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REVIEW PAPER

A review on nanostructured stainless steel implants for biomedical application

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ABSTRACT

Over the last two decades, many researchers have developed a variety of stainless steel-based medical implant types, taking full advantage of nanostructuring technologies. In this paper the application, fabrication and development of nanostructured stainless steel based materials with new composition for medical implants will be discussed. It is well established that application of severe plastic deformation (SPD) can decrease the grain size of metals and alloys significantly to the nanometer range. Among all the available SPD methods, equal channel angular pressing (ECAP) is very applicable. Stainless Steel became the raw structural material for the majority of the developed medical implants, and several techniques had to be studied and established in order to fabricate a feasible stainless steel-based neural probe. These nanostructured implants present a superior performance mechanically, biologically and electrically, when compared to the conventional implants. Finally, the effect of alloying elements on the bio-interaction of stainless steel will be explained.

Keywords: *Implants, Nanostructure, Stainless steel, Severe plastic deformation (SPD)*

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INTRODUCTION

Extensively, biomedical implants consist of: (i) cardiovascular implantable devices like stents, and etc. (ii) neural devices like deep brain stimulation (DBS), cochlear and retinal implants[1] (iii) orthopedic implants such as bone plates, and (iv) dental implants (Fig.1)[2]. By far metals are the oldest materials used in surgical procedures. The earliest records of the use of metallic implants in surgery went back to the 16th century[3, 4]. Rapid improvement of implant surgery together with the introduction of recently developed metals and alloys into clinical practice was visible in the following years[5]. Efforts have been made to implant different metal devices including wires and pins constructed of iron, gold, silver, platinum, etc. but they were largely unsuccessful because of infection after implantation. However, metals have been used in various forms as implants[4, 6]. Body has the capability to tolerate metals of manufacturing implants (e.g., Fe, Cr, Co, Ni, Ti, Ta, Mo, and W) for minute amounts[7, 8]. It is considerably important for implant metals to have biocompatibility because hostile body environment can corrode them. The results of corrosion are loss of material, which will enfeeble the implant, and probably more important, is that the corrosion products can insert the tissue, which results in undesirable effects [9-12]. One of the promising directions in the improvement of metallic implants with advanced properties is nanostructuring by different processing techniques. Severe plastic deformation (SPD) processes can be defined as processes in which an ultra-large plastic strain is

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introduced into a bulk metal in order to create ultra-grained metals[13-15]. Different SPD processes have been developed like equal channel angular pressing (ECAP), and accumulative roll-bonding (ARB). Severe plastic deformation can be introduced by an interesting method called ECAP [16-18]. The applicability of this method is production of materials with ultra-fine size grains in bulk. Samples faced with ECAP deform by simple shear and preserve the same cross sectional area[19]. A number of physical processes control the mechanical and biological features of nanostructured materials, these processes act and interact at many scale levels, from atomistic to the macroscopic level, and through different interacting physical mechanisms. Grain size reduction to nanoscales can influence corrosion behavior in several different ways[20]. In this review, we discussed about the nanostructured stainless steel implants for biomedical usages.

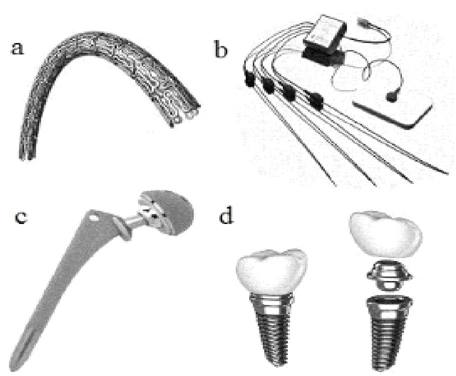

Fig.1. (a) cardiovascular, (b) neural, (c) orthopedic and (d) dental implants

Metal implants

Good formability, high strength and resistance to fracture are among the features that why metallic biomaterials have had wide application for surgical plants for decades[3, 4].

The important detriment of metals, is their willingness to corrode in physiological conditions (which limits the newly used metals to four main systems). Therefore, the list of metals currently used in implantable devices is limited to four main systems: iron-chromium-nickel alloys (austenitic stainless steels), cobalt-based alloys, titanium and its alloys and tantalum[5].

Cobalt-based implants

The other name of these materials is cobalt-chromium alloys. The applications of castable Co-Cr-Mo alloy are in dentistry and manufacturing artificial joints for many decades[21]. The wrought Co-Ni-Cr-Mo alloy has been used for making the stems of prostheses for heavily loaded joints. In the time of exposure to salt solution under stress, the alloy has a high degree of corrosion resistance. The strength of the alloy can be increased by cold-working significantly[22]. The superior fatigue and final tensile strength of the wrought Co-Ni-Cr-Mo alloy make it very appropriate for applications that need a long lasting service without fracture or stress fatigue. The modulus of elasticity for the cobalt-based alloys ranges from 220 to 234 GPa[3, 4, 23].

Titanium-based implants

Efforts to use titanium for implant construction turned back to the late 1930s. Great attempt has been made over the last few decades in the search for a suitable metallic biomaterial for orthopedic usages. The most generally used titanium materials for implant applications are commercially pure Ti and Ti–6Al–4V. Because of the prominent corrosion strength and good mechanical features, still one of the most extensively used alloys in the orthopedic scope is Ti-6Al-4V[24]. The modulus of elasticity of these materials is about 110 GPa, which has half of the value of Co-based alloys. The resistance of the Ti alloys is similar to 316 stainless steel or the Co-based alloys, in comparison to specific strength, the titanium alloy surpass any other implant materials[21]. Titanium, nevertheless, has poor shear strength, making it less desirable for bone screws, plates, and similar applications. In addition, the attendance of aluminum and vanadium in the alloy and, therefore, in the debris produced under conditions of extreme wear have led to potential safety concerns[23]. To reply to such concerns, aluminum and vanadium free titanium alloys have been developed to be used in the orthopedic application. Over the last three decades, the improvement of titanium and its alloys consisting zirconium and niobium as well as the alloyed tantalum for implant applications has continuously increased. Variation in the resistance of the different alloys in Ti–Nb–Ta–Zr system with varying alloying concentrations could be assigned to different deformation mechanisms functioning in these alloys[25]. These variations in the strength and modulus because of alloying additions are shown in Figs 2. Titanium deduces its resistance to corrosion by the constitution of a solid oxide layer. Under in vivo conditions, the only constant reaction product is the oxide (TiO_2). The oxide layer forms a thin adherent film and passivates the material [11, 25-27].

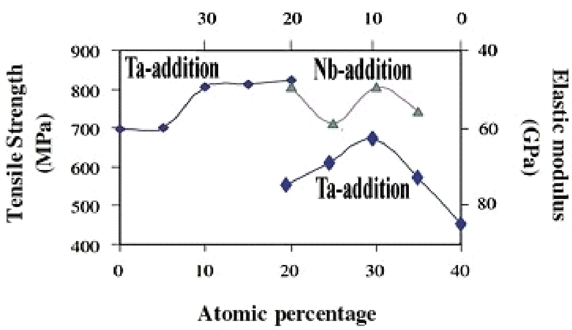

Fig.2. effect of element alloying on mechanical properties of titanium based implant[23]

Tantalum-based implants

Progression of tantalum (Ta) metal with bone-bonding ability is considered so much due to its absorbing features like high fracture stiffness, high workability and its prosperity on clinical usage[28, 29]. However, the relatively high cost of manufacture and an inability to produce a modular all Ta implant has confined its widespread acceptance. Ta has been represented to be bioactive and biologically bonds to bone by formation a bone like apatite layer in simulated body fluid (SBF). In several in vitro and animal studies porous Ta metal has arranged a structure for bone ingrowth and mechanical attachment[30]. Porous Ta implants suggest a low modulus of elasticity, high surface frictional characteristics and excellent bioactivity, biocompatibility and ingrowth properties. Moreover, one major constraint of these porous scaffolds is their significantly lower fatigue resistance in comparison with their equivalent fully dense materials [29, 31]. Authors previously showed that treatment with NaOH aqueous solution and subsequent firing at 300°C considerably accelerated the apatite formation on tantalum metal in SBF, while untreated tantalum metal spontaneously forms the apatite after a long soaking period[32].

Stainless steel-based implants

Stainless steel includes a vast range of steel types and grades for corrosion or oxidation resistance applications. The main need for stainless steels is that they should be corrosion resistance for a definite application or environment[21, 33]. 18-8sMo stainless steel was the first stainless steel used for implant materials, and it is stronger than the steel and more resistant to corrosion. “Sherman Vanadium Steel,” which was used to construct bone fracture plates and screws, was the first metal designed especially for human use[3, 4, 23]. Because of the insufficient corrosion resistance, Vanadium steel is not used any more in implants. On account of their great corrosion resistance, austenitic stainless steels (especially types 316 and 316L) are used in numerous industrial applications. Just cold-working can hardened these steels not heat-treatment. This group of stainless steels does not have the property of magnet but they contain better corrosion resistance than any others. The results can indicate that an extensive range of existing features depend on the heat-treatment or cold-working. 316L stainless steels may corrode inside the body under certain conditions, for example in a highly stressed and oxygen-depleted region[14, 34]. However an old application of stainless steels has been producing medical devices for the human body. Artificial joints and, especially during the past decade, vascular stents and neural implants have been among these devices. To manufacture such stents, commercial implant BioDur®316LS1 has been use specifically. These stent must have efficient mechanical and corrosion properties in blood plasma environments. As soon as placing in human body, Stainless steel implants can often be almost radiolucent to x-rays. Gold, platinum, or tantalum coatings applied to implants to increase radiopacity. A new method for increasing implant radiopacity is alteration to the composition of the stainless steel alloy[35]. This method contains alloying valuable metals, like platinum, with a stainless steel. The radiopacity and conductivity of stainless steel can be improved by such platinum additions, finally results in a new class of stainless steels, for medical applications. However, it must be shown that without considerable reduction in the mechanical characteristics or corrosion resistance of implants, such alloying can be carried out. Several studies have been conducted on the effect of metal additions on the corrosion performance of stainless steels. Some evidence shows that noble metal altered steels are more susceptible to stress corrosion cracking. In the following sections, the effects of alloying elements (including vanadium and platinum) on properties of stainless steel are reported. According to the specific grade, composition and application, stainless Steels contain a number of alloying elements. It is well known that adding the elements relevant to high oxygen affinity like Y, Ce, La, Er, Pt, V and other rare earth elements to steels in small amounts can increase their corrosion[36-38]. Moreover, new research has shown that one of the most practical methods to protect the stainless steel alloys against corrosion is using protective coatings[39].

Effect of vanadium on properties of stainless steel

This section follows the purpose of reviewing the role of V in microalloyed structural steels and our perception of how it influences microstructure evolution and mechanical features. Its role relevant to thermo-mechanical processing is especially focused[40]. Vanadium is a microalloying element mostly used to increase the strength and toughness rather than the hardenability of microalloyed steels; this process is realized through the precipitation strengthening of fine carbonitride particles that are shaped during cooling or tempering[41, 42]. Result showed that the hardenability multiplying factors of steels containing 0.1% vanadium can reach 1.2–1.6[43]. The hardenability curves of V-modified and V free steels at 860°C are represented in Fig. 3.

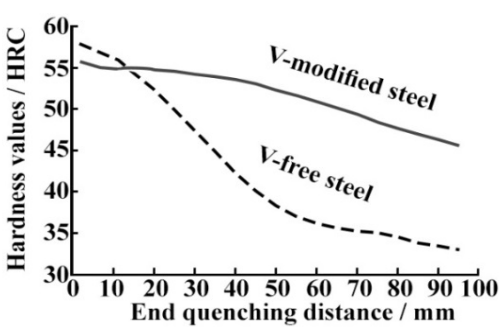

Fig. 3. Hardenability curves V-modified and V-free steels at 860°C[43]

Microalloy element vanadium has disparate effects on the strength and toughness of steel at various normalization temperatures[44, 45]. Some suggest that despite the fact that tensile strength remains constant, the V addition develops impact toughness, and some tend to conclude that small amount of V make trivial difference in steel and other researchers believed that V basically plays a role in increasing strength.Tao et.al investigated the mechanical characteristics of V-modified and V-free steels, their results show that by elevating reheat temperature, tensile strength increased and low-temperature impact toughness decreased. It can be also seen that by variation in reheat temperature, mechanical properties of V-modified steel has more fluctuation than those of V-free steel, which indicates that choosing an appropriate reheat temperature is of great importance for V-modified steel[44].

Another investigation attempt was made to study the effect of V up to 0.45% on the high-cycle fatigue properties of V-modified steel, in order to develop new crackable steel with best fatigue properties. The results show that the amount of V(C,N) precipitates increases as V content increases.As a result, the amount of hardness increase of ferrite by increasing V content is much more than that of pearlite. Therefore, both fatigue strength and fatigue strength ratio increase as V content increase and leads to excellent fatigue properties[46]. Recent researches on the fatigue crack initiation behavior of V-modified steel also indicated that almost all the fatigue cracks started mainly along the ferrite/pearlite boundary and progressed preferentially along that boundary (Fig. 4). However, on account of lack of enough corrosion resistance, vanadium steel is not used any more in implants. Based on this reason recently Pt-modified steel was introduced.

Effect of platinum on properties of stainless steel

The impact of alloying additions of platinum and palladium on the dissolution of stainless steels in different acids was reported by one of the primary investigators of stainless steels. Corrosion of iron alloys in sulfuric acid can be reduced by additions of 0.1 to 0.5 percent platinum and 0.1 to 1.0 percent palladium to stainless steels. It was found that these noble metal additions were efficacious in suppressing corrosion in formic and acetic acids[37, 47]. Tomashov et al.[48, 49] have focused their attention on the use of palladium additions to different stainless steel compositions as a means to reduce corrosion in acids. It was found that a stainless steel with 0.5 percent palladium remains passive in 10 percent sulfuric acid solution up to 100°C.

Some papers reviewed the effects of platinum metals additions on corrosion behavior stainless steels, Russian researchers have carried out most of these works. It is concluded that, improved corrosion behavior can be obtained by the addition of platinum group metals to stainless steels[50].

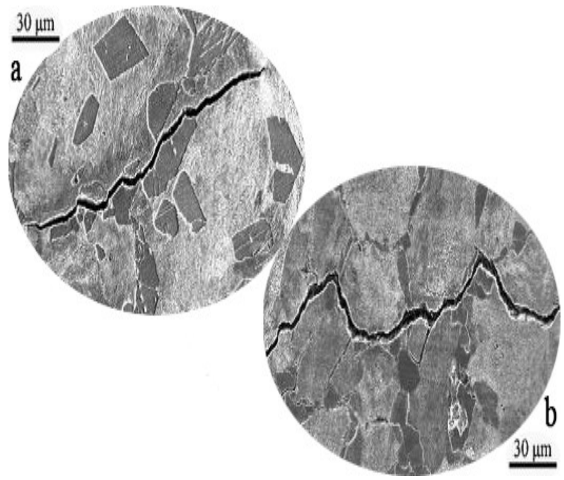

Fig.4. SEM image of rotating bending fatigued sample of V-modified steel in (a) as-annealed and (b) as-rolled conditions[46]

Many years ago, Greiss et al. investigate the effect of Platinum (0.5 percent) addition to stainless steel in uranyl sulphate or copper nitrate solutions. Their observation showed that corrosion rate was reduced from 0.035 inch/year to 0.015 inch/year through this addition[51]. Research on the effect of platinum additions on the stress corrosion cracking indicate with increasing platinum additions, life of 18Cr-8 Ni stainless steel in boiling magnesium chloride Gradually decreased[52]. Table 1 shows the results of platinum impact on the corrosion behavior of steel in some studies. Others showed stainless steels with at most 10% platinum providing homogeneous structures, moderate mechanical Properties and improvement of radiopacity compared to 316L. Efforts to find optimum percentage showed that compositions with 33% Pt, providing an optimal properties[53].

The greatest source of damage to stainless steels probably is chloride ion, bringing about quick degradation of passive films, then leads to pitting, crevice corrosion and possibly stress corrosion cracking of loaded components. With regard to the noble metal additions below a critical level deteriorate corrosion in boiling 10 percent sulfuric acid, but above the critical value they deeply passivate the steel[47, 50]. Researchers tested various alloys in hydrochloric acid and reported corrosion rates and electrochemical parameters. They suggest that while palladium additions may increase the tendency of steels to pitting, such additions also broaden the range of acid concentration and temperature over which the steels are passive. Outside this range, however, the palladium steels are those which have enhanced corrosion rates. Many authors, however, report noble metal-containing alloys generally which show a marked tendency to intergranular failure[54, 55].

Table1. effect of platinum addition on corrosion rate of steel in 10 % formic acid[47]

Platinum (%)	Time (h)	Corrosion rate ($g/m^2.h$)
0	1	343
	10	Complete dissolution
0.1	1	0.6
	10	0.15
0.5	1	2.2
	10	0.11

It appears that no systematic examination have been conducted on the effects of noble metals on the mechanical properties of stainless steels, though several workers have specified the mechanical properties of experimental alloys, to evaluate required loading for next stress corrosion testing. Irani et al.[56] has been studied the effect of different alloying elements, like platinum/palladium and gold, on the mechanical properties of deformable steels. Table 2 is the representative of the hardness and tensile test results at the various percent of Platinum. It seems that platinum have a slight solid solution hardening effect, with a hardness increase, in the annealed condition, of about 30 Vickers units for the addition of 10% of platinum. The work hardening response of all the alloys is similar. Table 2 clarifies that platinum does not appear to have an important effect on either the tensile or the yield strength[35, 53]. On the other hand, Platinum additions to stainless steel increased the radiopacity but for medical implant, it is required platinum equivalent to approximately 15 wt% to achieve parity with cobalt–chrome alloys. Moreover, Platinum additions decrease the tendency to form martensite on transformation[35, 53].

Corrosion and coating of metallic implants

The most common metals and alloys used in biomedical implants may get cytotoxic due to exposure to a process of corrosion in vivo[57]. The biocompatibility of metallic implants is basically associated to their corrosion behavior. The main factors in corrosion and biocompatibility of implants are surface coatings. To design protective coatings, the following requirements must be considered: great corrosion resistance, low oxygen permeability, low solubility in fused salts, and identical thermal expansion to that of the substrate and strong adhesion to the substrate[9, 10, 58, 59]. During the past two decades, superhydrophobic coatings on metallic substrates have shown remarkable corrosion resistance in highly aggressive media. The air retained on can prevent corrosive processes can be inhibited by retaining air on such super hydrophobic surface, e.g., chloride ions in body from attacking the metal surface, suggests a new efficient mechanism for anti-corrosion[60].Recent studies represent that electrochemical processes on steel and platinum electrode has been a method to compose poly (pyrrole-co-o-anisidine), poly (pyrrole-co-o-anisidine-co-o-toluidine) and poly (aniline-co-o-anisidine-co-o-toluidine) film. Poly (pyrrole-co-o-anisidine) and poly (pyrrole-co-o-anisidine-co-o-toluidine) films can protect better the corrosion of mild steel[61, 62]. In this regard, Yalcinkaya studied Synthesis of poly(o-anisidine)/chitosan composite film on the platinum and mild steel electrodes by electrochemical method. showed that the composite film with good stability, homogeneously formed on the surfaces of platinum and mild steel electrodes[63]. Furthermore, the addition of highly radiopaque materials such as tantalum, platinum or gold, in the form of coatings or marker bands may improve the radiopacity of 316L stainless steel stent's[64]. Coatings appeared to offer the ideal solution, allowing radiopacity to be tuned in proportion to coating thickness. A number of device companies explored gold coatings, but resulted in poor clinical performance as reflected in higher restenosis rates, compared to uncoated 316L stainless steel devices[65].

Biocompatibility of metallic implants

The most primary to be considered for the implant success is tissue compatibility. There has been no surgical study to be completely free of noxious reactions in the human body. Local tissue response to metal implants is nearly connected to the amount and toxicity of the corrosion products[66, 67]. It is found that titanium is well tolerated and mostly an inert material in the human body environment. Moreover titanium has the capability to integrate with bone in an optimal situation.

Table 2. effect of platinum addition on mechanical properties of steel in different condition[53]

Pt (wt%)	Tensile strength (MPa)	Yield strength (MPa)	Elongation (%)	As-cast (HV)	Annealed (HV)	Cold rolled: reduction in thickness 60% (HV)
–	650±17	274±5	60±5	129±5.4	112±3.2	332±11.7
1.21	604±6	250±1	55±1	132±4.0	137±3.2	355±9.6
3.04	703±13	347±3	55±1	138±3.7	138±3.7	395±7.4
6.46	660±18	297±7	67±4	130±2.5	130±2.5	362±11.2
10.14	704±12	355±42	52±0	139±7.8	139±7.8	381±11.0

Besides, titanium makes a very firm passive layer of TiO_2 on its surface and supply higher biocompatibility. Even if the passive layer is hurt, the layer will be reconstructed instantly[24, 68]. In comparison to the stainless steel and Cr–Co alloys, titanium alloys show superior biocompatibility[69]. In one study, in vitro cytotoxicity test using an established human osteoblast cell line hFOB aimed at assessing any possible toxic effects of Ta coating on Ti compared with the widely used Ti, as a control sample. Fig. 5 indicates the morphology of hFOB cells on Ti control and Ta coatings after 14 days culture. There is less cell spread on Ti surfaces. The cells on the Ta coating surface produced a great amount of extracellular matrix (ECM), which can be introduced as an early stage of osteoblast differentiation. In opposite, no confluent layer formation can be shown on the Ti control surface, even after 14 days[70].In another work, Pt-modified steel and 316L stainless steel resulted in endothelial cell growth on stents and then was evaluated by using human coronary artery endothelial cells grown on collagen gels. As is clear from Fig.6, for the Pt-modified steel, a considerable increase in the number of cells was observed at 14 days, compared to 7 days[35].

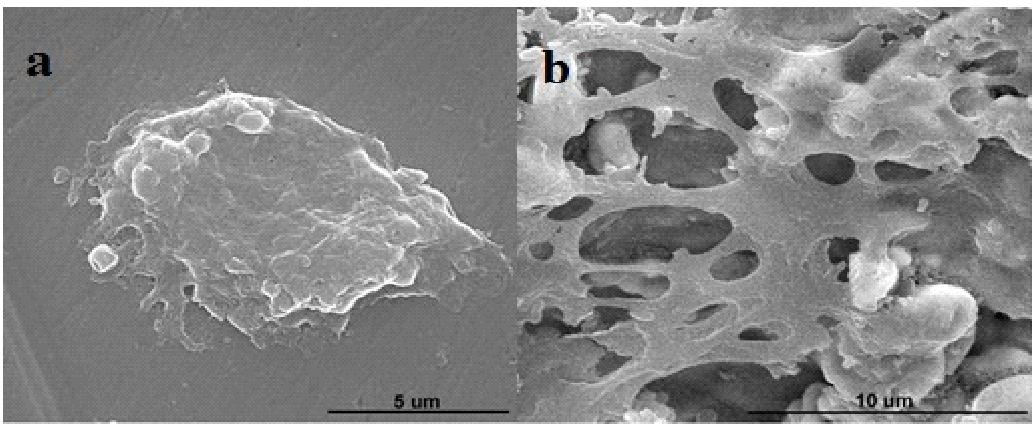

Fig. 5. SEM images of cell morphologies. (a) Ti surface and (b) Ta surface after 14 days[70]

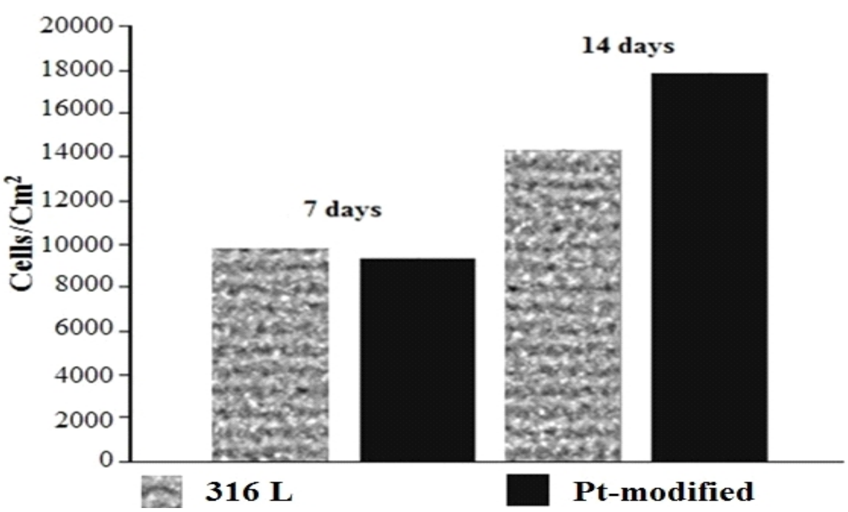

Fig. 6. Results of MTT assay for stents made from 316L stainless steel and from the Pt-modified steel[35]

Thus, according to cell culture studies, one of the best materials in terms of supporting endothelial cell growth and migration is Pt-modified steel.

Nanostructure stainless steel

It is expected that progress in metals construction technologies plays an important role in the improvement of the next generation of medical implants. Progress in nanotechnology now makes it possible to exactly design and modulate, at nanoscales, surface and bulk properties of materials used for different applications in medicine, which offers newer visions to patients[2]. The combination of nanotechnology with biomedical engineering promises a newer generation of implants. Implant industry can be revolutionized by designing and modulating their properties through the capability of nanotechnology. It should be noted nanostructuring can make mimicking the nanostructures in the body possible; Therefore. nanostructured implants have the unique capacity to positively influence the cellular phenomenon[14, 71]. These may be conveniently classified as implants with nanostructured bulk or surface topology (Fig.7).

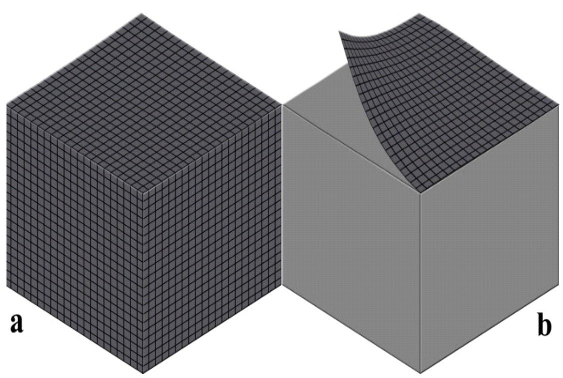

Fig.7. Schematic of materials with nanostructured (a) bulk and (b) surface topology

Biocompatibility is a crucial factor for biomaterials, i.e. they must be non-toxic, non-carcinogenic materials that do not demonstrate undesirable chemical reactions with body fluids[72]. They should also be mechanically resistant with long fatigue life and proper density. On the other hand, an ideal orthopedic implant requires having not only high corrosion resistance but also an elastic modulus agreeable with that of the bones[29]. Because of appropriate mechanical properties including relatively high corrosion resistance, easy produce, and comparatively low cost in comparison to many other alloys, the austenitic stainless steels have different usages as a biomaterial like human body implants and orthopedic devices among the present metal implants[33]. Despite its major advantages, a 316L stainless steel is prone to corrode in chloride environment, particularly localized corrosion (pitting corrosion). 316L stainless steel corrosion resulted in releasing metal ions such as nickel and chromium in the body and leads to allergies. Poor mechanical behavior of implant is the product of localized corrosion. Due to the fact that many mechanical, physical and chemical properties of metals sustain vital changes during their nanostructuring, researchers suggested construction of nanostructured materials during the two past decades[20]. Decreasing the grain micro-size intensifies the reaction of surface with corrosive environment; meanwhile reduction of nanocrystalline material decreases the reaction of surface to corrosive environment. The findings of some research show that, bulk and surface nano-crystallization develops the stability and corrosion resistance of the materials[73].

Authors show that the nanostructure stainless steel as the significant nucleation sites to fabricate more uniform passive film consisting more chrome, have greater corrosion resistance in sodium chloride solution in comparison to the microstructure one[34]. It is well established that application of severe plastic deformation (SPD) can filter the grain size of metals and alloys significantly to the nanometer range. Among all the available SPD methods, equal channel angular pressing (ECAP) is especially absorbing; because it requires simple facilities. The ECAP technique imposes large plastic deformation on a large billet by simple shear. The billet can be exposed to several ECAP passes in order to increase the total strain introduced into the billet[13, 74].

In another study, Jiang et al. found that in UFG structure, the corrosion behavior developed by the easier formation of an oxide layer with an improved adhesion force and protection efficacy. The relative dissolution or passivation of a surface can be connected to the total length of the grain boundary[75]. As shown by Orlov et al., an alteration in grain boundary length can either increase or decrease the corrosion rate, which rely on specific material/environment combinations[15].

Fattah-alhosseini and Imantalab has been examined the effect of accumulative roll bonding (ARB) process on the electrochemical behavior of pure copper in 0.01 M borax solution. The microhardness tests indicated that the values of hardness develop with increasing the number of ARB cycles by implementing the ARB process. Moreover, a drastic increase of microhardness was seen after the second ARB cycle[18]. In this work, corrosion test showed that increasing the number of ARB cycles offer better conditions for forming the passive films.

Maleki et al. studied the effect of Equal Channel Angular Pressing (ECAP) process on corrosion behavior of the 316L type austenitic stainless steel. ECAP was conducted on an 316L stainless steel up to eight passes. The results showed that after performing the eight passes of ECAP, an ultrafine-grained 316L stainless steel with a mean grain size of about 78 nm was gained. In their work, increasing of the number of ECAP passes improved significantly the corrosion resistance of 316L stainless steel. After performing the eight passes of ECAP process, the corrosion rate of 316L stainless steel measured to be 0.42 $\mu A.cm^{-2}$ which is greatly lower than that of initial coarse-grained material (3.12 $\mu A.cm^{-2}$)[34]. Hajizadeh et. al evaluated Corrosion and biological behavior of nanostructured 316L stainless steel processed by ECAP process. Results of their work after nanostructuring, revealed a substantial decrease of corrosion rate from 3.12 to 0.42 ìA.cm^{-2}. Furthermore, the cell proliferation on the surface of nanostructured steel enhanced Significantly compared with the conventional steel[20]. In this regard, the electrochemical and cellular behavior of commercially pure titanium with both ultrafine-grained (UFG) and coarse-grained (CG) microstructure was evaluated by Maleki-Ghaleh. Results of their investigations illustrate the improvement of both corrosion and biological behavior of titanium after ECAP process[71].

The Young's modulus E is the important technological and structure-sensitive parameter that gives integral information on structural changes in the volume of the materials under examination. Creation of fine textures during cold working (e.g., rolling, drawing or hydrostatic extrusion) lead to appreciable anisotropy of the Young's modulus because of the strong orientation dependence of elastic features[76, 77].

Fig.8 represents the relationship between proof stress and grain size of pure iron. The proof stress varies inversely with the square root of the grain size, following the Hall–Petch relationship. It is seen that the proof stress of the ultra-fine grained irons, with sub-micrometer grains, is five times greater than commercially pure iron[78].

Thus, on account of their high strength ,the conventional structural metals with ultra-fine grains are lighter. In addition, the improvements of the superplasticity, corrosion and fatigue properties of metals processed by SPD are expected. On the other hand, the ultra-fine grained metals are available only for micro-parts[13].

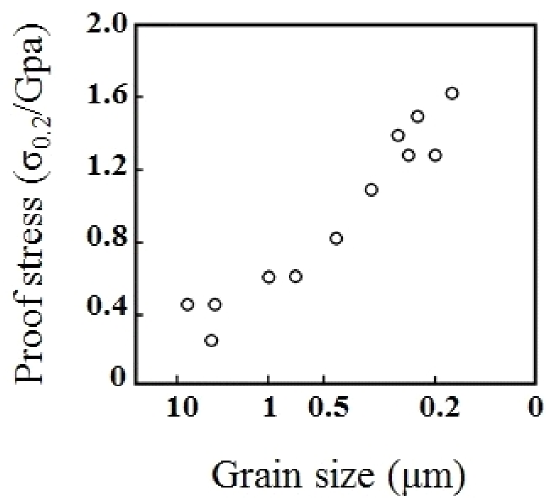

Fig.8. Graph illustrating relationship between proof stress and grain size of pure iron[13]

In another work, the capability of SPD-processing and subsequent heat-treatment to achieve a combination of high strength and good electrical conductivity was investigated. Heat-treatments were implemented in order to improve the electrical conductivity in the high-pressure torsion (HPT)-processed Cu–Cr alloys[79].

The change of the hardness and the electrical conductivity as a function of the heat-treatment temperature is shown in Fig. 9.

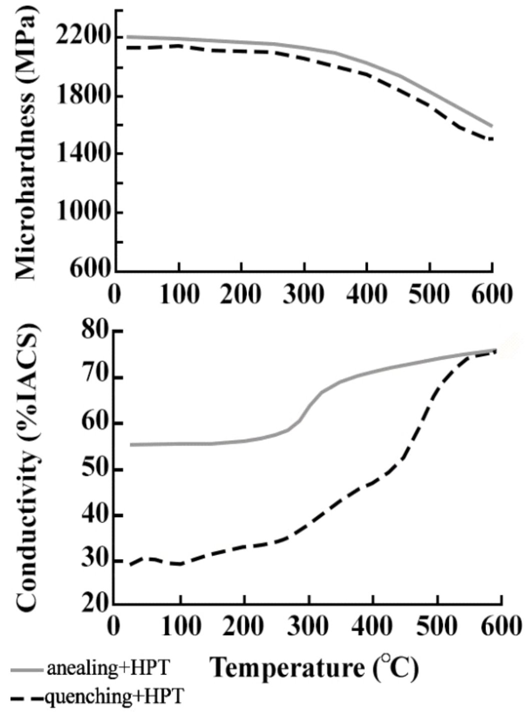

Fig. 9. Effect of SPD-process and heat-treatment on the hardness and the electrical conductivity[79]

In another previous studies of deformed 316L have indicated that diameter of steel wire reduced by drawing to 8 µm, it has a microstructure consisting of strain induced martensite and austenite. In this regard, previous studies indicated that rolling deformation of 316L induces the transformation of the austenite into á¹martensite.

Wang et. al showed that the grain structure is strongly textured and is approximated by space filling prisms elongated along the drawing direction in three dimensions.

Also It has been demonstrated that although the austenite can change completely into martensite under paraequilibrium conditions, it is not possible to do so in spite of huge strains, because of the onset of mechanical stabilization[80].

Nanostructure stainless steel properties

The excellent properties of the nanostructured stainless steel attracted the attention of a vast number of scientists especially in the field of manufacturing metallic implants. With their small grain size and high volume of grain boundaries, nanostructured stainless steel possess unique physical, chemical, and mechanical properties in comparison with that of the microstructured ones[34, 80].

Studies have shown that grains of the stainless steel after nanostructuring process are roughly uniform in size and distribution. As anticipated, the microstructure underwent a considerable refinement during nanostructuring process and evolved to an ultrafine-grained structure.

The distribution of grain size in the processed stainless steel was fairly large ranging from less than 20 to 200 nm[20].

Increasing the thickness and density of the passive layer on the surface of nanostructured stainless steel implants and also reducing the corrosion current density can improve the biological behavior and biocompatibility of the implants substantially. For example, polarization curves of conventional and nanostructured stainless steel in Ringer's solution are shown in Fig. 10.

Therefore, nanostructuring process considerably increased the corrosion potential, reduced the corrosion current density, and release of alloy elements. On the other hand, there is a significant decrease in corrosion rate of nanostructured stainless steel compared with conventional stainless steel[20, 73].

Also from metallographic observations found that the number, size and depth of corrosion pits on the conventional stainless steel surface are more than that on the surface of nanostructured stainless steel. This significant change in the corrosion behavior of the nanostructured stainless steel is mainly due to the change in the passive film structure. By increasing the thickness and density of the passive film, the metal corrosion resistance will enhance significantly. Therefore, as it is expected, the corrosion resistance of the nanostructured metals is much greater than the microstructure ones.

The results of studies demonstrated different concentrations of ions released from conventional and nanostructured stainless steel, i.e. nano-structured stainless steel could decrease the release rate of toxic elements, like iron, during the corrosion test by forming the stable oxide layer as an inhibitor[14, 20, 73].

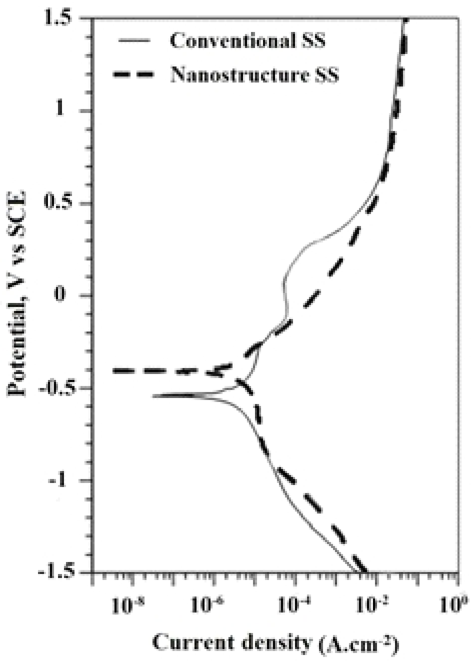

Fig. 10. corrosion behavior of conventional and nanostructured stainless steel[73]

Numerous studies have reported on the problems of fatigue fracture and wear of Stainless steel implants. The combined influence of corrosion and cyclic loading is known to affect the mechanical properties of stainless steels. The cracks frequently initiate from corrosion-induced surface defects, and it can accelerates the failure of the implant by fatigue. Fatigue characteristics are closely related with the microstructures. The microstructures in stainless steel implants change according to the employed processing method. nanostructured stainless steels are expected to have high strength as a result of structural refinement, according to the Hall–Petch relationship, where the yield stress varies with the reciprocal of the square root of the grain size. On the other hand, nanostructured stainless steels have limited ductility due to susceptibility to deformation localization. The grain refinement can produce through ECAP. This grain refinement can lead to drastic increases in yield stress, tensile strength and high cycle fatigue (HCF) strength. Fig. 11 depicts the S–N curves of conventional and nanostructured stainless steel in the Ringer solution. It is clear that, the fatigue strength of the stainless steel was increased after nanostructuring. On the other hand, the superior HCF performance of nanostructured stainless steel is explained by the very low surface defects, that leads to a reduction of fatigue crack nucleation[73, 81].

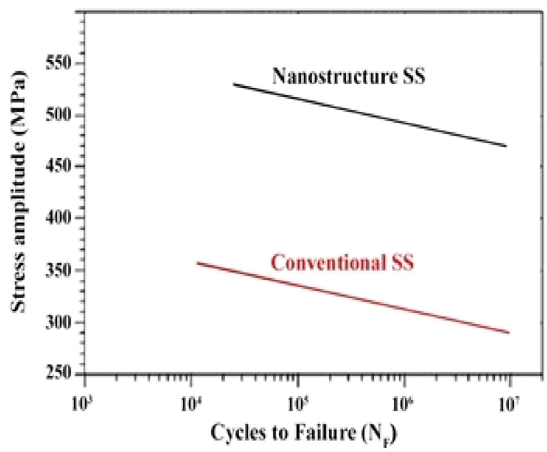

Fig. 11. S–N curves of conventional and nanostructured stainless steel in the Ringer solution[73]

The implant biocompatibility in the human body fundamentally depends on its reaction with surrounding environment. By reduction of the grain size and corrosion rate, the implant biocompatibility will increase drastically.

Figures 12 illustrate the optical microscopy image of the interface of culture environment with conventional and nanostructured stainless steel after 5 days. As can be clearly seen, the culture environment including the nanostructured stainless steel has much more cell aggregation com-pared with the medium with the conventional stainless steel. Unlike the conventional stainless steel, the nanostructured one increases the cell proliferation significantly. This significant cellular behavior difference between conventional and nanostructured stainless steel is due to the high corrosion resistance and reduction of release of iron ions.

Also, it can be found that the cells grew and attached well on the stainless steel substrate layer by layer, especially on the surface of the nanostructured stainless steel, while they show less activity and single thin cell spread on the conventional stainless steel, without significant proliferation[14, 20].

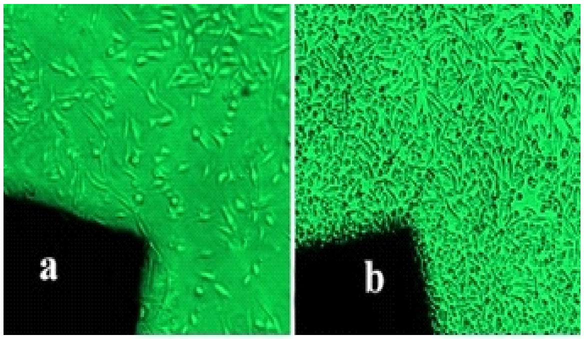

Fig. 12. images of interface of culture media with (a) conventional and (b) nanostructured stainless steel after 5 days[20]

Nanostructure stainless steel application

The use of metal as an implant material is most widely known for dental and orthopedic applications[82]. One example of a medical device is cardiac pace makers that use metal electrodes for electrical signal conduction into the cardiac muscle[83]. Neural interface prosthetics also use metal for the electrical conduction of signals at the tissue interface[84].

Stainless steel is commonly used for recording sites on intracortical microelectrode wire. Tungsten, platinum and stainless steel wires made commercial microelectrode wire as well as much noncommercial wire from various research groups, such as the authors'[85]. The microwires can be inserted into neural tissue without buckling[86]. However, tungsten is not impervious to corrosion. The attachment sites for the tungsten wires and stainless steel nuts were coated with insulating epoxy and PDMS. Later designs changed the recording-site metal from gold to platinum or iridium, incorporated parylene rather than Si cables and added wireless capability[87, 88].

Desai et.al describes a simple, inexpensive and reliable method to manufacture bipolar electrodes containing an insulated stainless steel wire (Fig.13-a)[89]. While the commercially available electrodes are quite expensive, earlier in-house fabrication methods use cumbersome procedures and costly metals like gold or platinum.Performing a wide variety of measurements of bioelectric signals requires electrodes[90]. The basic needle electrode shown in Fig.(13-b) includes a solid needle, usually made of stainless steel, with a sharp point. An insulating material coats the shank of the needle up to a millimeter or two of the tip so that the very tip of the needle remains exposed. When this structure is placed in tissue like skeletal muscle, electrical signals can be picked up by the exposed tip[1, 91].

Otherwise, coronary stents may be made from austenitic stainless steel. These stents are not sufficiently visible, radiographically, under certain operational conditions, thus a range of Pt-modified steel alloys were improved, which are more visible when used as stents. Nowadays, authors developed the new alloys to ensure that the properties are those required for coronary stents. These properties contain an ability to be cold worked, mechanical strength and ductility identical to those of implant grades of austenitic stainless steel, an absence of magnetic phases, like ferrite and martensite, also an absence of brittle intermetallic phases[35, 53, 64].

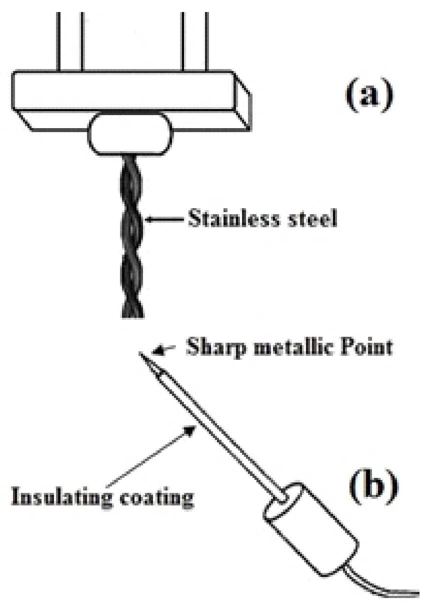

Fig.13. Examples of different electrodes: (a) bipolar electrode[89] , (b)needle electrode[90]

CONCLUSION

In this review, the application, fabrication and development of nanostructured stainless steel based materials with new composition for medical implants are discussed. Studies confirm that, modifying the composition of the stainless steel alloy is a new method for improvement of implant properties. This method consists of alloying precious metals, such as platinum, with a stainless steel. Results show that platinum additions leading to a new class of stainless steels, for medical applications. Reviews show that nanostructured implant presents a superior performance electrochemically, mechanically, biologically and electrically, when compared to the conventional implants. Also, mechanical and biological properties of nanostructured materials are controlled by parameters of severe plastic deformation processes. The results showed that an nanostructured stainless steel was obtained after performing the eight passes of ECAP. As a result, the corrosion resistance of stainless steel was improved considerably by increasing of the number of ECAP passes. Finally, properties of nanostructured stainless steel and Pt-modified steel must also be acceptable, comparable to conventional stainless steel. Therefore, new generation of metallic implant can be achieved by nanostructuring Pt-modified steel.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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