for Cr and Mo alloyed surface was found to be 780 mV [10].

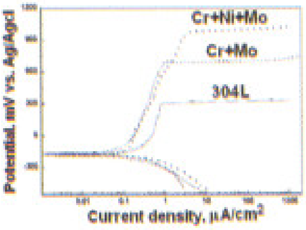


Fig.T.2.4: Potentiodynamic polarization plots of laser surface treated Cr+Mo and Cr+Ni+Mo alloyed and untreated type 304L SS (substrate) specimens in 0.5 M NaCl solution.

4. Laser surface alloying with Si for improved corrosion resistance of type 304L SS

Type 304L SS is a major material of construction in chemical and reprocessing plants involving extensive use of nitric acid (HNO_3). Normally protective Cr_2O_3 film on the surface of SS is rapidly dissolved under aggressive HNO_3

environment or at temperature above 353 K [11]. The stability of Cr_2O_3 film is enhanced by Cr and Ni addition. Si is another important alloying element influencing corrosion resistance of austenitic SS in HNO_3 environment. Si offers excellent corrosion resistance when its concentration is either below 0.2 wt% or above 1.6 wt%. With 0.4 -1 wt% Si content, the alloy suffers excessive inter-granular corrosion (IGC) [12]. ASTM specifications allow upto 1 wt% Si in type 304L SS. Hence, surface enrichment of Si above 1.6 wt% is an effective means of enhancing corrosion resistance of type 304L SS in concentrated boiling HNO_3 environment. Laser surface alloying with Si was achieved by laser cladding type 304L SS substrate with pre-mixed powders of type 304L SS and Si. The results of polarization study performed on Si-alloyed specimens in 6N HNO_3 solution demonstrated that in contrast to untreated substrate, laser surface-alloyed specimens exhibited significant reduction in passive current density from 1μ A/cm^2 to less than 0.1μA/cm^2, as shown in Fig.T.2.5, signifying greater stability of protective film on laser alloyed surface [13].

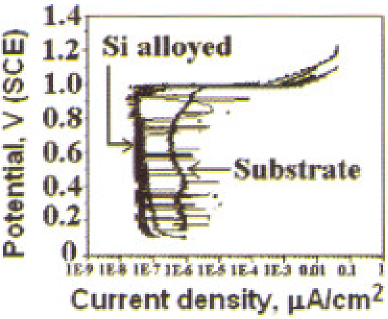


Fig.T.2.5: Potentiodynamic polarization plots of Si-alloyed and untreated type 304L SS (substrate) specimens.

5. Laser surface treatment to enhance inter-granular corrosion resistance of type 304 SS

Austenitic stainless steels, in spite of having good general corrosion resistance, strength, and formability [14-16], are particularly prone to localized corrosion like crevice, pitting, inter-granular corrosion (IGC) and stress corrosion cracking (SCC). In nuclear fuel reprocessing, waste management industries and in many chemical industries, using nitric acid as the process fluid, the main corrosion problem is IGC [17,18]. The basic cause of IGC is sensitization of SS. IGC of austenitic SS arises from inter-granular precipitation of Cr-rich carbides $M_{23}C_6$ during exposure to the temperature regime of 773- 1073 K. Inter-granular carbide precipitation is accompanied by the development of Cr-depleted zones adjacent to grain boundaries. Cr-depleted, zones, being anodic with respect to grain interior, are preferentially attacked in the corrosive environment leading to IGC [14-18]. Sensitization is also a main reason for inter-granular stress corrosion cracking (IGSCC) of SS weldments in certain environments e.g. oxidizing water chemistry in boiling water reactors [19].

Present study demonstrated that laser surface melting (LSM) treatment of type 304 SS brings about significant increase in its resistance against sensitization and IGC during subsequent exposure to susceptible temperature regime [20]. Fig.T.2.6 compares exposed surfaces of base metal and laser treated specimens after undergoing ASTM A262 practice B test. Degree of sensitization (DOS) of laser surface melted specimens remained largely unaffected by exposure to severe sensitization heat treatment at 923 K for 9 hours. In the best conditions, laser melted surface, even after undergoing this heat treatment, exhibited comparable or even lower DOS than the base metal in as-received condition (refer Table-1). Figure T.2.7 compares Double-loop Electrochemical Potentiokinetic Reactivation (DL-EPR) plots of base metal and laser melted specimens after undergoing 9-hour long sensitization heat treatment at 923 K. Enhanced resistance against sensitization of laser-treated surface is attributed to its duplex microstructure (involving austenite and -ferrite) and higher fraction of low angle grain boundaries (refer Table-2). The message of the investigation is that LSM treatment of unstabilized austenitic SS brings about significant reduction in its risk sensitization and IGC, arising out as a result of subsequent exposure to susceptible temperature regime. The technique has also been applied as a pre-welding treatment to suppress sensitization in the heat-affected zone (HAZ) of type 304 SS weldment [21].

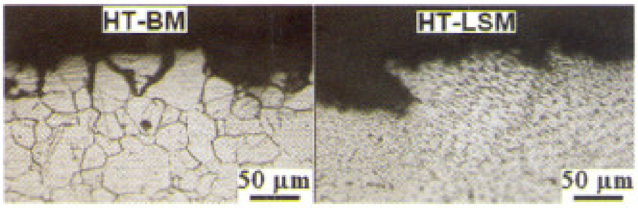


Fig.T.2.6: Transverse cross-sections of heat-treated (923 K for 9 hours) base metal and laser surface melted specimens after undergoing ASTM A262 Practice B test. Clear IGC attack on the exposed base metal surface (left) is in contrast to un-attacked laser treated surface (right).

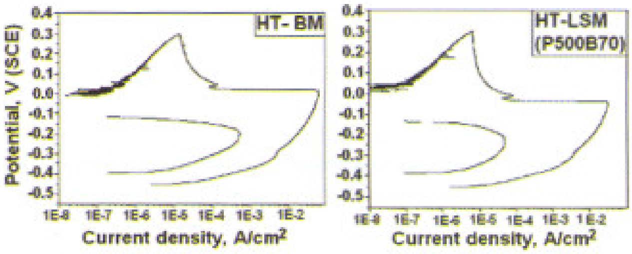


Fig.T.2.7: Comparison of DL-EPR plots of hea treated (923 K for 9 hours) base metal and laser surface melted specimens.

Specimen	Without heat treatment	After heat treatment
Base metal	0.36	4.52
Laser treated 1	0.09	0.107
Laser treated 2	0.24	0.327

Table-1: Effect of heat treatment on degree of sensitization (DOS) of base metal and laser surface melted specimens.

Nature of grain boundaries	Base metal	Laser melted surface
Low angle grain boundaries, $2^0 < \theta < 5^0$	0.042	0.17

Table-2: Grain boundary character distributions, as determined by orientation imaging microscopy, in base metal and on laser treated surface.

6. Laser surface treatment to suppress sensitization in mod. type 316(N) SS weld metal

AISI 316 LN SS with 0.024-0.03% C and 0.06-0.08% N is the primary structural material for 500 MWe PFBR. Welding of this material is being carried out using modified E316-15 electrode with 0.045-0.055% C and 0.06-0.10%N. Welded SS components are subjected to solution annealing heat treatment for achieving full stress-relief and restoration of mechanical properties and corrosion resistance. Higher C content of the filler metal makes the weld metal prone to sensitization during cooling from the solution annealing temperature. It has been shown that in order to avoid sensitization of the weld metal, weldment needs to be cooled at a rate higher than 75 K/h. However, rapid cooling of the weldment carries associated risk of distortion and reintroduction of residual stresses. A study had been taken up to develop a laser surface treatment to evolve a surface microstructure which would be more resistant against sensitization during post weld solution annealing treatment with cooling at a slow rate of 65 K/h

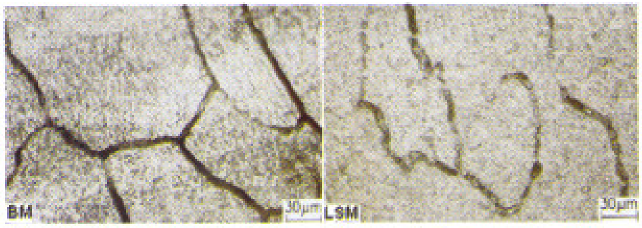


Fig.T.2.8: Comparison of the microstructures of solution annealed as-deposited (BM) and laser surface melted 316(N) weld metal specimens. Discontinuity in inter-granular carbide network in laser-melted specimen reflects its lower susceptibility to IGC.

Experiments involving LSM were carried out with 150 W average power pulsed Nd:YAG laser and 10 kW CO_2 laser, in both continuous wave (CW) and pulse modulated (100 Hz) modes. LSM treatment parameters have been found to have a profound effect on the IGC resistance of the resultant microstructure after subsequent solution annealing treatment. Best results were obtained when LSM was performed with high frequency pulse modulated CO_2 laser beam. Laser treatment of type 316(N) SS weld metal with high repetition rate pulse modulated CO_2 laser successfully induced greater resistance against IGC during solution annealing treatment involving cooling at the rate of 65 K/h Laser treated weld metal remained un-sensitized after solution annealing involving slower rate of cooling at 65 K/h [22]. Figure T.2.8 compares microstructures of untreated and laser treated 316(N) weld metal specimens after undergoing solution annealing treatment. Numerical simulation study performed with ANSYS 7.0 software to understand the physical reason behind difference in sensitization behavior of laser surface melted specimens under CW and high frequency pulse modulated conditions and the predictions were subsequently validated by electron back scattered diffraction (EBSD) analysis. In contrast to formation of long columnar grains growing from the fusion boundary in CW laser surface melted region, LSM with high frequency pulse modulated laser beam resulted in the evolution of fine grains near the fusion boundary region which is believed to be the cause for enhanced resistance against sensitization. The direct implication of these results is that the a laser surface melted type 316LN SS weldments can be cooled at a slower rate during subsequent solution annealing with reduced risk of sensitization and thus minimizing distortion and reintroduction of thermal stresses.

7. Laser beam shaping for improved microstructure during laser surface melting

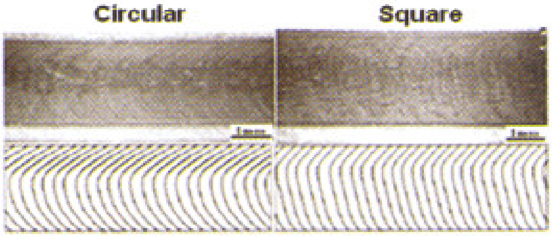
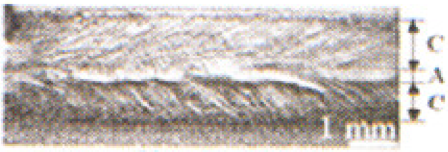
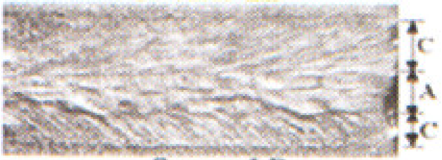


Fig.T.2.9: Comparison of the shapes of solidification fronts produced during LSM with circular and square shaped laser beams. Re-constructed profiles of associated solidification fronts are provided on the bottom of the figure.

Laser surface melting of austenitic SS at high-speed carries the risk of centerline solidification cracking due to the formation of tear-drop shaped melt pool. Laser beam shaping can be effectively employed to engineer surface microstructure of laser-melted region by controlling the shape of associated melt pool. Results of the present study demonstrated that by using a square laser beam in place of a circular one for LSM, the orientation of the solidification front associated with the resultant melt pool can be made flatter and more steeply oriented with respect to the direction of laser scanning (Fig.T.2.9). Development of this kind of melt-pool during LSM results in the growth of smoothly curved columnar grains with broader region of axial grains at the centre-line of laser surface melted track, as shown in Fig.T.2.10. Surface microstructure generated by LSM treatment with square laser beam should enhance resistance of against centerline solidification cracking (over that obtained with circular laser beam) even at higher processing speed [23].



Circular LB



Square LB

Fig.T.2.10: Comparison of surface microstructures produced by LSM with circular and square shaped laser beams. (A: axial grained region; C: columnar grained region)

8. Laser surface treatment to control end grain corrosion of austenitic stainless steel

Apart from IGC, another form of corrosion to which particularly bar, wire, and tubular products of SS are susceptible to in nitric acid environment, is end-grain corrosion. It takes place on the tubular and forged surfaces that are perpendicular to hot-working direction and occurs as localized pitting like attack that develops along the hot-working direction and finally corrosion occurs as intergranular attack [18, 24-27]. It has been identified as a major form of corrosion in those components in which cross-sectional surfaces are exposed to oxidizing process [25]. In reprocessing plants, using sensitization resistant low carbon grade or nitric acid grade (NAG) stainless steels, end-grain corrosion is shown to be a major degradation mode in components like instrument tubing and tube-to-tube sheet welds. There are also reports of end grain corrosion in forgings and set in pipe branches [24]. Exposure studies carried out in a dissolver in a reprocessing plant (in vapor phase) showed very heavy corrosion rates of 0.2-0.6 mm/year even for NAG grade of SS and this was attributed mainly to end-grain corrosion [24]. Directional nature of end-grain attack has been explained by the dissolution of aligned sulphide inclusions along the hot-working direction [18, 24-27]. Segregation of P, Cr and Si along the flow lines during the fabrication stage is another proposed mechanism for end-grain corrosion [18, 26-28]. The end-grain corrosion of a material is related to the defect in manufacturing and processing stage such as a high-inclusion content in the material or use of an improper solution annealing heat treatment. Instead of discarding these defective materials against end-grain corrosion, some suitable methods can be used to avoid or minimize such type of attack

In the present work LSM treatment was evaluated for its effectiveness to reduce end-grain corrosion in type 304 SS. Laser surface treated specimens of two heats (A and B) were subjected to ASTM A262 practice C to find out the susceptibility of these materials against IGC. LSM brought about significant reduction in the corrosion rates of both the heats with respect to corrosion rates observed for corresponding specimens in as-received conditions (refer Table-3). The reason for improvement in the resistance against end-grain corrosion is brought about by removal / redistribution of elongated MnS inclusions (refer Fig.T.2.11) and elimination of segregation of Cr, Si, and P along the flow lines. Another contributing factor for increase in IGC resistance is the presence of δ-ferrite on the laser treated surface, which makes the austenite grain network discontinuous [29].

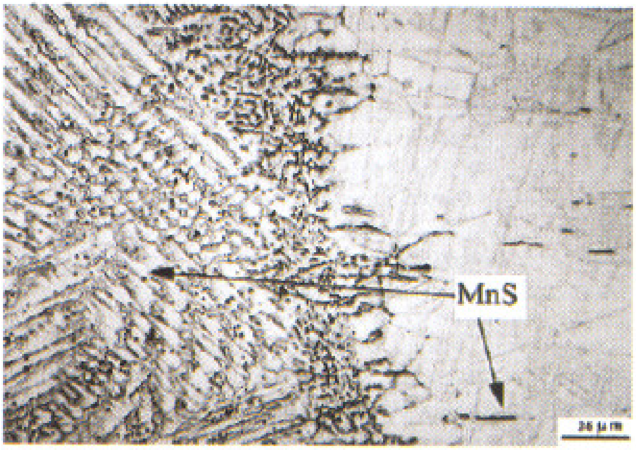


Fig.T.2.11: Transverse cross-section of laser surface melted specimen of heat B. Arrows indicate change in the morphology of MnS inclusions by laser melting. Laser melted region is on the left side of the photomicrograph.

Specimen	As-received	Laser melted surface
Heat A	1.858	0.185
Heat B	3.5763 (after 3 periods)	0.208

Table-3: Corrosion rates (in mm/yr) measured after 5th period of ASTM A262 practice C test for type 304L SS specimens

Conclusions

Laser surface treatment studies performed so far have demonstrated unique capability of laser to exercise control over surface composition and microstructure for yielding enhanced performance characteristics. After building this initial foundation, our present research activity focuses on developing laser surface treatments for enhancing or extending life of engineering components operating under fatigue and corrosive conditions through modification in surface microstructure and state of stress. Efforts are also being made to couple laser with conventional processes to make resultant hybrid process more capable and versatile.

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