APPENDIX 6
METALLURGICAL PHENOMENA

6-100 GENERAL

The properties of steels and nonferrous alloys are influenced by the processing history, heat treatment, melting practice, and level of residual elements.

6-200 CREEP-RUPTURE PROPERTIES OF CARBON STEELS

Previous studies suggested that carbon steel produced to a coarse austenitic grain size melting practice exhibited superior creep properties compared to those produced to a fine austenitic grain size melting practice (aluminum treated). However, studies by Glen[1] have shown that the 100,000 hr rupture strengths of steel made to either fine or coarse austenitic grain size melting practices are about the same at temperatures above 850°F. More recent studies have shown that the superiority of the "coarse grain" steels is associated with "free" nitrogen. Once the free nitrogen is removed from solid solution by precipitation, the differences in creep properties are negated. Precipitation of nitrogen may occur prior to service by heat treatment (tempering or postweld heat treatment) or by service at elevated temperatures. The amount of precipitation is dependent on both the temperature and the time at temperature.

In addition to deoxidation practice and heat treatment, the creep and creep-rupture properties of carbon steel are influenced by residual elements. For example, a small addition (0.10%) of molybdenum can markedly increase the strength of carbon steel.

Because of the superior notch toughness of normalized steel made to a fine austenitic grain size melting practice, it is often desirable to forego any possible creep strength advantage of the steels made to "coarse grain" practice. However, when considering fine austenitic grain size materials, it should be recognized that aluminum-treated steels have been shown to be more prone to graphitization than silicon-killed steels not treated with aluminum.

The existing data base for carbon steels does not permit a quantitative assessment of the various factors affecting the strength of these steels. To a large extent, the existing allowable stresses are based on service experiences rather than on individual test data.

6-300 HIGH ALLOY AND STAINLESS STEELS

6-310 STRUCTURE

The composition, mechanical working, heat treatment cycle, and the solidification rate in castings and weld metal largely determine the degree to which ferrite, carbide, and sigma phases are formed in austenitic stainless steels. The type of structure and the thermal and mechanical treatment it receives are determining factors in its resistance to intergranular corrosion, stress corrosion cracking, and crack susceptibility, and in its ductility and toughness.

6-320 INTERGRANULAR CORROSION

When austenitic steels are held for a sufficient time between 800°F and 1600°F, chromium carbide tends to precipitate preferentially at austenite grain boundaries. This type of precipitation is referred to as sensitization. Intergranular corrosion takes place when a sensitized material is exposed to a sufficiently strong corrosive medium for a long enough time.

Methods for combating intergranular corrosion include the following:

(a) An anneal at 1850°F to 2050°F followed by rapid cooling through the sensitization range. Subsequent operation of a vessel in the sensitization range may resensitize the material.

(b) Stabilizing with columbium, titanium, or tantalum. These elements have a strong affinity for carbon

[1] Glen, J., Factors Controlling the Rupture Strength of Carbon Steel, Metallurgical Developments — Carbon Steel, Iron and Steel Institute, Special Report No. 81, 1963.

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and, in sufficient quantities, prevent the precipitation of chromium carbides.

(c) Use of types of steel having a low enough carbon content that the chromium depletion at the grain boundaries is kept within safe limits.

6-330 STRESS CORROSION CRACKING

Austenitic chromium–nickel steels that are highly stressed in tension may develop transcrystalline or intercrystalline cracks when exposed to certain corrosive media. The stresses may be produced by external loads, welding or cold forming operations, or by uneven cooling. Methods of reducing susceptibility to stress corrosion cracking include the selection of a composition that will have a stable austenite structure in the operating range and heat treatment to reduce the magnitude of the residual stresses.

6-340 SIGMA PHASE EMBRITTLEMENT

The existence of sigma phase in stainless steels (austenitic, ferritic, martensitic, and austenitic–ferritic) may significantly reduce their ductility and toughness. The sigma phase is formed in the temperature range between 1050°F and 1700°F. Factors contributing to the rate of formation of sigma phase include the amount of ferrite, time in the sigma phase transformation range, prior cold working, variation in composition due to progressive solidification, high chromium content, and the presence of ferrite stabilizing elements, particularly molybdenum, columbium, and titanium. Formation of sigma phase may be minimized or prevented by a proper selection of composition, or the sigma may be transformed into austenite and ferrite by suitable heating, followed by water quenching or rapidly cooling by other means.

6-350 HEAT TREATMENT OF AUSTENITIC CHROMIUM–NICKEL STEELS

In recognition of controversial opinion relative to the effects of postweld heat treatment of austenitic stainless steels, mandatory requirements for such have been omitted. Service experience is too limited to permit comparison between the relative safety of as-welded and postweld heat treated austenitic steel weldments, particularly in thick sections. It is recognized that the stability of austenitic steels and their optimum behavior in service are influenced by the mechanical and thermal treatment they have received; however, it is a basic principle that the Code rules are intended to provide minimum safety requirements for new construction, not to cover deterioration which may occur in service as a result of corrosion, instability of the material, or unusual operating conditions such as fatigue or shock loading.

Where maximum corrosion resistance is required, it is advisable to heat treat in such a fashion as to place all chromium carbides in solution. For such service it is recommended that the following procedure be followed: hold the vessel within the solution temperature range prescribed by the governing material specifications for not less than 1 hr/in. of thickness. Quench all parts of the vessel uniformly and as rapidly as possible. Material not stabilized with columbium or titanium should be cooled through the range from 1700°F to 1000°F in not more than 3 min. The rapid cooling should be continued to below 800°F. Slower cooling rates may be just as satisfactory for some compositions of the material and conditions of service.

6-360 885°F EMBRITTLEMENT

Upon exposure to elevated temperatures, high-chromium steels and the ferrite phase of austenitic and austenitic–ferritic stainless steels are subject to embrittlement characterized by an increase in hardness and a loss in tensile ductility and toughness at and below the service temperature. The phenomenon is observed at chromium levels in excess of about 12%. The severity of embrittlement increases with increasing chromium content, the effect of which is enhanced by some alloying elements, notably aluminum, molybdenum, and tungsten, and with increasing ferrite content. While the maximum rate of embrittlement occurs at 885°F, a typical C curve time–temperature behavior is observed and some alloys with as little as 15% to 18% chromium have shown significant embrittlement with a few thousand hours exposure at temperatures as low as 500°F. Table 6-360 provides precautionary guidelines with respect to ferrite content and temperature of exposure.

6-400 NONFERROUS ALLOYS

6-410 MAGNETIC PROPERTIES

Both aluminum and copper are practically nonmagnetic, but nickel, like steel, is strongly magnetic at room temperature. The Curie temperature (the temperature at which a metal loses its magnetic properties) of nickel

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TABLE 6-360
CAUTIONARY FERRITE GUIDELINES

% Ferrite	Temperature, °F 500	600	700	800	900	1000	1100 and higher
0	...	...	...	...	...	...	C
5	...	...	...	...	...	...	C
10	...	...	...	...	C	C	C
15	...	...	...	C	C	C	C
20	...	...	C	C	C	C	C
25	...	C	C	C	C	C	C
30	...	C	C	C	C	C	C
35	C	C	C	C	C	C	C
40	C	C	C	C	C	C	C

GENERAL NOTES:
(a) C stands for caution.
(b) At the ferrite levels and temperatures identified with the letter C, the subject alloy will have significant reductions in Charpy V-notch toughness values at room temperature and below following service exposure. This reduction indicates the potential for brittle fracture with high rate loading in the presence of sharp notches or cracks.

is 680°F. Nickel–copper alloy is slightly magnetic at room temperature and has a Curie temperature of 110–140°F, depending on slight variations in copper content and other alloy elements. Nickel–chromium–iron alloy is nonmagnetic at room temperature and has a Curie temperature of −40°F. These statements suggest a simple magnetic test for differentiating the nickel alloys.

6-420 ELEVATED TEMPERATURE EFFECTS

The nonferrous alloys, in general, do not harden when quenched from an elevated temperature. The cooling rate from an elevated temperature does not usually affect mechanical properties. Heating for forming should be within temperature ranges recommended by the material producers. If the material is reannealed following hot or cold working, annealing per the material specification is recommended. Other heat treatments should be agreed upon by the user and Manufacturer.

6-430 LOW TEMPERATURE BEHAVIOR

The nonferrous alloys listed in Tables 1B and 2B do not exhibit a transition range at low temperatures as do some ferrous materials and hence do not suffer a loss of impact resistance at low temperatures. The static tensile strength increases as the temperature decreases, and the ductility as measured by percent elongation is not adversely affected to any significant degree. For these reasons low temperature impact tests of nonferrous materials are not required.

6-440 CORROSION

(a) General. The nonferrous materials listed in Tables 1B and 2B offer resistance to corrosion for many engineering applications. For specific information concerning the corrosion resistance, reference may be made to nonferrous materials producing companies and/or trade associations, as well as the following sources:

(1) National Association of Corrosion Engineers (NACE), Houston, Texas;

(2) Corrosion Data Survey-Metals, National Association of Corrosion Engineers, Texas, 1974;

(3) Process Industries Corrosion, National Association of Corrosion Engineers, Texas, 1975;

(4) Corrosion, Vols. 1 and 2, 2nd Ed., edited by L. L. Shreir, Newnes-Butterworth, London, 1976;

(5) Metals Handbook, Ninth Edition, American Society for Metals, Ohio, 1977-79;

(6) Corrosion and Oxidation of Metals, V. R. Evans, Crane-Russak Company, London, 1971;

(7) Corrosion Engineering, M. G. Fontana and N. D. Greene, McGraw-Hill, New York, 1967;

(8) The Corrosion Handbook, edited by H. H. Uhlig, John Wiley & Sons, New York, 1948.

(b) Stress Corrosion. Because of the occasionally contingent danger from the failure of pressure vessels by stress corrosion cracking, the following seems pertinent. The materials listed in Tables 1B and 2B are suitable for engineering use under a wide variety of ordinary corrosive conditions, with no particular hazard in respect to stress corrosion. However, few alloys are completely immune to stress corrosion cracking in all combinations of stress and corrosive environments and the supplier of the material should be consulted. Reference may also be made to the following sources:

(1) Stress Corrosion Cracking Control Measures, B. F. Brown, U.S. National Bureau of Standards (1977). Available from NACE, Texas.

(2) The Stress Corrosion of Metals, H. L. Logan, John Wiley & Sons, New York, 1966.

(c) Galvanic Corrosion. By virtue of their relative solution potentials, some materials are anodic to others in the presence of an electrolyte. The extent of galvanic attack will vary with the nature, concentration, and temperature of the environment, and with the inherent characteristics of the dissimilar metals and their relative

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TABLE 6-452
LIMITING SERVICE TEMPERATURE, °F

Material	Spec No.	Sulfur-Free Atmospheres			Sulfurous Atmospheres		
		Oxidizing	Reducing H_2	Reducing CO	Steam	Oxidizing	Reducing
Nickel	SB-160, SB-161, SB-162, SB-163	1900	2300	2300	800	600	500
Low-Carbon Nickel	SB-160, SB-161, SB-162, SB-163	1900	2300	2300	800	600	500
Nickel–Copper	SB-127, SB-161, SB-163, SB-164, SB-165	1000	2000	1500	700	600	500
Ni–Cr–Fe	SB-163, SB-167, SB-168	2000	2100	2100	1500	1500	1000
Ni–Fe–Cr	SB-163, SB-407, SB-408, SB-409	2000	2300	2100	1800	1500	1000

areas. Where practicable avoid dissimilar metals or select special precautions, such as insulation between dissimilar-metal parts. The use of protective coatings should be considered.

6-450 SPECIAL COMMENTS

6-451 Aluminum

Threaded Connections. Under some conditions of loading, aluminum and aluminum-alloy threaded connections seize so that repeated tightening and loosening are impossible. All threaded connections should be treated with a suitable antiseize compound.[2]

Dissimilar Metals. If dissimilar metals must be used in combination with aluminum alloys, the best choices would ordinarily be galvanized steel and stainless steel, austenitic types preferred.

6-452 Nickel

Sulfur Embrittlement. Nickel combines with sulfur at elevated temperatures to form a brittle sulfide. This phenomenon takes place preferentially at the grain boundaries, and results in embrittlement which exhibits itself as a network of cracks when the material is stressed or bent. Nickel is affected most, nickel–copper somewhat less, and nickel–chromium–iron still less. Table 6-452 lists the normal limiting service temperatures. The more sulfur present or the higher the temperature, the more rapid and deep will be the attack.

Material which has been sulfur embrittled cannot be salvaged. It must be scrapped.

Prior to any operation which involves heating to a higher temperature, such as welding, brazing, annealing, hot forming, and forging, it is imperative to remove all sulfur-containing substances, such as oil, grease, marking pencil marks, paint, and drawing or threading lubricants. In addition, the atmosphere of the furnace in which heating is done should be essentially sulfur-free. A city gas or natural gas containing less than 25 grains of sulfur per 100 cu ft or a fuel oil containing less than 0.5% sulfur will be satisfactory for heating. Coal and coke are not satisfactory.

Lead Embrittlement. Lead causes embrittlement in all nickel-base alloys in much the same manner as sulfur. Lead-containing drawing or threading lubricants must be removed prior to a heating operation. Welding must not be done adjacent to or over soft solder. “Buttering” of threads with a lead-containing antigalling compound is to be avoided if the temperature of operation will exceed 400°F or if seal welding is done.

6-453 Titanium and Zirconium

(a) Heat treatment of zirconium Grade R60705 after welding is mandatory for Section VIII, Division 1 fabrication. Heat treatment of all other titanium or zirconium alloys after welding is not mandatory, but is recommended after forming operations.

For titanium, it is recommended that heat treatment be performed in a furnace and at a metal temperature of not less than 900°F or more than 1200°F, with time at temperature of 1 hr. The stress-relieving heat treatment usually recommended is 900°F to 1100°F for $\frac{1}{2}$ hr for Grades 1, 2, 3, and 7, and 1 hr for Grade 12.

For zirconium, postweld heat treatment is mandatory for Grade R60705 (see Section VIII, Division 1, UNF-56). Heat treatment is generally recommended after forming operations for all grades of zirconium (R60702 and R60705). It is recommended that the heat treatment be performed in a furnace and at a temperature of not less than 950°F or more than 1150°F, for not less than $\frac{1}{2}$ hr/in. of thickness.

[2] Army-Navy Aeronautical Specification AN-C-53 Amend. It may be obtained from Supt. of Documents, U.S. Printing Office.

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For reactive metals such as titanium and zirconium, prolonged exposure at temperatures above 1100°F will result in heavier surface oxide films that are not satisfactorily removed by acid pickling. It is required that a descaling treatment be employed for removal of the thicker oxide film.

(b) In certain environments associated with pickling and annealing, as well as under actual operating conditions, absorption of hydrogen may cause embrittlement of titanium or zirconium.

In addition, oxide thickening will result from excessive annealing time and temperatures in oxidizing environments. In any heat treatment operation, reducing furnace atmospheres shall not be used. Suitable procedures are available from the manufacturers and other sources to minimize scaling and/or hydrogen pickup during the various steps associated with fabrication and heat treatment.

(c) Titanium or zirconium weld metal in its molten state or at elevated temperature will react readily with air. Contamination during welding by oxygen, hydrogen, and nitrogen increases the weld metal hardness and decreases the ductility and notch toughness.

(d) When zirconium is placed in rotating or sliding contact with itself or other materials, it may suffer surface damage. Galling or seizing of zirconium threaded or rotating parts can be prevented by an oxidation treatment of the finished part by heating in air at 950°F to 1150°F for 2–4 hr at temperature. If the part is required to be welded following the oxidation treatment, the oxide layer must be removed or contamination of the weld will occur.

6-460 COLD FORMING OF AUSTENITIC MATERIALS

Cold forming operations performed during the manufacture of austenitic stainless steel pressure parts may cause impaired service performance when the component operates in the creep range (above 1000°F). This impairment may entail either:

(a) recrystallization to a finer grain size, leading to an increase in creep rate and a decrease in rupture strength; or

(b) a decrease in ductility which renders the component vulnerable to premature failure from the formation of cracks, particularly at attachments and stress concentrations.

With regard to the first impairment mechanism, the major variables governing recrystallization kinetics are extent of cold work, temperature, time, and alloy composition. For a given amount of cold work, the recrystallization kinetics are broadly described by an Arrhenius type of relationship in which recrystallization occurs in a short time (minutes to hours) at a high temperature or in a long time (hundreds to thousands of hours) at a lower temperature. At forming strains below about 20%, recrystallization is not likely to occur during the service life of an austenitic steel component if the temperature is sufficiently low (about 1050°F or lower for simple alloys like TP304H or TP316H, or about 1150°F or lower for a more complex material like Alloy 800H). At a sufficiently high level of cold forming strain and service temperature, recrystallization during operation becomes a threat to the long-term serviceability of an alloy. Because of the relationship between grain size and creep-rupture strength, the finer-grained recrystallized material has lower stress-rupture strength, higher creep rate, and higher rupture ductility. The consequence is premature failure relative to an equivalent unstrained material which does not recrystallize during service. Heat treatment after cold forming at temperatures given in the material specification will restore the intended properties of the material and will minimize the threat of premature failure due to recrystallization during the time of operation.

With regard to the second impairment mechanism, as austenitic alloys are cold worked, the hardness and strength are enhanced, but the ductility is reduced. At temperatures below the creep range, this tradeoff between strength and ductility can be exploited without significant risk of service problems related to low ductility. However, as operation intrudes into the creep range, another problem besides recrystallization emerges, which involves failure due to impaired stress-rupture ductility. This phenomenon is operative below the recrystallization threshold. It is characterized by premature creep crack growth in the cold worked material and is exacerbated by the presence of stress concentrators (e.g., notches, welded attachments, etc.).

The alloys that are most susceptible to premature failure from ductility impairment are those which have been strengthened by the addition of a potent carbide former such as columbium (TP347H) or by the addition of gamma prime formers such as titanium and aluminum (Alloy 800H). Titanium is a carbide former in TP321H, but it has less effect on the ductility impairment mechanism than does columbium in TP347H. Even when solution treated, these particle-strengthened alloys are typically stronger but have less stress-rupture ductility than the simpler substitutionally strengthened alloys such as TP304H and TP316H. Failures by ductility impairment are always intergranular and occur with little or no macrodistortion of the component; i.e., there

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is no obvious necking down or swelling of the failed component.

The ductility impairment damage mechanism is not fully understood, but it is generally thought to involve deformation of the grains by cold work, followed by precipitation at intragranular dislocation sites created by the cold work during service exposure. This produces a matrix with a very high creep strength, so that most creep deformation must be accommodated at the "weaker" grain boundaries. Such strain concentration at the grain boundaries greatly increases the risk of low ductility creep-crack growth type fractures. In the most extreme cases, the rupture ductility cannot accommodate the inelastic strains associated with redistribution of the cold-forming residual stresses; fracture initiates soon after service begins and failure occurs within months or even weeks. This same phenomena has been observed in heavily constrained thick section weldments in materials such as TP347H and Alloy 800H, and has been referred to as *relaxation cracking* or *strain-induced precipitation hardening* (SIPH). As was the case with recrystallization, heat treatment after cold forming at the temperatures indicated in the material specification restores the intended properties of the material and minimizes the threat of premature failure by ductility impairment.

In adopting rules restricting cold forming, the Code recognizes that a simplified treatment has been given to a complex subject, and that application of these rules is not an absolute guarantee that premature failures will be avoided in all situations. Likewise, violation of the limits defined in the rules will not inevitably result in premature failures. Factors such as melting practice, consolidation and heat treatment practices of the material producer, initial grain size, and the presence of certain deleterious residual elements are believed to play an important role in explaining both good and bad service experiences with cold formed material. However, the rules represent a consensus achieved by parties representing disparate interests and are viewed as a step in the right direction. As with all Code rules, the limits are subject to modification and revision as new laboratory data and field experience are gathered.

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