Development of Cryogenic Structural Materials

Li L.F.[1], Zhang Y.T.[2] , Li Y.Y. [2]

1 Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, China
2 Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China

During the last decades, cryogenic structural materials have experienced a sustaining development by institutes, universities as well as industries. Besides cryogenic metals and alloys, significant progress has been made in cryogenic composites and cryogenic ceramic materials. The world development in cryogenic material research and applications is overviewed. Firstly, an overview of the applications of cryogenic materials will be presented. Cryogenic materials are being used in a wide variety of fields, such as space technology, high energy particle accelerator, fusion reactor development, cryocoolers and gas industry. Secondly, the microstructures and properties of cryogenic structural materials will be discussed. Among the cryogenic structural materials, metallic base materials take on a predominant role. The chemical composition and the mechanical properties of different alloys at low temperatures as well as their advantages and disadvantages are compared with each other. Composites and ceramic materials are the prospective structural materials for cryogenic application and their microstructures and properties as well as potential applications at cryogenic temperatures are also discussed in this paper.

INTRODUCTION

Cryogenic structural materials are used at temperatures below 120K in order to meet the development of cryogenic engineering.

Cryogenic engineering started near the end of the 19th century. The main task during the first half of the 20th century was in connection with the building up of the modern gas industry through the application of cryogenic separation of gaseous mixtures. Once started, this technology of air separation played crucial roles in the development of the steel industry and the chemical industries[1]. As refrigeration techniques improved and liquid gas became readily available, suitable materials were needed for storage dewars, industrial processing equipment, and refrigerators[2].

In 1911 Onnes discovered the superconductivity, which stimulated the fundamental studies of condensed matter physics and superconductors. Both low temperature superconductivity (LTS) and high Tc superconductivity (HTS) attracted great interests for researchers. LTS superconductors are used extensively today in many applications where high magnetic fields are required, including superconductive magnets for controlled thermonuclear fusion, for nuclear magnetic resonance, for high energy physics research, for magnetic refrigeration, for Maglev system as well as for magnetic ore separation. For HTS[1], studies today concentrate on the material side, which is certainly the fundamental issue. Claims about future applications abound, some are being tested, and it takes time, at least, to check on their practicality. In applied superconductivity, high strength/thermal conductivity ratio, adequate toughness, and weldability alloys are required, and also for insulating purpose, nonmetallics, structural composites were also developed.

Another chief application field of cryogenic structural materials is the space technology. Cryogenic materials specific for the rockets and the spacecrafts has been largely developed in some countries in the world. Use of liquid oxygen and liquid hydrogen fuels, led to the development of high strength, lightweight materials and heat insulating composites, Chinese efforts in space technology started in late 1950s. Manned spacecraft with LH_2/LO_2-engine was launched in 2003..

Although many materials have been successfully used for a wide range of structures and devices that operate at low temperatures, in recent years, many large cryogenic engineering projects bring new requirements on materials. This is a new challenge for cryogenic materials R&D, the practical way is how to design and how to tailor present materials, upgrading them to a higher level by combining the considerations of good performance, environmental-friendly, and less-cost. With the developments of the advanced material synthesizing method, the new structure characterization and computer simulation technology, it will be possible to realize this task.

In this paper, we will give an overview on applications and developments of cryogenic structural materials. Focusing on some specific applications, metal, composites and ceramics materials will be discussed by emphasizing mechanical and thermal properties as well as microstructures.

APPLICATIONS OF CRYOGENIC STRUCTURAL MATERIALS

Table 1 is a brief summary of cryogenic structural materials used in different fields. It indicates the order of preference with asterisk marks.

Table 1 Various of cryogenic structural materials used for different fields

Fields	Structural steels	Al alloys	Other alloys	Composites	Ceramics
Space					
● Ground and rockets	□ □ □ □	□ □ □			
● Spacecraft	□	□ □ □	□ □	□ □	□
Superconducting engineering	□ □ □ □	□ □ □		□ □	
Gas industry	□ □ □ □	□ □ □ □			
Cryocoolers	□ □		□ □	□	□

Materials used for space technology

Materials used for space technology mainly involve in large power launch vehicles for liquid oxygen and liquid hydrogen storage tanks and rocket engine components such as valves, turbopump, conduits, bearings and seals. Space cryogenic materials include metal and composites materials. For metal materials, the high strength/weight ratio, high toughness, weldability, high resistance to hydrogen brittleness at cryogenic temperature are required. Typical materials are Inconel 718, Ti-5Al-2.5Sn, Ti-6Al-4V, Al-Mg alloys, Cu-Zr alloys. There were lots of Ti-alloys used in USA Apollo project for liquid hydrogen tank, conduit and high pressure vessels. Inconel 718 was also widely used for space shuttle of USA, H-2 rocket of Japan as key materials for LH_2/LO_2 engine in recent year.[3] For polymer composite materials, high specific strength, high heat insulation value, high modulus and low density is required. Typical materials are GFRP, CFRP, polyimide, epoxy and CFCs (CFC-11 has high ozone depletion potential and thus, many companies such as Solvay Germany, Elf Atochem France and Allied Signal USA are searching new substitutes, for example, HFC-245fa、HFC-365mfc and liquid CO_2).

Space cryogenic materials are highly related to the special application environments, including temperature, pressure, load, medium and medium state, so that the research activity on mechanical, physical properties under practical using environment is very important. Since 1960, researchers from US, USSR, China, France, Japan, et al. have made a lot of investigations on mechanical properties as strength, modulus, fatigue, toughness, creep, impact, and on thermal properties as expansion, thermal conductivity, specific heat as well as on electromagnetic properties, cryotribology and hydrogen embrittlement. Current research mostly focuses on how to further decrease the weight and how to decease environmental pollution. Attempts to use composites instead of metallic alloy for LH_2/LO_2 tank and use low ozone depletion potential value materials instead of CFCs are carried up.

Structural materials in applied superconductivity

Structural materials are used for structural support and electrical insulation in large superconducting devices. In addition to HTS power cable, most of applications focus on superconducting magnets. Structural materials related to superconducting magnet technology, are mainly austenitic stainless steels and composites.

For fusion application, nowadays, many projects are on establishing in the world, such as ITER (multi-country joined project), LHD-Japan, EAST-China and KSTAR-Korea. Austenitic stainless steels and epoxy base resin composites as candidates will be used for supports and insulating materials. For instances, both ITER and EAST have decided to use 316LN as CICC conduit and winding case materials, 316L as upper and lower supports, and resins developed in Rutherford Appleton Laboratory as vacuum pressure impregnation (VPI) insulation. It is estimated that hundreds of tons of austenitic stainless steels and epoxy resins will be used for EAST device.

For particle accelerator, there are also many big projects on establishing, such as LHC (CERN), TESLA(DESY), CEBAF (USA), VLHC(USA), KEKB(Japan), BEPCII (Beijing), and SSRF (Shanghai). Similar to fusion applications, structural materials used for high field magnets are also austenitic stainless steels and composites.

Structural materials for gas industry

The need to transport and store large quantities of liquefied natural gas (LNG) led to the development and use of tough 9Ni steel and Al alloys that are less expensive than the austenitic stainless steels . The safety and long service lifetime demanded of these large containers required an increased understanding of materials properties at low temperatures.

In addition to traditional materials, modern gas industry brings materials to some new requirements because modern gas industry has been extended to many fields. For example, Japan's WE-NET(the world energy network system) projects are aiming at constructing clean energy systems using hydrogen as fuel, focusing on the development of hydrogen production, transport, storage and utilization since 1993. They have established goals for Japan with respect to fuel cell vehicles and stationary fuel cell systems of 50,000 vehicles by 2010, and 5 million vehicles by 2020. The R & D work on various of properties of austenitic stainless steels and Al alloys under liquid hydrogen environment has been carried up these years for WE-NET projects[4].

Structural materials for cryocoolers

Cryocoolers, especially small scale coolers become much more important in novel refrigeration technology since they will be deeply involved in information technology.

Basically, cryogenic environment is essential to high quality information handling. As we keep finding new information carriers, bearing the signature of quantum physics, turning up in physics research, we should expect the field of 'cryoelectronics' to become widened with 'electronics' in a broad sense. We might also expect that more subtle cryogenic backup will be required besides the cooling function, and cryogenic structural materials will be part of the 'electronics' system[1].

We have to accept the facts that there really exist some barriers between person engaged in cryocooler investigations and person engaged in materials and /or physics studies. The former does not pay more attention on the development of materials and selections on proper materials. The latter, does not know much about refrigeration and its appropriate requirements on materials. In recent years, ICMC and CEC are regularly held together, and sometimes they were also held together with ICEC. These connections are helpful to reduce the obstacles between the two subjects. We are glad to see some progresses on pulse tube cooler in which some components are instead by ceramic materials and composites[5-6]. An attempt to use toughening ceramics to fabricate the rotary valves in G-M cooler is undergoing[7].

MICROSTRUCTURES AND PROPERTIES OF CRYOGENIC STRUCTURAL MATERIALS

Cryogenic structural alloys

Commonly used cryogenic structural alloys are austenitic stainless steels and Al-alloys. Ti-alloys is under further developing and the application is very limited.

a) Austenitic stainless steels

The austenitic stainless steels are Fe-Cr (16-26%)-Ni (8-24%) alloys sometimes with Mn and N in order to stabilize the austenitic phase. They have higher ultimate strength, toughness at cryogenic temperatures coupled with reliability, ease of fabrication, and good service. Their disadvantages are that they are more expensive and their machinnability is poorer than that of Al-alloys. According to the strengthening mechanism, austenitic alloys can be classified as basic type (AISI 300-series), nitrogen-strengthened type (21-6-9,22-23-5), and precipitation-hardened type (A286, Inconel 718). Inconel series are nickel based alloys, however, their cryogenic mechanical behaviors are very similar to austenitic stainless steels.

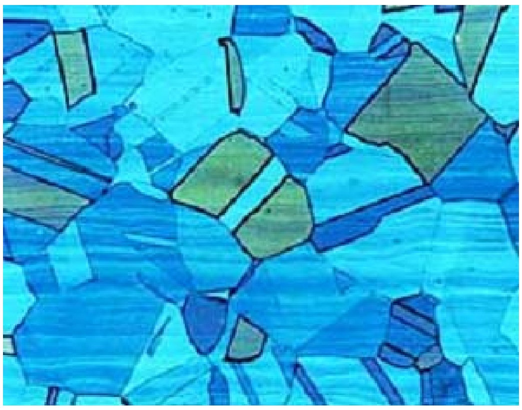
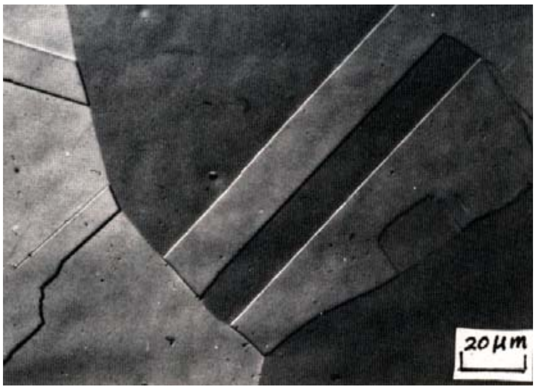


Figure 1 Microstructure of austenitic phase[8]

Table 2 Typical compositions of austenitic stainless steel

Type	Cr (%)	Ni (%)	Mn (%)	N (%)	C (%)	Others (%)
304	18-20	8-12			<0.08	
304LN	18-20	8-12	2.0	0.10-0.16	< 0.03	
316	16-18	10-14			< 0.08	2-3Mo
316L	16-18	10-14			< 0.03	2-3Mo
316N	16-18	10-14	2.0	0.10-0.20	< 0.08	
316LN	16-18	10-14	2.0	0.10-0.20	< 0.03	
21-6-9	19-21.5	5.5-7.5	8-10	0.15-0.40	< 0.08	
A286	14-16	23-27			< 0.08	1-2Mo
JBK-75A	15.0	29.0			0.015	Al0.3,Ti 2.4
Inconel 718	19.0	bal	0.35	Mo3.0 Nb5.0Fe18.0	0.08	
Incoloy 907	-	37.4		-		Co 13.0



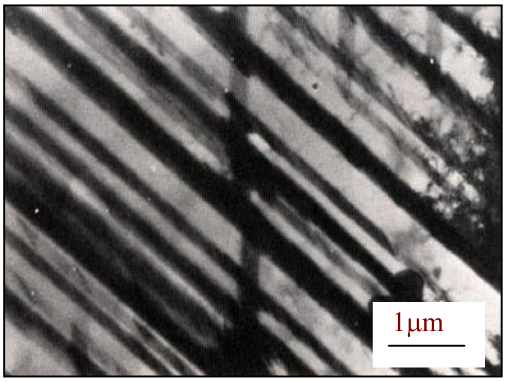


Figure 2 Microstructures of Alloy 21-6-9 [9]: (a) After solution at 293K, (b) Lath martensites after deformation at 4K

Table 3 Tensile properties of 316LN and 21-6-9

Alloy	Temp. (K)	Yield Strength (MPa)	Tensile Strength (MPa)	Charpy Impact (J/cm^2)	Elongation (%)	Reduction of Area (%)
316LN	298	318	626	477	67	84
	77	802	1364	277	59	71
	20	964	1624	285	51	61
	4.2	1067	1592	283	51	58
21-6-9	298	384	701	484	68	79
	77	881	1360	289	66	70
	20	1076	1596	300	52	61
	4.2	1163	1576	293	51	59

Typical compositions of austenitic stainless steels are summarized in Table 2. Basic microstructure of austenitic phase is shown in Figure 1. Meta-stability austenite steels deformed or cooling at low temperature, will experience stress induced martensitic transformation, so as to enhance the strength and decrease toughness. Figure 2(a) is the austenite steel 21-6-9 after solution treatment. Figure 2(b) shows lath martensites after deformation at 4Kfor the same steel..

Mechanical properties of austenitic steels are excellent at cryogenic temperatures, one can easily get relevant the data from many handbooks. Here listed some materials' data obtained recently from IMR and TIPC (see Table 3).

b) Al-alloys

Commonly used aluminum alloys are Al-Cu (2000-series, Cu: 4-6.5%), Al-Mg (5000-series, Mg:2.5-6%), Al-Mg-Si (6000-series, Mg: 0.6-1%, Si: 0.6-1%) as well as Al-Li alloys developed in 90s. They have been used for many structural applications such as rocket propulsion tanks (LH_2, LO_2), LNG tanks, and superconducting structural supports.

Aluminum alloys have moderate strength, high toughness and ductility at cryogenic temperatures. They have low density, nonmagnetic behavior, stable microstructure and good machinability. The disadvantages of aluminum alloys are low strength in weldments, low elastic modulus, and high thermal expansion, which limited their use in large structure, such as land-based storage tanks. Typical microstructure of Al-Li alloy is shown in Figure 3.

Generally, Aluminum alloys strengthening mechanisms are precipitation-hardened. Their ultimate strength is in a level of 300-700MPa, yield strength 150-520MPa, no big change at cryogenic temperatures.

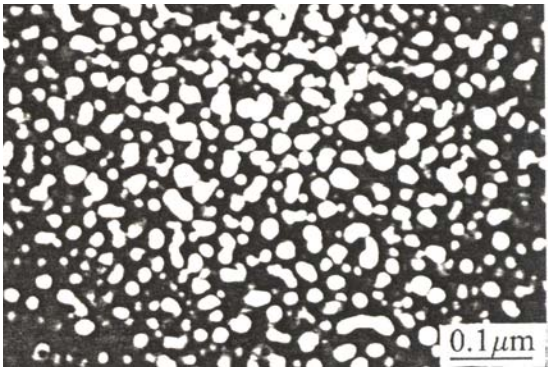


Figure 3 Microstructure of Al-Li alloys[10]

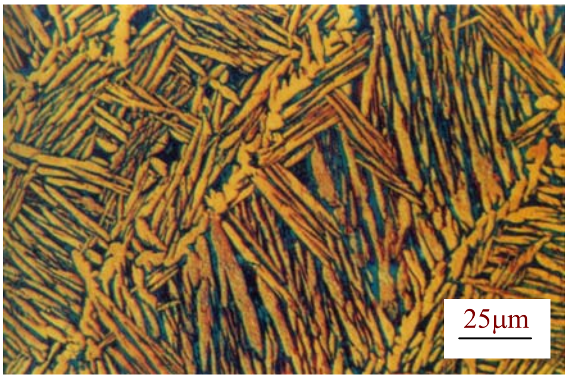


Figure 4. Micrograph picture of Ti-6Al-4V alloy showing α+β phase [11]

c) Titanium alloys

Titanium alloys are classified as three types according to their compositions. They are α type (Ti-5Al-2.5Sn), β type (Ti-13V-11Cr-3Al), and α+β type (Ti-6Al-4V). Among them, Ti-6Al-4V alloys have excellent strength, ultimate strength in a level of 1200MPa (RT), 1600MPa (77K), 1900MPa (4K), and yield strength in a level of 1000MPa (RT), 1300MPa (77K), 1800MPa (4K). Typical micrograph of Ti-6Al-4V alloy is shown in Figure 4. Although Ti-alloys have high strength both at room and cryogenic temperatures, the use at cryogenic temperatures has been limited to aerospace applications where strength to weight ratio is primary concern. This is due to their high costs and difficult to fabricate. In addition, Ti-alloys have low ductility, low fracture toughness. So it is limited to use widely.

Studies on metallic base materials in the future will be concentrated on enhancing their mechanical properties to another order of magnitude through grain-refined, homogenized and purified, so as to satisfy the requirements of large cryogenic engineering.

Cryogenic Composites

Composites always act as both structural and functional materials used for cryogenic technology. Superconducting technology, space technology, and fusion technology push the development of cryogenic composites since 1970s. It is mainly due to that composites can satisfy the requirements of reduced weight and increased electrical/thermal insulations. The advantages of composites can be described by using strength to thermal conductivity and density ratio, i.e., $\sigma/(\lambda.\rho)$, the higher the ratio value, the less refrigeration cost. The ratio of composites is about 2 order of magnitude over stainless steels. However, composites also have many disadvantages[12-13]: low toughness, heterogeneous strength and high thermal contraction, neutron radiation damage and low bonding strength between fiber and matrix.

Composites are classified as fiber reinforced and particle reinforced plastics. Commonly used fibers are E-glass, S-glass, Kevlar, boron, carbon, alumia; particles are SiC, SiO_2, Al_2O_3; matrices are epoxy, polyester, Teflon, polyimide. Glass fiber reinforced plastics (GFRPs) are well-developed, commercial products are G-10, G-10CR, G-11CR. Carbon fiber reinforced plastics still need to be improved. It is noted that some materialists are trying to use new materials as reinforced agents (such as carbon nanotube) and new technology (such as nanotechnology). It has been shown in laboratory scale tests that the physical properties and performance of composite materials can be tremendously improved by the addition of small percentages ~2% of carbon nanotubes. However, there have not been many successful for large applications that show the advantage of using nanotubes as fillers over traditional carbon fibers. The main problem is in dispersing the nanotubes. The other problem is not match well between the nanotube and the polymer matrix [14-15]. Plasma polymer coating on fibers or particles might be a good method to solve the dispersing problem (see Figure 5).

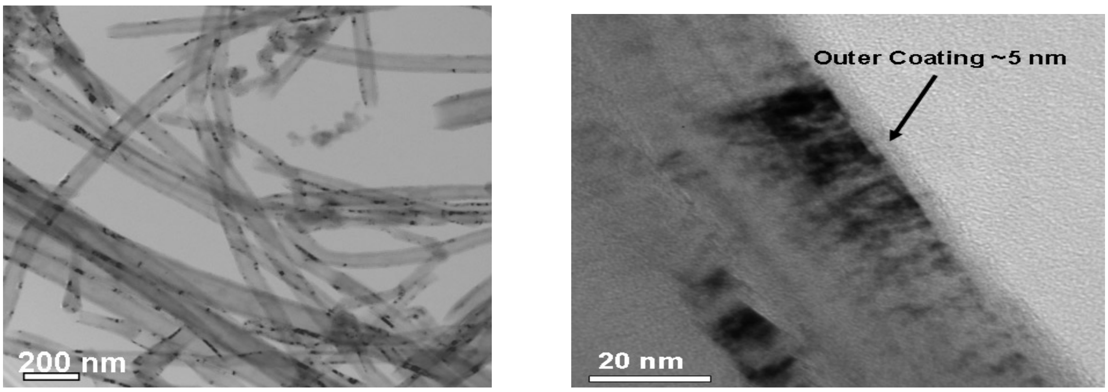
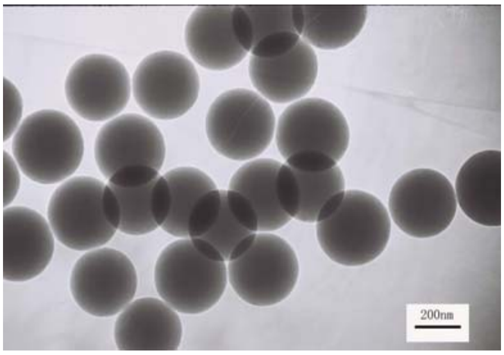


Figure 5 Thin polymer film plasma coating of the carbon nano-tubers (left). The magnification picture (right) shows the thickness of coating[15].

Recently, under the application backgrounds of EAST project and HTS power cable project in China, researchers in TIPC (Technical Institute of Physics & Chemistry, CAS) are carrying on the modification of epoxy resins and polyimide films by the addition of various shapes and sizes of nanometer SiO_2 particles and fibers (see Figure 6). Mechanical property tests on these synthesized composites show that there are more than 30% increases both in tensile strength and modulus. For HTS power cable, polyimide insulating films shall satisfy the matching of the thermal expansion to that of Ag-shield BSCCO conductor at ~77K. This work is undergoing at TIPC. A novel type of toughening epoxy resin for low temperature application was studied.

Another significant progress developed in TIPC is about active toughening epoxy resin[16]. An active toughening component was used to improve the properties of bisphenol-A-epoxy resin and form two-phase structure in the reaction. A complex amino cure agent was investigated to control the inhomogeneity of molecular cross-links in the chemical structure, in which the combination of stiffness and flexibility decreased the sensitivity to temperature, so that the system can be used at low and middle high temperature. The excellent bonding at interface between the dispersed phase and matrix phase is performed by adding the ether-chain coupling in the curing reaction. The applied temperature region is from 4.2 K to 373 K. The mechanical property such as lap shear strength is 20 MPa at 4.2 K. The glass transition temperature (Tg) is at 393 K. The coefficient of liner thermal contraction is 3.88×10^{-5} (1/K) in the region of 300K to 77K. It has the excellent vacuum hermetic property and the leakage rate is less than 1×10^{-8} Pa M^3/S. It has been successfully applied in EAST project of IPP, CAS.



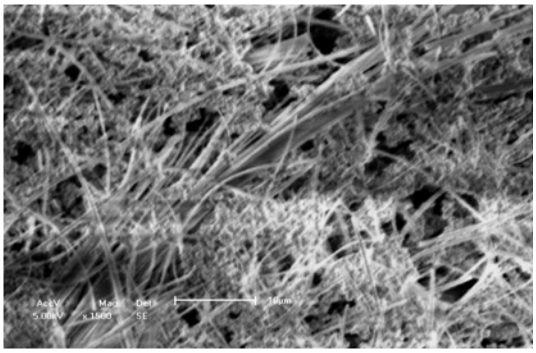


Figure 6 Fillers to be added to epoxy resin and polyimide, the left picture is the uniform spherical nano silica particles by sol-gel technology; the right picture is the silica tubes by self assembly.

Cryogenic ceramic materials

Ceramic material is comparatively a new approach. Comparing ceramics to FRPs and metals, ceramics appear to be feasible as cryogenic structural materials because they have high strength, elastic moduli and low thermal expansion coefficients, as well as low thermal conductivity and high electrical resistivity. However, the brittleness of most ceramics seems to be a significant disadvantage in engineering application. The ZrO_2 based system is suitable for gains in toughness and strength because the character is stress-induced toughening. Since the phase transformation temperature can be held significantly below room temperature by carefully controlling the chemical composition and grain size, the toughening and strengthening are able to occur at cryogenic temperatures.

Table 4 Property dada of some materials (the average values of 4-77K)

Materials	Density ρ (g/cm^3)	Strength σ (MPa)	Thermal conductivity λ(W/m.K)	σ/(ρ.λ)	K_{1c} ($MPa.m^{1/2}$)
14.5Ce-Zirconia	5.77	730	0.6	211	12
16.5Ce-Zirconia	5.69	720	0.6	211	13
50CeZTA	4.62	710	0.6	256	6.5
CFRP-T60	1.50	1050	0.15	4667	3-5
GFRP-P	2.00	978	0.29	1686	3-5
SUS 304	8.03	490	5	12	300

Experimental results obtained by researchers at Cryogenic Laboratory of TIPC, CAS, show a great increase of fracture toughness and strength from 298 to 4.2K for ceria stabilized tetragonal zirconia polycrystals (Ce-TZPs)[17], and then researchers at Japan also found similar results in yttria stabilized tetragonal zirconia polycrystals (Y-TZPs)[18]. Mechanical properties of some ceramics, steels and composites are compared in Table 4. It is clear that the ceramic materials have moderate values both on ratio of strength to thermal conductivity and fracture toughness. In fact, they have already been examined in small scale cryocoolers[5-7]. In final, we give two micrographs of ceramic materials in Figure 7.

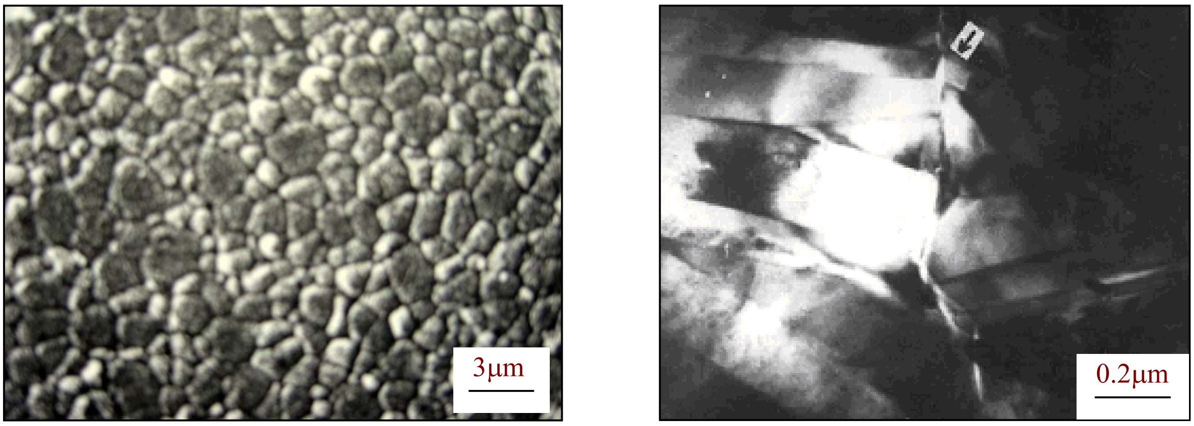


Figure 7 Micrographs of ceramics. The left one is SEM picture of the as sintered Ce-TZP ceramics. It shows high sintering density with tetragonal phase and the average grain size is about 1 micrometer. The right one is TEM picture on the fracture surface of Ce-TZP ceramics fractured at 4.2K, which shows that the crack propagation was blocked by t to m phase transformation.

SUMMARY

Among the cryogenic structural materials, metal cryogenic materials are still in a predominant position. However, how to decrease the grain size and increase the strength without change of the composition is the aim of metallic scientists. So, the developments of metal materials in the future are purification, homogenization and grain-refinement. Composites and ceramics will be prospective structural materials for cryogenic applications in the future. Anyhow, the cryogenic structure materials have to continue into a higher level.

REFERENCES

1. Hong, C.S. , "Cryogenics for China Tomorrow? --a reverie--", Proc. of ICEC 18, Mumbai, India, edited by K.G. Narayankhedkar, (2000), 59-62.
2. "Materials at low temperatures", edited by Reed, R.P. and Clark, A.F. , 1983.
3. Liu, C.L., et al, "Study on Physical and Mechanical Properties of Materials Under Hydrogen Circumstance Conditions in USSR and USA", Chin. Cryogenics, (2000), 113, 1-6
4. Ohria, K., "Research and Development Work on Liquid Hydrogen Technologies in Japan's WE-NET projects", Proc. of ICEC 19, Grenoble, France(2002), 557-562.
5. Ju, Y.L., Zhou, Y., "On the Development of Non-Metallic Non Magnetic Minature Pulse Tube Cooler", Proc. of 12th Inter. Cryocooler Conf. , Cambridge, Massachusetts, USA(2002).
6. Dang, H.Z., Ju, Y.L., Zhou, Y., "Design and Construction of a Non-metallic, Non-magnetic Miniature Pulse Tube Cooler", Proc. of ICEC 19, Grenoble, France (2002), 423-426
7. Li, L.F., Su, X.T., Gong, L.H., et al, "A Kind of Ceramics Ued at Cryogenic Temperatures", Chin. Patent, No. 03160054.9, 2003.
8. From:http://www.outokumpu.com/

9. Li, Y.Y., Chai S.S., Xu, Y.K., Qian, B.N. et al. The microstructure and properties of a cryogenic steel Fe-21Cr-6Ni-9Mn-N. Advances in Cryogenic Engineering Materials, 30, Edited by A.F.Clark and R.P.Reed, Plenum Press, New York, (1994), 237-244
10. Jiang, X.J. et al. The effect of Zn, Ag, Sc on microstructure and fracture mechanism of Al-Li alloy. Ph.D dissertation of IMR, 1993
11. In: Colour metallographic technology. Defence industry press, 1991
12. Nishijima, S. "Cryogenic Properties of Advanced Composites and their Applications", Proc. of ICEC16/ICMC, Kitakyushu, Japan, (1996), 19-26
13. Evans, D., Reed, R.P. ,"Low temperature adhesive bond strength of electrical insulation films", Adv. Cryo. Eng. (Mat.), (2000), 46A , 243-250.
14. Thostenson, E.T., Ren, Z.F., Chou, T.W., "Advances in the science and technology of carbon nanotubes and their composites: a review," Composites Science and Technology, (2001), 61, 1899-1912.
15. Shi, D., Ooij, W.J., "Uniform Deposition of Ultrathin Polymer Films on the Surface of Aluminum Nanoparticles by a Plasma Treatment," Appl. Phys. Lett, (2001) , 78, 1234 -9.
16. Zhao, L.Z., A novel toughening epoxy adhesive for cryogenic application, In: Interface of Composites, Harbin Univ. Press, Harbin, China (1997)72-77.
17. Li, L.F., Hong, C.S., Li, Y.Y. et al., "Strength and Toughness of ZrO_2-based Ceramics at Cryogenic Temperatures", Cryogenics,(1994), 34, Suppl., 469-472, and "Martensitic Transformation in ZrO_2-based Ceramics at Cryogenic Temperatures", Cryogenics, (1996), 36, 7-11.
18. Ueno, S., Nishijima, S., Nakahira, A., Sekino, T, Okada, T., Niihara, K., "Mechanical and Thermal Properties of Zirconia at Cryogenic Temperature", Proc. of ICEC16/ICMC, Kitakyushu, Japan, (1996) 2041-4.