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Materials for cryogenics applications

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Cryogenics is one of field in which the materials play an very important role in its advancement. Cryogenics-based technologies have applications in wide variety of areas as metallurgy, chemistry, power industry, medicine, rocket propulsion and space simulation, food processing by refrigeration, to name but a few of them. The topic of the-state-of the art and future developments in cryogenic materials areas looking toward the next century has several aspects to it. First, is to look at the history of the development of cryogenics materials. Secondary, is to evaluate where we are today in this science and to look at research and development trends in this area which can give us some clues to future developments. While it is easy to write a history of a topic and even to evaluate the present state of cryogenic materials, it is very difficult to predict the future. To the extent possible this paper will deal with the past, the present and the future of cryogenics materials for the 21st century.

1. INTRODUCTION

The science and technology of producing a low-temperature environment is generally referred to as cryogenics. It is perhaps appropriate to start with some definitions. The word cryogenics has its origin in the Greek language where "cryos" means frost or cold and "gen" is a common root for the English verb to generate. Strictly speaking, cryogenics means to produce cold, yet the term has developed a more general connotation over years of usage by engineers and scientists. Today, the word cryogenics is associated with the production and study of low-temperature environments. Thus, a cryogenic engineer is a person who specializes in these areas. The expertise of a cryogenic engineer can vary considerably within this discipline. Expertise in cryogenic engineering is in demand in a wide variety of technical fields including advanced energy production and storage technologies, transportation and space programs, and a wide variety of physics and engineering research efforts.

Over the years the word cryogenics has developed several common usages. A cryogenic fluid is one that is used in the production of cold, while cryogenic machinery is the hardware used in achieving low-temperature environments. At first it would appear that all machinery and fluids used in cooling would be identified as cryogenic. Generally, however, it is accepted that the word cryogenics is reserved for those processes that take place below about 100-150K. This distinction is established because it represents the point where permanent gases such as N_2 and O_2 begin to liquefy. Sometimes, cryogenics is used in reference to liquid natural gas and its liquifaction technology. The points of liquefaction for some cryogenic liquids are presented in table 1.

Table 1
Liquefaction temperatures for some systems

System	CH_4	O_2	Ar	CO_2	N_2	Ne	H_2	He
Liquefaction temperature (K)	111.7	90.1	87.4	81.1	77.3	27.2	20.4	4.2

Cryogenics is a multidisciplinary science, based on fundamental science of the nature like, chemistry, physics, and which has a wide range of possibilities of development in the field of engineering research and development into the field of cryogenics began slightly more than 200 years ago[1]. An evolution in time of the low temperature records obtained are shown in table 2.

Table 2
Evolution in time of the low temperature records

Year	1800	1840	1877	1878	1885	1889	1900	1908
Temperature (K)	223	163	90	77	50	20,3	14	4.22

Year	1910	1919	1922	1932	1933	1935	1945	1956	1965
Temperature (K)	1.04	1.0	0.83	0.71	0.27	0.004	0.00114	0.00002	0.000012

The obtaining of these low and very low- temperatures had depended of development of the cryogenics techniques, but especially of achievements in materials field, materials playing an important role in this direction.

As motivation to discussion of the materials used in cryogenic field and their properties at low-temperature, it is useful to identify the major applications for cryogenics technology today. Some of these are commercial enterprises, while others are still in the stages of research and development. It is possible to separate these applications into next categories: 1) Storage and transport of liquid cryogenics;2) Separation and production of gases;3) Biological and medical applications;4) Altering material properties by reduced temperature; 5) Space applications (rocket propulsion, space simulation); 6)Superconductivity.

Before presenting some materials used in cryogenics applications, it is useful to have a working knowledge of the properties of materials at low temperatures. This knowledge is useful because materials have behaviour that must be taken into account when considering the problems of refrigeration, heat transfer, or cryogenic liquids storage. Equipments operating in cryogenic environments are required to be strong and hard wearing and they must be manufacturing from materials with special properties [2,3].

2. MATERIALS DEMANDS FOR CRYOGENICS APPLICATIONS

For cryogenics applications, materials must be carefully selected because of the drastic changes in the properties of materials when they are exposed to extreme low temperatures [4,5]. Materials which are normally ductile at atmospheric temperatures may become extremely brittle when subjected to temperatures in the cryogenic range, while other materials may improve their properties of ductility. Once the materials are selected, the method of joining them must receive careful consideration to insure that the desired performance is preserved by using the proper soldering, brazing, or welding techniques and materials [6-8]. When properties of materials which are being considered for cryogenic uses are unknown, or not to be found in the known guides, experimental evaluation should be performed before the materials are used in the system.

Material characteristics change significantly with temperature [9,10]. Although at low temperature the strength and stiffness of most materials increase, they tend to shrink in size and become rather brittle. Warming solid body from absolute zero requires energy. In a free body, this energy manifests itself in two ways: an increase in temperature and a change in volume. Both of these are directly related to the additional vibrational energy of the individual atoms. The ratio of the change in energy to the change in temperature is the specific heat. The ratio of the change in volume to the change in temperature is the thermal expansion. Between two extremely important properties, specific heat and thermal expansion there is a significant relation [10,11] The specific heat of solids is given of the following equation:

$$C= Q/M\delta t \quad (1)$$

In general, at cryogenic temperatures, C decreases rapidly with decreasing temperature. This has two important effects: systems cool down faster as they get colder; at cryogenic temperature, small heat leaks may cause large temperature rises. When the materials are cooled to cryogenic temperatures large contractions in volume occur. All materials experience a change in physical dimension when cooled to low temperatures. This effect, normally referred to as thermal contraction in the field of cryogenics, is of the order of a few tenths of a percent change in volume in most materials. It can have profound effect on the design of engineering devices operating in a low-temperature environment, largely because the thermal contractions of different materials vary considerably. Since most devices constructed to operate in cryogenic systems are fabricate out of a number of different materials, one of the major concerns is the effect of the differential thermal contraction and associated thermal stress due to material differences.

Differential contraction is especially important to the design of vacuum seals, structural supports, and electrical and thermal insulation. [12,13].Integral thermal contraction of some materials are presented in table 3.

Table 3
Integral Thermal Contraction for some materials at low temperatures

Material	ΔL/L(300-100K)	ΔL/L(100-4 K)
Stainless Steel	$296x10^{-5}$	$35x10^{-5}$
Copper	$326x10^{-5}$	$44x10^{-5}$
Aluminium	$4156x10^{-5}$	$47x10^{-5}$
Iron	$198x10^{-5}$	$18x10^{-5}$
Invar	$40x10^{-5}$	-
Brass	$340x10^{-5}$	$57x10^{-5}$
Epoxi/Fiberglass	$279x10^{-5}$	$47x10^{-5}$
Titanium	$134x10^{-5}$	$17x10^{-5}$

At low temperatures the heat capacity of materials is differently. For insulators, the dominant temperature is proportional to T^3 while at very low temperatures, $T \leq 1K$, metals have heat capacities that are linearly to temperature. The mechanical properties of materials are considerable importance in the design of cryogenic systems. The two properties that are most often of concern are the level of stress σ within the material and the modulus of elasticity, E. These material properties enter into calculation of failure modes in mechanical structures [16.For most common structural materials, the yield and ultimate stresses increase with decreasing temperature. The magnitude of this increase varies from around 10% in some metallic alloys to several 100% in polymeric materials [14]. Young's modulus E, also increases with decreasing temperature. Unlike the limiting stress values, Young's modulus is not as strongly affected by material treatment and form [15].

Many metallic elements and a larger number of alloys transform into a state with essentially zero electrical resistance when cooled to temperatures close to that of the boiling point of liquid helium [13,16]. More recently, with the discovery of high-field superconductive materials, technical applications have come to fruition. In particular, large-scale superconductive magnets and superconductive electronics are now fairly well-established applied subfields of superconductivity[1,17,18].Superconducting materials require helium temperature environments to achieve their properties, but more importantly, the behaviour of superconductive devices are governed largely by problems of heat transfer, efficient cooling and safety. For example, the properties of a superconductor are conductive to carrying electric current provided the material remains below the local critical temperature and field. Thermal equilibrium is not always possible so superconductors must be fabricated in a low-resistance matrix material like copper or aluminium to provide the current-carrying capacity should the superconductor enter the normal state.

The first materials used in low temperature area were copper, brass, carbon [19]. After 1774 when was discovered the carbon steel by Tobern Bergmann, this material was used in application at low temperatures. In time, the quality of carbon steels was improved and in 1878, when was obtained temperature of 77K (liquid nitrogen) this materials used for testings. In 1913, when steel researchers were experimenting with different types and qualities of alloys, Harry Brearley discovered stainless steel. While experimenting with increasing levels of chromium, he found out that at over 12 percent chromium, the steel gained presents an exceptional resistance to acid corrosion and temperature. By the late 1920's two types of stainless steel had been found to be most versatile and useful: martensitic stainless steel (chromium content of 13-18 percent) and austenitic stainless steel (18 percent chromium and 8 percent nikel). Today, stainless steel is a generic term given for a group of corrosion resistant steels containing a minimum of 10.5 percent of chromium, which creates a passive, self renewing film of chromium oxide around the steel at the atomic level, thereby impeding the iron from rusting, that is a suitable material in cryogenic applications. Technical development over the decades has followed two paths: the incremental improvement of standard grades invented in 1920's as well as the development of entirely new grades. However, the core attributes of stainless steel i.e. strength, heat and corrosion resistance, formability, aesthetic appearance and low maintenance have not changed with technical developments. Stainless steel producers still continue to do research into chemical composition and innovations in stainless steel materials.

Based on their properties determinated at low temperature, only some suitable materials are used in cryogenics field. Some materials which are suitable for cryogenic temperatures are stainless steel (300 series and other austenitic series), copper, brass, monel and aluminium and its alloys, invar (Ni/Fe alloy) useful in making washers due to its lower coefficient of expansion, indium (used as an Oring material), teflon,kapton and mylar (used in multilayer insulation and as electrical insulation), quartz (used in windows).Metallic materials exhibit the best relationship between strength and plasticity compared with those of other structural materials [3].A disadvantage of ceramic materials in their low plasticity as against metalic materials. Composites occupy an intermediate position between ceramics and polymers in the specific characteristics of strength and plasticity. Due to the indicated advantages of metalic structural materials, the fraction of steel in the total amount of structural materials used in cryogenic applications exceeds 80%. By the end of the twentieth century, the world production of steels continously grew and achieved about 800 million tones per year [4].

Steel was and is the most material used at low temperature in world. Carbon and alloy grades for low-temperature service were required to provide the high strength, ductility and toughness in equipments that must serve at 225K and lower. Because a number of steels are engineered specifically for service at low temperature (about 173K), selecting the optimum material calls for thorough understanding of the application and knowledge of the mechanical properties that each grade provides [14]. At temperature below ambient, metals behaviour is characterized somewhat by crystalline structure. The yield and tensile strengths of metals that cristallize in the body-centred cubic from iron, molybdenum, vanadium and chromium deper greatly on temperature. These metals display a loss of ductility in a narrow temperature region below room temperature. The tensile strength of metals with face-centred cubic structures - aluminium, copper, nickel and austenitic stainless steel -is more temperature dependent that their yield strength, and the metals often increase in ductility as temperature decrease[20]. Transformation occurring in compositions that are normally stable at room temperature, but metastable at cryogenic temperatures, can greatly alter their behaviour. For example, the combination of gross plastic deformation and cryogenic temperatures can cause a normally ductile and tough stainless steel, such as 301,302,304,321, to partially transform to bcc structure, resulting in a impairment of ductility and toughness. A fully stable stainless steel 310 cannot be transformed at cryogenic temperatures. The 300 series steels offer a fine combination of toughness and weldability for service to the lowest temperatures. In the annealed condition, their strength properties are adequate for ground-based equipment but inadequate for lightweight structures. For aerospace applications, fabricators can take advantage of the alloys strain-hardening characteristics and use them in highly cold-worked condition. The principal shortcomings of cold-worked materials are: low weld-joint efficiencies caused by annealing during welding and the transformation to martensite that occurs during cryogenic exposure. Selection of fully stable grade type 310, overcomes the transformation problem. Precipitation-hardening A 286 stainless has even higher strength when cold worked before aging.

The alloy steel recommended for cryogenic service is also 9% nichel steel [21]. It is satisfactory for service down to 77 K and is used for transport and storage of cryogenics because of its low cost and ease fabrication. Other alloy steels are suitable for service in low-temperature range. The steels A201 and T-1 can suffice to -45^{o}C, nichel steels with 2,25% Ni can suffice to 215 K, and nickel steel with 3,5% Ni to 172 K. A grade with following chemical composition shows good mechanical properties at cryogenic temperatures: C-0.072%; Mn-16%; P-0.02%; S-0.008%; Si-0.41%; Ni-5,85%; Cr-17.8%; N-0.36%; Fe-remainder. This composition is given for plates with 12.7 thickness [14]. The material combination of high strength, good toughness and weldability should prompt designers to specify it for welded pressure vessels for the storage of cryogens. Much better as material for cryogenics field proved to be aluminium and aluminium alloys, that represent a very important class of structural metals for subzero-temperature applications and are used for structural parts for operation at temperatures as low as 77 K. Below 77 K, most aluminium alloys show little change in properties, yield and tensile strengths may increase, elongation may decrease slightly, impact strength remains approximately constant. Consequently, aluminium is useful material for many low -temperature applications.

In cryogenic applications very important are the insulation systems. Some materials were and are used in this way. The aluminized mylar with low-density fibrous insulating spacers between layers, represents a special case of a multilayer insulation system. Since there is interlayer material present, it is no longer possible to assume that each of the n shields are isolated from the others except for radiant heat transfer. Thus, superinsulation systems are required for application at very low-temperature, under 77K [10,11]. In superinsulation there are two contributing heat transfer mechanisms which are both functions of density and total number of shields. There is radiant heat transfer that decreases with increasing number of radion shields, that is, layers of superinsulation ,however, as the packing density increases, the heat transferred by conduction though the fibrous insulating spacers begins to make a larger contribution to the total heat leak. Thus, there occurs an optimum layer density for practical multilayer insulations. Note that the solid-state conduction heat leak can be reduced by increasing the spacing between walls for the same packing density while the radiation contribution is only a function of number of layers. Therefore, the optimum number of layers should also be a function of the total insulation thickness. The existence of a minimum in the layer density dependence of the heat transfer through superinsulation has been demonstrated experimentally [10,11]. Superinsulation at low densities, less than 0.5 layers/mm, can be modeled fairly accurately by pure radiant heat transfer. The best choice for the emissivity of aluminized mylar is ε=0.011at 4.2 K nd 0.03 at 77K[11].

Glass powder insulation or perlite materials also are used to fill spaces between vacuum walls in insulating cryogenic vessels. These materials generaly are comprised of glass microspheres with diameters in the range 100-1000μThey have advantages over superinsulation in that the material is easier to install, cheaper, and the residual vacuum requirements are not as high. However, the disadvantages of powder insulation technology are that is requires long and careful pump-down procedures and that the residual effective thermal conductivity is considerably higher than can be achieved with properly installed superinsulation. Powder insulations are only considered for containers operating in the range of liquid nitrogen temperatures and above.

The apparent thermal conductivity of perlite materials is a reasonably well-known quantity. Experimental measurements have been carried out on the variation of this quantity with residual gas pressure and diameter of glass spheres. Most results are reported in the range of 77-300 K, where it is of interest in liquid nitrogen and oxygen storage container design. Minimum conductivity for this material is achieved for pressures less than 10^{-2} torr. At high pressures, $p \geq 10^{-1}$ torr, superinsulation actually has higher thermal conductivity than the powders. [1].

3. FUTURE TRENDS

There are several trends today that can help us look into the future of cryogenics materials. These include: 1) computationally designed materials and processing; 2) unique nanophase materials systems for new applications at low temperatures; 3) smart materials and systems based on new alloys; 4) durability and performance, 5) quality assurance and testing etc.

The future trend will favor the use of low density materials, for this there will be a permanent competion for to develop these types of materials. The key of development in cryogenic materials area will be the emergence of a computational design approach based on knowledge of the physical and mechanical properties of materials at the atomic level. This approach will lead to the development and manufacturing at low cost of smart materials and nanophase materials that will, in turn, be anablers of new materials development. Simulation of materials characteristics using this approach will include modeling of microstructure, defects, surface structure, interface properties, prediction of adhesion and bonding, thermodynamic properties, and general mechanical behaviour.

Among the candidate materials is the new generation of low density alloys. These low -density alloys are attractive to the cryogenics applications, since structural weight reduction is a very efficient means of improving cryogenics performance. For example, the addition of Li to Al offers the promise of substantially reducing the weight of cryogenics alloys, since each 1% Li added to Al reduces density by 3% and increase in elastic modulus by about 6%. Al-Li alloys use in cryogenics applications, where the weight savings effected by using these low-density alloys greatly reduce the equipment costs and increases performance. In contrast to new materials systems such as fiber-reinforced composites, low density Al alloys do not require large capital investements by the cryogenics equipments producer in new fabricating facilities. This cost savings can more than offset the greater performance increment, which composites may offer, resulting in Al-Li alloys being substantially more cost effective than composites in some applications. Fatigue crack growth resistance in Al-Li alloys generally is very high, this is important in damage-tolerant structures such as lower cold surfaces.

The new properties of Al-Li alloys are given by:

- excellent fatigue and cryogenic toughness properties;
- higher stiffness;
- superior fatigue crack growth resistance;
- reduced ductility;
- low fracture toughness.

Al-Li alloy is a candidate material in future for cryogenic tankage of booster systems. Also these alloys are used in cryogenic applications for example, liquid oxygen and hydrogen fuel tanks for aerospace vehicles.

In future the effort will be directed toward developing cryogenic vacuum insulation systems, that will be efficient, easy-to-use alternatives to the present evacuated multylayer insulation systems. The new thermal insulation systems for cryogenic applications typically will consist of an evacuated annular space filled with layers of radiation shields and space materials, fine powders, fiberglass blankets, teflon, or graphite/epoxy material. These superinsulation systems could provide apparent thermal conductivity (k) values below 0.4 milliwatt per meter-kelvin (mW/m-K) if residual gas pressures below $1x10^{-4}$ torr will be maintained. The optimization of the new insulation systems will require a better understanding of the heat transfer contributions. Of equal importance will be the overall cost effectiveness of the insulation systems, thermal performance, durability. The advanced insulations should also allow for more flexibility in the design and implementation of cryogenic systems.

4. CONCLUSION

The future of cryogenics materials will be very exciting and dynamic. It will be driven by traditions, trends, costs, performance, legislation. Of these, the most critical issue is costs. Logical, creative and inovative ideas will have little chance of success if the economics are not positive. Cryogenics materials will be part of the dynamic future. By considering the entire cryogenics materials, we are not limited to just one type of materials, but metal materials, composites and fluorinated polymers will remain the major materials for applications at very low temperatures. We are no longer limited by shape, density, size, composition, we are only limited by our imagination and our knowledge and understand of how to achieve the highest level of performance from cryogenics materials. We must not only continue to make incremental improvements in present materials but develop whole new technologies of manufacturing and processing for to achieve the highest performance in cryogenics materials field.

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