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Introduction of fullerenes in industrial steel production

Bojan Senčič

Žalec, 2010



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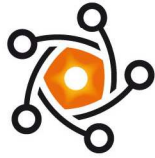
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Abstract

Fullerenes are discussed in this paper from the time of their discovery to present day applications. Some production methods, properties and industrial applications of fullerenes are reviewed.

The focus of this report will be on nanostructured steels and their processing strategies. Also some key players in production of nanostructured steels and patents regarding production are presented.



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1 Introduction

The most versatile element that exists on the earth is carbon. Carbon has different properties which can be used in many ways depending on how the carbon atoms are arranged. Carbon has been used for the reduction of metal oxides for many years. Carbon in the form of graphite was discovered in 1779, and 10 years later in the form of a diamond. It was then determined that both of these forms belong to a family of chemical elements. It was not until about 200 years later that the next advancements in carbon took place. In 1985 Kroto, Smalley and Curl discovered fullerenes [1].

Multi-walled carbon nanotube were discovered a few years later in 1991 by Iijima. Carbon nanotubes are a completely new type of carbon fibre which comprises coaxial cylinders of graphite sheets, which range from 2 to 50 sheets [2]. In 1993 single wall nanotubes were observed by Iijima along with Ichihashi [3].

Single wall nanotubes are basically a single fullerene molecule that has been stretched out so their length is a million times its diameter. In 1996 Smalley synthesized bundles of single wall carbon nanotubes for the first time.

The name carbon nanotube is derived from their size which is only a few nanometers wide. By definition carbon nanotubes are cylindrical carbon molecules with properties that make them potentially useful in extremely small scale electronic and mechanical applications. These tubes consist of rolled up hexagons, 10,000 times thinner than a human hair. Ideal nanotubes can be described as a seamless cylinder of rolled up hexagonal networks of carbon atoms, which is capped with half a fullerene molecule at the end. Their strength is one to two orders of magnitude and weight six times lighter than steels [4].



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2 Fullerenes

Fullerenes are a form of carbon molecule that is neither graphite nor diamond. Fullerenes are the third allotropic form of carbon material (after graphite and diamond). They consist of a spherical, ellipsoid, or cylindrical arrangement of dozens of carbon atoms. Fullerenes were named after Richard Buckminster Fuller, an architect known for the design of geodesic domes which resemble spherical fullerenes in appearance. A spherical fullerene looks like a soccer ball, and are often called "buckyballs," whereas cylindrical fullerenes are known as "buckytubes" or "nanotubes."

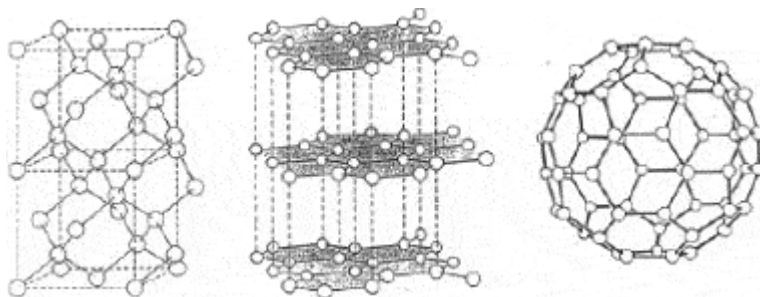
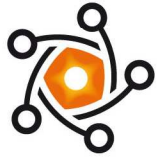


Figure 1: From left to right: Diamond, graphite, and fullerene.

Fullerenes were discovered as an unexpected surprise during laser spectroscopy experiments at Rice University in September 1985. The 1996 Nobel Prize in Chemistry was awarded to Professors Robert F. Curl, Jr., Richard E. Smalley, and Sir Harold W. Kroto for their discovery. Fullerene molecules consist of 60, 70, or more carbon atoms, unlike diamond and graphite, the more familiar forms of carbon.



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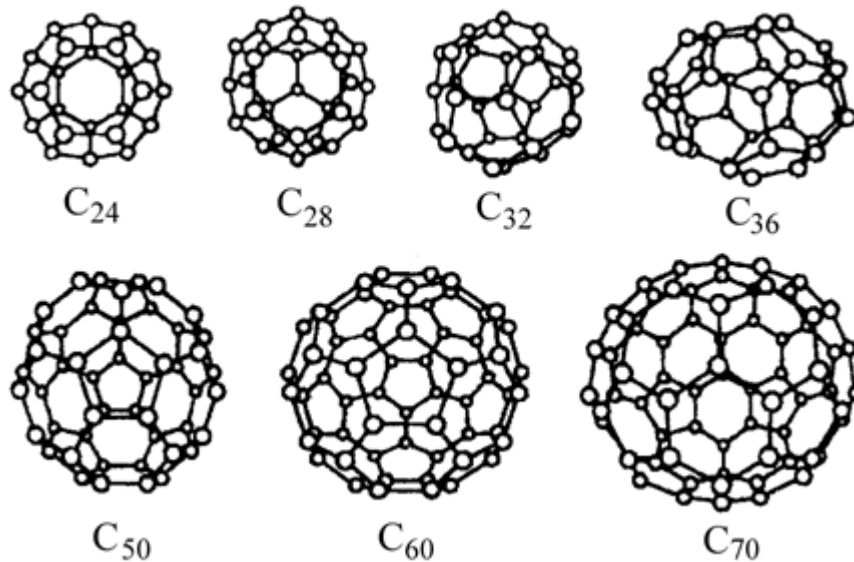


Figure 2: Some examples of the fullerenes

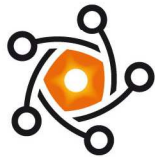
3 Properties of carbon nanotubes

Carbon nanotubes (CNT) are acicular single crystals of high aspect ratio which contain only a few defects. Because of this low density of defects carbon nanotubes have that excellent electronic and mechanical properties.

These characteristics have sparked great interest in their possible uses for nano-electronic and nanomechanical devices. Properties of carbon nanotubes can also be expanded to thermal and optical properties as well.

Carbon nanotubes are predicted to have high stiffness and axial strength as a result of the carbon-carbon sp^2 bonding. Studies exploring the elastic response, inelastic behaviour and buckling yield strength and fracture need to be conducted [4].

The mechanical properties of a solid must ultimately depend on the strength of its interatomic bonds. With knowledge of known properties of crystal graphite the mechanical properties of carbon nanotubes can be



predicted with some confidence. Experimental and theoretical results have shown an elastic modulus of greater than 1 TPa (that of a diamond is 1.2 TPa) and have reported strengths 10–100 times higher than the strongest steel at a fraction of the weight. It has been predicted that carbon nanotubes have the highest Young's modulus of all different types of composite tubes such as BN, BC₃, BC₂N, C₃N₄, CN, etc. (Table 1). The definition of Young's modulus involves the second derivative of the energy with respect to the applied stress/strain. In general, the strength of the chemical bonds determines the actual

value of Young's modulus and smaller diameters result in a smaller Young's modulus. However, in tests conducted on carbon nanotubes show that little dependence exists on the diameter of the tube with Young's modulus, which does help to hypothesize that carbon nanotubes do possess the highest Young's modulus which is expected around 1 TPa. Experiments conducted have resulted in tensile strengths in the range from 11 to 63 GPa, with dependence on the outer shell diameter, which is not far from the theoretical yield strength of 100 GPa.

Due to high in-plane tensile strength of graphite, both single and multi wall carbon nanotubes, are expected to have large bending constants since they mostly depend on Young's modulus. The nanotube has been found to be very flexible. It can be elongated, twisted, flattened, or bent into circles before fracturing. Simulations conducted by Bernholc and colleagues indicate it can regain their original shape. Their 'kink-like' ridges allow the structure to relax elastically while under compression, unlike carbon fibers which fracture easily.

The unique elastic and inelastic properties have brought about more studies on the durability of carbon nanotubes.

For single wall nanotubes simulations of deformations showed that each shape change corresponded directly to an abrupt release in energy and a singularity in the stress/strain curve. The nanotubes were found to have an extremely large breaking strain which decreased with temperature.

However, it was concluded single wall nanotubes were subject to buckling under high pressure, which is responsible for the pressure induced abnormalities of vibration modes and electrical resistivity. The elastic modulus, Poisson's ratio and bulk modulus were all found to be directly affected by the tubes radius. A max bulk modulus was found to be 38 GPa with samples having a radius of 0.6 nm. For multi-wall



nanotubes the properties were a little more complicated to calculate. An empirical lattice dynamics model was used, which showed that multi-wall nanotubes were insensitive to parameters such as the chirality, tube radius, and the number of layers [5].

Thermal properties including specific heat and thermal conductivity of carbon nanotubes are determined primarily by the phonons. A phonon is a quantum acoustic energy similar to the photon. Phonons are a result of lattice vibrations observed in the Raman spectra. Especially at low temperatures the phonon contribution to these quantities dominates and is due to the acoustic phonons. The measurements of thermoelectric power of nanotube systems give direct information for the type of carriers and conductivity mechanisms.

Theoretical and experimental results show superior electrical properties of carbon nanotubes. They can produce electric current carrying capacity 1000 times higher than copper wires. For 1D systems cylindrical surface, translational symmetry with a screw axis could affect the electronic structures and related properties. The electronic capabilities possessed by carbon nanotubes are seen to arise predominately from interlayer interactions, rather than from interlayer interactions between multilayers within a single carbon nanotube or between different nanotubes.

These optical properties have proved to be especially unique with capabilities of acting as either a metallic or semiconductor, which depends on tubule diameter and chiral angle. Studies have shown that metallic conduction can be achieved without introduction of doping effects. For semiconducting nanotubes the band gaps have been found to be proportional to a fraction of the diameter and without relation to the tubule chirality. The I-tight-binding model within the zone folding scheme shows, one third of carbon nanotubes are found to be metallic while two thirds are semiconducting, depending on their indices. Calculations based on the use of r and P bands, due to curvature induced mixing of these bands, are used to predict that some metallic nanotubes are very-small-band-gap semiconducting nanotubes. The symmetry of the structures basically relates all the calculations in both single and multi-wall carbon nanotubes. Electronic properties of bundles of single wall nanotubes can be derived, assuming the intertube interactions are not strong enough to change the band structure. Broken symmetry caused by interactions between tubes in a bundle create a



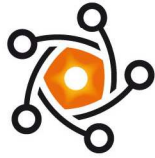
pseudogap of about 0.2 and 0.1 eV. This pseudogap, which is created can modify electronic properties such as semimetallike temperature dependence of the electrical conductivity and a finite gap in the infrared absorption spectrum is predicted [5].

Table 1 : Mechanical properties of carbon nanotubes

	Material Young's modulus (GPa)	Tensile strength (GPa)	Density (g/cm ³)
Single wall nanotube	1054	150	
Multi wall nanotube	1200	150	2.6
Steel	208	0.4	7.8
Epoxy	3.5	0.005	1.25
Wood	16	0.008	0.6

4 Carbon nanotubes applications

Carbon nanotubes have attracted a great deal of attention world wide with their unique properties which are leading to many promising applications like electrical, thermal, magnetic and optical applications. Potential practical applications have been reported such as sporting equipment, displays, auto parts, conductive polymers, fibers and yarns, batteries, super capacitors, thermal management systems, chemical sensors, field emission material, catalyst support, electronic devices, transistors, high sensitivity nanobalance for nanoscopic particles, nanotweezers, reinforcements in high performance composites, and as



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nanoprobes in meteorology and biomedical and chemical investigations, anode for lithium ion in batteries, nanoelectronic devices, nanotube radio, supercapacitors and hydrogen storage [7,9,10,11].

New applications are likely in the diamond industry since experiments have shown the conversion of carbon nanotubes to diamond under high pressure and high temperatures with the presence of a certain catalyst [5,6]. These are just a few possibilities that are currently being explored. As research continues, new applications will also develop.

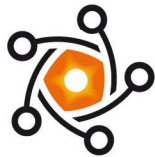
The market for CNT-composite is growing at a rapid rate. According to a BCC report published in 2007, the global CNT-composite market was 43 million US\$ in 2006 and the projected market in 2010 was estimated to be 451 million US\$, with an average annual growth rate of 80%.

CNT have also a great potential as reinforcing elements for composites. Currently, there is a growing awareness about the potential benefits of nanotechnology in the modern engineering industry, and a lot of leading R&D institutes and companies are researching in the area of nanostructured steels.

5 Nano-engineered steels for structural applications

Steel is one of the most widely used engineering materials in the world. Its eminent position amongst the engineering materials arises due to the abundance and low cost of its main constituent, i.e. iron, and its ability to produce a wide variety of engineered microstructures with superior properties, and recyclability [8].

The focus of the ongoing research has been largely manipulation of microstructures at the nano-scale through innovative processing techniques and adoption of novel alloying strategies. This is being aided by employing advanced characterization methods like high resolution transmission electron microscopy (HRTEM), atom probe tomography



(APT) etc. and computational design of materials. Steel is synonymous with strength. The theoretical strength of steel is 27.30 GPa (in $\langle 111 \rangle$ direction). There are two ways of achieving ultra high strength in steels. The first one is to reduce the size of a crystal to such an extent that it is devoid of any defects, like in the case of a whisker. Brenner in 1956 could achieve a tensile strength of greater than 13 GPa in an iron whisker. The second alternative is to introduce a very large density of defects in a metal sample that act as an obstacle to the motion of dislocations. This has been illustrated by drawing high carbon pearlitic steel wire, which is subjected to intense plastic deformation, thereby, introducing dense dislocation substructure. The carbon steel wire is a remarkable example of nanostructured steel produced on a mass scale. The strengthening arises due to the presence of nanoscale cementite/ferrite lamellar structure. The ferrite phase in this structure contains very high dislocation density and supersaturated carbon atoms, and the cementite phase contains amorphous and nano-crystalline regions. The high carbon steel wire is an important engineering material used for reinforcing automobile tires, galvanized wires for suspension bridges and power cable wires. In fact, the suspension cables of the world's largest suspension bridge, Akashi Strait Bridge built in Japan in the year 1998, were made of pearlitic steel wires of 1800 MPa strength. To inhibit softening during hot-dip galvanizing, high-Si and high Si-Cr steel wires have also been developed for high-strength galvanized suspension-bridge wires. Similarly, the pearlitic wire for automobile tyre cords exhibits strengths of about 4000 MPa. The main challenge in realizing the immense potential of nano-engineered steels is to manufacture large components of bulk nanocrystalline steel having superior properties and at a reasonable cost. To meet this challenge, a number of innovative approaches are being developed to produce nanostructured steels. Very important is dispersion of nanoparticles in steel.

Nanostructured steels, on account of their outstanding strength, high toughness, remarkable corrosion resistance, excellent erosion and wear resistance etc. have significant potential to improve the performance of various systems. By virtue of the above, they are also likely to have a major impact in a variety of sectors including defence, aerospace, transportation, power, construction, infrastructure and medical.



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Table 2: Key Benefits and Market Drivers for Nanostructured Steels.

Increased strength levels(ultra-fine grain size steels)

High toughness and high ductility at higher strength levels (TRIP-Maraging Steels)

Greater degree of radiation – induced embrittlement resistance, greater survivability in neutron radiation environment and higher creep strength (nano-cluster strengthened ODS ferritic alloys)

Improved erosion, corrosion and wear resistance (devitrified glassy ferrous alloys)

Enhanced corrosion resistance for high strength/high toughness steels (Nano-precipitation strengthened computationally designed steels)

Transportation Sector:

Vehicle weight reduction, increase in fuel efficiency and corresponding reduction in CO2 emissions.

Transportation Sector:

Lighter vehicles with improved impact resistance and safer to drive.

Improved formability leading to lower processing costs.

Nuclear Industry:

(FBRs and Fusion Reactors) Higher operating temperatures would help in improving economic performance and provide means to support thermo-chemical production of hydrogen. Also would result in higher safety, reliability and reduced emissions.

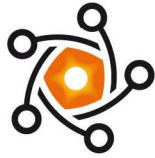
Power Generation, Mining, Cement and Concrete Industries:

Improved performance and extended service life.

Aerospace and Navy (Landing gear and other Aircraft and Naval Components):

<http://www.questek.com>

Eliminates the need of providing toxic and carcinogenic cadmium coating, which prevents the problems of hydrogen embrittlement and stress corrosion cracking associated with Cd plating.



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Table 3: Applications of Nanostructured Steels

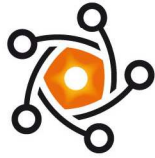
Defence	Ballistic armour
Aerospace	Aircraft landing gears
Medical	Surgical needles and clips
Sports	Mountain bicycle frames
Consumer	Razors for shaving machine
Oil and Gas	Pipeline steels for the transportation of natural gas
Nuclear	Fuel cladding tubes for nuclear reactors
Infrastructure	Concrete reinforcing rebars
Power	Advanced exhaust components for heavy duty diesel engines
Automotive	Automobile body-structural and safety parts, chassis and suspension parts and TWBs
Industrial	Cutting tools and bearings

5.1 Processing procedures

The different processing procedures and alloy development aspects being currently explored for the manufacture of nanostructured steels are briefly outlined below.

Severe Plastic Deformation (SPD) Processing

SPD processing is one of the promising routes for grain size refinement to nano-scale levels. Non-traditional processes, such as equal channel angular processing (ECAP), accumulative roll bonding, torsion under very high pressures, multiple compressions etc. have been developed for this purpose. The ultra-fine ($<1\mu\text{m}$) grain sizes lead to exceptionally high strengths in conventional steels; however, there is a drastic reduction in



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tensile ductility, especially uniform elongation in tension. Therefore, a number of processing routes are being developed for the improvement of ductility.

Thermomechanical Controlled Processing (TMCP)

TMCP is based on microstructure control during hot rolling and subsequent cooling. Many of the microstructural events are controlled at the micron level while other events like precipitation hardening are at the nano-scale level of control.

Nanostructured Steels with High Work Hardening Rate by Exploitation of TWIP Effect

The high-manganese TWIP steels are subjected to plastic straining to introduce thermally stable nanometre-scale mechanical twins in the structure. Subsequent recovery treatment results in an excellent combination of high yield and ultimate tensile strengths, and work hardening.

Phase-reversion Induced Nano-grained/Ultra-fine Grained Steels

Microstructures comprising an optimized combination of nano- and ultra-fine grains are obtained in austenitic stainless steels by controlled annealing of heavily cold-worked metastable austenite. Reversion annealing of strain-induced martensite in severely deformed metastable austenitic steels results in nano-grained/ultra-fine grained structures with excellent combination of strength and ductility.

Computational Designing of Steels

A new class of martensitic stainless steels are being developed by following a system's design approach. This approach combines predictive control of the alloy chemistry, transformation temperatures, cryogenic treatment and multi-step aging to produce radically new high-strength, high toughness corrosion resistant stainless steels.

Devitrification of Glassy Ferrous Alloys

Metallic glasses based on the specialized formulation of ferrous alloys have been developed. These glasses are subjected to devitrification



treatment by subsequent heating above crystallization temperature to obtain nanoscale microstructures. These amorphous steels can also be used in the form of powders to produce amorphous/nanocomposite thermally sprayed coatings to enhance the wear and corrosion resistance of engineering components.

Advanced ODS Ferritic and Martensitic Steels

Ferritic or martensitic alloy powders are ball milled with Y₂O₃ and subsequently compacted and hot extruded to obtain nano-structured ferrous alloys. These alloys contain a large number density of ultra-fine cluster of atoms containing predominantly Y, O and Ti, called nano-clusters, which resist coarsening and prevent grain growth following isothermal aging.

Mechanical Alloying and Consolidation

Mechanical alloying via high energy ball milling of iron and carbon powders (or other alloying elements) is carried out and the powders are subsequently consolidated by various techniques such as spark plasma sintering, warm compaction, HIP etc. This approach can result in nano-crystalline/ultra-fine grained structures with excellent mechanical properties.

An example of that approach is Mechanical Alloying and Powder Consolidation in SiC and Hydroxyapatite.

The reaction ball milling can produce the solid state amorphization of covalent ceramic, SiC, including the mechanical alloying (MA) of the elemental crystalline powder mixture of Si and C and the mechanical grinding (MG) of the commercial β -SiC particle and MG of the nanocrystalline β -SiC powder as synthesized via 'high-energy' MA. An increase in amorphous volume (X) by decreasing crystallite size (d) during MG is expressed by a relation of $X = 1 - \{d/(d+\Delta)\}^3$ with the intercrystal thickness (Δ) of 1 nm. The rotating-arm reaction ball milling is used to synthesize nanocrystalline (nc) hydroxyapatite by MA of the powder mixture at 303 K, according to a reaction of $6\text{CaHPO}_4 \cdot 2\text{H}_2\text{O} + 4\text{Ca}(\text{OH})_2 \rightarrow \text{nc-Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + 8\text{H}_2\text{O}$ with JMA exponent of 1. By employing the pulse electric discharge consolidation, the amorphous SiC powder compact shows a rapid densification during Newtonian viscous flow as expressed by an Arrhenius relation with the



activation energy of $495 \text{ kJ} \cdot \text{mol}^{-1}$, and then obtain the full densification at 2033 K under 100 MPa. The nanocrystalline hydroxyapatite powder with the crystallite size of 8 nm can be consolidated at full-density at 1023 K under 150 MPa, following a rapid shrinkage during superplastic flow from 900 K. The fracture toughness (KIC), as deduced from the indentation microfracture method, is the high level of $13 \text{ MPa} \cdot \text{m}^{0.5}$ for nanocrystalline SiC with 12 nm.

Combination of TRIP Effect with Maraging Treatment

This approach combines the TRIP mechanism with maraging treatment in a Fe-Mn base alloy system. These steels contain a low-carbon martensitic matrix with precipitates of intermetallic (Ni, Ti, Al, Mo) nanoparticles.

Surface Nanocrystallization of Steels

A nanostructured surface layer can be fabricated by subjecting the steels to various surface treatment techniques, such as ultrasonic shot peening and surface mechanical attrition treatments (SMAT). SMAT provides a simple, flexible and low cost approach to enhance the bulk properties of steels, without any change in the chemical composition.

Advanced Bainitic Steels by Low Temperature Isothermal Transformation

New generation bainitic steels (e.g. Fe-0.98C-1.46Si-1.89Mn-0.26 Mo-1.26Cr- 0.09V) are designed using detailed phase transformation theory for the bainitic reaction. The bainitic transformation occurs at low temperatures (200–300°C), which avoids the diffusion of iron or any substitutional solutes. As a consequence, the plates of bainite are extremely slender, 20 – 40 nm thick, making the steel very strong [13,14].

TRIPLEX Steels

TRIPLEX steels are designed on the basis of Fe-Mn-C-Al with Al > 8%. Mn is usually > 19%. The alloy consists of an austenitic FCC matrix and about 8% ferrite and nano-size κ -carbides regularly distributed in the FCC matrix in an orderly fashion. The TRIPLEX alloys exhibit low density, high strength level, excellent formability and high energy absorption

capacity.

5.2 Key Players in production

Currently, interest in nanostructured steels is just beginning to gather momentum. However, with the entry of industrial giants like Nippon Steel, Sandvik, Arcelor Mittal, Exxon, JFE Steel and others, there is a good scope that broader industrial adoption could occur in the near future. Moreover, some of the new players such as QuesTek Innovations, Max Planck Institute for Steel Research, MMFX Technologies and Cambridge University are able to demonstrate significantly greater benefits in nanostructured steels at a reasonable cost with their innovative approaches and this is likely to change the scenario quickly. A few key players active in the field of nanostructured steels are listed below:

The NanoSteel Company, Inc., U.S.A.

Has developed nanostructured ferrous alloys by devitrification of metallic glass. The alloys are used in the form of thermal spray coatings or weld overlay to tackle the problems of wear, corrosion, erosion etc.

QuesTek Innovations LLC, U.S.A.

Has developed computationally designed high strength and environmentally friendly corrosion resistant steels.

Sandvik Materials Technology, Sweden

Has developed nanostructured 'Nanoflex' stainless steels.

JFESteel Corp., Japan

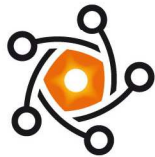
Has developed hot rolled, high strength nanosize carbide precipitation strengthened 'NANOHITEN' steel for automobile industry.

Kawasaki Steel Corp., Japan

Has developed non-heat treated ultra-low carbon, Cu precipitation strengthened bainitic steels produced by thermo-mechanical precipitation control process (TPCP) [12].

Kobelco Research Inc., (Kobe Steel), Japan

Has developed ODS 9Cr martensitic steel (12YWT) for fuel cladding tubes of nuclear reactor.



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Exxon Mobil Upstream Research Co., U.S.A.

Has developed high strength pipeline steel for the transportation of natural gas in collaboration with Nippon Steel and Mitsui & Co. It is 20-50% stronger than the currently used pipeline steel. A mile-long section in the TransCanada Pipeline utilizes this nano-steel under -40°C temperature conditions.

MMFX Technology Corp., U.S.A.

Has developed the microcomposite Fe/Cr/Mn/C steels with superior combination of strength-toughness-corrosion properties for concrete members reinforced with high-strength rebars.

Nippon Steel Corp., Japan

Has developed nanostructured steels for various applications: • Fatigue resistant steels containing Cu nano-precipitates for transportation and bridges • High strength steels with resistance to delayed fracture (by hydrogen trapping with nano-size precipitates) for bolts to be used in automobiles and high-rise buildings • High HAZ toughness steel 'HTUFF' using nano-size dispersion of oxides and /or sulfides • High strength steel wires for reinforcing automobile tires, galvanized wires for suspension bridges and power cable wires.

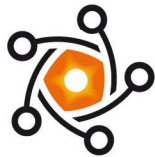
Arcelor Mital

The world's largest steel maker, has a new nanostructured steel which is not inherently lighter, but it's so strong that automakers can use thinner gauges and that's where part of the weight savings comes from. Another part of the weight savings comes from not having to use additional brackets, gussets or panels to strengthen the structure.

A-pillars are becoming so big these days due to roof crush standards that they are actually becoming a safety hazard. The fat A-pillars can partially block your view to side traffic or pedestrians. But with this nano steel, A-pillars could be made much thinner with no sacrifice to structure or safety.

The new steel is not cheaper than other grades of steel. In fact, it's probably a little bit more expensive. But by eliminating all those brackets and extra panels, the total tooling cost of a car goes down, and that's where the costs savings comes from.

To get the maximum 188-pound reduction in the BIW, an automaker would have to design-in the nano steel's capabilities using a clean sheet



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approach. But ArcelorMittal says that some applications, especially cross-members, lend themselves to running changes on existing designs.

The nano steel does require a newer manufacturing technique called hot stamping. That's where automakers heat up the steel blanks that go into a stamping press to the point where they're literally glowing red. Then they feed the red hot blanks into a press and stamp them into body panels. Heating up the steel makes it much more pliable and enables it to be formed into more complex shapes. Actually, this is a fairly common process already in use today, used to form the high-strength steels that have been available for the last decade and a half. So, while the nano steel requires hot stamping, it's not as if automakers need to make a big investment in manufacturing technology.

The nanostructured steels (particularly, manufactured by SPD processing) exhibit extraordinary strength levels. However, their ductility is inadequate, and therefore, makes them unsuitable for certain applications. This drawback is a major hurdle in bringing nanostructured steels from laboratory to commercialization. In view of this, it is of paramount importance that innovative approaches are developed to improve the ductility of nanostructured steels. Consequently, nanostructured steels require non-traditional processing methods and specialized machinery, which calls for significant investments and application development to make them commercially viable.

5.2 Intellectual Property Scenario

Since the technologies pertaining to nanostructured steels are mainly based on process innovations, they are relatively difficult to actually protect despite the legal cover that patents are intended to provide. Therefore, the technology developers are often inclined to maintain trade secrets rather than rely on patents for protection. This strategy helps them in avoiding IP conflicts and also protects their technologies from being exploited in other countries where IP protection is weak. Of



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course, this strategy makes the producers vulnerable if a competitor develops a similar process independently. Notwithstanding the above, the following patents relating to nanostructured steels are pertinent to mention:

Precipitation hardenable martensitic stainless steel

Patent Number: US 2008 / 0210344 A1 Filing / Publication Date: Dec.22, 2005 / Sep.4, 2008

Assignee: Sandvik Intellectual Property AB, Sweden

Inventor(s): Hikan Holmberg, Sweden

Key Features: A precipitation hardenable stainless Cr-Ni steel with high strength, high ductility and excellent formability. Exhibits very good corrosion resistance and finds applications as springs, surgical needles, dental instruments etc.

Nanocarbide precipitation strengthened ultra-high strength, corrosion resistant structural steels

Patent Number: WO 03 / 018856 A2 Filing / Publication Date: Feb.11, 2002 / Mar.6, 2003

Assignee: Questek Innovations LLC, USA

Inventor(s): Kuehmann, Charless, J., Olson, Gregory, B., Jou, Heing-Jeng, USA

Key Features: Ultra-high strength (UTS > 1930 MPa) precipitation strengthened structural steel possesses out-standing combination of corrosion resistance and strength. The alloy is strengthened by nano-scale M₂C carbides. Potential applications include aircraft landing gear, machinery and tools used in hostile environment

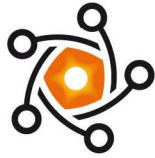
Nano-composite martensitic steels

Patent Number: EP 1 461 466 B1 Filing / Publication Date: Dec.12, 2002 / July 23, 2008

Assignee: MMFX Technologies Corp., USA

Inventor(s): Ku Sinski, Gregorz, J., Pollack, David, Thomas, Gareth

Key Features: Steel alloys with high strength, toughness and cold formability. Unique microcomposite micro structure comprising of nano sheets of austenite between laths of dislocated martensite. Highly corrosion resistant steels resulting in extended service life of rebar in



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corrosive environments. t e C H n o l o g y w a t C H

High strength hot rolled steel sheet and method for manufacturing the same

Patent Number: US 7527700 B2 Filing / Publication Date: April 21, 2004 / May 5, 2009

Assignee: JFE Steel Corp., Japan

Inventor(s): Nobusuke Kariya, Shusaku Takagi, Tetsuo Shimizu, Tetsuya Mega, Kei Sakata, Hiroshi Takahashi

Key Features: High strength (780MPa) hot rolled steel sheet with low carbon (0.04 to 0.15% C) having excellent elongation and stretch flangeability. Microstructure comprising nano-scale (20nm) Ti-Mo carbide precipitates within ferrite matrix. The steel sheet is suitable for reinforcing members of automobile cabin and crash worthiness member of automobile.

Nano structured steel alloy

Patent Number: US 5589011 Filing / Publication Date: Feb. 15, 1995 / Dec. 31, 1996

Assignee: The University of Connecticut, USA

Inventor(s): Kenneth E. Gonsalves, USA

Key Features: The invention relates to nanostructured M50 type steel synthesized by chemical methods, which has improved mechanical and physical properties such as hardness, strength and durability. The steel finds particular utility in the manufacture of cutting tools and bearings.



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