### LOW TEMPERATURE METALS\*

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Before we consider how low temperatures affect the engineering properties of specific metals and alloys, we should review the general effects of low temperature upon the properties of metals. As the temperature is lowered, the hardness, yield strength, tensile strength, modulus of elasticity, and fatigue resistance of almost all metals and alloys increase.

Unfortunately, many engineering metals and alloys become embrittled at reduced temperatures so that structures fabricated from them fracture or shatter unexpectedly at low temperatures when loaded to stress levels at which performance would be satisfactory at normal temperatures. Brittle fracture is generally characterized by little or no deformation of the metal in the vicinity of the fracture, or by a distinctive fracture having bright crystalline appearing facets.

Considerable confusion has, unfortunately, existed about the nature of the behavior that is the opposite of brittle. Some refer to this as "ductile," while others use the term "tough." Although both terms are correct, they do not describe the same characteristic of a material's behavior.

Ductility is commonly expressed in terms of percentage elongation in gauge length, and reduction in area, of a tensile specimen that is tested to fracture. Ductility is thus a measure of the deformation undergone by a smooth test specimen of uniform cross. section that is slowly and uniaxially stressed until fracture occurs. Toughness, on the other hand, is a characteristic that permits a metal to absorb energy by undergoing plastic deformation rather than fracturing in the presence of high stress concentrations (cracks or notches) and multiaxial stress distributions, under high rates of loading, or at low temperatures.

It is possible for a metal to exhibit high ductility in a tension test, yet behave in a catastrophically brittle fashion in service at moderate temperatures; witness the plague of fractures in Liberty ships during World War II, when many ship plates broke apart with virtually no deformation anywhere near the fracture, and yet tensile test coupons removed from adjacent areas exhibited 40% elongation and 60% reduction in area.

While ductility is measured as deformation occurring in a tension test of a uniaxially loaded smooth specimen, toughness is commonly measured in terms of the energy absorbed in breaking, under impact loading, a test specimen that is notched with a circular or sharp groove on the side where fracture initiates. At a given test temperature, a metal may manifest high ductility in the tensile test and practically no toughness in a notched-bar impact test. Consequently any statement regarding the effects of low temperature upon the tendency of metal to behave in a ductile or brittle fashion must be qualified by the conditions under which the fracture is produced.

In general, metals fall into two distinct classes with respect to the influence of low temperatures upon their ductility and toughness: a relatively small class of

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metals that retain a high order of ductility and resistance to brittle fracture down to very low temperatures, and a much larger class of metals that, at some temperature or in some range of temperature, undergo a transition from ductile to brittle behavior. As pointed out above, the temperature level where this transition in fracture behavior occurs is influenced by the test conditions.

The metals that remain ductile at extreme subzero temperatures include nickel, copper, aluminum, lead and silver, among others. These metals all have a face-centered cubic crystal structure, and ductility at low temperatures appears to be a characteristic common to them. The explanation of this phenomenon is as yet obscure. Metals having a body-centered cubic structure (iron, chromium, molybdenum, tantalum, tungsten, etc.) undergo a marked decrease in ductility over a range of temperatures (upper chart of Fig. 1) and the range of transition temperatures may occur from well above boilingwater temperature to several hundred degrees below  $0^{\circ}F$ . Several common metals - for instance, magnesium, zinc, titanium and beryllium - have a hexagonal crystal structure, and these metals, except for titanium, are generally brittle or have limited ductility at room and at moderately elevated temperatures. Titanium and several of its alloys may exhibit high ductility and toughness down to very low temperatures.

The different effects of low temperatures upon the ductility of metals is explained in terms of the influence of low temperatures upon two characteristics of the metal. These are the flow strength (stress level at which plastic yielding starts) and the fracture strength (stress level at which undeformed metal fractures). Low temperatures cause an increase in both flow and fracture strengths of metal, but they may increase at characteristically different rates. In the cases of aluminum and copper, as well as other face-centered cubic metals, the fracture strength increases at a rate equal to or greater than the flow strength. Greater spreads between the flow and fracture strengths permit more deformation to occur prior to fracture; hence these metals retain or increase their ductility at low temperatures.

Iron, however, exhibits a more rapid increase in flow strength than in fracture strength as the temperature is lowered. As the spread between flow and fracture strengths decreases, less plastic deformation occurs. Finally, at some reduced temperature, fracture takes place with no plastic deformation, and the flow and fracture strengths coincide. The two charts of Fig. 1 show how the low temperature affects the ductility and flow strength of several metals.

In the metals that undergo a transition from ductile to brittle performance with decreasing temperature, it is found that a large number of factors may have a marked influence on the temperatures where this transition occurs. As discussed earlier, at a given test temperature a metal may be ductile in the tension test and brittle in an impact test.

In the case of mild steel, Fig. 2a shows the wide variations in transition temperature revealed in torsion, tensile and impact tests. Heindlhofer<sup>1</sup> explained the difference in transition behavior in the three tests in terms of the ratios between maximum principal and shearing stresses.

Other mechanical factors that influence the temperature level where brittle fracture transitions occur are geometry of test specimen, rate of load application, and the presence and sharpness of notches. Large or wide specimens, as illustrated in Fig. 2b, tend to raise the temperatures of brittle fracture because of the greater degree of restraint imposed upon the deformation capabilities of the material. Increasing the rate of load application also raises the temperature of transition from ductile to brittle behavior, as shown in Fig. 2c.

1. K. Heindlhofer, Trans. AIMME 116, 232 (1935).

Armstrong and Gagnebin<sup>2</sup> studied the effect of increasing the sharpness of notches upon the transition from ductile to brittle fracture in notched-bar impact tests. The notched-bar impact test, by combining complex stress distributions, high rates of loading and a sharp notch, provides a sensitive index of the tendency of materials to perform in a brittle fashion at extreme subzero temperatures.

In addition to crystal structure, a considerable number of metallurgical factors influence the low-temperature toughness of alloys; for example, increasing amounts of nickel up to 13% significantly raise the notched-bar impact properties of low-carbon steels (Fig. 3a). For this reason, low-carbon alloy constructional steels containing up to 9% nickel are commercially employed for cryogenic-fluid storage tanks and transport equipment. Similarly, increasing the carbon content of alloy steels lowers the toughness and raises the ductile-to-brittle transition temperature of alloy steels as shown in Fig. 3b.

Microstructure also greatly affects the low-temperature mechanical properties of alloys, especially toughness. In the case of heat-treatable low- and medium-alloy steels, heat treatment to a tempered martensitic microstructure develops the best combination of strength and toughness at subzero temperatures, with tempered bainite being less tough, and tempered pearlite still less tough, at temperatures below approximately  $50^{\circ}F$  (see Fig. 3c).

Nonmetallic inclusions, intermetallic compounds, and other impurity constituents that may form or precipitate at grain boundaries, will reduce the toughness of metals, especially at low testing temperatures.<sup>3</sup> We have determined at General Dynamics/Astronautics that impurity levels causing no apparent embrittlement in titanium alloys when tested at room temperature may cause excessive embrittlement at extreme subzero temratures.

The embrittlement effects of oxygen, nitrogen, sulfur and phosphorus in carbon and alloy steels have been long  $recognized^{4-6}$  and attempts are made to keep these impurities at low levels in quality steels intended for critical service applications.

Grain size also has a marked effect upon the toughness of metals at reduced temperatures. At any given strength level, fine-grained metals and alloys generally possess significantly higher notched-bar impact properties than coarse-grained metals. They also retain higher toughnesses down to lower testing temperatures. The effect of grain size upon the impact resistance of a heat-treated low-alloy steel is shown in Fig. 4.<sup>7</sup>

Many other factors also influence the notch-toughness of metals. Wrought products (sheet, plate, forgings, etc.) are generally tougher in the direction longitudinal to the direction of hot or cold working than in the transverse direction. However, in thick plates or forgings, the toughness in the direction through the thickness (short transverse) is often considerably reduced. Tensile ductility generally parallels this

- 2. T.N. Armstrong and A.P. Gagnebin, Trans. ASM 28, 1 (1940).
- 3. S.A. Herres and C.H. Lorig, Trans. ASM <u>40</u>, 775 (1948).
- 4. C.H. Lorig and A.R. Elsea, Trans. AFA 55, 160 (1947).
- 5. C.E. Sims and F.B. Dahle, Trans. AFA 46, 65 (1938).
- F.T. Sisco, <u>Alloys of Iron and Carbon, Vol. II, Properties</u>, p. 468 (Mc-Graw Hill, New York, 1937).
- 7. L.D. Jaffe, Trans. ASM <u>40</u>, 805 (1948).

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same behavior. Cast metals and alloys generally exhibit somewhat lower toughness than wrought products at the same strength levels, but are less prone to directional effects.

The lower toughness of cast metals is attributable to the generally coarser grain structure, segregation of alloys, intermetallic compounds and nonmetallic inclusions around grain boundaries (or around the primary solidification structure) and to casting defects. Hot working generally eliminates these casting defects, refines and homogenizes the structure and improves the ductility and toughness.

Similarly, heat treatments can drastically affect both ductility and toughness at given strength levels by changing grain size and the size, shape and distribution of phases and intermetallic compounds.

As should be evident from the preceding discussions, welding produces a cast structure and can exert a profound effect upon the ductility and toughness of metals. This is especially true at reduced temperatures. Welding introduces geometrical factors that promote brittle behavior, notches and stress concentrators. It also causes complex stress distributions resulting from weld undercutting, changes in section thickness at the weld crown on one or both surfaces, and from slag entrapment, porosity, or weld cracks. Some of the metallurgical structures thus formed may be very notchbrittle and prone to crack propagation, especially if minute flaws occur in such zones.

Another possible source of weld embrittlement is contamination by atmospheric gases in contact with the hot solid or liquid metal in the weld zone. Titanium, for example, can be severely embrittled by the absorption of oxygen and nitrogen during welding. This metal and its alloys must be welded either in vacuum or inert atmosphere chambers, or with inert atmosphere shielding applied to both sides of the weld joint when welding in air.

Steel weldments may undergo severe reductions in ductility and become prone to cracking by absorption of hydrogen resulting from the decomposition of moisture in organic electrode coatings or in the welding atmosphere. Special low-hydrogen electrode coatings have been developed for the welding of steels subjected to critical service applications. Post-welding stress-relieving heat treatments are often applied to weldments not only to relieve stresses but also to temper or to age brittle, heat-affected zones to improve their toughness.

### TESTS FOR MATERIAL SELECTION

While the standard tensile test, if conducted at sufficiently low temperatures, shows the effect of reduced temperatures upon the behavior of metals, it is not by itself sufficient or satisfactory for use in selecting materials for low-temperature. applications. As described previously, the simple, uniaxial stress distribution, absence of stress concentrators, and low rate of loading, enhance the tendency toward ductile behavior in the tension test. A number of other tests were consequently developed to evaluate the embrittlement of metals as influenced by metallurgical, mechanical, and physical conditions of the test. Practically all of these tests possessed at least two features in common: stress concentrators and multiaxial stress distributions, both of which result from notches located within the test section.

The earliest tests (between the turn of the century and World War I) generally involved impact since at that time high-speed loading was considered to be a major factor in brittle fracture. The keyhole and V-notch Charpy and the Izod impact tests are representative of the early tests used to evaluate the effects of low temperature upon the behavior of metals.

The V-notch Charpy impact test is the most widely used of the three tests and

finds extensive use to this day. Here a  $60^{\circ}$  V-notch is machined across one face of the specimen. The bar is broken by being supported at both ends and struck by a pendulum-supported weight impacting the face opposite the notch. The energy absorbed in rupturing the bar is determined by measuring the loss in kinetic energy of the pendulum.

The notched-bar impact test is generally considered to be qualitative in nature. Materials specifications incorporating notched-bar impact-test requirements have been • developed for many critical applications. Generally, requirements have been established on the basis of experience gained by correlating notched-bar impact properties with simulated or actual service behavior of full-size or scale-model structures.<sup>8,9</sup>

A group of researchers at Watertown Arsenal<sup>10</sup> has attempted to employ the V-notch Charpy impact test quantitatively in materials specifications covering low- and mediumalloy steels required for critically stressed applications at room and moderately low temperatures. The approach is based upon the equivalence of low temperature and high strain rate in causing transition from ductile to brittle fracture (Fig. 2c). From an estimation of the maximum strain rate and lowest service temperature to which an engineering structure or part will be subjected, it is possible to calculate, or pick off from a special graph the temperature at which a V-notch Charpy impact-test specimen should be tested to behave the same as regards ductile or brittle fracture as the part in question. Several Army Ordnance specifications based on this approach have since withstood the searching test of time.

While the notched-bar impact test is very useful for evaluating the toughness of forgings, plate, and bar stock, it is not applicable to very thin sheet materials such as are often employed in aerospace vehicles and airborne pressure vessels. Another type of test specimen that has been employed to evaluate the brittle-fracture tendency of heavy sections of steel, and more recently of sheet alloys, is a tensile test specimen notched on both sides. In round specimens, the notch is circumferential.

A variety of notches has been employed by various investigators, with stress concentrations ranging from 3 for mild notches to as high as 18 for severely notched specimens (ASTM and NASA standard specimens). At General Dynamics/Astronautics, we have standardized on a notched tensile-test specimen having a stress concentration factor of 6.3, since this specimen has been found to yield results that correlate with the fracture behavior of full-scale, thin-skinned cryogenic pressure vessels and with the behavior of large specimens containing complex welded joints.<sup>11,12</sup> With materials that are notch-tough, the effect of the biaxial stress distribution at the notched section is to increase the effective strength of the material, and the notched tensile strength may range from 1.0 to approximately 1.5 times the smooth tensile strength. In notch-brittle or notch-sensitive steels, the effect of the notch is to induce premature brittle fracture, and the notched tensile strength will be less than the smooth tensile strength. The ratio of the two strengths thus serves as an index of the brittle fracture characteristics of materials.

- 8. A. Hurlich, ASTM Special Tech. Publ. No. 158, p. 262 (1954).
- 9. A. Hurlich and A.F. Jones, Metal Progress 71, 65 (1957).
- 10. L.D. Jaffe et al., SAE Journal 59 (Mar. 1951).
- 11. J.F. Watson, J.L. Christian, T.T. Tanalski, and A. Hurlich, ASTM Special Tech. Publ. No. 302, p. 129 (1961).
- 12. A. Hurlich, ASTM Special Tech. Publ. No. 287, p. 215 (1960).

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More recently, with the development of the concepts of fracture mechanics, <sup>13,14</sup> it has become possible to employ notched tensile tests in a quantitative manner to determine the critical crack-extension force, the critical crack length beyond which catastrophically rapid crack propagation ensues, or the stress level where a cracklike flaw or defect will propagate to result in failure.

Other tests of importance in evaluating the mechanical properties of materials at reduced temperatures include both notched and unnotched fatigue tests, bend tests (particularly of weld joints), and notched and unnotched tensile tests of fusion weldments.

Notched and unnotched tensile fatigue, bend and impact tests can be readily performed over a range of temperatures down to the boiling point of liquid helium  $(-452^{\circ}F)$ to evaluate the effect of low temperatures upon the brittle fracture characteristics of metals. For the sake of convenience and economy, low-temperature mechanical-property tests are generally conducted at some of the following temperatures:  $-100^{\circ}F$  (dry ice and alcohol);  $-320^{\circ}F$  (liquid nitrogen); or  $-423^{\circ}F$  (liquid hydrogen).

Temperatures between room and -100°F can be achieved and maintained constant by adding appropriate amounts of dry ice to the alcohol as may be needed.

A typical test facility for conducting tensile tests at temperatures down to that of liquid hydrogen is shown in Fig. 5. The liquid hydrogen is contained in a doublewalled, vacuum-jacketed Dewar, surrounded by a liquid-nitrogen bath that in turn is insulated with polyurethane foam. Pull rods extend through Teflon-sealed holes in the bottom and top cover of the liquid-hydrogen Dewar. Hydrogen gas boil-off is vented through a flexible steel hose attached to the cover. The test equipment is located in a room fitted with a sealed sheet-steel ceiling pierced with vents fitted with explosion-proofed motors and fans to provide rapid air changes within the room. All electrical connections more than a few feet off the floor are explosion-proofed, while a sheet-steel room having positive air pressure is erected round the console of the tensile machine since the many electrical connections in this unit could not be explosionproofed. More than 15 000 tests have been performed with liquid hydrogen in this facility at General Dynamics/Astronautics since 1959 without a single serious incident.

A large outdoor liquid-hydrogen test facility is shown in Fig. 6. This installation includes a tensile-test facility (far left), larger bend and compression-test fixtures (center) fitted with double-walled vacuum-jacketed liquid-hydrogen chambers, and a cryogenic test setup for cyclic fatigue testing of the large coupons of thin materials used for cryogenic propellant storage. In all of these test fixtures, loading is applied by means of hydraulic load cells calibrated to read loads directly.

13. G.R. Irwin, Naval Res. Lab. Report 4763 (1956).

14. G.R. Irwin, J.A. Kies, and H.L. Smith, Proc. ASTM 58 (1958).

## METALS FOR CRYOGENIC APPLICATIONS

References 15 to 20 give data on a variety of low-temperature materials. A very comprehensive compilation of data on the mechanical and physical properties of a large number of metallic alloys, as well as nonmetallic materials, is included in the "Cryogenic Materials Data Handbook." This handbook was initially compiled by the Cryogenic Engineering Laboratory, National Bureau of Standards, Boulder, Colorado, but it now being kept up to date by the Martin Co., at Denver, under contract to the Aeronautical Systems Division, Air Force Systems Command, Wright-Patterson Air Force Base, Dayton, Ohio.

Typical of such data is the accompanying table of results obtained at General Dynamics/Astronautics on sheet nickel alloys.

Figure 7 lists the more important steels, aluminum, nickel, and titanium-base alloys that are suitable for critically stressed applications at reduced temperatures. It places them in order corresponding to the lowest temperatures at which they may be reliably used. This method of presentation, borrowed from J.M. Hodge,<sup>21</sup> provides a ready reference to the comparative usefulness of metallic alloys at low temperatures. It should be borne in mind, however, that high toughness is not always an essential requirement for low-temperature applications. Many parts subjected to extreme subzero temperatures are not subjected to high stresses, multiaxial stress distributions, or impact loading. Magnesium-alloy castings, which are extremely notch brittle, have served very satisfactorily as pump housings, valve bodies, and in other applications at liquid-hydrogen temperatures. The alloys listed in Fig. 7 were selected on the basis of their suitability for critically stressed applications where notches, sharp changes in section, complex stress distributions, and high rates of loading may be involved in addition to the reduced operating temperatures. Another factor that entered into their placement in Fig. 7 was consideration of the alloys' weldability, and toughness of the weld joints at reduced temperatures.

The various alloys will be briefly discussed in the following sections where the low-temperature ranges are divided into four classifications for uses down to  $-50^{\circ}$ F, to  $-150^{\circ}$ F, to  $-320^{\circ}$ F, and below  $- 320^{\circ}$ F.

<u>Metals for use to  $-50^{\circ}$ F.</u> The temperature range from ambient down to  $-50^{\circ}$ F is of interest because it essentially encompasses the minimum temperatures encountered on the earth's surface — as well as the boiling temperatures of ammonia, propane and freon, materials that are of considerable interest to the chemical processing and refrigeration industries.

Most of the standard constructional carbon steels such as the ASTM A7, A36, or A373 grades cannot be reliably used at temperatures down to  $-50^{\circ}$ F. These steels are

 M.P. Hanson, G.W. Stickley, and H.T. Richards, ASTM Special Tech. Publ. No. 287, p. 3 (1960).

16. J.F. Watson, J.L. Christian, and J. Hertz, Electro-Technology (Sept.-Nov. 1961).

17. J.L. Christian and A. Hurlich, ASD-TDR-62-258, Part II (1963).

- J.L. Christian and J.F. Watson, <u>Advances in Cryogenic Engineering</u>, Vol. 7 p. 490 (Plenum Press, New York, 1962).
- 19. J.L. Christian, ASD-TDR-62-258 (1962).

20. J.E. Campbell and L.P. Rice, ASTM Special Tech. Publ. No. 287 (1960).

21. J.M. Hodge, ASTM Special Tech. Publ. No. 302, p. 96 (1961).

not subject to notched-bar impact test requirements and may or may not be aluminumkilled to develop fine grain sizes. Their cooling rates during processing are not controlled. They may vary from tough to brittle at ambient temperatures. There are, however, several fine-grained carbon steels available for low-temperature applications down to  $-50^{\circ}F$ . These are the ASTM A334-61T, A333-61T and A420-61T grades that are required to meet  $-50^{\circ}F$  notched-bar impact-test requirements. In addition, silicon-killed fine-grained carbon steels of the ASTM A-201 and A-212 grades have good toughness properties down to  $-50^{\circ}F$ , but are not required to meet notched-bar impact tests except when specified to meet the test requirements of A-300. In the latter case, they may be and are widely used in refrigeration and transport equipment.

Quenched and tempered low-alloy steels are, of course, applicable at temperatures down to  $-50^{\circ}$ F, and many of them are suitable for use at temperatures down to  $-100^{\circ}$ F or  $-150^{\circ}$ F, but these will be discussed more fully in the next section.

Practically all aluminum and titanium alloys may be used in critically stressed applications at temperatures down to  $-50^{\circ}$ F, except for some of the highest-strength aluminum alloys such as 7178-T6 and 7075-T6. These are not recommended, especially where sharp changes in section, complex stress distributions or impact loads are involved. Similarly, the all-beta 13V-11Cr-3Al-titanium alloy (120VCA) and the 8 Mn-titanium alloy tend to be notch-brittle at moderately reduced temperatures.

Nickel and copper-base alloys are virtually all suitable for use at temperatures down to  $-50^{\circ}$ F, and generally much lower.

<u>Metals for use to  $-150^{\circ}$ F.</u> Low-alloy steels suitable for use at temperatures down to  $-150^{\circ}$ F fall into two categories: quenched and tempered steels having essentially fine-grained, tempered, martensitic microstructures, and nickel-alloyed ferritic steels. Most of the lower carbon (0.20 to 0.35% C) low-alloy steels having sufficient hardenability to achieve martensitic microstructures through the section thickness when either water- or oil-quenched are, after tempering at appropriate temperatures, sufficiently tough for most critical service applications at temperatures down to at least  $-100^{\circ}$ F. Many of these steels contain several alloying elements such as manganese, nickel, chromium, molybdenum and vanadium. Several contain small quantities of zirconium or boron, the latter having a potent effect on increasing hardenability. These steels include proprietary grades such as T-1 and N-A-XTRA, among others, as well as standard grades such as AMS 6434, 4130, 4335, etc.

Although the above steels are usable to at least  $-100^{\circ}$ F, they may, depending upon steel-making practice, tempering temperature, etc., undergo the tough-to-brittle transition at some temperature between  $-100^{\circ}$ F and  $-150^{\circ}$ F. For more reliable performance at the lower end of this temperature range, it is necessary to employ somewhat more highly alloyed quenched and tempered steels such as HY-80 or HY-TUF, both of which are proprietary steels.

Low-carbon  $3\frac{1}{2}\%$  nickel steel is widely used in large land-based storage tanks to contain liquefied gases at temperatures down to  $-150^{\circ}$ F. This steel falls under ASTM A203, Grades D and E, and is subject to impact tests in accordance with the requirements of A-300.

As shown in Fig. 7, a large number of aluminum, nickel, and titanium-base alloys are suitable for critically stressed applications at temperatures down to  $-150^{\circ}$ F and lower. The high-strength 7079-T6 aluminum alloy may be used down to  $-200^{\circ}$ F, but is not recommended for lower-temperature applications. In the case of titanium alloys, the 6A1-6V-2Sn-Ti alloy in the heat-treated condition may be used at temperatures down to  $-40^{\circ}$ F, and the 16V-2.5A1-Ti alloy may be used down to  $-100^{\circ}$ F, but neither is recommended for use at temperatures lower than these.

<u>Metals for use at -320°F.</u> Increasing the nickel content of low-carbon steel progressively reduces the temperature of transition from duetile to brittle fracture as shown in Fig. 3a. In the normalized and tempered condition, a steel with 9% nickel has a keyhole-notch Charpy impact energy of 30 ft-lb at -320°F. In the quenched and tempered condition the same steel will show 50 ft-lb impact energy at this temperature. ASTM A353-58 covers the 9% nickel grade and requires the normalized and tempered heat treatment. Revision of current pressure-vessel codes to permit quenched and tempered steel of this grade for pressure vessels will result in improved reliability of low-temperature storage tanks.

The austenitic stainless steels of the Type 300 series are all suitable for use at  $-320^{\circ}$ F, as is the heat-treatable A-286 stainless steel. Precipitation-hardenable stainless steels of the PH series are not recommended for subzero temperature applications since they evidence notch embrittlement at temperatures between  $0^{\circ}$ F and  $-40^{\circ}$ F.

The recently developed maraging steels of the 20% and 25% nickel varieties, with various amounts of cobalt, molybdenum, titanium, aluminum and columbium added, exhibit notch toughness at temperatures down to at least  $-320^{\circ}$ F, and possibly down to liquid-hydrogen temperature. The maraging steels are readily formable and weldable, and are hardened by a relatively low-temperature aging at 900°F.

A large number of aluminum alloys, including 2024-T6, 7039-T6, 2014-T6, and 5456-H343 have excellent resistance to brittle fracture at  $-320^{\circ}$ F, although weld joints in the 2014-T6 alloy tend to exhibit brittle behavior at low temperatures. Other aluminum alloys of the 5000 series aluminum-magnesium type are also tough at  $-320^{\circ}$ F and at lower temperatures, as are the 6061-T6 and 2219-T87 alloys.

Nickel-base alloys are almost all tough at -320°F, as shown in Fig. 7. Titanium alloys such as the 6A1-4V-Ti (both in the annealed and heat-treated conditions), the 8A1-2Cb-lTa-Ti, and the 5A1-2.5Sn-Ti alloys are ductile and tough at -320°F. It has been found that impurity elements such as oxygen, nitrogen and carbon, as well as iron, can embrittle these alloys at low temperatures; care should be taken to keep these impurities as low as possible in materials intended for critical applications at very low temperatures. Cooperative work at General Dynamics/Astronautics and Titanium Metals Corp. of America led to the development of the ELI (extra low impurity) grades of the 6A1-4V-Ti and 5A1-2.5Sn-Ti alloys.

<u>Metals for use below  $-320^{\circ}$ F.</u> There is a large gap between the temperature of liquid nitrogen,  $-320^{\circ}$ F, and that of the next lower-temperature liquefied gas of importance, liquid hydrogen, which boils at  $-423^{\circ}$ F. Liquid helium, boiling at  $-452^{\circ}$ F, is the only other cryogen that fills this low-temperature range. Liquid hydrogen, because of the space program, has become of wide commercial significance, and a production capacity in the tens of thousands of tons per year has been established here within the past few years.

Among the steels, only the more highly alloyed austenitic stainless steels are suitable for use at liquid-hydrogen or helium temperatures. Types 304 and 310 stainless steels fall within this classification, and the low-carbon grades of these steels are recommended, especially when welding is to be performed. There are a number of low-carbon stainless-steel casting alloys containing generally 18 to 21% chromium and 9 to 14% nickel that may be used for piping, valve bodies, flanges, etc., at -423°F or lower.

The aluminum alloys that may be safely used at liquid-hydrogen temperatures include several of the 2000 and 5000 series, as well as the 6061-T6 alloy. Weldments of the 2219-T87 alloy have demonstrated excellent resistance to brittle fracture at  $-423^{\circ}$ F, while the lower-strength 5052-H38 and 5083-1138 alloys have also showed good notch-toughness at this temperature. Monel, K-Monel, both annealed and aged, electroformed nickel, TD (thorium dispersion hardened) nickel, and heat-treatable nickel-base alloys such as Inconel X, Inconel 718, and René 41, and cold-rolled-to-strength Hastelloy B, all exhibit excellent ductility and notch toughness down to -423°F.

In titanium, only the very low interstitial unalloyed titanium, Ti45A (AMS 4902), and the 5A1-2.5Sn-Ti ELI grades are recommended for use at  $-423^{\circ}F$  or lower. Both base metal and weld joints exhibit good ductility at very low temperatures.

While the preceding discussion was confined to steel and aluminum, nickel, and titanium-base metals, other metals and alloys are used in many cryogenic-temperature applications. Copper and its alloys are used for bushings, valve components, and other parts subjected to lower temperatures. Most copper alloys retain their ductility and toughness down to very low temperatures. These include 70-30 brass, beryllium copper, and aluminum and iron-silicon bronzes. Magnesium alloys are generally a little more brittle at subzero temperatures than at room temperature, with some tendency for lower elongation at extreme subzero temperatures. As stated previously, magnesium alloys can be used in low-stress application at reduced temperature with care in design to reduce stress concentrations and multiaxial stress distributions.

# CORROSION RESISTANCE

Metals used in the chemical processing industry must often exhibit a high order of resistance to corrosion by chemicals. The higher chromium-nickel base alloys and stainless steels exhibit somewhat lower resistance to corrosion but still provide a high order of corrosion resistance. Aluminum alloys are resistant to corrosion attack by organic acids, halogenated hydrocarbons, ethers, esters, amines and ketones, and hence are widely used in the chemical processing industry. The cryogens listed in Fig. 7 are all compatible with aluminum alloys insofar as chemical attack is concerned. Nickel and nickel-base alloys also exhibit a generally high degree of corrosion resistance.

Carbon and low-alloy steels, as well as the high-nickel maraging steels, have generally poor corrosion resistance; there may be cases where, despite good mechanical properties at subzero temperatures, these alloys will be eliminated because of poor corrosion resistance.

# Mechanical Properties of Nickel Alloys at Cryogenic Temperatures

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(Tests on sheet material 0.01.5 to 0.050 in. thick. Notched specimens were double edge-notched with  $K_{\rm f}=6.3$ )

Alloy	Test Temp., °F.	Base Metal						
		Yield Point, M Psi.	Ult. Tens. Strength, M Psi.	Elong., %	Notched Ult. Tens. Strength, M Psi.	Notched/ Unnotched Ratio	Ult. Tens. Strength; M Psi.	Elong., %
K-Monel	75	97.3	154	. 22	144	0.93	141	11
(aged)	-100	107	166	24	155	0.93	154	14
	-320	120	183	30	174	0.95	170	15
	-423	136	200	28	198	0.98	190	14
Inconel 718	75	183	204	13.2	226	1.11	114	5.0
(Cold rolled and	-320	214	254	21.0	262	1.03	151	5.3
aged)	-423	228	281	22.0	286	1.02	174 .	3.5
Hastelloy	75	118	171	18.0	148	0.87	164	12.7
R-235	-100	124	184	18.3	154	0.84	154	8.0
(aged)	-320	138	189	11.7	166	0.88	181	6.7
	-423	144	188	9.0	183	<b>0.97</b> .	187	7.7
Electroformed Nickel	75	85.9	139	7.5	169	1.21		••••
	-423	109	184	15.9	216	1.17	•••	•
TD Nickel	75	58.6	79.7	12.0	89.5	1.12		
	-320	70.4	111	27.5	112	1.01	•••	
	· -423	72.9	132	31.5	125	0.95	•••	••••
Rene 41	75	131 ·	189	21.3	168	0.88	132	3.0
(aged)	-100	139	205	20.0	176	0.86	154	4.6
	-320	155	229	17.0	192	0.84	174	4.8
	-423	171	255	14.9	209	0.82	192	3.3
Hastelloy B	75	177	191	3	220	1.15	107	2
(40% cold rolled)	-100	207	222	5	245	1.10		
	320	208	228	12	265	1,16	•••	••••
	-423	240	283	16	308	1.09	145	2



Fig. 1. How temperature affects ductility (top) and yield strength (bottom) of body-centered cubic metals compared with Ni, a face-centered cubic metal.



Fig. 2. Effect of mechanical factors (a, plastic displacement; b, specimen width; and c, impact velocity) on embrittlement of ferritic steels.



Fig. 3. How chemical composition and microstructure (a, nickel; b, carbon; and c, microstructure) affect the toughness of wrought steels.





 Influence of grain size on toughness of 8640 steel, heat treated to R<sub>0</sub> 34.



Fig. 5. Indoor test facility with liquid hydrogen cooling requires careful design to avoid explosions.



Fig. 6. Outdoor test facility permits tensile, bending and fatigue testing of specimens at -423°F.



## Fig. 7. Metals suitable for use from atmospheric temperature to the lowest available are here spotted at lowest applicable temperatures.