

# A REVIEW OF THE RESEARCHES ON THE TECHNICAL PROPERTIES OF THE MATERIALS USED IN MACHINERY AND EQUIPMENT IN THE PETROCHEMICAL INDUSTRY

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**Abstract:** Unconventional reserves must be explored and exploited safely and profitably to meet the world's rising energy demand. Some of these unusual prospects present severe environments that test the limits of conventional engineering alloys as well as our comprehension of the basic degradation processes that could cause a failure. The most significant source of innovation in terms of material technology is found in high-temperature, high-pressure, ultra-deep and pre-salt reservoirs, notwithstanding their complexity. With an emphasis on advanced materials, this paper offers a broad review of current development and research trends in materials. For the oil and gas industry, the cutting-edge polymers stand out above their conventional equivalents with improved hardness or strength. Modern metallic materials, unconventional materials (metal or non-metal), or a combination of these are all examples of advanced materials. Numerous stronger, lighter, and multifunctional materials have been created in laboratories over the past few decades. Advanced materials are those with at least one characteristic that is much better than that of standard alloys. The three most promising innovative material types for use in petroleum production are chosen.

**Keywords:** Advanced Materials, Polymers, Modern metallic, Petrochemical

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## INTRODUCTION

Oil and gas production is very important for our world's moving forward, because we mostly rely on the oil and gas for producing or continuing our operations. This is accomplished by the extraction and transportation of raw materials from subterranean reservoirs, the processing of these materials into fuels, and the delivery of the finished goods to end users worldwide. But this sector covers more than just fuels. Numerous other vital materials are also made from the hydrocarbon molecules which this industry mines from the soil. The majority of synthetic materials, such as plastics, polymers, synthetic rubber, detergents, solvents, and other items, are produced by the petrochemicals sector. Bitumen, lubricants, and waxes are all products of the refining business. Fertilizers, medications, and other vital compounds are made using more specialized petroleum processing. [1] Additionally, the fuels sector of the industry receives a variety of high-value gasoline additives that are produced by the petrochemicals sector. The distinction between fuels and petrochemicals has therefore grown less distinct due to the complex link among refining, natural gas processing, and the petrochemicals industry. A refinery transforms the crude into a variety of refined petroleum products (RPPs) to provide a range of hydrocarbon products that best satisfy users' needs. Distillation, which is the fundamental refinement procedure, vaporizes various hydrocarbon elements in crude oil at various temperatures, allowing for their separation. The resulting condensed components are then put through a variety of additional chemical industrial operations to produce a wide range of distinct RPPs, ranging in weight from the extremely low (refinery gases) to the very weighty (asphalt). [2] For the materials, which we used in petrochemical industry, they are selected first based on the application types and it varies application to application and equipment to equipment. Which materials we want to use, they are examined before according to our application that for which purpose and where we want to use them, then we see the mechanical and physical properties of materials.

## MAJOR MATERIALS USED IN PETROCHEMICAL INDUSTRY

There are some materials which used in petrochemical industry mostly. And we deal those most of the time and there's a relation between these materials and corrosion and here's a list of those materials and will explain which is good for corrosion.

- Ferrous Alloys
- Cast Iron & Steel
- Nickel based Alloys

Ferrous alloys are categorized in two forms. One of them is steel in which carbon quantity is less than 2% and second is cast iron which also named high carbon alloy in which carbon quantity is more than 2%. Further steel is categorized in more three forms named as plain carbon steel, low alloy steel and high Alloy steel. And, so on cast iron high carbon alloy is categorized in four forms named as Gray CI, White CI, and malleable CI and high Si CI. [3] Plain carbon steel is further divided in three different types on the basis of carbon quantity, which is listed below. 1) Low CS 2) Medium CS 3) High CS In low carbon steel, carbon quantity is less than 0.2% which is in mathematically as  $C < 0.2\%$  In Medium carbon steel, carbon quantity is between 0.2% to 0.5% which is in mathematically as  $C = 0.2\% - 0.5\%$ . In High Carbon steel, carbon quantity is more than 0.5% which is in mathematically as  $C > 0.5\%$ . Low Alloy steel is the type of steel in which steel is formed with other alloying elements for making steel useable according to our different applications. In low alloy steel, alloying element is lower than 8%. And its good example is Cr-Mo steel. Cr is for chromium and Mo is for Molybdenum Examples: Cr-Mo. In High alloy steel, alloying element is greater than 9%. And its good example is stainless steel, in which cr quantity is more than 9%. Cr is for chromium. E.g. Stainless Steel

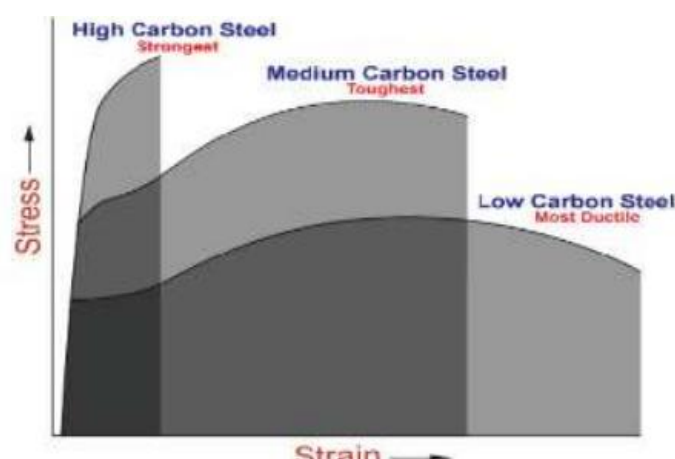


Fig.1 Plain carbon steel properties graph between Temperature vs Strength [4]

Here's a graph which will show the effect of temperature on plain carbon steel.

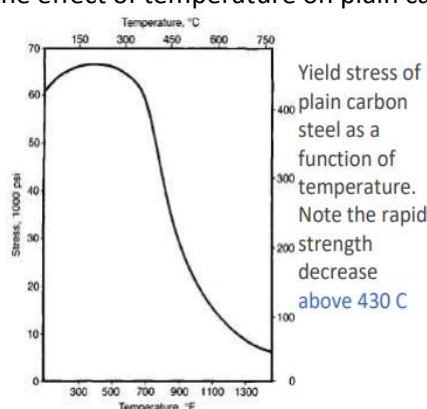


Fig. 2 Yield stress of carbon vs Temperature [3]

**Classification of Steel:** In oil and gas industry we make classification of steel according to our need and our strength. And on the basis of their composition we categorized on above three forms. High strength steel is carbon steel in which carbon quantity is higher to all of these three. Intermediate strength steel is the steel which is mixture of chromium and molybdenum, in this alloying elements quantity is greater than 8%. And mostly it is used for creep resistance. In low strength steel, alloying elements quantity is greater than 9% and its best example is stainless steel and it is widely used in oil

and gas industry for different applications, it is used for high temperature applications, for corrosion resistance etc.

**High Strength Materials:** In order to meet the designing requirements forced by the high pressures of HPHT wells and the arctic areas' subfreezing temperatures, Materials with increased fatigue life and high strength are preferred, if not necessary. Unfortunately, as strength increases, so does EAC resistance and, more specifically, the performance of hydrogen assisted cracking. Thus, there is a maximum level for the secure usage of engineering metals in oil and gas environment of production, which is perhaps more cautious than in other sectors.[5] The definition of a high strength material varies depending on a number of variables, such is the application, the family of alloys, and the component's size or weight. High strength in this section is defined as materials with Specific Minimum Yield Strength (SMYS) values greater than the average maximum generally advised for LAS and forged carbon subjected to manufacturing fluids, i.e., 550-586 MPa (80–85 ksi).[6]

**Low alloy steels:** Contrary to popular belief, LAS are some of the most cutting-edge technical materials. By volume, LAS is used in more important O&G applications than any other alloy family. Therefore, improvements in LAS performance and characteristics may have a significant effect. Despite their benefits, LAS have nevertheless seen catastrophic environmental assisted failures, such as those caused by hydrogen produced by CP systems and settings containing H<sub>2</sub>S.[8] It is crucial to comprehend the underlying processes that result in appropriate EAC resistance, particularly when H<sub>2</sub>S is present. If qualified, low alloy steel and carbon steel that don't fulfill the necessary standards can still be utilized for durability, toughness, and chemical composition. However, hardness is a poor predictor of SSC resistance. The sensitivity to EAC varied greatly across different microstructures even at the same levels of hardness and strength. Despite these drawbacks, limiting the base metal and weld hardness significantly decreased the frequency of the early SSC failures. [7]

**Moving beyond current limitations:** Within the parameters of ISO 15156, SMYS values for Cr-Mo steels up to 760 MPa (110 ksi) are commonly acceptable. However, in fact, LAS with SMYS of 550–586 MPa or higher (80–85 ksi) are rarely used for large forgings since restricting the strength reduces the possibility of reaching 250HV in weldments. Similarly, commercial LAS with an extraordinary mix of qualities, including strength, toughness, weldability, fatigue life, and hardenability, are not covered by ISO 15156's restriction on the permitted nickel concentration.[9] Similar to ASTM A707, ISO 15156 forbids the copperbearing, low-carbon, precipitation hardenable LASs35, which combines high strength, weldability and toughness as stated in the table below. These kinds of LAS could be altered for use in sour service applications, for instance by reducing their amount of carbon, adjusting their carbon equal amount, and trying to impose strict control of the factors that cause temper embrittlement. This could lead to significant weight savings, improved through-thickness properties, and extended fatigue life.[10] The impact of the intricate LAS microstructures on SSC and HSC performance is still a hot topic of discussion in this area. According to their threshold stress (th) in H<sub>2</sub>S-saturated electrolytes, tempered martensite and lower bainite are the microstructures that are most resistant to SSC. Hydrogen has a negative impact on new martensite steels and normalized and tempered LAS. Snape has shown that small levels of untempered martensite have significant influence on SSC performance, even on steels that met the macroscopic hardness limit required by ISO 15156. Furthermore, Fig. 3 shows that the QT and bainitic steels' threshold stress was greater than the permissible stress in Pressure Vessel Design Code and Division 2 of the ASME Boiler, equivalent to an AYS of around 700 to 750 MPa. Above 750 MPa, the threshold stress significantly dropped.

Alloy designation	Standard nominal composition (wt%)										SMYS		
	Cr	Mo	Ni	W	N	Fe	Nb or (Nb + Ta)	Ti (Al)	Cu	C	Si	Mn	MPa (ksi)
Carbon and low alloy steels													
API 5L-X65Q (PSL 2)	-	-	-	-	-	bal.	§	§	-	0.18 (max.)	0.45 (max.)	1.70 (max.)	450 (65)
ASTM A694 F65	-	-	-	-	-	bal.	-	-	-	0.30 (max.)	0.15-0.30	1.60 (max.)	450 (65)
ASTM A508 Gr. 4	1.50 to 2.0	0.40 to 0.6	2.80-3.90	-	-	bal.	-	-	-	0.23 (max)	0.40 (max)	0.20 to 0.40	690 (100)
UNS K32047	1.50 to 1.90	0.50 to 0.65	3.00-3.50	-	-	bal.	-	-	-	0.14 to 0.20	0.15-0.38	0.10 to 0.14	690 (100)
10GN2MFA	0.30 (max.)	0.40 to 0.70	1.80-2.30	-	-	bal.	-	-	-	0.08 to 0.12	0.17-0.37	0.80 to 1.10	414 (60)
UNS K21590	2.00 to 2.50	0.90 to 1.10	0.25 (max)	-	-	bal.	-	-	-	0.11 to 0.15	0.10 (max)	0.30 to 0.60	517-586 (75-85)
UNS G43200	0.40 to 0.60	0.20 to 0.30	1.65-2.00	-	-	bal.	-	-	-	0.17 to 0.22	0.15 to 0.35	0.45 to 0.65	414 (60)
Precipitation-hardened low alloy steels													
ASTM A707-LS	0.60 to 0.90	0.15 to 0.25	0.70 to 1.00	-	-	bal.	-	-	1.00 to 1.30	0.07 (max.)	0.35 (max.)	0.09 (max.)	517 (75)
Solution annealed nickel-based alloys													
UNS N06625	20.0 to 23.0	8.0 to 10.0	58.0 (min.)	-	-	5.0 (max.)	(3.15 to 4.15)	-	-	0.10 (max.)	0.50 (max.)	0.50 (max.)	290-414 (42-60) <sup>a</sup>
Precipitation-hardened nickel-based alloys													
UNS N07718	17.0 to 21.0	2.80 to 3.30	50.0 to 55.0	-	-	bal.	(4.87 to 5.20)	0.80 to 1.15	0.23 (max.)	0.045 (max.)	0.010 (max.)	0.35 (max.)	827-965 (120-14)
UNS N07725	19.0 to 22.5	7.00 to 9.50	55.0 to 59.0	-	-	bal.	2.75 to 4.00	1.00 to 1.70	-	0.030 (max.)	0.20 (max.)	0.35 (max.)	827 (120)
UNS N07716	19.0 to 22.0	7.00 to 9.50	59.0 to 63.0	-	-	bal.	2.75 to 4.00	1.00 to 1.60	0.23 (max.)	0.030 (max.)	0.20 (max.)	0.20 (max.)	827-965 (120-14)
UNS N06059	22.0 to 24.0	15.0 to 16.5	bal.	-	-	1.50 (max.)	-	(0.1 to 0.40)	-	-	0.10 (max.)	0.50 (max.)	450 (65ksi) <sup>b</sup>
UNS N06680 <sup>c</sup>	20.5	6.5	bal.	6.5	-	0.1 (max.)	3.5	1.5	-	0.010 (max.)	-	-	550-665 (80-95)
UNS N06686	19.0 to 23.0	15.0 to 17.0	bal.	3.0 to 4.0	-	5.0 (max.)	-	-	-	0.010 (max.)	0.08 (max.)	0.75 (max.)	760 (110) <sup>d</sup>
Duplex and super duplex stainless steels													
UNS S32205	21.0 to 23.0	2.50 to 3.50	4.50 to 6.50	-	0.08 to 0.20	bal.	-	-	-	0.03 (max.)	0.2 to 0.70	2.0 (max.)	450 (65)
UNS S32750	24.0 to 26.0	3.0 to 5.0	6.0 to 8.0	-	0.24 to 0.32	bal.	-	-	-	0.03 (max)	0.8 (max.)	1.2 (max.)	550 (80)
UNS S32760	24.0 to 26.0	3.0 to 4.0	6.0 to 8.0	0.50 to 1.0	0.20 to 0.30	bal.	-	-	0.5 to 1.0	0.03 (max.)	1.0 (max.)	1.0 (max.)	550 (80)
UNS S39274	24.0 to 26.0	2.50 to 3.50	6.0 to 8.0	1.5 to 2.5	0.24 to 0.32	bal.	-	-	0.20 to 0.80	0.03 (max.)	0.8 (max.)	1.0 (max.)	550 (80)
Austenitic and highly alloyed austenitic stainless steels													
UNS S31603	16.0 to 18.0	2.0 to 3.0	10.0 to 14.0	-	-	bal.	-	-	-	0.03 (max.)	1.0 (max.)	2.0 (max.)	182 (27) <sup>a</sup>
UNS S31254	19.5 to 20.5	6.0 to 6.5	17.5 to 18.5	-	0.18 to 0.22	bal.	-	-	0.50 to 1.0	0.020 (max.)	0.80 (max.)	1.0 (max.)	310 (45)
Martensitic and precipitation hardened-martensitic stainless steels													
UNS S41000	11.5 to 13.5	-	-	-	-	bal.	-	-	-	0.15 (max.)	1.0 (max.)	1.0 (max.)	550 (80) <sup>e</sup>
UNS S17400	15.0 to 17.5	-	3.0 to 5.0	-	-	bal.	0.15 to 0.45	-	3.0 to 5.0	0.07 (max.)	1.0 (max.)	1.0 (max.)	724 (105) <sup>f</sup>

Table.1 Nominal composition of typical low alloy and carbon steels for use in oilfield applications [7]

It's interesting to note that the dispersion in Fig. 3, especially for bainitic steels, is linked to an incorrect microstructure characterization. Since most authors did not indicate the kind of martensite, such as plate, lath, or a mixture of both, or the type of bainite, such as upper or lower, it was necessary to make assumptions based on the published heat treatment techniques and alloy compositions to create Fig. 3. Even today, there are important parts of the bainitic and martensitic phase transitions in steels that are still unclear and may hinder technical advancement, such as the mechanisms for carbide precipitation. According to phenomenological observations, hydrogen dislocation interactions may be facilitated by untempered martensite's high residual strain, the ferrite-carbide interface present in ferritic-pearlitic alloys, as well as the carbides present at the GB in upper bainite needles.

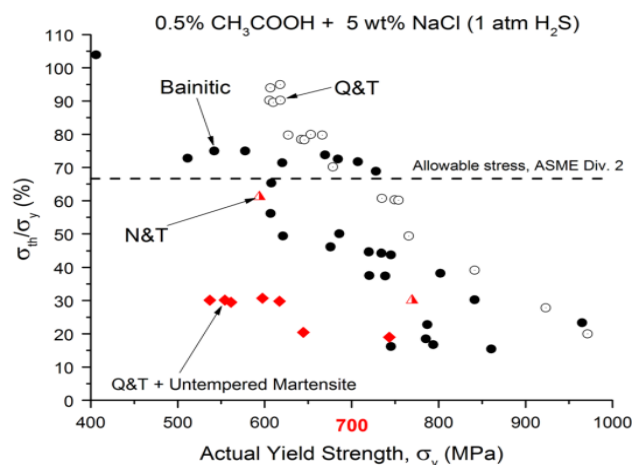


Fig. 3 Threshold stress ( $\sigma_{th}$ ) of low alloy steels with different microstructures exposed to 0.5 wt%  $\text{CH}_3\text{COOH}$  + 5 wt% NaCl in 1 atm  $\text{H}_2\text{S}$  at 24 °C, normalized to the actual yield strength ( $\sigma_y$ ) versus  $\sigma_y$  [1]

Precipitation hardened (PH) corrosion resistant alloys (CRA) Generally speaking, huge bore (i.e., having an internal diameter more than 50 cm) components used in subsea production, including valves, connections, and pipelines, are frequently constructed from LAS covered or clad with a CRA. The strength and affordability of the LAS core are benefited by fully or partially clad designs, while the CRA inlay reduces the corrosion risks brought on by LAS exposure to aqueous electrolytes including  $\text{CO}_2$  and  $\text{H}_2\text{S}$ . [11] Although other stainless steels and nickel alloys may be utilized, in subsea oil and gas production, LAS are commonly welded topped with UNS N06625 (NA625), a nickel-based seawater resistant CRA. Despite the fact that the surface in contact with production fluid is formed of a CRA, the base LAS must nevertheless meet ISO 15156's standards for strength, hardness, and alloy chemistry. When an application calls for strength values greater than those permitted by ISO 15156 for LAS, i.e., SMYS above 690-760 MPa, PH CRA are employed (100–110 ksi). Numerous uses for stainless steel and PH nickel-based alloys (PHNA) can be found in the production of oil and gas. Due to its strength and EAC resistance, PHNA in particular are often employed in wellbore components. [12] Although not all PHNA families can survive seawater, all PHNA are capable of withstanding the hardest industrial environments. Uns N07718 (NA718), a super nickel alloy with a composition of 50–55 percent Ni, Nb, Ta, and Ti, is the most popular PHNA. It contains 17–21% wt% Cr and 2.8–3.3 wt% Mo. (Table 1). The NA718's intermediate Cr and Mo content causes pitting and crevice corrosion in situations with oxidizing halides, despite the material's excellent performance in sour manufacturing environments. According to ISO 21457, NA725 and NA716 are classified as seawater resistant due to their ability to withstand the harshest sour situations. There is currently no standard that specifies the highest temperature at which NA725 and NA716 can be used in seawater, although NA625 is limited by ISO 21457 to 30 °C because of concerns about crevice corrosion in chlorinated systems. Although it is generally known that NA718's HSC and SSC resistance is substantially compromised by the presence of  $\gamma$ -phase56, PHNA has traditionally been thought to be resistant to hydrogen embrittlement under the age-hardened conditions found in O&G applications. [7] However, throughout installation and operation, reports of rapid cleavage failures of the subsea components NA71857, NA71658, and NA72559, all linked to HE, have been made in comparatively benign conditions. Although the source of the hydrogen in these failures has not always been clearly identified, it is thought that either CP, electroplating, galvanic coupling to carbon steel, or fluid deterioration from non-production fluids may have contributed to the H. More concerning, the majority of materials and production techniques complied with international standards, indicating that current best practices may not account for all the factors that influence an ideal microstructure. After appropriate sample preparation procedures, GB ornamentation was evident in the scanning electron microscope (SEM) and could only be identified by transmission electron microscopy (TEM). [5]



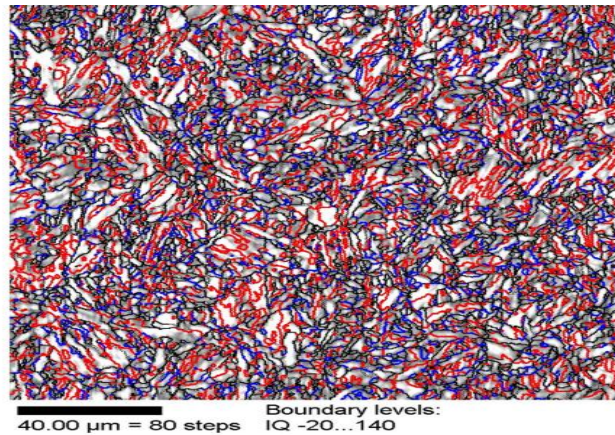


Fig.4 An electron backscatter diffraction analysis of a QT pipeline steel revealed the qualitative distribution of specific grain boundaries (: 3 in red: 11, 25b, 33c, and 41c in blue). [7]

### Materials Advancement in Petrochemical Industry

In the last a couple of decades, there have been a number of stronger, lighter and multifunctional materials developed in the laboratory. Advanced materials are those with at least one characteristic that is much better than that of standard alloys. Without exception, their distinctive features result from either the non-equilibrium microstructure or the novel chemical composition. Three types of advanced materials are picked as the most promising for applications in oil and gas production.

**NANOCRYSTALLINE MATERIALS:** Enhancement of both strength and toughness can be achieved simultaneously by reducing the grain size, schematically shown in below Figure 5. In contrast to conventional metallic alloys with typical grain sizes in the range of 10 to 100  $\mu\text{m}$  or even higher for some cast materials, Nano crystalline (NC) materials are characterized by grain size of typically 10-100 nm. However, a softening effect by grain boundary sliding begins to take a dominant role when grain size is further reduced under 10 nm.[13] In principle, processing of bulk Nano crystalline alloys can be accomplished by either the “two step bottom up” methods which assemble Nano scale clusters and subsequently consolidate into bulk material, or the “one step top-down” methods which break down the bulk microstructure into the Nano scale, as illustrated in Figure 6. The consolidation step involved with high pressure and heat should be carefully done without significant coarsening of the grain size and introduction of artifacts. In contrast, “one-step” processes such as electrode position and mechanical attrition, are beneficial for the dense and artifact-free NC materials.[14]

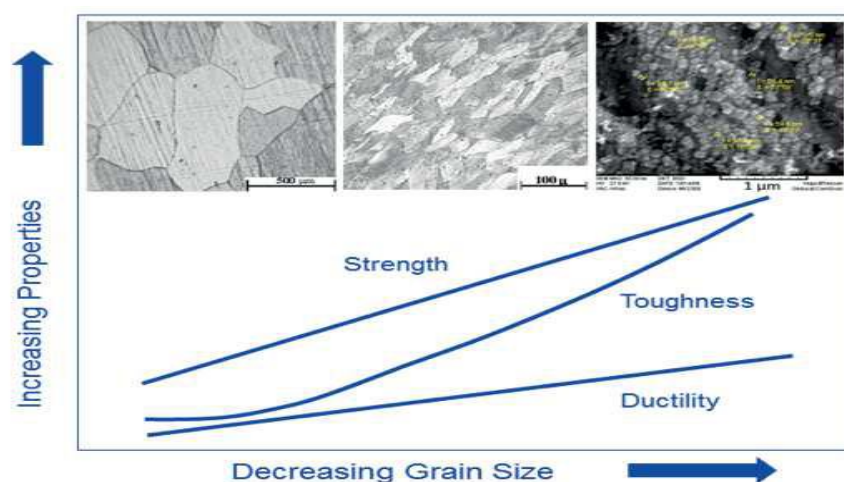


Fig.5 Schematic representation of how various material properties are affected by smaller grains.[15]  
Optical image of coarse-grained iron specimen: (left) annealed, (middle) as cast, and (right) SEM image of Nano crystalline iron deposit.[16]

Compared to their microcrystalline counterparts, NC metals in general exhibit high yield strength and hardness, excellent wear resistance, and enhanced super plasticity. However, the expected

ductility increase is typically limited by processing artifacts. Fracture and fatigue resistance are found to be superior as well. Due to the high portion of grain boundaries, high temperature creep rate of NC materials may be increased by the enhanced diffusivity. NC materials are therefore not heat treatable. The increased diffusivity of NC materials, on the other hand, contributes to faster protective passive film formation and thus increases corrosion resistance. NC materials are mainly limited to coatings and thin films due to the difficulty of retaining the ultra-small grain sizes in thick cross-sections. NC coatings are used to improve hardness and toughness coupled with better corrosion and wear resistance for structural applications, i.e. Fe/Ni-W, WC-Co- Cr, TiN/TiCN, yttrium-stabilized zirconia (YSZ) and other metallic or cermet nanostructured coatings. It is likely that NC materials would see service in specialty applications such as valve seats and stems, components of compressor or pump, and surfaces such as the riser tensioning system where wear and corrosion resistance are required. Nowadays, more than a dozen of companies in U.S. are involved in the manufacture of nanostructured materials on an industrial scale and probably more than 1600 organizations world-wide are involved in the development, production, and services related to such materials. [17]

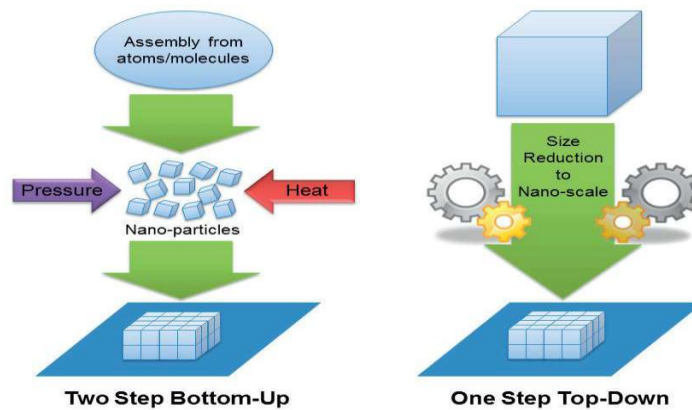


Fig.6 Schematic drawing to illustrate “bottom-up” and “top-down” fabrication methods of nanocrystalline materials.[13]

**BULK METALLIC GLASS** Bulk metallic glasses (BMG) have appealing features that come from their amorphous condition when combined with some desired qualities of metals and the processability of glasses. Theoretically, every metallic alloy can achieve a glassy state through incredibly quick solidification. However, such extreme cooling rates yield thin materials in small quantities. BMG strictly refers to those multicomponent alloys system developed since 1980's with high glass forming ability (GFA). GFA refers for the capability of creating materials with a glassy state thickness more than 1 mm at a reasonably slow cooling rate. ( $< 100$  K/s). [18]

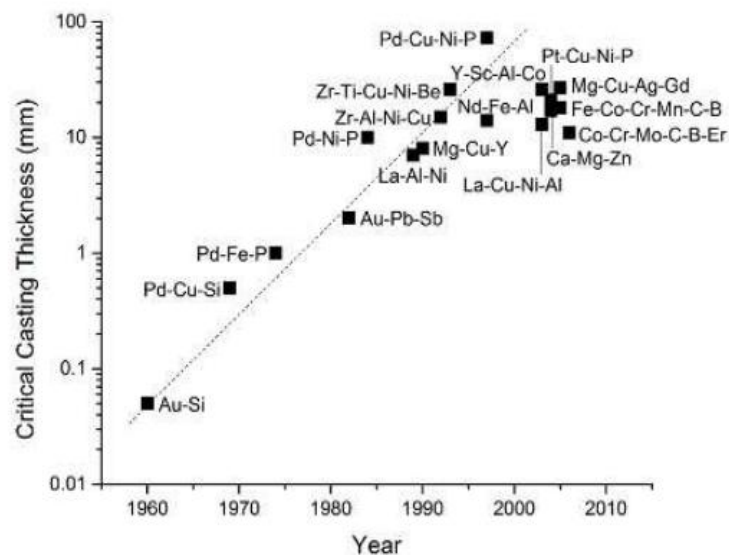


Fig. 7 Typical various alloy systems of BMG's were reported with critical casting thickness for glass formation and the calendar year when the first synthesis was discovered. [19]

Fabrication methods of BMG's all result from different non-equilibrium processing techniques to avoid crystallization. Solidification processes via direct casting and thermoplastic forming (TPF) are the most widely used. Direct casting requires relatively rapid cooling from melting temperature to glass transition temperature by bypassing crystallization. Thermoplastically formed BMGs with high GFA can be produced in the TPF while still being supercooled liquids above their glass transition temperature.[20] Because of the absence of grain microstructure, well-defined crystal defects, and chemical in-homogeneities, BMG's possess outstanding mechanical properties compared to their crystalline counterparts, such as much higher tensile strengths and hardness, near theoretical high yield strength with more than 2% elastic deformation, lower Young's modulus, low internal friction and wear coefficients, high fracture strength, and superior fatigue resistance. Some BMG alloy systems, e.g. Zr-, Pd-Cu-, Fe-, and Mg based systems, also possess excellent corrosion resistance and repassivation ability under extremely corrosive environment.[21] However, due to the highly constrained plastic flow and the lack of microstructural features, BMG's usually are "brittle" and lack plasticity under tension, which results in low fracture toughness and impact resistance. It is suggested that applications with small dimension would benefit the most from BMG's with enhanced plasticity and the low material cost. In oil and gas production, BMG can be used on valves and springs, strengthened edges of tools, wear resistant surface of drill head, high corrosion resistant coating, pipes for mass flow meter, precise miniature parts of pressure sensors, etc. Due to their high cost and low impact toughness, the principal applications for BMG will be constrained to small, crucial components with high performance requirements. A recently developed Fe-based BMG (Fe-Ni-Cr-C-B) with an exciting combination of moderate cost and properties may have a greater resistance to localized corrosion than a conventional Ni-22%Cr-9%Mo-3%W alloy. Thermal spray-coated layer of high performance Fe-based BMG's (SAM2X5, SAM1651) were developed to protect substrate under fairly aggressive conditions, in Figure 7. It has been suggested that 316L stainless steel plates coated with these Fe-based amorphous metals layer outperform conventional Ni-Cr-Mo alloys, but at a third of the cost.[22]



Fig. 8 High Velocity Oxy-Fuel (HVOF) process is used to coat a container with SAM1651 amorphous metal with quality assurance monitoring the thickness and roughness of BMG coating. [23]

**DIAMOND-LIKE CARBON:** A range of amorphous carbon compounds that have a large portion of carbon-carbon bonds with the  $sp^3$  electron configuration make up diamond-like carbon (DLC), lending these materials similar mechanical performance of diamond. The properties of DLC films are determined by the ratio of  $sp^3$  and  $sp^2$  electron configuration of bonding and hydrogen content, as shown in Figure 9. DLC films often exhibit better mechanical properties when their  $sp^3/sp^2$  ratios are high, whereas their optical and electrical properties are better when their  $sp^3/sp^2$  ratios are low. [24] The excellent chemical inertness of DLC films makes them a promising coating material in corrosive environments as a physical barrier. The most attractive features of DLC films are: i) their



wide range of properties that can be tailored by deposition methods with doping, ii) low cost to coat, and iii) low deposition temperature, i.e. almost any materials can be DLC coated at room temperature. Depending on the carbon source and deposition process, there are two main types of DLC films in Table 2: i) hydrogenated amorphous carbon (a-C:H) and ii) hydrogen-free tetrahedral amorphous carbon (ta-C). The a-C:H was earlier developed from hydrocarbon plasma. The hydrogen is required to tie-up the dangling bonds and to keep the carbon in  $sp^3$  bonding configuration for obtaining “diamond like” properties. The a-C:H films are relatively soft Compared to diamond, and exhibit some of the lowest friction coefficients (0.001-0.1) and wear coefficients in the dry and lubricant-free conditions (but increase considerably with humidity). Recently improved by a filtering technique, ta-C films were able to be deposited from pure carbon source with good quality at comparable growth rates of a-C:H film. Due to a predominant fraction of  $sp^3$  carbon, ta-C film exhibits high hardness and wear resistance close to those of diamond. As complement to a-C:H, ta-C shows lower friction coefficients for most surfaces (0.1–0.15) especially in a humid environment, and much higher thermal stability. The only drawback of ta-C films is their high intrinsic compressive internal stress arising from the ion bombardment for the formation of metastable  $sp^3$  bonding, which often limits the maximum thickness of an adhesive ta-C film to less than 1  $\mu m$ . [25]

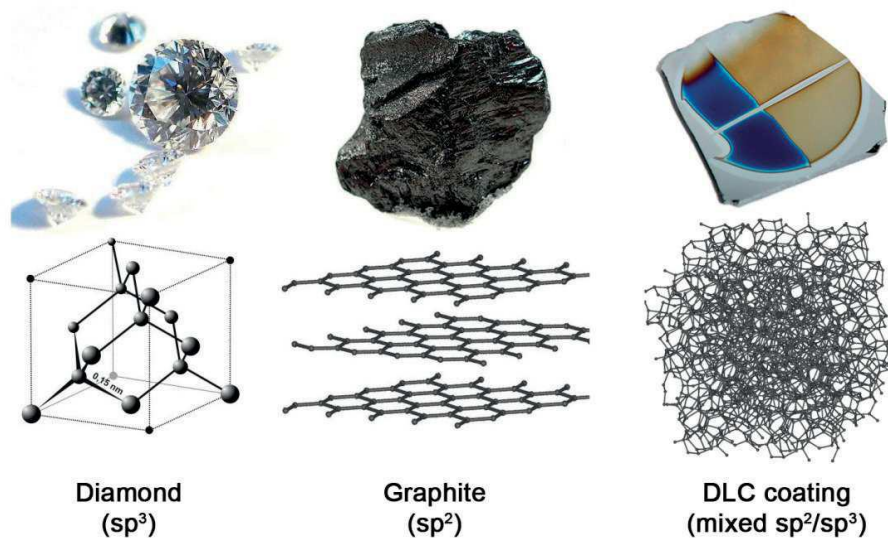


Fig. 9 Structure and carbon-carbon bonding of diamond ( $sp^3$ ), graphite ( $sp^2$ ), and DLC coating (mixed  $sp^2/sp^3$ ) are compared. [13]

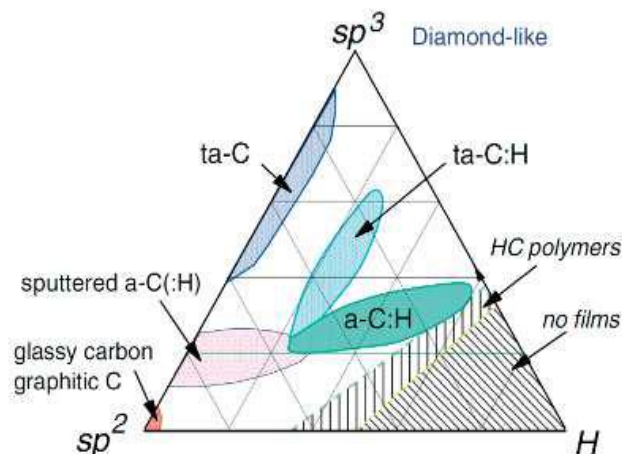


Fig. 10 a-C:H, ta-C, and other types of DLC film are shown in the ternary phase diagram of the C, H system. [26]

In addition to carbon and hydrogen, DLC films can be doped with nitrogen (N-DLC or  $CN_x$  films), silicon (Si-DLC), fluorine (F-DLC), and metal atoms (Me - DLC). Most modifications have been made to DLC are to reduce its high internal compressive stresses, to increase the adhesion between film and substrate, to decrease its surface energy for further lowered friction coefficients, or to modify its electrical properties.

	sp <sup>3</sup> content, %	H content, %	Density, g cm <sup>-3</sup>	Hardness, GPa	Young's modulus, GPa	Fracture toughness, MPa m <sup>1/2</sup>	Residual stress, GPa	Thermal stability, °C
Graphite	0	0	2.267	0.2	9-15	-	-	-
a-C:H	20-60	20-50	1.2-2.2	<20	50-200	1.2-3.3	<3	<250 <sup>1</sup> , <350 <sup>2</sup>
ta-C	70-90	<5	1.9-3.1	40-90	300-900	-	<12	<500 <sup>1</sup> , <1100 <sup>2</sup>
Diamond	100	0	3.515	100	1144	3.4	-	<700 <sup>1</sup> , <1700 <sup>2</sup>

\* 1 oxidation temperature in air, 2 oxidation temperature in vacuum or inert gas. Table 2: Comparison of structure and properties of a-C:H and ta-C DLC films with those of diamond and graphite. [27] [28]

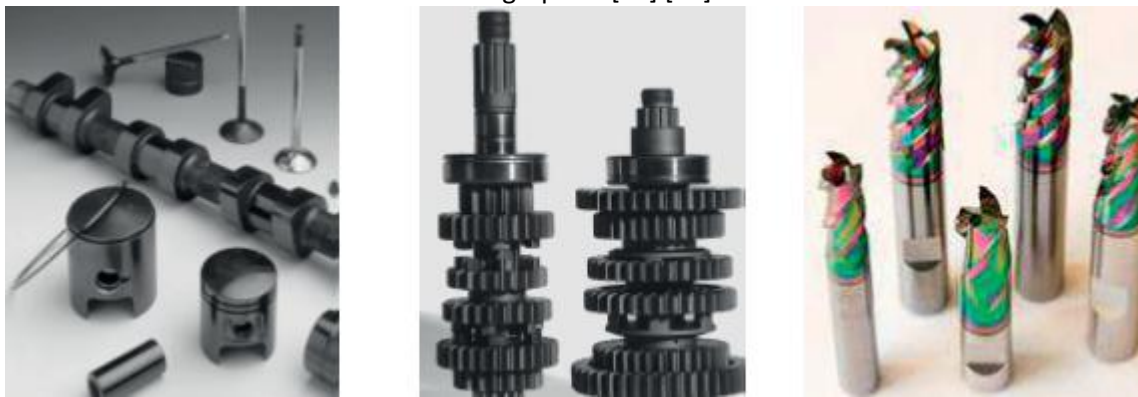


Fig. 11 a) Selection of automotive engine components that have been coated successfully with DLC. b) DLC (WC/C multilayer) coated spur gear. c) Hydrogen-free DLC coating for tools. [29]

The major application for DLC is as a tough, low-friction, durable, wear- and corrosion-resistant coating material. Commercial providers provide DLC coatings with various compositions that are applied using various techniques. The automotive sector has made extensive use of DLC film as a trustworthy tri-biological coating. The uses of DLC films in the oil and gas industry can be broadened to include drilling instruments, chemical pumps or multiphase pumps, valves, thread connections, elastomer seals, and other components.

## CONCLUSION

In order to address the material challenges involved in the extraction of hydrocarbons from unconventional sources, high strength materials, such as LAS and PH-CRA, are required. The two main types of degradation that affect the alloys required for the safe and effective operation of sour, HPHT, and Arctic fields are localized corrosion and EAC. The performance of engineering alloys' macroscopic corrosion at the Nano-and micro-scales can still be improved with more research. This paper compares three different types of advanced materials, DLC, BMG, and NC, to traditional metals and ceramics to highlight specific mechanical features of each type. It is desirable for the oil and gas industry that these new materials outperform more than traditional materials in terms of hardness or strength. High catalytic activity nanoparticles can operate as catalysts for chemical reactions upstream and high performance inhibitors for upstream chemical reactions. The idea behind a smart coating is comparable to that of a chromate conversion coating, which was created with the ability to "smartly" heal or release a corrosion inhibitor from coating damage. Unique heat-treated strength and corrosion resistance are combined in precipitation hardenable CRA. For these materials, systematic solutions still need to be found for problems like performance limitations and quality inconsistencies caused by the manufacturing process. Major aluminum producers are investigating the potential of aluminum alloys in offshore drilling procedures as lighter weight alternatives to steel. The vulnerability of

proprietary aluminum alloys to corrosion in sour and sweet environments must be addressed, and preventative coatings or other treatments must be developed. For applications like as drilling risers or high pressure heat exchangers, titanium alloys have been investigated as a lightweight, highly corrosion-resistant alternative to CRA. However, there are currently only a few facts on titanium alloy.

### ACKNOWLEDGEMENTS

The capability of aluminum alloys in offshore drilling processes is being explored by major aluminum producer as lighter weight alternatives to steel. However, there is a need to address the susceptibility to corrosion of proprietary aluminum alloys in sour and sweet environments and develop preventive coatings or other treatments. Titanium alloys have been explored as lightweight, highly corrosion-resistant alternative to CRA, ideal for applications of drilling risers or high pressure heat exchangers. The data of titanium alloy are however still limited. Increased use of titanium alloy is dependent upon the scale of availability at reduced cost.

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