NIOBIUM: FUTURE POSSIBILITIES – TECHNOLOGY AND THE MARKET PLACE

Friedrich Heisterkamp(1) and Tadeu Carneiro(2)

(1) Niobium Products Company GmbH, Steinstrasse 28, D-40210 Düsseldorf 1, Germany.
(2) Reference Metals Company, Inc.,1000 Old Pond Road, Bridgeville, PA 15017-0217, U.S.A.

Abstract

Although niobium is now two hundred years old, it has been only during the past four decades that it has been consumed as an industrial material. During this time, niobium has been established as part of the engineering solution in numerous cases for its own technical merits. The most important of these cases are in the field of oil and gas transportation, automotive industry, high-rise buildings, aircraft engines and medical diagnosis devices. The future will see niobium as an increasingly important technological solution in a broad spectrum of end-uses as specific niobium properties continue to be investigated. The bulk of niobium will continue to go into steel since its present position is unchallenged in the three main microalloyed steel domains (pipe, automotive and structurals). In pipe steels niobium will remain a chief microalloying element in all steel grades. In automotive steels it will remain the most important microalloying element in all hot and cold rolled HSLA steels with a good chance to penetrate the new and important group of multi-phase steels. In addition, it is expected that all thermomechanically processed high strength steels for structural components will contain niobium as the first microalloy choice in the future. With regard to the non-ferrous applications niobium will be rather used for high value-added products. There will be new opportunities for niobium in nickel-based superalloys for the automotive industry, for optimised alloys in aircraft engines, land base turbines and a variety of applications requiring improved abrasion and corrosion resistance. Examples of other areas where niobium can have its presence further developed due to economical and technological changes are electronics (electrolytic capacitors and battery alloys), medical (implant materials), photonics (thin films) and chemical (catalytic applications). Intensified research and development in these expanding and highly promising areas bears the chance of outstanding results and thus might turn into a market expansion with growth in added value rather than in added tonnage.

Introduction

The breakthrough for niobium as an industrial material came in 1933 with the development of technology to stabilize stainless steels against intergranular corrosion (1) and in the late 1950's, early 1960's with the microalloying of mild steels to enhance simultaneously strength and toughness (2). In the 1970's it also became a material of choice for several advanced technology applications. The vast majority of the metal is still used in microalloyed steels. Nickel-based superalloys constitute the second largest application of niobium.

High strength microalloyed steels are today essential for the transportation of oil and gas through pipelines from remote areas, for building lightweight automobiles thereby reducing fuel consumption, for high rise buildings and for a variety of other special steel applications. Niobium in Nickel-based alloys are the most important superalloys for a wide range of applications including aircraft engines, land-base turbines, chemical and petrochemical equipment and even automotive parts. Niobium-based alloys also have important commercial applications. Niobium-titanium and niobium-tin are present in the superconducting magnets used in Magnetic Resonance Imaging-MRI and Nuclear Magnetic Resonance-NMR devices as well as in particle accelerators. Niobium-based alloys are well established as high-temperature materials. The most important of which contains 10% Hf and 1% Ti and is currently used in rocket thrust cones, high-temperature valves and thrust augmenter flaps of turbine engines. Moreover, Niobium metal, niobium-zirconium, niobium-tantalum and titanium-niobium are currently used to resist different corrosive environments.

The future will see niobium playing an increasingly important role, because the spectrum of promising sectors that benefit from niobium and in which numerous key innovations only became possible by niobium, is extremely broad. It ranges from sophisticated multiphase steels to aeronautics and space technology, from medical usage to modern information technology. In the area of steel and its applications niobium will remain the most important microalloying element and has great opportunities to penetrate new promising sectors. In the field of "high-tech" nonferrous applications niobium will be used exclusively for high value-added products. There will be new opportunities for niobium in nickel-based superalloys for the automotive industry, for optimised alloys in aircraft engines, land base turbines and a variety of applications requiring improved abrasion and corrosion resistance. The future generation of materials for the hotter part of aircraft turbines operating at 1,300 °C will find niobium-based alloys and niobium silicides as possible candidates. In the same field, the low density Gamma-Titanium Aluminides with niobium may play an important role due to the improvement in oxidation and creep resistance. Economical and technological changes see niobium used for electrolytic capacitors, as a medical implant material with excellent biocompatibility, for thin films in optical applications, in shape memory alloys, in battery alloys and in chemicals especially for catalytic applications.

This paper covers briefly the market situation of niobium in steel as the so far most important business area, outlines the present niobium technology in steel and future aspects regarding existing niobium alloyed steels and also the development trends to preserve and expand this market segment. In the field of the "high-tech" application of niobium the state of the art for a variety of alloys and their applications will be described. Based on this, there will be areas outlined, where niobium may play an important role in the future as the element of choice for technological progress based on its own merits. Some of the most promising of such applications will be analysed in some detail. As a result of this exercise it will be explained, why intensified research and development in these expanding and highly promising areas bears the chance of outstanding results and thus might turn into a market expansion with growth in added value rather than in added tonnage.

Niobium Market

General

History considerations can be helpful to understand the past in order to make the right decisions for the future. Twenty years ago, at Niobium '81, there were two forecasts for the consumption of niobium. A realistic one predicted 3 to 3.5% p.a. (3) and an optimistic one with 8 to 10% p.a. (4). Both were wrong; as from 1980 till 2000 the niobium market grew by a very moderate 2.6%. Therefore, our considerations will outline the context between technological progress and its potential impact on the future market. In the last 20 years an optimisation process took place in steel making, rolling and alloy design, which has lead to reduced raw material consumption per ton of finished product; which means that the application of niobium microalloyed steel increased without reflection on niobium consumption. New saving potentials are coming up with thin slab casting and direct rolling.

Small additions of niobium have a substantial effect e.g. on grain refinement via retardation of austenite recrystallisation. A long-term stable price policy made niobium the reliable partner of the steel and other niobium consuming industries for research projects in all fields of possible niobium usage. These technological and economic advantages resulted in niobium being the first choice in alloy design for many application areas. In this context it is interesting to note that the technical development of new niobium containing steel products supported the striving of the steel industry to maintain or even strengthen its competitive position against competing materials in the automobile industry. The emergence of niobium as a widely used industrial metal for alloys of the aircraft and electrical industry is also directly related to outstanding results of technical development. The relative importance of the three main consuming areas of niobium is given by the ratio of its application, steel: superalloys: metal = 100: 10: 1. However, this consideration might look more favourable in the future for non-steel products in terms of added value and future potential.

Steel

The world market for niobium in steel exceeded in 1997 for the first time the level of 20,000 tons of niobium and reached in 2000 about 23,000 tons. Approximately 90% of this is consumed in the industrialised countries of Europe, North America and Japan, Figure 1, the remaining 10% by the rest of the world.

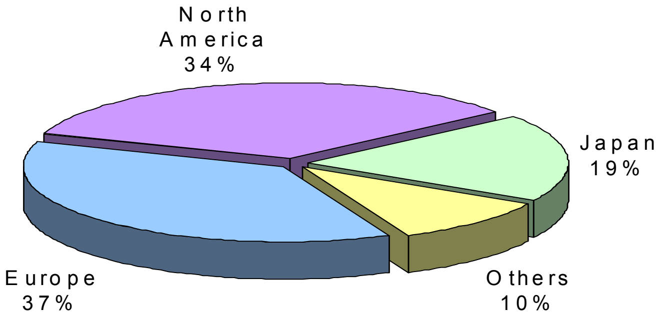


Figure 1: Niobium consumption by geographical areas.

Also the specific consumption is well over 50 g FeNb/ ton steel in the industrialised countries, substantially higher than in Russia, China and the Developing Countries with 10–20 g/t. As these latter countries increase their share of the world steel market they represent another potential growth for niobium. These emerging markets have increased already in the last 10 years by almost 50% due to the export of niobium metallurgy into them. An important precondition is the emergence of a modern steel consuming industry in these countries.

The consumption of niobium by products falls into three main areas: microalloyed steels, stainless steels and superalloys plus metal, Figure 2.

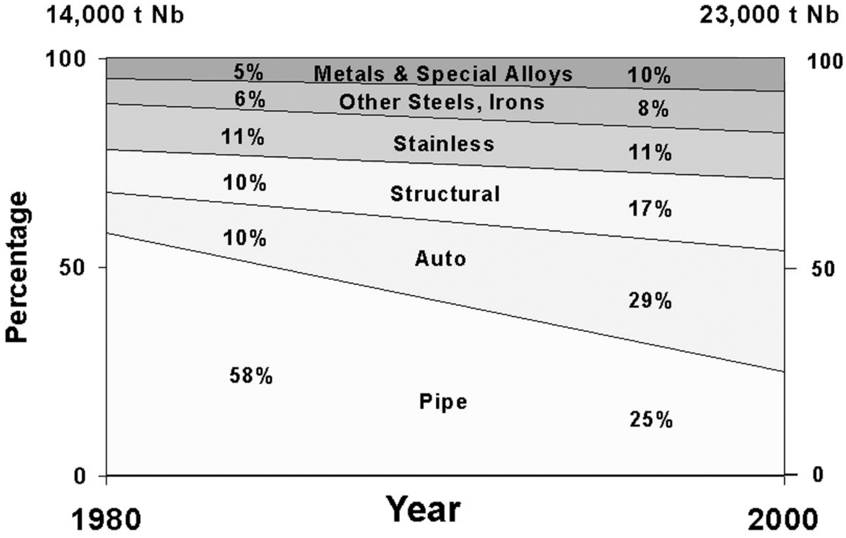


Figure 2: Niobium consumption by products.

Microalloyed steels for pipelines, automotive industry and structural applications account for about 70% of the total and thus reflect the importance of the steel producing and steel consuming industries for niobium. The application of niobium in other areas such as engineering steels, tool steels and castings reach 8%. Including the stainless grades, steel applications account for 90% of the total niobium consumption. Superalloys, metal and special oxides are responsible for the remaining 10%, but with higher value added products. Figure 2 shows also that over the last 20 years this consumption pattern has changed substantially towards increased diversification. In those days, the dependence of niobium on steel amounted to 95%, and almost 60% of the total niobium would be consumed in pipe steels, making the market very volatile and strongly dependent of pipeline projects. Extensive research in all steel areas has lead to the present diversification with niobium steels for the automotive industry now being the main consuming area. Even though the share for pipe dropped to 25%, the total tonnage remained rather high, because the total niobium market grew substantially within this period of time. Also, structural steel applications became increasingly important for niobium.

Superalloys and Metal

The market for this important segment of the niobium business doubled between 1980 and 2000 from about 1,100 tons Nb to 2,300 tons. The most important driver for the growth was the aircraft industry. The motivation to cut back on the widely used cobalt containing superalloys in the 1960's and early 1970's led to the development and consumption of nickel based alloys, which made use of the group V B and VI B elements, e.g. niobium, as a precipitation strengthener of coherent phases and carbides and as a solid solution strengthener in a lesser extent. In addition, for decades niobium metal and alloys have been used in industry for a variety of applications based on its corrosion resistance and high temperature properties. Due to the highest critical temperature of all superconducting metals and its ease of processability, NbTi and Nb_3Sn became the only commercially relevant alloys for technical superconductors, which resulted in the further enhancement of the importance of niobium as a technical choice. Besides the regular MRI and NMR business the metal market depends to a great extent on projects associated with particle physics of DESY, CERN and other Research Institutes. Pure niobium also has a good market prospect for superconducting RF cavities in linear accelerators.

The following chapters discuss the state of the art technology and application of the main niobium containing products. The impact of technological development on the future market of these products and thus on niobium is also examined.

Pipe Steels

General

According to energy analysts the transportation of oil and gas from remote areas will become increasingly important in the coming decades in order to meet the expected growth in energy consumption. As in the past, and also in the foreseeable future, pipelines will serve as the most economic method of transportation for oil and gas, Figure 3.

Figure 3: X80 pipeline construction in Germany. Courtesy of Europipe.

Over the last few decades the operating pressure of pipelines has been increased to 120bar, thus raising the throughput at a constant pipe diameter by 50%, Table I. Increased pressure requires a thicker wall for a given steel grade, which results in a higher pipe weight. With pipe material of higher yield strength the wall thickness and thus the pipe weight can be reduced substantially. The economic benefits include lower steel consumption, lower welding and transportation costs. With the forthcoming exploitation of oil and gas fields in deep water and with the transportation of gas through deep sea, like the considerations for an Oman-India line, a new type of heavy wall pipe in excess of 40 mm will be required, which has little in common with present pipe steels (5). In the future, even higher pipe diameters of up to 1620 mm do not seem to be impossible.

Table I Trend in operating pressure, pipe diameter and gas throughput

Year	**Operating pressure** in bar	**Diameter** in mm	**Annual capacity** in million m^3
1930	20	500	650
1965	66	900	8,300
1980	80	1,420	26,000
2000	120	1,420	39,000
2020	120	1,620 ?	50,700

Alloy Design and Properties of Pipe Steel Grades

The currently available pipe steels can meet the necessary requirements for all known applications. The progress of the last 20 years in pipe steel development and production became possible due to the enormous achievements made in steel and plate making technology in combination with niobium metallurgy and thermomechanical rolling. As a result of the retardation of recrystallisation by niobium during hot rolling, an enhanced grain refinement can be achieved, whereby strength and low temperature toughness are improved simultaneously. This rolling process can be combined with accelerated cooling, which adds further to grain refinement as a result of the austenite-ferrite transformation taking place at a lower temperature. Due to these strengthening mechanisms the carbon content can be reduced and thus weldability and upper shelf impact energy noticeably improved. The ductility and the resistance against hydrogen induced cracking of pipe material are strongly dependent upon the cleanness of steel, i.e. a low volume fraction of sulphides and oxides, preferably in globular form. Modern steelmaking achieves this even in mass production. The development in the field of high strength pipe steels over the last few decades is summarised in Figure 4, indicating the importance of grain refinement.

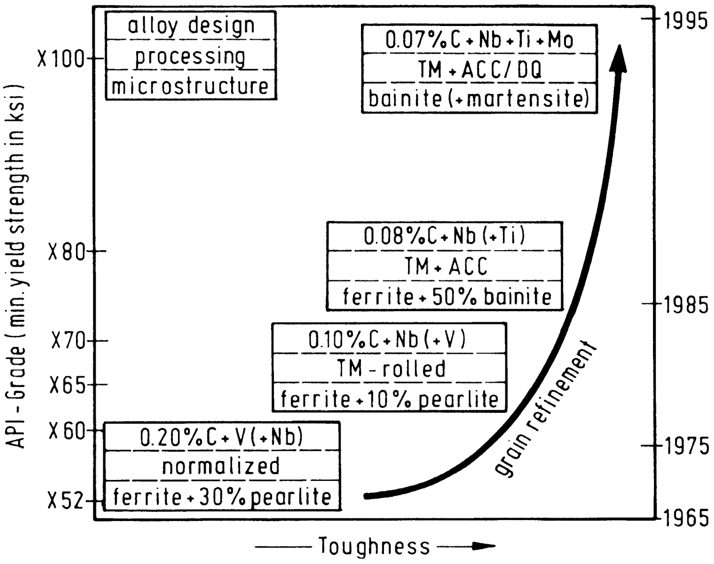


Figure 4: Development of pipe steels over the years.

The improved knowledge of the relationship between processing-microstructure-properties allowed improvements of rolling schedules leading to leaner compositions. The work horse of steel for pipelines until today is the standard grade X70, initially a low carbon-manganese-niobium-vanadium steel with 0.10% C, 1.55% Mn, 0.007% S, 0.03% Nb and 0.05% V for 15-20 mm wall thickness. However, due to the high price of vanadium this alloy design was changed and the precipitation hardening effect of vanadium-carbonitride was replaced by dislocation strengthening. In the 1990's grade X70 was further improved by a reduction in carbon content to about 0.08% and sulphur content below 0.005%. At the same strength level an increase of impact toughness was achieved. Accelerated cooling after rolling, with cooling rates of 15 to 20°C/s, and a cooling stop temperature of approximately 550°C, led to new possibilities for X70 and higher strength pipe steels such as X80. A typical X70 has a microstructure of ferrite with a certain amount of bainite after accelerated cooling. In order to increase the strength towards X80, without impairing the toughness, a higher volume fraction of bainite is aimed for by increasing the hardenability, i.e. by adding more manganese or, if need be, molybdenum or nickel. The effect of niobium on austenite conditioning and transformation is improved by stoichiometric titanium additions to fix nitrogen.

Based on this concept several X80 pipeline projects have been carried out so far and due to the economic and technical advantages this grade might become the pipeline steel for the coming decades. However, this is still not the end. In order to further increase the strength above the X80 level a fully bainitic microstructure has been aimed for. At a cooling rate of about 20°C/s the microstructure of a low C-Mn-Mo-Ni alloyed steel consists of 100% fine bainite, even if thermomechanical rolling with a finish rolling temperature in the metastable austenite region and a cooling stop temperature of approximately 500°C has been applied. The strength level of such steels is X100. With the introduction of higher cooling rates of e.g. >35°C/s the desired microstructure can be achieved with a leaner alloy (6).

Increasing strength is not the only driving force for pipe steel development. In recent years new gas deposits with high contents of sour constituents have come on stream. This requires steels with resistance against hydrogen induced cracking (HIC). The majority of these pipe steels are restricted to the X65 strength level and the pipes are of rather heavy wall. For good HIC resistant steel, sulphur levels below 10ppm and sulphide shape control are prerequisites. Any formation of banded pearlite has to be avoided and can be suppressed by accelerated cooling during transformation. In order to achieve a very homogeneous microstructure, carbon contents below 0.05% together with limited manganese levels are common. For special applications, in a very corrosive environment, high strength, high toughness clad pipe is used. In order to achieve the required corrosion resistance of high alloy austenitic material, finish rolling of the pipe plate at temperature above 800°C followed by accelerated cooling is necessary. For such special applications, also as an alternative for standard X70/X80 alloy design, a new concept has been developed. Reducing the carbon content in the steel to approximately 0.03 percent will reduce segregation and result in further improvement of toughness, ductility and weldability. Such low carbon content permits the solution of higher niobium content than those traditionally experienced. With a higher niobium content austenite processing can be undertaken at higher rolling temperatures. Additional strength increase is observed by niobium's role in retarding the transformation to ferrite, thus promoting a higher volume fraction of bainite, and by forming NbC precipitates in ferrite. This concept is ideally suited to produce high strength via accelerated cooling or X65/X70 strength levels at finish rolling temperatures around 800/850°C necessary for HIC and clad pipe properties (7).

Future Trends

Given this favourable scenario for niobium the question then arises, how the future for niobium in pipe steels will look like? In particular, in view of technological trends, Table II.

This table reveals, importantly that there is no relevant information known, yet, which indicate that the existing pipe steels from grade X52 to standard X70 will be replaced by non niobium containing steels. On the contrary, it is fair to assume that in the future niobium will remain the first and most important microalloying element. Increasing operating pressure requires a thicker wall for a given steel grade, or the application of X80, or even X100. Higher strengths and/or higher wall thickness generally requires increased niobium additions to pipe steels. Based on observation in the 1960's of long running brittle cracks, the Batelle Drop Weight Tear Test-BDWT test was developed and is now a standard for gas lines. A typical acceptance criterion is 85 % shear fracture at –20 C. With the tendency towards higher pressures and larger pipe diameters the stored energy increases substantially causing the danger of long running ductile cracks. It turns out that an "in-body-arrest" of such cracks can only be achieved, if the pipe body has minimum impact energy. Both, resistance against brittle failure and against unstable ductile fracture can be met only by thermomechanically treated niobium microalloyed steels with a fine ferritic or even better, with an ultra-fine low carbon bainitic microstructure. For the latter requirement one needs in addition high cleanness, i.e. low sulphur content and sulphide shape control. The tendency towards HIC resistant pipes is also favourable for niobium, because they generally have a higher wall thickness and require relaxed rolling schedules to avoid any banded microstructure. For a very corrosive environment, as mentioned before, clad pipe is applied. The necessary high finish rolling temperature to obtain the desired microstructure in the austenitic clad material is also advantageous for niobium. The overall conclusion is that the position of niobium in pipe steels is unchallenged and growing due to technological developments.

Table II Technological progress and the future of niobium in pipe steels

Grade	**Alloy design**	**Average Nb content (%)**	**Application**	**Future production**	**Probability of future Nb application**
X52 – X65	0.08C-Nb, (+V)	0.02 – 0.05	Standard	+++	+++
X70	0.08C-Nb, (+V) or dislocations	0.03	Standard	+++	+++
X80	0.08C, Nb (+Ti) TM + ACC	0.045	For increased pressure or reduced wall thickness	++ *increasing*	+++
X100	0.07C, Nb+Ti+Mo TM + ACC (DQ)	0.05	Possible; depends on in-body-arrest behaviour	+ *if applied*	+++ *if applied*
X65 HIC resistant	0.04C, Nb, V	0.045 – 0.09	Sour media transportation	++ *increasing*	+++
Clad pipe	0.04C, Nb, V	0.08	Highly corrosive environment	+	+++

low: +, medium: ++, high: +++

Automotive Steels

General

The automotive Industry has always been one of the most important users of a variety of hot and cold rolled steel products. The urgent need for fuel efficiency, safety considerations and improved corrosion resistance has been the major driving forces in the development of new automobiles. The trend to light weight vehicles became a special requirement and its continuation can be expected especially in newly designed models. The search for new materials brought up serious competition for steel. This was the beginning of an unprecedented development of new steels by the steel industry, a new attitude of the automotive industry towards the application of new materials and a chance for niobium to foster its position in current automotive steels and find its way into new ones. Hot and cold rolled high strength steels with niobium were developed in the 1970's. Whereas hot rolled material has been basically used in the manufacturing of trucks, it gradually became increasingly applied for automotive under-body components; which require good press formability and ductility as well as acceptable surface appearance despite being hidden away. Cold formable high strength steels had its breakthrough into passenger cars as the main material with the introduction of new and stringent requirements. The use of some of these high strength low alloy steels together with modern fabrication techniques like hydroforming and laser welding was, some years ago, investigated through the initiative of the Ultra-Light-Steel-Auto-Body-Advanced-Vehicle-Concept and provided an insight into the growing use, demand and requirements of high strength strip steels destined for automotive markets. Figure 5 shows a break down of the materials used in the ULSAB development program, of which 46% are high strength (8).

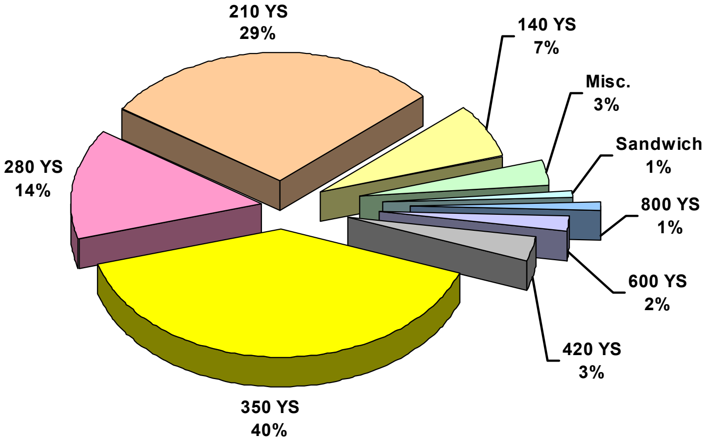


Figure 5: Material strength used in the ULSAB structure.

Hot Rolled Steels (9)

Microalloyed Steels. This type of material applies grain refinement and precipitation hardening as the most commonly used strengthening mechanisms achieved in the hot rolled condition. Its field of usage is growing, because of the rapid growth of mini-mill technology over the last decade, which has lead to the encroachment of hot rolled grades into cold rolled territory. Hot rolled microalloyed high strength strip has successfully been produced to gauges of 1.4mm and have the potential to reach gauges as low as 0.8mm. Examples of the chemical composition and related mechanical properties for commercially available modern Nb-bearing high strength strip steel grades destined for cold forming applications are given in Table III.

Table III Alloy design and guaranteed properties for commercially available high strength hot rolled strip steel

Grade	Chemical composition (%)				Mechanical properties		
	C	Mn	Al	Nb	Y.S. (MPa)	T.S. (MPa)	El. (%)
350	0.06	0.60	0.04	0.025	350	430	26
400	0.06	0.70	0.04	0.030	400	460	22
420	0.06	0.80	0.04	0.030	420	460	20
450	0.06	1.00	0.04	0.035	450	500	18
500	0.07	1.35	0.04	0.040	500	550	15
700 *	0.07	1.35	0.04	0.050	700	750	15

* V or Ti and Mo/B additions

All these steels are based on a low C-Mn concept with niobium as the first and main microalloying element, because of its ability to act simultaneously as a grain refiner and a precipitation hardener. Niobium additions up to levels of 0.06% will generate yield strengths of up to 500MPa. For higher strength and heavier strip gauges, above 6mm, niobium must be supplemented with additions of titanium or vanadium.

All strip steels for cold forming applications are required to possess good levels of formability, even if the bend axis is parallel to the rolling direction of the strip. Therefore, low oxygen and sulphur levels are a prerequisite including sulphide shape control by calcium. Modern hot strip mills provide excellent process control to minimize scatter of mechanical properties over the width and the length of a hot strip, which minimizes problems, e.g. spring back, during the production of automotive parts. The application of accelerated cooling on the run out table promotes further grain refinement. From the CCT diagram of a given grade the mechanical properties can be tailored according to the cooling strategy employed by exploiting the highly conditioned structure rich in ferrite nucleation sites. If the accelerated cooling exceeds a critical level, low temperature transformation products are obtained, which means that for a given steel composition the strength level of thin strip grades can be made on the run out table.

Multiphase Steels. This is another group of high strength steels for hot rolled strip products, whose strength increase does not depend on grain refinement and precipitation hardening, as in the microalloyed steels, but on the development of a fraction of a hard phase, e.g. martensite, in a ductile ferritic matrix. As a result they show excellent mechanical properties, in particular low initial yield strength, continuous yielding, high tensile strength, a high work hardening rate and an excellent uniform elongation. Only in the last decade has this family of steels developed into industrial products as a result of the ULSAB project.

Dual Phase-DP steels are manufactured as hot and cold rolled strip. The actual DP microstructure is obtained by cooling the steel from the intercritical range at a sufficient rate for the transformation of austenite to martensite to take place. The average DP steel composition contains about 0.1%C, 1-1.5%Mn, 0.1-0.5%Si, 0-1.2%Al, in certain cases also chromium, but has no niobium. The higher silicon and manganese levels promote ferrite transformation. Thus, the chemical composition of the steel is of paramount importance in not only determining the start of the austenite transformation but also the hardenability of the austenite phase. A typical DP microstructure consists of up to 80% ferrite and 20% martensite. As in microalloyed strip the mechanical properties are developed via a sophisticated cooling strategy on the run out table.

Recent developments have highlighted the positive aspects of small additions of niobium to conventional DP steels (10, 11), where the addition of niobium permitted a degree of deformation to take place below the recrystallisation stop temperature. This enhances the ferrite nucleation potential and means that a continuous cooling strategy can be applied. For an identical base composition, the addition of niobium resulted in a significant strength increase of almost 100MPa. The use of 0.030%Nb addition with heavy strain accumulation, aiming at metadynamic recrystallisation, develops a fine-grained DP steel (11). Moreover, conventional DP steels are very demanding of the hot strip mill, because very low coiling temperatures, as low as 250°C, are required to obtain martensitic phase. Furthermore, the introduction of a specific volume fraction of bainite besides martensite will enhance the ductility without significantly lowering the tensile strength (12). These steels, although exhibiting DP characteristics, are termed tri-phase steels. The required coiling temperature of 450°C is by far less demanding and the addition of niobium is seen to enhance both the strength and ductility as a result of a fine-grained structure.

Transformation Induced Plasticity-TRIP steel is another member of this family. The outstanding properties, a combination of high strength with excellent formability, are attained via the deformation-induced transformation of metastable austenite into martensite. Thus, the stability of retained austenite is crucial to enhance the TRIP phenomenon. Carbon is the crucial element in this type of steel to stabilise the retained austenite. The necessary carbon enrichment in the austenite and the prevention of iron carbides are achieved by the addition of elements such as silicon or aluminium at higher than normal levels. The average TRIP composition is as follows: 0.2%C, 0.3-1.5%Si and 1.0-1.5%Al. Originally, TRIP steels have been developed without niobium additions. However, it has been experienced that a small amount of niobium enables processing to proceed below the recrystallisation stop temperature. The fine elongated austenite grains will tend to accelerate the ferrite transformation at the grain boundaries resulting in the concentration of carbon to austenite (13). This will, in turn, increase the volume fraction of retained austenite whilst also leading to quicker stabilisation of austenite. It has also been reported that niobium additions will tend to deter the precipitation of cementite in bainite, which is further favourable to concentrate carbon in austenite (14). The presence of stable retained austenite naturally will enable the TRIP phenomenon to take place at a later stage of plastic deformation, and thus giving excellent elongation values at the higher tensile strength, where ductility becomes paramount. Like DP steels, the production of hot rolled TRIP steel is demanding for a hot strip mill and requires an optimum three stage cooling strategy with an intermediate temperature to promote ferrite nucleation and growth. The holding and subsequent cooling below 500°C is not only crucial to the carbon enrichment of austenite, but to its volume fraction and the stability of the retained austenite.

Cold Rolled Steels.

Microalloyed Sheet. Steels with higher yield stress than 280MPa, predominantly over 340MPa, for car body structural parts are in the domain of microalloyed steels and the volume fraction of this type can be as high as 20% of the total weight of the body-in-white. The metallurgical concept of cold rolled microalloyed sheet steels is based on microalloyed hot strip with niobium as the main microalloying element and the additional processing steps of cold deformation followed by annealing. The role of microalloying elements in cold rolled sheet is similar as that in hot strip. Due to the annealing process after cold rolling, the strength is substantially lower than in the hot strip of the same chemical composition. For strength levels above 350MPa the combination of niobium plus titanium is often applied with higher additions of solid solution hardening elements. Microalloyed cold rolled sheet can be processed by batch annealing or on a continuous annealing line; the latter giving a higher strength, and thus presenting the possibility of a leaner composition.

Interstitial Free-IF Steel. These steels have been known for decades; they became important with the introduction of continuous annealing lines, continuous hot dip galvanising and other metal coating lines. Steels processed on such lines exhibit a reduced formability in deep drawing and stretch forming. To counteract this disadvantage, very often IF steels with inherent better cold forming properties than conventional batch annealed deep drawing qualities are used. Modern steel making achieves carbon and nitrogen levels typically below 30ppm C and 40ppm N in mass production. In order to achieve an IF steel, the remaining C and N atoms have to be fixed by elements, which form stable carbides and nitrides like titanium or niobium. The precipitation behaviour of titanium is rather complex due to its reaction with C, N, and S and the resulting formation of Titanium-carbosulphides. Therefore, titanium stabilised IF steel may exhibit several disadvantages, e.g. surface defects, powdering in galvannealed sheet, outburst phenomena and a poorer adhesion of the zinc layer in galvanised sheet; moreover, titanium-only stabilisation has a negative effect on deep drawability and spot weldability as well. Dual stabilising with titanium and niobium overcomes these problems and therefore this alloy design has become increasingly important. A typical dual stabilized IF steel of the given interstitial level contains titanium plus niobium - around 0.015% Ti, stoichiometric to nitrogen and 0.020% Nb, stoichiometric to carbon.

High strength IF steel with a high Lankford value and strain hardening values are niobium only stabilised. This generates a finer grain size, hence a higher yield strength. Moreover, in rephosphorised IF steel grades the strength increase by phosphorus is much higher in the presence of Nb than of Ti (15). In addition, the continuous annealing of Nb containing IF steels can be performed in a way as to partially dissolve Nb to generate a bake hardening-BH effect during painting. The extra strength increases after forming and paint baking at 170°C / 20 min is around 50MPa and as high as in normal BH steels (16).

Multi phase steels. Cold rolled DP steels have a microstructure of 5 to 30% martensite embedded in polygonal ferrite and are produced on continuous annealing lines applying a slightly higher annealing temperature into the two phase region to get the desired austenite content, which will transform into martensite after fast cooling. Due to their poor Lankford value of around 1.0, like microalloyed steels, their application is limited to bending and stretching, but not to deep drawing. Like in hot strip, the DP steels have been originally developed without niobium additions. However, it has been demonstrated that an alloy design of DP steel involving niobium microalloying generates grain refinement with a resulting improvement of ductility. In addition, continuous cooling instead of a holding period after finish rolling can be applied to maximize ferrite formation. This favourable microstructure is transmitted to the microstructure of the cold rolled and annealed material, giving improved strength and ductility. Even though the sheet material exhibits yield strength of only 550MPa, the characteristic high work hardening coefficient of the dual phase steel results in an enormous yield strength increase during the forming operation, and the final product after bake hardening shows a yield strength as high as 800MPa. In this context it should be mentioned that both types of high strength sheet, the microalloyed and the dual phase steel, exhibit a higher strength in the cold formed and painted material than in the recrystallised annealed condition. This yield strength gain derives from work hardening plus a certain BH effect.

Cold rolled TRIP steels have a relatively high C-content and even higher amounts of Mn and Si than the DP steels (17). Their microstructure exhibits a certain percentage of retained austenite, which is stable at room temperature because of the enrichment by carbon. Due to the positive experience with niobium in dual phase steels, TRIP steels have also been investigated in their response to niobium microalloying. A positive effect might derive from the preservation of austenite at room temperature and from improved carbon enrichment of the austenite, mandatory for austenite stabilisation (13). These steels are produced via a two-step heat treatment. The TRIP effect guarantees an outstanding high uniform elongation, deriving from the transformation of the retained austenite during the cold forming operation into martensite, which is correlated with an additional dilatation. The addition of niobium results in a fine-grained microstructure, causing a yield strength increase of about 15MPa per 0.01% Nb. As expected, the volume fraction of retained austenite increases with higher niobium additions and these higher values are obtained in a much wider field of annealing conditions during the second heat treatment (18).

Figure 6 gives an overview of the various cold rolled high strength steels and their ductility (19).

<u>Future Trends.</u> Conventional microalloyed high strength hot rolled steel grades with strength levels from 350 to 800MPa are well established in the automotive industry. For their production niobium is the microalloying element of first choice. The cold formability of these steels is paramount, especially for the automotive industry. Even for tensile strength levels above 500MPa microalloyed HSLA steels are quite acceptable for a wide range of applications. However, for applications requiring superior formability, hot and cold rolled dual-phase steels are now widely available. For the optimisation of these steels it has been established that microalloying with niobium further improves the mechanical properties, especially through refinement of the microstructure. This not only generates higher tensile properties, but the ductility is further improved resulting in an exponential increase in the characteristic product of tensile strength and elongation with higher niobium levels. TRIP steels are likely to be a new candidate for the automotive industry. Similar to DP steels niobium also improves the properties of this material. Consequently, optimised multiphase steels are also increasingly relying upon microalloying with niobium.

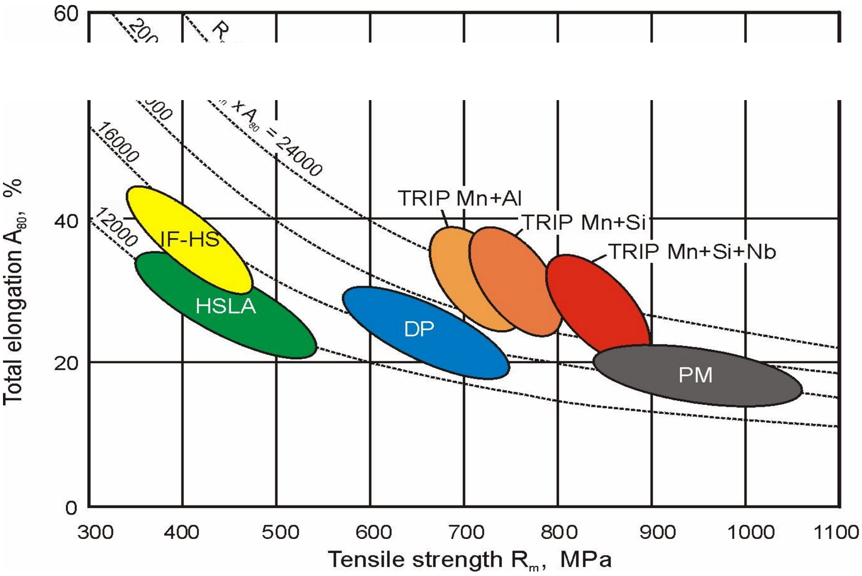


Figure 6: Ductility-strength relationship of cold rolled steels.

Regarding the various IF steel grades, it is very likely that those grades, which do not yet contain niobium additions, will do so in the future, table IV.

Table IV Technological progress and the future of niobium in automotive steels

Steels	Alloy design	Average Nb content (%)	Future production	Probability of future Nb application
a) Hot rolled				
HSLA, Re up to 1000MPa	Low C-Mn-Nb (Ti, V) *	0.025 – 0.06	+++	+++
DP, Rm up to 1200MPa	C-Mn-Si (Al, Nb)	0.04	+++	+
TRIP, Rm up to 1200MPa	C-Mn-Si (Al, Nb)	0.04	+	+
b) Cold rolled				
IF	30ppm C, N-Ti, (Nb)	0.025	+++	+
IF, galvannealed	30ppm C, N-Nb	0.025	++	+++
IF, BH	30ppm C, N-Ti, (Nb)	0.025	++	+
IF, high strength	30ppm C-Nb	0.05	++	+++
HSLA up to 600MPa	Low C-Mn-Nb (Ti)	0.025 – 0.06	+++	+++
DP up to 1000MPa	C-Mn-Si (Al, Nb)	0.04	+++	+
TRIP up to 1000MPa	C-Mn-Si (Al, Nb)	0.04	++	+

* Plus Mo, Ni, B for Re >500MPa. Low: +, medium: ++, high: +++

A continuation in the trend towards high strength steel for the automotive industry can be expected in the future, because it allows remarkable weight savings. The increasing use of tailored blanks, Figure 7, is supporting this trend, because it allows HSLA steel sheets to be put into places, where a high strength is required and low formability can be tolerated.

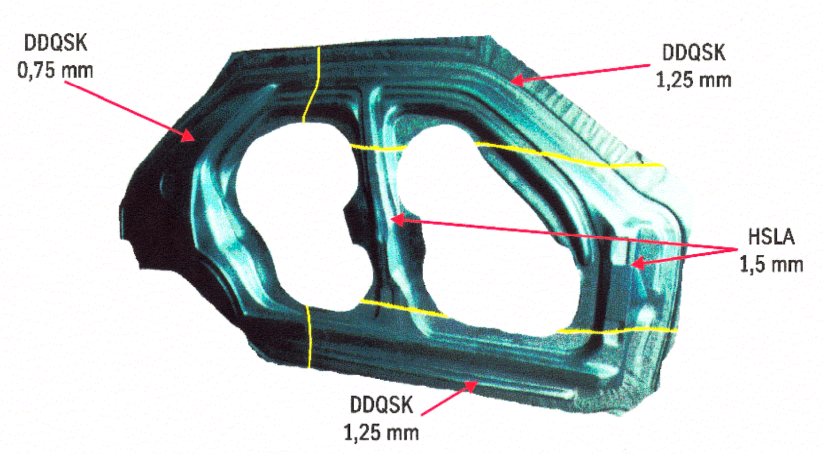


Figure 7: Tailored blanks made of different steel grades and thicknesses.

Steels for Welded Constructions

General

For many years in Europe there was a preference for concrete rather than steel constructions. This has started to change over the last two decades for specific types of constructions, with the result of high strength steels being increasingly applied. The advantages are obvious: by applying such steels a reduction in material thickness and thus in weight can be achieved, in particular under uniaxial loading. Furthermore, the lower weight reduces transportation and handling costs and economises welding due to the reduction in weld metal volume. A prerequisite is the ductile behaviour of the construction at operating temperature with a ductility level withstanding any crack propagation. Therefore, the safety analysis of steel constructions of the European design code is based on fracture mechanics.

Alloy Design and Processing Route

At present, the bulk of high strength structural steel grades applied are S 355 and S 460 in the normalized and thermomechanically treated condition, whereby the latter can be additionally accelerated cooled or direct quenched-DQ. The base compositions in table V show various carbon-manganese steels with niobium as the first microalloying element of choice and standard sulphur content below 40ppm. Due to this low sulphur level, the amount of non-metallic inclusions is very low and the ductility, in particular, in through thickness direction of rolled steel has been drastically improved, making “lamellar tearing” a rare event. Most of the modern HSLA steels are pearlite reduced or even pearlite free steels. Their rolling process is in fact a conditioning of the recrystallized austenite grain, which after transformation gives a good refinement of the ferrite grain. This processing route is called recrystallisation controlled rolling and it is used for non-severe requirements of low temperature toughness. Recrystallisation controlled rolling is included as the first stage in the thermomechanical rolling process. The characteristic step of this process is a certain degree of deformation below the temperature of austenite recrystallisation, which is retarded by niobium additions. This results, under practical rolling conditions, in a heavily deformed elongated austenite grain with a high amount of nucleation sites, which leads after transformation to a much finer ferrite grain size than in normalized steels and consequently to higher strength and toughness.

Table V Examples of base composition, 50 mm plate thickness

Steel grade	S 355 N	S 355 TM	S 460 N	S 460 QT	S 460 TMCP	S 460 TMDQ
% C	0.15	0.07	0.15	0.10	0.07	0.06
% Si	0.40	0.30	0.40	0.35	0.25	0.30
% Mn	1.50	1.50	1.50	1.45	1.55	1.50
% Cu	none	none	0.60	0.30	none	none
% Ni	none	none	0.60	0.60	0.25	none
% Nb	0.03	0.02	0.03	0.025	0.02	0.02

Modern plate mills and some profile mills often have equipment for accelerated cooling. Recently, some companies have even installed direct quenching devices. Higher cooling rates offer the possibility to further increase the strength in low carbon steel or allow a reduction in the amount of carbon and other alloying elements for the steel whilst achieving the same strength level. A comparison of the chemical composition between the normalised, respectively quenched and tempered steels and the thermomechanically rolled steels, eventually in combination with accelerated cooling or direct quenching, shows a reduced carbon content and a low carbon equivalent of the latter steels. The preheating necessary to guarantee crack free weldments can be reduced or even avoided in such steels, resulting in a remarkable cost saving in the total steel construction, Figure 8. For girders and wide flange beams the same basic metallurgical and economic considerations apply as for plates.

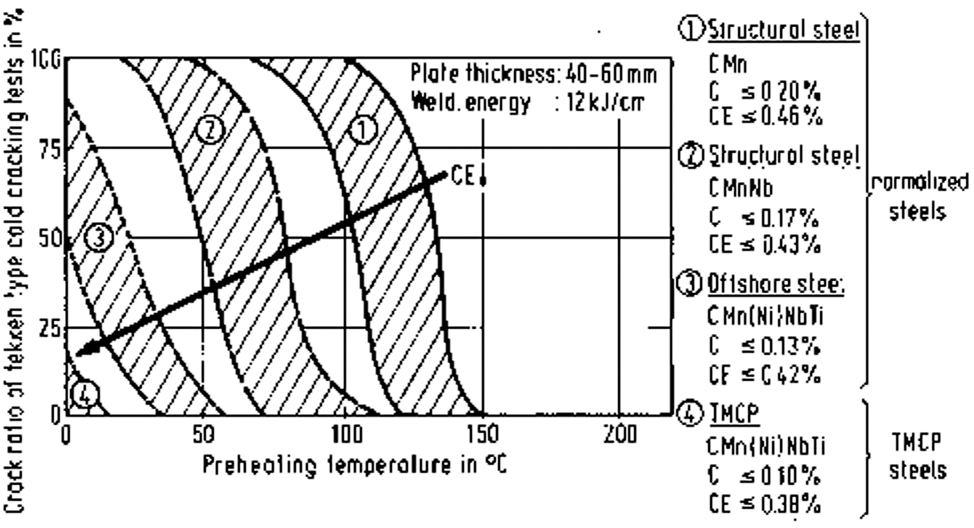


Figure 8: Effect of carbon equivalent on pre-heating temperature for crack-free weldments in steels with Re > 355Mpa.

Higher Strength Steels and Safety Considerations

Even though the majority of HSLA steel used in the construction industry today is limited to a yield stress level of 460MPa, thermomechanically processed steels up to a minimum yield stress of 690MPa relying on a low carbon bainitic microstructure are readily available. For safety considerations the application of such steels have to take into account the regions of poor toughness observed in a welded structure, which is often the grain coarsened heat affected zone-HAZ. Two microstructural features influence the HAZ toughness: the fracture facet size and the volume fraction of martensite-austenite constituents, which result in local brittle zones and act as initiation sites for brittle failures. This problem can be minimized in steels with carbon content below 0.09%C and alloy content giving the desired acicular microstructure.

Future Trends

All thermomechanically processed high strength steels for structural components will contain niobium as their first microalloying element of choice and there are no technological trends that would alter this in the near future. The cost savings of steel structures made of these low carbon HSLA steels, for which next to no preheating is necessary, very likely will lead to an increase in application. These cost and weight savings are substantial, when increasing the yield stress from mild steel via 355MPa yield strength to the 460MPa level as Figure 9 shows. The result is elegant constructions, Figure 10. The widespread application of these modern steels is supported by the actual design code for steel constructions (5), which covers the necessary safety considerations with a fracture mechanics concept. The technical and economic benefits will also support the application of these modern types of steel in geographical areas, where today, for traditional reasons, still the old fashioned quenched and tempered steels are used. Further development towards DQ steels with 690 or even 960MPa yield strength show microalloying with up to 0.1%Nb to be very advantageous. This might even lead HSLA steels with niobium into the domain of the conventional high carbon QT grades.

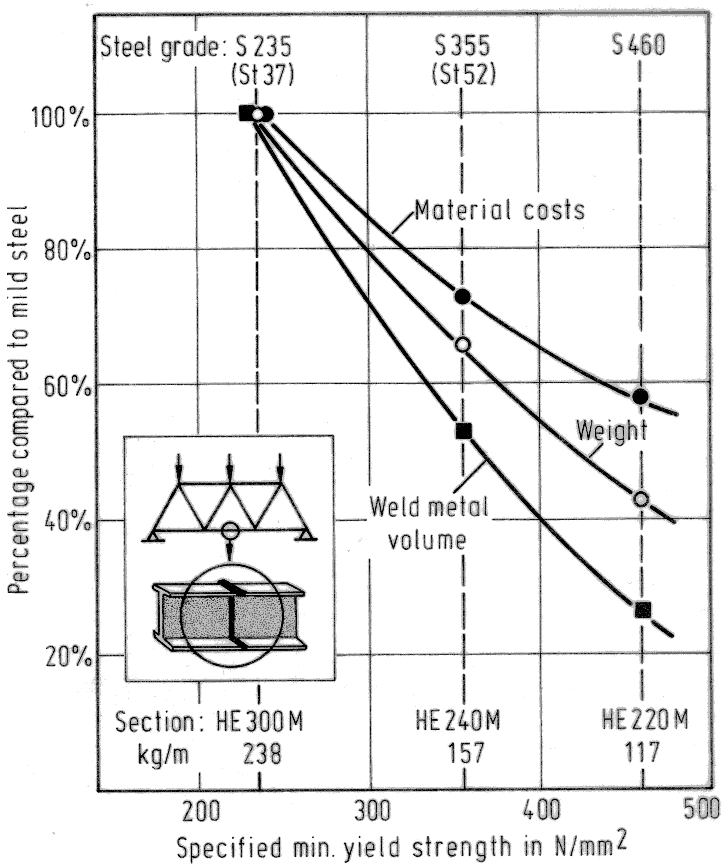


Figure 9: Weight and cost reduction by applying HSLA steels.

Figure 10: The Öresund Bridge.

Stainless Steels

General

The application of stainless steels for household goods, in the food and chemical industry, for architecture and automobiles has been growing over the last few decades, but the technical progress in steel making via the Argon-Oxygen-Decarburising process, which leads to very low levels of the interstitials carbon and nitrogen, made stabilisation for such applications either unnecessary or has substantially reduced the additions of niobium and/or titanium to such steels. Only the improvement of the high temperature properties of niobium containing ferritic and austenitic stainless steels make them a continuing and secure application for niobium.

Alloy Design and Properties

Ferritic stainless steels with chromium contents from 12 to 26% are gaining importance over austenitic steels due to their cost advantage. However, their disadvantage is the inherent low toughness, reduced formability and ductility and also the poor corrosion resistance and properties of the weldments. For specific applications this can be overcome by a fit for purpose construction and by a specific alloy design, in particular by the stabilisation with titanium and/or niobium. The dual stabilisation with niobium and titanium has the advantage that the lower Ti addition reduces surface defects stemming from large TiN inclusions, the formability is improved via a favourable texture development and a good mean r-value (20) at an over-stoichiometric niobium content, which improves both spot and MAG weldability (21). Despite many advantages, application of dual stabilisation is stagnant, if not decreasing and it remains to be seen, whether this trend can be reversed by intensified research to demonstrate the inherent advantages.

Due to the emission control for cars, the automotive industry has been forced to install exhaust systems with catalytic converters. The catalytic converter can and the manifold at the hot front are typical consumers of ferritic stainless steels, Figure 11. The advantage of a fully ferritic system is the same thermal expansion of all parts and a generally 50% lower thermal expansion coefficient than the austenitics, thus reducing thermal stresses, fatigue cracking and oxide spalling. Moreover, in particular for the manifold oxidation resistance, creep resistance, good weldability and formability are required. For this purpose such a ferritic stainless steel: 0.02C-18Cr-0.3Ti-0.7Nb is preferably alloyed with over-stoichiometric additions of niobium, because the niobium in solution forms a Laves phase, which improves the creep behaviour, whereas the niobium precipitates give higher elevated temperature strength. In many cases for this application a 409-type material with titanium is used, but the anticipated higher exhaust gas temperature of fuel efficient cars will replace this material in the future.

Austenitic stainless steels contain 18 to 30% chromium and 7 to 25% nickel with additions of molybdenum, niobium and titanium. Modern steels have a carbon content of 0.03% and below and are, for general purposes, not stabilized, because at such carbon levels chromium carbide, $Cr_{23}C_6$, remains dissolved at temperatures up to 800°C. A considerable amount of these unstabilized low carbon austenitic stainless steels is for the fabrication of cold formed parts in kitchen-ware, containers for soft drinks and beer and also for architectural application. The main application for niobium in austenitic stainless steels is for elevated temperatures with a base composition of 18%Cr and 11%Ni. The precipitation of niobium carbides provides the elevated temperature strength and improved creep resistance. With decreasing carbon and equivalent niobium levels in such steels their inherent disadvantage such as weld decay and intergranular corrosion in the HAZ could be avoided. For years a two-phase austenite-delta ferrite stainless steel has been available on the market. This material exhibits a higher strength, because of its inherent finer grain deriving from the duplex structure; niobium additions are helpful to prevent grain growth during production and fabrication steps.

Figure 11: Complete automotive exhaust system.

Future Trends

The increasing demand for power generation requires steels for power plants with good high temperature oxidation resistance and creep properties. Since niobium is beneficial for the required property combination and no adverse technological development can be expected, this application will remain a small, but stable part of the niobium market. The relatively new steels with duplex structure, which require niobium additions for grain size control may provide a new application for niobium. Dual stabilisation of ferritic stainless steels is still a small market at present in the USA with little growth, but a future potential, if surface quality requirements become of paramount importance. Legislation for the emission control of automobiles has provided new fields of high temperature applications in the exhaust system of cars. In such steels, niobium is indispensable to generate the required properties like creep resistance and elevated temperature strength. The complete ferritic system of the exhaust pipe and converter can provide additional advantages deriving from the uniform thermal expansion and the lower thermal expansion coefficient. Therefore this type of steel has a future growth potential.

Microalloyed High Carbon Steels

General

The development of low carbon HSLA steels and the successful replacement of heat treatment by thermomechanical rolling generated already in the 1970's the idea of a similar development for high carbon engineering steels with microalloying additions, which attain their mechanical properties in the as forged condition rather than after a heat treatment. The driving force for such a development was the saving of energy by the elimination of any heat treatment and the better machinability of the predominantly ferritic-pearlitic microstructure. Machining costs accounts for about 50% of the final parts. However, unlike in HSLA steels, where the retardation of recrystallisation by niobium made this element indispensable in such steels, this effect does not yet play any practical role in high carbon steels under practical rolling and forging conditions. Moreover, the low solubility of niobium in austenite at high carbon contents further limits its metallurgical advantage. Therefore, in many cases vanadium rather than niobium is the first choice microalloying element and niobium acts basically by precipitation hardening, in controlling the austenite grain size and to some extent in refining the microstructure.

Microalloyed Forging Steels

The traditional forging steels for many applications have a base composition in the range of 0.25-0.50%C, 0.3-0.6%Si and 0.7-1.3%Mn. The addition of about 0.1%V gives an incremental strength by precipitation hardening of the proeutectoid and pearlite ferrite via VN precipitates resulting in a tensile strength level of 800-1000MPa in the as forged condition. Even in such high carbon steels niobium has a remarkably higher strengthening potential than vanadium, provided the austenitising temperature prior to forging is high enough to get sufficient niobium in solution. The dissolved niobium influences the transformation behaviour towards a microstructure with small amounts of low transformation temperature products such as bainite and eventually martensite, which deteriorate the toughness. On the other hand the very stable NbC precipitates are pinning the austenite grain boundaries to prevent austenite grain coarsening. This is beneficial for the toughness and in particular for the fatigue strength, because the fatigue crack follows the ferrite network of the prior austenite grains. The combination of vanadium plus niobium is therefore used in many practical applications for as forged automotive parts such as crank shafts, connecting rods and anti-sway bars (22, 23).

Case Hardening Steels

For heavy-duty applications of forged steels the surface of components like gears, shafts and other rotating parts is in many cases carburised. Hardness, wear resistance and fatigue are improved by this treatment. The carburising process is time and energy consuming and causing at too high temperatures an exponential austenite grain coarsening and thus property degradation. Due to the pinning effect of NbC, austenite grain growth can be prevented up to rather high carburising temperatures. This means that the carburising process can take place at much higher temperatures than for non-niobium microalloyed steels and treatment time and cost can be substantially reduced for the same carburising depth, with the additional advantage of a reduced distortion of the carburised parts, Figure 12. The economic and technical advantages like energy saving, improvement of fatigue, impact properties and distortion will provide enough driving force for a wider application in the future, provided the required heat treatment facilities allow higher carburising temperatures.

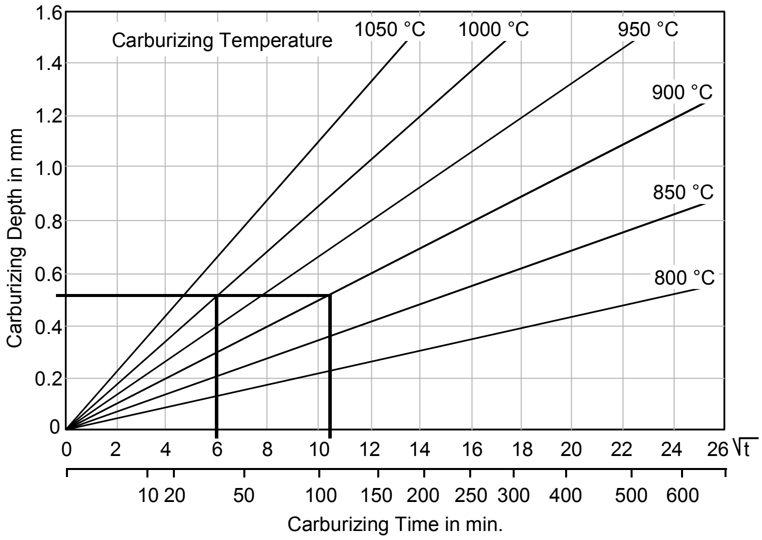


Figure 12: Time-Temperature-Interaction in gas carburising for a surface carbon content of 1%.

Cold Heading Steels

High strength bolts and fasteners with tensile strength of 800 and 1000MPa require for their production various heat treatment steps: spheroidizing annealing, quenching and tempering. The use of low carbon-manganese-niobium-boron steels with a bainitic microstructure containing a certain percentage of evenly distributed martensite can eliminate this costly process. The microstructure is generated by the combined effect of boron and niobium on the transformation characteristics of steel (24) and exhibits sufficient ductility and work hardening potential for wire drawing and cold heading.

Tool Steels and High Speed Steels

The development of high performance tool steels and high speed steels dates back many decades, when niobium was not available as an alloying element for steel and therefore was not part of the empirical research. However, in the last 20 years remarkable progress was made. As a strong carbide forming element, with a low solubility in high carbon steels, niobium is basically present as primary carbide to improve the wear resistance. On the other hand, niobium has a general impact on the alloying concept of tool steels, because it influences the solubility of alloying elements in the steel by removing the carbon in solution and allowing higher austenitising temperatures. The complexity of the tool steel and high-speed steel metallurgy requires time for further development. A state of the art report and an outlook into the future is part of these proceedings (25).

Future Trends

Microalloying of as rolled or as forged high carbon steels with niobium offer outstanding advantages for the production and application of these steels. The optimisation of such steels will be further pursued in order to get the right balance between the chemical composition and the resulting precipitation hardening behaviour, austenite grain size control and avoidance of low temperature transformation products under practical rolling, forging and cooling conditions. For a variety of applications this has been obtained and these steels have been in place for a long time (23, 24). The narrow range of production parameters to get optimal products makes future research and development work mandatory to optimise the structure-property-fabrication relationship. This will provide a steady, although slow growing application for niobium. The obvious cost advantage and technical benefits of niobium in steels for carburising in particular in the modern argon-propan plasma process, will provide additional growth. For historic reasons niobium was not part of the empirical development of tool steels and high-speed steels. This and the complexity of the tool steel metallurgy make fast inroads of niobium into these steels impossible. However, the progress of the last two decades was substantial and will continue steadily to provide a further diversification of niobium applications.

Niobium in Superalloys

In the late 50's, industry was confronting important technological challenges related to aircraft engine manufacture. These involved difficulty in forging alloy Rene 41 and the impossible task of avoiding strain-age cracking in welded fabrications of this alloy (26). Alloy 718 introduced by Inco Alloys in 1959 showed much better performance than the other precipitation-strengthened superalloys available at that time. Alloy 718 also presented better creep properties in the range 540-650°C than alloy Rene 41 and Astroloy. 718's residual strength and ductility properties were not impaired by exposure in this temperature range.

Niobium was added to nickel-based alloys to increase strength at high temperatures. The strengthening mechanism involved precipitation of an intermetallic compound (Ni_3Nb) in the nickel matrix during heat treatment. Although there were other alternatives to niobium as a strengthener, niobium was found to be unique in its ability to avoid strain-age cracking during fabrication of the final components, especially during welding. Because niobium provided a slower aging response, parts could be thermally stress relieved without cracking.

Alloy 718 was one of numerous new alloys offered by industry and being evaluated by engine manufacturers such as GE, P&W and Allison.

As a consequence of General Electric and its supply industry commitment to focus a significant part of their resources to making Alloy 718 work in all its forms, the alloy became the backbone of the superalloy business. This alloy had been selected as the material for GE's new family of engines called GE-1 (which became the core of the military TF39 and the commercial CF6) and GE-4 (Super Sonic Transport Program).

After more than forty years since first being introduced by Huntington Alloys, IN718 is still the most important all-purpose nickel-based superalloy. The dominant position of Alloy 718 in the aircraft engine applications is presented in Table VI (26-28).

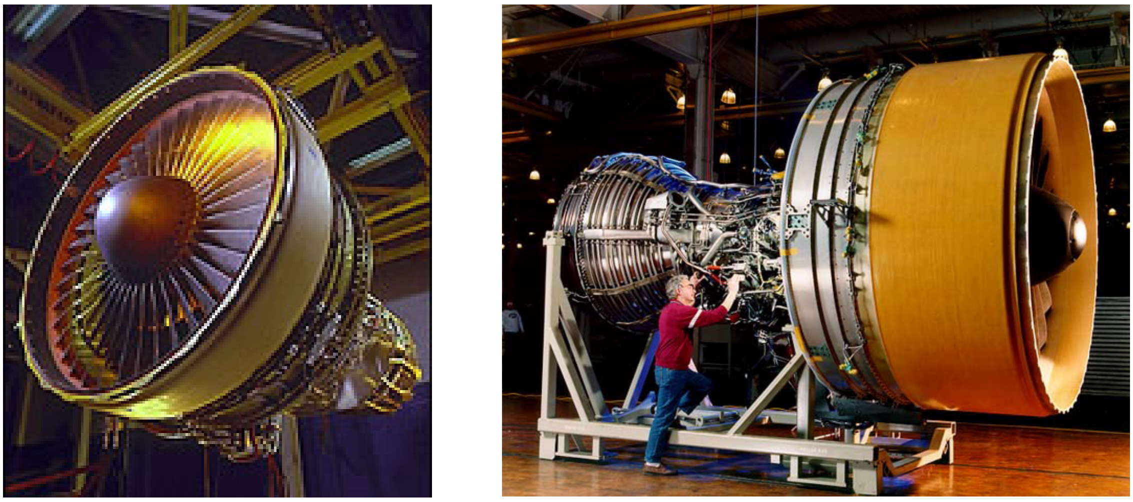
Table VI Materials input weight in aircraft engines (26-28)

	GE – CF6	**PW 4000**
Alloy 718	**34 %**	**22 %**
Other superalloys	13 %	17%
Titanium	25 %	26 %
Aluminium	8 %	8 %
Steel	16 %	24 %
Other materials	4 %	3 %

The table shows that alloy 718 alone, corresponds to 34% of finished component weight for the General Electric CF6 aircraft engine, Figure 13a. In addition, under other superalloys niobium will also be present as an alloying element. As an example, for the Pratt & Whitney PW4000 engine, Figure 13b, 6.5% correspond to alloy IN713C, which contains 2%Nb in its chemical composition.

In the near future the dominance of alloy 718 should not be changed significantly due to the characteristics of the aircraft engine business. New alloys must be thoroughly tested before their practical implementation, which takes several years and considerable resources to do it. Furthermore a forecast by Boeing and Airbus for the world's aircraft deliveries in the next two decades shows that more than 23,000 aircraft of all types will be delivered in the period.

Thus, it is expected that superalloys containing niobium for aircraft engines will continue to be an important segment of the niobium business in the future.



(a) (b)

Figure 13: a) GE CF6-80C2 aircraft engine (left). More than 2,000 aircraft are currently flying with engines from the GE CF6 family. b) PW4000-112" aircraft engine (right). This engine covers the 74,000 to 98,000-pound-thrust class to meet the current requirements for the Boeing 777 twinjet.

An important technological challenge in the aircraft engine industry is the development of an alloy 718 derivatives that would allow an increase of 40 to 50°C in its temperature capability. The immediate penalties of replacing alloy 718 to accomplish this task are an increase in cost and in the weight of the final component. The development of alloy Rene 220 at GE was a response to this challenge. The alloy provided encouraging technical results but was eliminated due to high elemental costs (27, 28). A Metals Affordability Initiative Program funded by the U.S. Air Force and involving General Electric Aircraft Engines, Pratt & Whitney, Ladish, Allvac, Carpenter Technology and Honeywell is in the works for the development of a low cost, high temperature structural material (27, 28). The objective is to develop a new alloy, in the next 5 years, with the characteristics of fabricability and weldability of alloy 718, and with stability to the same higher temperature range as Waspaloy and Rene 41. The most important requirements for this new alloy are summarized in Table VII (27, 28).

Table VII Critical requirements for a new High Temperature Structural Material to replace Alloy 718 (27, 28)

- Component costs 75% less than Waspaloy
- Comparable metallurgical stability at 704°C (1300F) as alloy 718 at 612°C (1150F)
- Creep resistance and tensile strength at 649°C (1200F) and 704°C (1300F) at least equal to Waspaloy
- Stress rupture properties equal or higher to Waspaloy under selected conditions
- Ductility at processing temperatures equivalent to alloy 718
- Ductility at running engine part temperatures equivalent to alloy Waspaloy
- Wear resistance and weldability equivalent to alloy 718 at the selected conditions

Superalloys containing niobium are not limited to the aircraft engine industry. Table VIII shows the chemical composition for the most important nickel-based superalloys containing niobium.

Table VIII Nominal chemical composition (wt%) of the most important superalloys containing niobium

Alloy	Chemical composition (%)										Others
	Ni	Cr	Co	Nb	Mo	W	Ti	Al	Fe	C	
Inconel 718	52.2	19.0	--	5.1	3.0	--	0.9	0.5	18.5	--	--
Inconel 706	41.5	16.0	--	2.9	--	--	1.8	0.2	37.5	0.03	--
Inconel 625	61.0	21.5	--	3.6	9.0	--	0.2	0.2	2.5	0.05	--
René 95	61.0	14.0	8.0	3.5	3.5	3.5	2.5	3.5	<0.3	0.16	0.01B; 0.05Zr
Udimet 630	50.0	17.0	--	6.5	3.0	3.0	1.0	0.7	18.0	0.04	0.004B
Inconel 751	72.5	15.5	--	1.0	--	--	2.3	1.2	7.0	0.05	0.25Cu max
Inconel X750	73.0	15.5	--	1.0	--	--	2.5	0.7	0.7	0.04	0.25Cu max
Alloy 713C	74.0	12.5	--	2.0	4.2	--	0.8	6.1	--	0.12	0.012B; 0.10Zr
IN-738	61.0	16.0	8.5	0.9	1.7	2.6	3.4	3.4	--	0.17	0.010B;0.10Zr; 1.7Ta
MAR-M 200	60.0	9.0	10.0	1.0	--	12.0	2.0	5.0	--	0.15	0.015B; 0.05Zr
Inconel 907	38.0	--	13.0	4.7	--	--	1.5	0.03	42.0	--	0.15Si
Inconel 909	38.0	--	13.0	4.7	--	--	1.5	0.03	42.0	0.01	0.40Si

Of increased importance is the application of nickel-based superalloys in land-base turbines for power generation. GE developed their F-machine with an introductory firing temperature of 1230^{o}C (2250F) in the late 1980’s (29, 30). The new machine operated at a firing temperature more than 140°C (250F) higher than the previous generation of industrial gas turbines. Thus, there were two possibilities to decide on the materials for GE's F-machine. In order to use the existing wheel materials it would be required to invest in a cooled compressor discharge cooling air system. The other option would be to avoid investing in the cooling system by using a higher temperature capability alloy, and alloy 706 was chosen for use in the wheels and the spacers. Prior to this, all the turbine wheels had been made from steel (30).

Although the most important alloy in this industry is still alloy 706, the increase in operating temperatures to achieve higher efficiencies is driving the industry to look at alloy 718 to replace alloy 706. Figure 14 shows an H-type land-base turbine. The biggest challenge in this case is to obtain large diameter ingots (760mm) without segregation defects that would compromise the performance of the final component. Alloys 706 and 718 are considered to be the two only solutions for this specific application because of the slow kinetics of growth for the γ' (Ni_3Nb) strengthening phase. This is very important in components with large cross section to avoid over aging during heat treatment (30).

Schielke et al (30) estimate that more then 12,000 tonnes of alloy 706 have been melted for gas turbine applications to date and this number will continue to increase. Power generation will have to show increased efficiencies on a continuous basis. In addition, the old plants will have to be replaced for economic reasons. Thus, this application segment also presents itself as an opportunity for niobium in the near future.

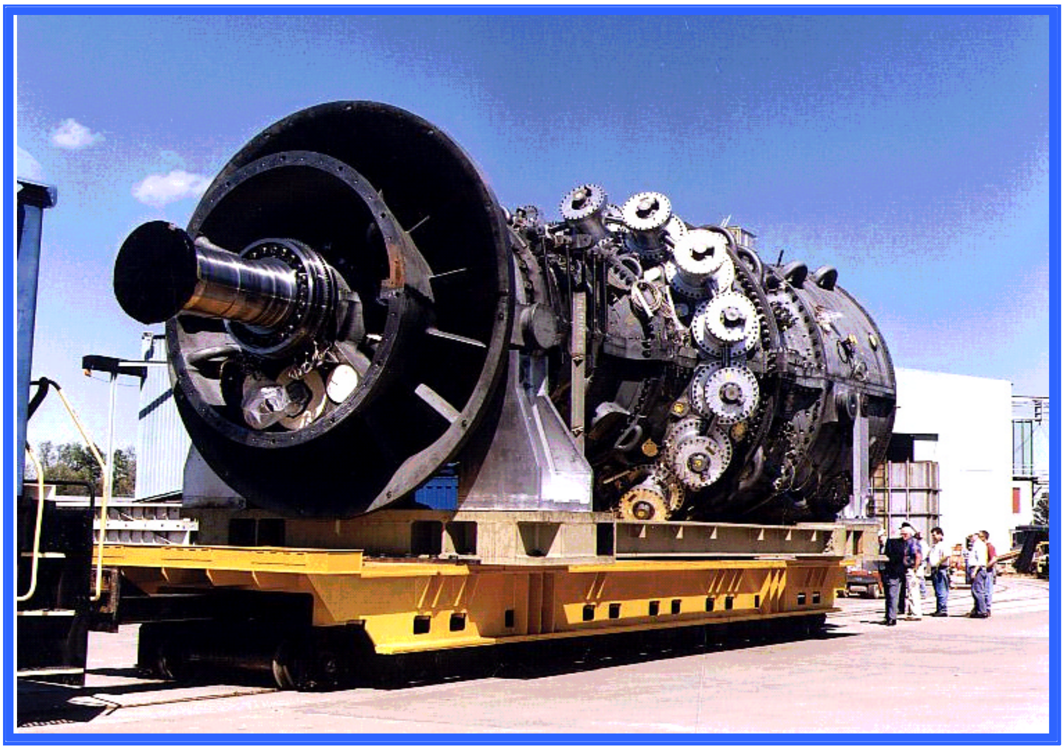


Figure 14: First MS9001H gas turbine at GE's facilities (Greenville, SC). Courtesy of General Electric Power Systems.

Alloy 625 completes the group of the most important nickel-based superalloys, along with 718 and 706. A significant portion of the several thousand tonnes of alloy 625 manufactured per year is consumed by applications on seawater, aerospace and the chemical processing industries (31). Smith et al (31) confirm the fact that alloy 625 and its derivatives are the solution to numerous environmental problems in a wide variety of industrial applications. The authors predict that alloy 625 will play a major role in the future worldwide growth of municipal Waste-to-Energy and Refuse-Derived-Fuel plants.

The previous data presented for alloys 718, 706 and 625 show that the future potential for niobium in superalloys is much more associated to the use of already developed alloys to solve recent design and engineering problems than to the development of new alloys.

None-the-less, several examples of new alloy development involving superalloys can also constitute future potential for niobium in this area. Fahrmann et al have presented data on recent developments of nickel-based alloys containing niobium emphasizing the help of computational tools (32, 33). In the first case, a new alloy is to be developed for superheater tubing in advanced power plants. In this case, a niobium addition in the range of 1.0 to 1.5% was effected in order to improve the weldability of the alloy (32). In another development, the authors designed a low-cost diesel truck exhaust valve alloy (33). Niobium levels of up to 2.5% are considered to be the optimum in this case. Niobium additional role in this alloy is related to the formation of NbC to improve the abrasion resistance of the alloy. Furthermore, niobium was found to significantly improve the alloy's resistance to hot salt corrosion.

In addition, efforts are under way to study the possibility of substitution of tantalum for niobium in superalloys. Again, the recent turmoil in the tantalum supply chain is the most important driving force for this development and may result in additional opportunities for niobium in the superalloy industry.

Niobium-based Alloys for High Temperature Applications

Even the most advanced nickel-based superalloys cannot meet new challenges imposed by the need for increased performance at higher temperatures in aircraft engines, because of the natural ceiling imposed by the melting temperature of nickel. Niobium and its alloys will most likely be the next generation of materials for temperatures exceeding 1,100^{o}C.

It is well known that niobium has been a factor of major importance in the evolution of materials for high temperature uses. Niobium-based alloys were studied exhaustively during the height of the space race of the 50's and 60's and the use of both Nb-1wt%Zr and alloy C-103, which is a Nb-10wt%Hf-1wt%Ti alloy, were important consequences of this work. Niobium uses have centered mainly on missile and spacecraft propulsion systems. All recent applications of niobium involve the lower strength binary or ternary alloys, which can be readily welded and formed into complex shapes such as Nb-1Zr, PWC-11, and C-103. The most important niobium alloy in this area is the alloy C-103, which is used for rocket thrust cones, high temperature valves, and some special close-die forgings. Another important current application of silicide-coated C103 is in the thrust augmenter flaps used in one of the Pratt & Whitney turbine engines (34).

In developing new materials for high temperature applications, especially those of relevance to aerospace, industry must deal with the optimization of properties such as high-temperature strength, creep resistance, environmental stability, and room temperature toughness. In addition, characteristics such as material's processability, density, cost and materials availability are also crucial in developing new alloys for these applications. Niobium has been viewed over the years as an element that contributes to achieving the demanding overall goals imposed by high temperature applications. Whether it is used as an alloying element to improve a specific property or as a metal to operate at higher temperatures, niobium has always been considered an important option due to its overall properties, but also because niobium is the lowest-density refractory metal with excellent characteristics of fabricability and ductility at room temperature.

Resistance to oxidation has been the most important obstacle to the expansion of the uses of niobium-based alloys for high temperature applications. The surface layer of niobium pentoxide (Nb_2O_5) formed during the oxidation process is not protective and repeatedly cracks and spalls. Although niobium forms several other oxides none of them are protective. A solution to the oxidation problem is the use of protective coatings such as the silicide-based coating used for C103 components. These coatings also contain chromium, hafnium, iron and nickel in addition to silicon. As design engineers do not rely only on coatings, especially when it comes to aircraft engine applications, a niobium-based alloy with a minimum resistance to oxidation needs to be developed to withstand temperatures approaching 1,300^{o}C. To achieve the oxidation resistance required by the design parameters, the niobium alloy must form a protective oxide. Thus, niobium will need to be alloyed with an element that will oxidize preferentially to form the protective scale. The two most successful candidates would be aluminum and silicon.

Bishop and Olson (35) opted for the aluminum solution to form the protective scale in their approach. This on-going research focuses on the design of a high-temperature niobium-based alloy for use in the hottest section of the aircraft engine (T4 high pressure turbine blades) with requirements defined in phase III of the Integrated High Performance Turbine Engine Technology (IHPTET) Program fostered by the US Air Force (36). These guidelines have very stringent requirements with regard to creep properties and oxidation resistance at maximum temperature of 1,300^{o}C. Results obtained to date show that it is possible to design a niobium-based alloy using alumina as the protective coating and a Heusler phase to achieve high temperature mechanical properties via precipitation strengthening. Bishop (35) suggests that in addition to aluminum for the protective scale formation, the new alloy should contain palladium and hafnium for strengthening via formation of Pd_2HfAl Heusler phase, ruthenium to decrease oxygen solubility and to increase the stability of Heusler phase, tungsten and chromium to decrease the lattice parameter and decrease the precipitate/matrix misfit.

Another approach involves the system niobium-silicon to achieve the required high-temperature performance for the alloy. The Nb-Ti-Si is the most important system in this class of materials. Such an alloy system offers a potential advantage over Beta titanium-based alloys in that the introduction of intermetallic phases can result in reasonable high-temperature properties, while the ductile constituent can impart good low-temperature toughness (37). Two-phase Nb-Nb5Si3 alloys represent a model material system in this class. The inability of this system to achieve the goal of performance up to 1,400°C is related to its resistance to oxidation. In order to overcome this problem, research strategies are considering multi-component alloys involving additions of other elements such as aluminum, titanium, chromium and hafnium to the Nb-Si base. Although the studies by Subramanian et al (37) and by Bewlay et al at GE (38) indicate that a useful balance of low-temperature and high-temperature properties may be obtained through appropriate alloying, processing, and microstructural control, the alloy development efforts are still in the exploratory stage. Some of the important alloys studied in this system are Nb-27Ti-8Cr-9Al-15Si (at%) and Nb-26Ti-8Cr-9Al-17Si (at%) in the studies at the Wright Laboratory (WPAFB) and Nb-25Ti-8Hf-2Cr-2Al-16Si at General Electric.

An important observation of Subramanian et al (37) is that even if the oxidation goals are realized through alloying efforts, the materials will require oxidation-protective coatings (as for all other long-life engine alloys) for any long-term use in the temperature range of proposed service (1,200-1,400°C). Thus, coating development for advanced alloys will require further research on new coating compositions as well as coating techniques.

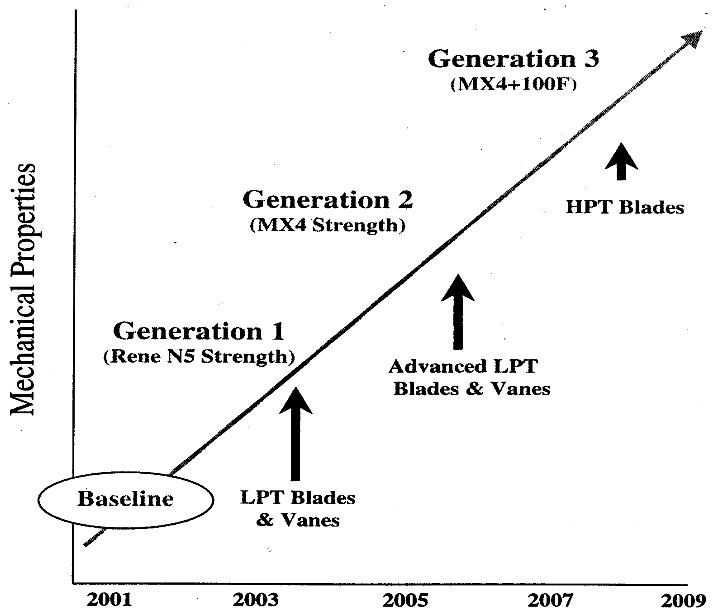


Figure 15: Niobium Silicide Program at General Electric (39).

Also relying on a design approach with the use of simulation and modeling tools, General Electric is heavily involved in a high-temperature capability material development within the niobium silicide system. GE's roadmap associated with their Niobium Silicide program is presented in Figure 15 (39). GE's strategy (39) involves the development of a first generation alloy with similar properties to the single crystal Rene N5 alloy for application in low pressure turbine blades and vanes. The second generation alloy would have as baseline the MX4 latest generation of single crystal superalloy and would be targeted for more aggressive low pressure turbine applications. The alloy for high temperature turbine blade and vane applications would come with an alloy of third generation, which would show a much improved temperature capability.

Gamma Titanium Aluminides Containing Niobium

The Integrated High Performance Turbine Engine Technology (IHPTET) initiative, established as a target performance for advanced engines, a thrust to weight performance that must be twice that of current aircraft engines (37, 40, 41). Under these circumstances, several advanced materials initiatives have been created in recent years, aiming at identifying the "missing link" for high-temperature applications, i.e., a material or a system showing higher temperature capability with reduced weight. Once again, due to its overall properties, niobium has been part of most of these initiatives, and it is certainly a participant in those that are showing promise. Figure 16 (42) shows the temperature limitation and density for different materials used in jet engines.

With density in the range 3.7 to 3.9 g/cm^3, which is less than half of that of superalloys (8.3g/cm^3) and more than 10% lower than titanium (4.5g/cm^3), gamma titanium aluminides have an enormous potential for aerospace application. This is especially true since these alloys also exhibit a good combination of properties for high temperature applications, such as high temperature strength, modulus retention, resistance to oxidation and hydrogen absorption and creep properties. It is generally accepted that gamma titanium aluminides have temperature capability of 700°C with limited prospects to reach 900°C for structural uses (37). The main problem with these alloys is their poor ductility and fracture toughness at room temperature.

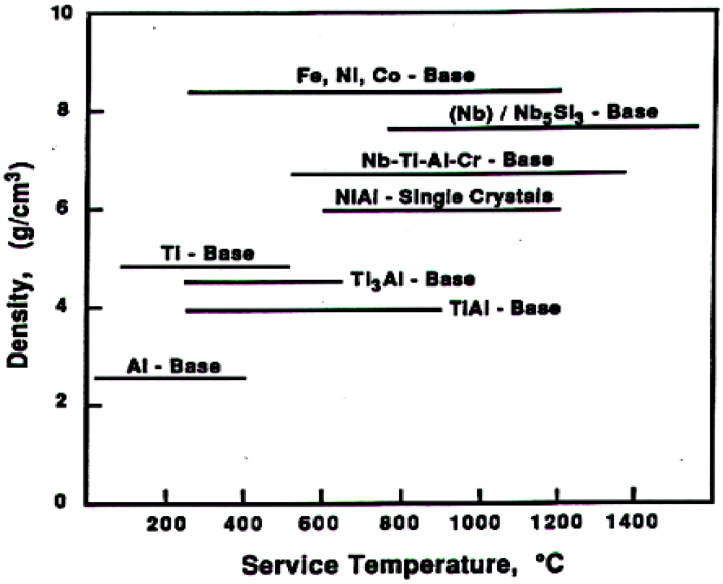


Figure 16: Temperature range for service as a function of density for different materials (42).

Titanium aluminide alloys can be classified into single phase alloys (γ-TiAl) and two-phase alloys (α_2-Ti_3Al + γ-TiAl). The α_2 phase has an ordered DO19 hexagonal superlattice structure while the γ phase has an ordered $L1_o$ face centered tetragonal structure (43). Tensile properties and fracture toughness of both are strongly dependent on microstructure (44). Microstructure control in the (α_2 + γ) alloys results in improved mechanical properties when compared to the single phase γ alloys. Thus, the former are more interesting as practical structural materials. As potential materials for aircraft engines, gamma titanium aluminides have three distinct commercial attributes: stiffness, high temperature strength and burn resistance (45). Gamma titanium aluminides show specific stiffness 50% greater than commonly used alloys such as IN718 and Ti-6Al-4V (45); and they have higher specific strength especially beyond the limits of alloy 718 (45). Although their burn containment is marginally better than titanium, their burn ignition is nearly as good as that of nickel-based alloys (45).

The main role of niobium in titanium aluminides is to improve their resistance to oxidation by promoting the formation of a continuous surface layer of Al_2O_3 that is absent in oxidation-prone alloys (46). Figure 17 (46, 47) illustrates the pronounced effect of niobium in reducing the oxidation of gamma titanium aluminides. This figure also emphasizes how the presence of vanadium instead of chromium as a promoter of better ductility impairs the properties of niobium in improving oxidation resistance. With the niobium addition, it becomes possible to use gamma alloys at 800 C without coating (46). Recent work by Varma et al (48) have further demonstrated the importance of niobium additions to improve the oxidation resistance of these alloys. The authors concluded that the largest effect in improving the oxidation resistance is observed with additions of up to 4at%. Increasing the niobium concentration from 4 to 11at% will only gradually reduces the net weight gain at a given temperature for both static and cyclic heating. The role of niobium as a promoter of better resistance to oxidation in these alloys is clear and well accepted. Furthermore, niobium additions are known to increase the strength and the creep resistance of TiAl alloys, simultaneous with improvement of oxidation resistance (49).

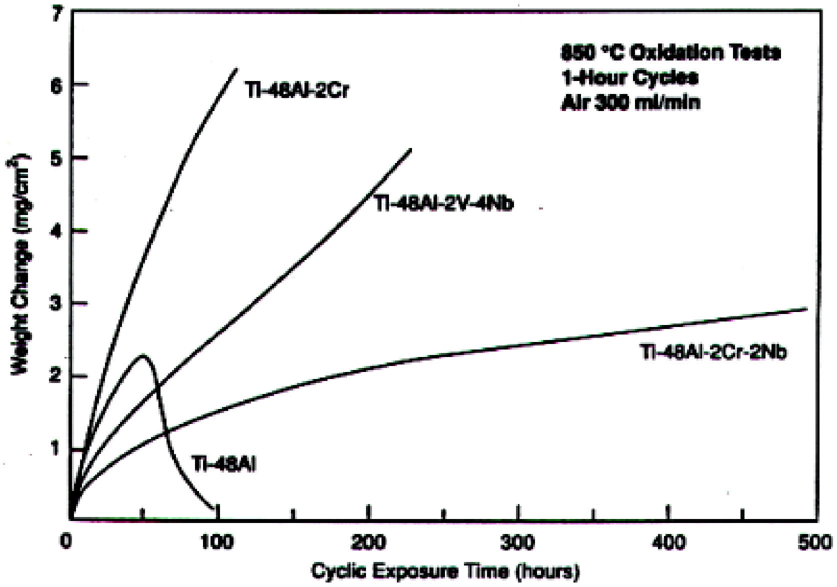


Figure 17: The effect of niobium in improving the oxidation resistance of Gamma TiAl alloys (46, 47).

Recent work by Chen et al (50) has demonstrated that additions of niobium as high as 10at% to the system Ti-45Al lead to significant improvements in high-temperature strength. Microstructural observations showed that higher niobium content alloys result in increased critical resolved shear stress (CRSS) for ordinary slip in γ phase due to a higher niobium content in solution. In addition, higher niobium in solution in γ phase lowers the stacking fault energy (SFE) of these alloys. High CRSS for ordinary slip and the difficulty of dislocation climb due to the low SFE appear to be the major factors responsible for the excellent high-temperature strength of high niobium Gamma TiAl (50).

Additional work by Appel et al (51-53) confirmed the improved strength properties for Gamma TiAl with higher niobium content and concluded that the strength increase is mainly a result of a structural refinement due to reduced aluminum content, since this is consistent with the site occupancy of niobium in gamma TiAl. This site occupancy argument was also endorsed by computational and simulation analysis recently published in the literature (54). Niobium additions lead to an increase of α_2 volume fraction in the transformed regions and to a refinement of the microstructure. The observations presented in Figure 18 (52, 53) support this rationale. Appel et al (51-53) additionally concluded that large niobium additions seem to also reduce the diffusibility of Gamma TiAl which certainly is beneficial for creep resistance.

The gamma titanium aluminide alloy most studied in the literature is the one developed by General Electric with the nominal atomic composition of Ti-47Al-2Cr-2Nb (46, 47, 55). GE initiated efforts at several titanium casting suppliers to produce cast gamma components in 1989 (56). In their 1993 implementation program, GE successfully tested low-pressure turbine blades manufactured from this alloy in a factory CF6-80C2 engine at full power (56). During the implementation GE adopted a risk-phased approach and a small non-critical component (GE90 transition duct beam) was selected. Certification was finished in 1995 and this component was ready for use in the GE90 engines (56). This component was normally made from René 77 (Ni-15Cr-18Co-5Mo-3.5Ti-4.25Al)(wt%). Following the first publicly disclosed engine test involving gamma titanium aluminide in 1993, a series of other completed engine tests was reported (57) involving several other components such as F414 carbon seal supports, blade dampers, 14th stage compressor blades, low pressure turbine side plates and advanced engine radial diffusers (57). The majority of the work has been concentrated in the GE alloy Ti-47Al-2Cr-2Nb.

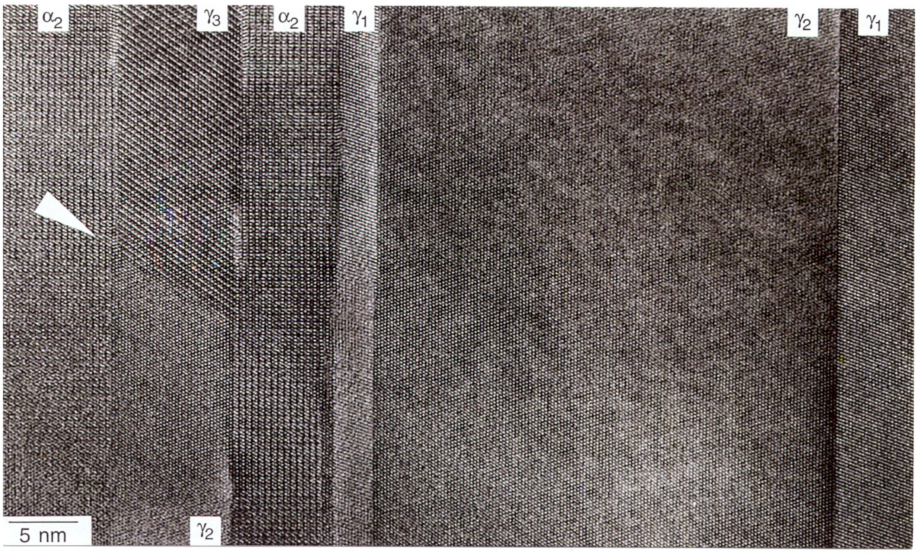


Figure 18: High-resolution TEM micrograph showing the lamellar microstructure observed in an alloy Ti-45Al-10Nb (at%). Note the small lamellar spacings and the high density of α_2 lamellae (52, 53). Courtesy of GKSS.

A second very important gamma titanium aluminide also extensively studied and present in implementation programs is that developed by Howmet Corporation, making use of a process invented by Martin Marietta to incorporate TiB_2 in cast alloys. To avoid GE's patented alloy, the other two big engine manufacturers, Pratt & Whitney and Rolls Royce adopted this alloy in their programs. Each engine manufacturer concentrated on one aluminum content for its specific alloy composition. The base alloy in atomic percentage is Ti-45Al(or 47Al)-2Nb-2Mn-0.8vol.% TiB_2XD^{TM} (58). The TiB_2 dispersoids are added as a grain refiner to improve strength and ductility of the alloy. These two alloys, Ti-47Al-2Cr-2Nb and Ti-45Al(or 47Al)-2Nb-2Mn-0.8 vol.% TiB_2 XD^{TM} are classified as Stage 1 alloys and have reached the engineering technology level after decades of concentrated effort in their scientific development.

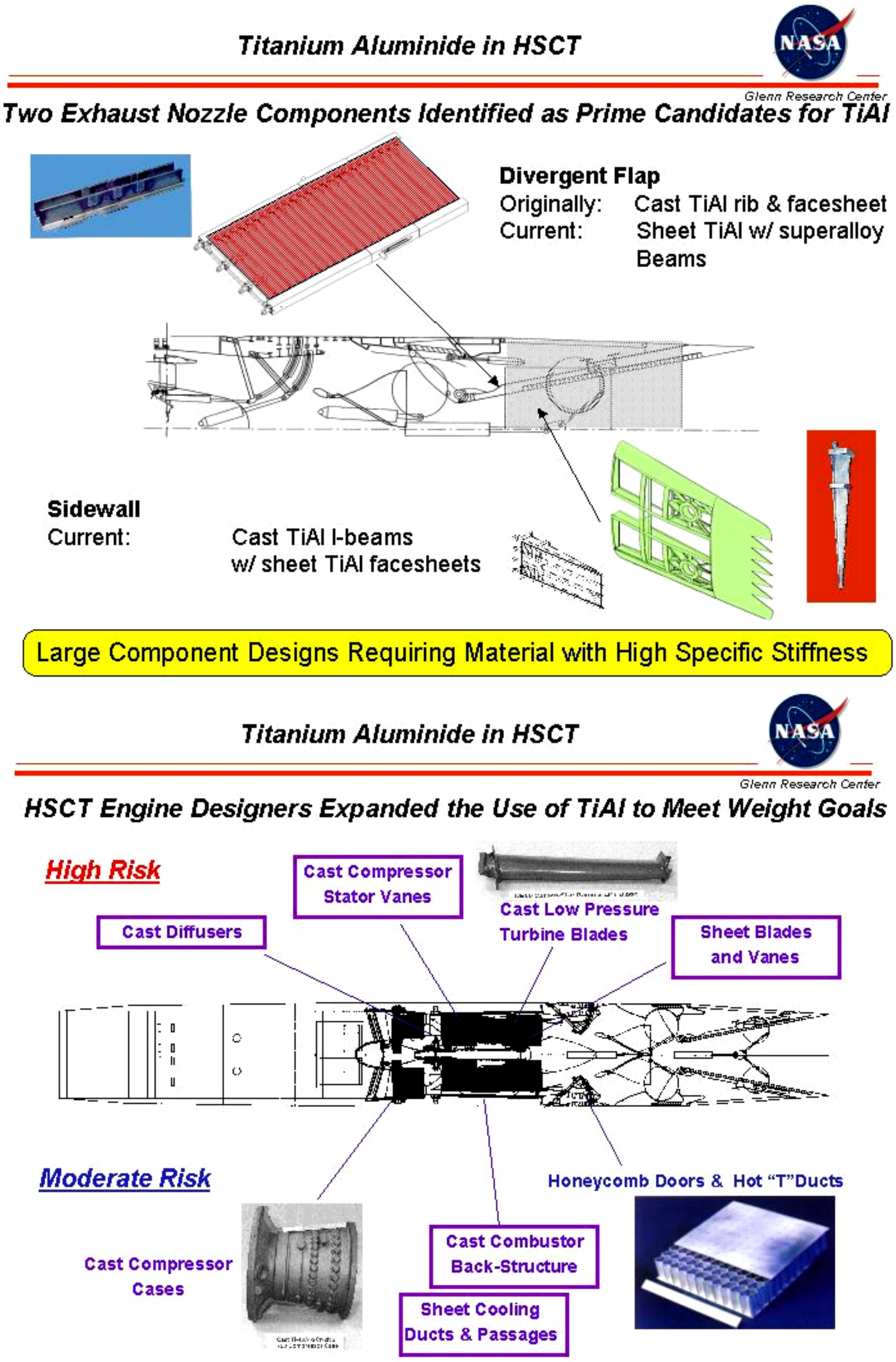
There are presently several other Stage 2 and Stage 3 alloys under study, to replace Stage 1 alloys in specific applications. Alloy K5 with a nominal composition (in atom %) of Ti-46.5Al-2Cr-3Nb-0.2W (59) and K5CBS (60) where interstitial elements (carbon, silicon and boron) were added to the base material (K5) in different combinations. They are both wrought gamma alloys developed at the USAF Wright Laboratory Materials Directorate. Specific alloys in this development show superior creep performance at high temperatures when compared to other fully lamellar gamma titanium aluminide alloys. Alloy 7 with a nominal composition (in atom %) of Ti-46Al-5Nb-1W (61) was developed by the Allison Gas Turbine Division of General Motors, before the formation of the present entity Rolls Royce - Allison. This alloy is regarded as one of the best wrought gamma titanium aluminide alloys presently available.

Other examples are given as follows, with composition in atom percent:

- Alloy 395 (Rockwell-Boeing-Pratt & Whitney): Ti-47Al-2Cr-2Nb-1.5Mo-0.5Si
- Alloy WMS (Allied Signal): Ti-47Al-2Nb-1Mn-0.5Mo-0.5W-0.2Si

- Rolls Royce: Ti-45Al-4Nb-4Zr-0.2Si-0.3B
- Alloy NCG359E: Ti-47Al-2Cr-1Nb-1.5Ta

As can be seen, niobium is present in all the alloys considered to be significantly important for future development and implementation in high temperature applications, notably in aircraft engine components.



Titanium Aluminide in HSCT

Glenn Research Center

Two Exhaust Nozzle Components Identified as Prime Candidates for TiAl

Divergent Flap

Originally: Cast TiAl rib & facesheet

Current: Sheet TiAl w/ superalloy Beams

Sidewall

Current: Cast TiAl I-beams w/ sheet TiAl facesheets

Large Component Designs Requiring Material with High Specific Stiffness

Titanium Aluminide in HSCT

Glenn Research Center

HSCT Engine Designers Expanded the Use of TiAl to Meet Weight Goals

Figure 19: Titanium Aluminide Applications in the Exhaust Nozzle for the High Speed Civil Transportation developed by NASA Glenn Research Center. Courtesy of NASA Glenn Research Center.

The following examples of applications support the view of a promising future for the gamma titanium aluminides containing niobium as high-temperature engineering materials. Recent structural casting innovations by PCC Structurals (62) are approaching the implementation stage for the very large engine of the High Speed Civil Transport (HSCT) where the enabling technology goals are to be reached within 20 years. A new outlet-nozzle has been designed which must provide special features for emission and noise abatement. It can be described as a very large, long box that basically acts as a muffler. Major nozzle components are the welded assembly of several closeout beams and corner I-beam casting segments which form the nozzle sidewall and flap construction. Figure 19 from NASA Glenn Research Center shows the outlet-nozzle and the components to be manufactured with niobium containing gamma titanium aluminides. Figure 20a shows a detailed view of the closeout beam castings that are around 102 cm long and 0.10 to 0.60 cm wall thickness. A corner beam casting section is shown in Figure 20b. It is a substantial casting weighing around 32kg, around 70 cm length and up to 1.58 cm section thickness. The examination of these castings in meeting design requirements is now underway and rig testing of an outlet nozzle section for the HSCT is anticipated.

(a) (b)

Figure 20: a) Close-out beam castings of γ-TiAl produced by PCC Structurals foroutlet-nozzle of HSCT engine (left). b) Cast I-beam and track of γ-TiAl produced by PCC Structurals foroutlet-nozzle of HCST engine (right). Courtesy of PCC Structurals, Inc.

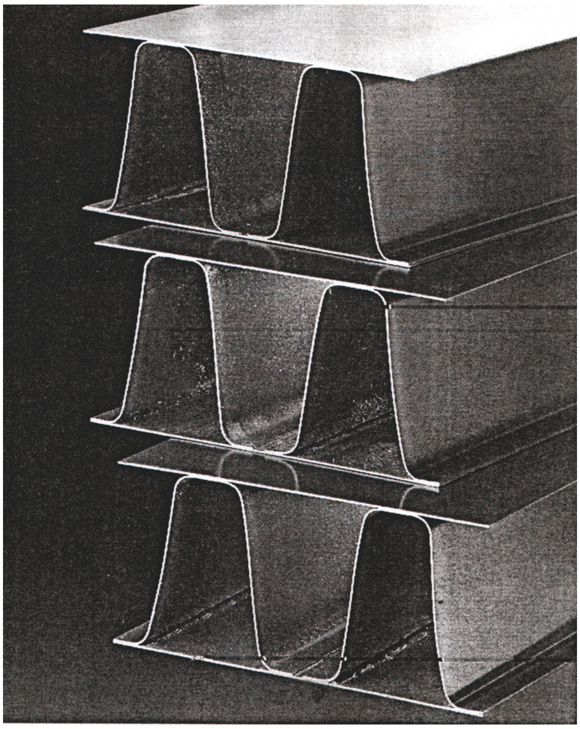


Figure 21: Truss core made by BF Goodrich Aerospace from TiAl sheet for NASA Glenn contract (63). Courtesy of NASA Glenn Research Center.

Recent studies suggest that a divergent flap fabricated from wrought TiAl sheet may provide cost and weight savings. Also, the nozzle sidewall may be a hybrid of cast TiAl substructure and wrought TiAl sheet. Plansee AG has produced sheet, which is being fabricated into various configurations, and these shapes have reached the implementation stage.

NASA has also announced (63) that BF Goodrich Aerospace successfully manufactured the truss core of TiAl sheet (0.625 mm thick) from separately formed corrugations, or hats, covered top and bottom with face sheets of the same material. In cross section, it looks much like a corrugated box, per Figure 21. This production process supports the potential use of TiAl for the skin of the future X-33 space plane and thermal protection system for a reusable launch vehicle, Venture Star (63).

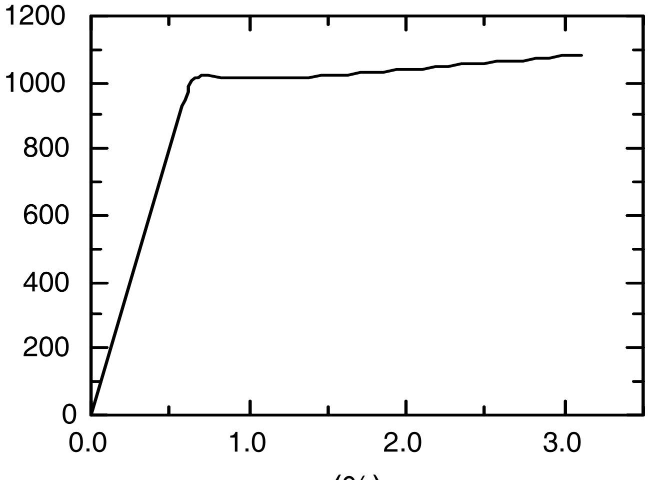


Figure 22: Stress-strain curve as obtained on room temperature tensile testing (MPa) of a specimen Ti-45 Al-(5 – 10) Nb-X (at.%) (52), (53). Courtesy of GKSS.

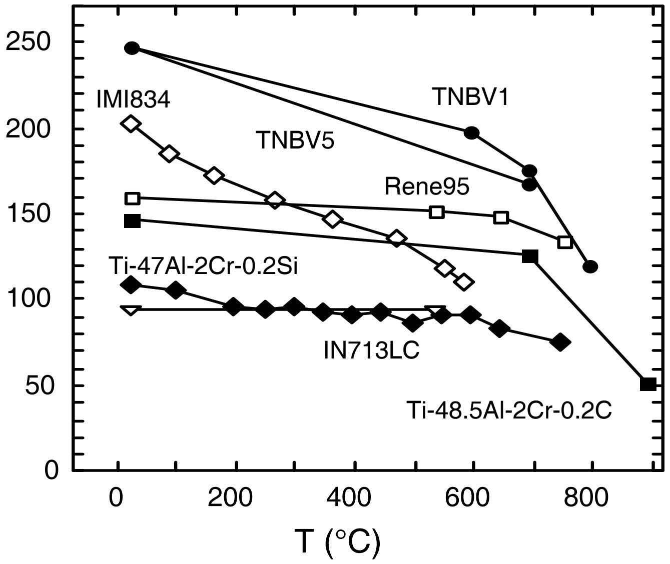


Figure 23: Temperature dependence of the density compensated tensile yield strength (MPa.cm^3/g) of different gamma titanium aluminide alloys. Extremely high specific yield strengths can be obtained for extruded alloys Ti-45 Al-(5 – 10) Nb- X (at.%) denoted as TNBV1 and TNBV5. For comparison the values of Ni-basesuperalloys and a titanium alloy are given 27, 28. Courtesy of GKSS.

Rolls Royce has initiated a program to develop gamma titanium aluminides for low pressure turbine blades in their aircraft engines several years ago. It has become clear in this development that application in turbine engines with strength requirements higher than 1GPa require a wrought version of gamma titanium aluminide. The alloy development done at GKSS by Appel et al (52, 53) was chosen for this specific program. The specific alloy TNB, which belongs in the system Ti-45Al-5-10Nb with carbon additions is the latest generation of high niobium gamma titanium aluminide developed by the group. Figure 22 (52, 53) presents room temperature stress strain curve for GKSS's TNB alloy. Figure 23 (52, 53) shows specific yield strength as a function of temperature for different materials to evidence the superiority of these latest generation alloys, which can contain up to 10at%Nb. Figure 24 (53) shows high-pressure compressor blades successfully manufactured with an earlier version of this gamma-titanium aluminide containing niobium, which is evidence that the future for the application of this specific alloy in aircraft engines is very promising.

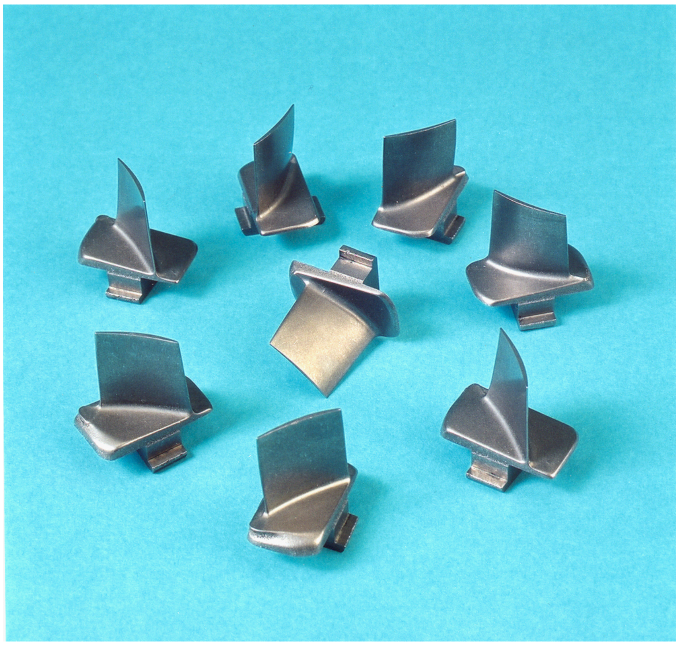


Figure 24: High pressure compressor blades of gamma TiAl manufactured by hot extrusion followed by closed-die forging and electro-chemical milling by GKSS (53). Courtesy of GKSS.

Another example of a special composition refinement of Gamma TiAl alloys for a specific application is the case of Mitsubishi's development involving turbine wheels in turbochargers for passenger vehicles manufactured with Gamma TiAl. The driving force to try Gamma TiAl in this application was the potential improvement in responsiveness and rotating speed of turbocharges when the disks of the turbine is made from lighter materials (64). In addition, lighter disks have the potential to simplify and improve the efficiency of the overall system (64). To evaluate the influence of the microstructure on the rotating strength of TiAl alloys (65), nearly lamellar (NL), fully lamellar (FL) and near gamma (NG) structures were studied. Due to the importance of oxidation resistance in the application, the NL and FL alloys were chosen to contain up to 8at% of niobium in their composition. The NG alloy corresponded to the 1st generation alloy patented by GE and containing 2at% Nb. The best rotating strength was achieved in the near lamellar structure. Further work by Mitsubishi (66) to study the influence of composition and microstructural effects on endurance of TiAl used in turbochargers was done with two alloys containing 0.4at% Nb (Low-Nb) and 7.1at% Nb (High-Nb). The work evidenced that erosion occurred at the wheel blade tips of the low-niobium alloy, but not in the case of the high-niobium alloy. The fully lamellar structure, characterized by very fine colony size and narrow lamellar spacing with superior mechanical properties which was formed in the blade of the high-niobium alloy, is thought to have resulted in the superior resistance to erosion that was observed (66). Figure 25 (67) shows the high-niobium gamma titanium aluminide turbocharger developed by Mitsubishi.

Another development involving gamma titanium aluminides and the automotive industry is associated with engine valves. In this case a casting approach is of fundamental importance in order to make the development economically viable. Loretto et al. (68) have been studying cast versions of gamma titanium aluminides containing up to 8at% niobium for this application with emphasis in both alloy development and process improvement. Figure 26 shows machined gamma TiAl alloy valves used in race cars and manufactured with the alloy 45XD (Ti-45Al-2Mn-2Nb-0.3B) by Howmet Corporation.

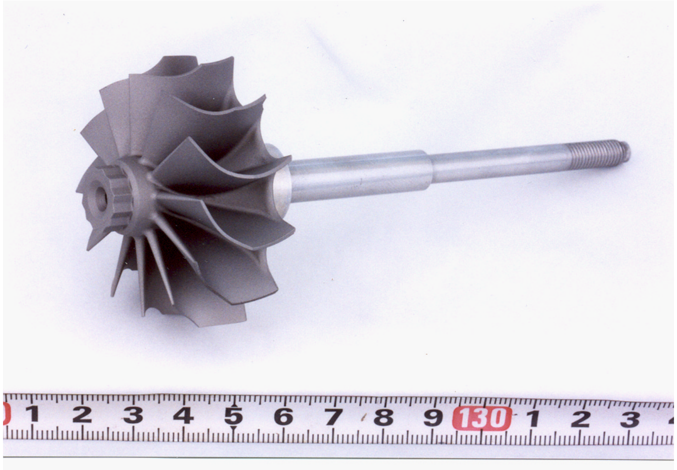


Figure 25: High Nb content γ-TiAl turbine wheel casting and complete assembly of automotive turbocharger by Mitsubishi (67). Courtesy of Mitsubishi Heavy Industries.

Figure 26: γ-TiAl automotive valves manufactured by Howmet Corporation. Courtesy of Howmet Castings.

Compared to aircraft engines, the implementation of this automotive product is much shorter, and perhaps the largest potential markets for γ-TiAl over the next five years are in turbocharger wheels and automotive valves. The extension to large diesel turbochargers will be the next consideration. If an application such as the ones involving the automotive industry were successful, even as a niche market, the learning curve for manufacture of aero-components could be significantly reduced.

Niobium in Thin Films

More recently, niobium has developed into an important material for thin film applications. Although niobium metal is used as the starting material, the great majority of the commercial niobium thin films are actually one of several niobium oxides. Niobium oxide films can be formed with different stoichiometries to attain different final properties. Niobium pentoxide (Nb_2O_5) is a semiconductor with a band gap of about 3.5eV, whereas NbO has metallic conductivity and appearance (69, 71). NbO_2 is used in microelectronics for switching devices(70). Nb_2O_5 can be used as a dielectric because of its high dielectric constant (11 to 100) or as an antireflection coating, because of its high refractive index (2.2 to 2.6) (69). In addition, it can also be used as a barrier layer in Josephson junctions and for decorations since the whole spectrum of colors can be achieved by varying the thickness of the oxide layer. In addition to its optical and dielectric properties, niobium was also found to be an important material for improving the adhesion of diamond-like-carbon (DLC) coatings onto stainless steel substrates, such as that used in razor blades.

Niobium oxide thin films can be present in “stacks” of optical coatings to accomplish different tasks. However, the application where niobium is mostly used is related to the anti-reflection coatings. Anti-reflection is achieved as a direct result of light reflections from interfaces between very thin films that destructively interfere with light resulting in a low total reflectance from the coated transparent object. A coating with a thickness a quarter the wavelength of light, with a refractive index equal to the square root of the refractive index of the substrate, will yield an anti-reflection coating (71). In practice it is difficult to achieve anti-reflection with a single layer as dictated by theory because it is almost impossible to find the materials with matching refractive indexes to obtain the necessary destructive interference. Instead, a multiple stack of optically transparent inorganic materials accomplishes the task. Typical materials used in these stacks include TiO_2, ZrO_2, Nb_2O_5, SiO, SiO_2, Ta_2O_5 and MgF_2 (72).

Table IX (73) shows the configuration of a four-layer anti-reflection coating on glass. These stacks are usually built with a sequence of pairs of low-refraction-index/high-refraction-index materials. The specific coating of Table IX reduces the average reflectance of the system by a factor of 10, when compared with plain glass, i.e., from 4.3% to 0.4%.

Table IX Example of anti-reflection coating for glass for visible light (73)

Layer Nr.	Thickness (µm)	Refractive index (n)
Air		1
1	0.0866	1.47
2	0.1176	2.3
3	0.0348	1.47
4	0.0125	2.3
Glass		1.52

The use of anti-reflection thin films is finding increasing acceptance in several applications. The main importance of these anti-reflecting coatings is to enhance visual acuity by increasing the amount of light transmitted through the transparent object in question.

In lenses made of glass or plastic, anti-reflection coatings can promote such increase in visual acuity. A standard plastic lens can reflect as much as 8 percent of the incident light. Adding an anti-reflection stack to the lens can increase transmittance to greater than 98 percent (72). It is also accepted that the normal reflectance on the front surface of glass is approximately 4.5 percent. Thus, anti-reflection coating can improve the performance of computer screens by reducing photopic reflectance to a minimum. BOC Coating Technology (74) has developed a thin film system for this purpose, which is also conductive and therefore eliminates static electricity buildup on the display. Another example is OCLI's recently patented absorbing anti-reflection coating for computer displays that relies on niobium pentoxide as the high-refractive index material (75).

Examples of additional markets where anti-reflective coatings can be useful are those involving glass in museum displays and shop-windows (74). The high refractive index of niobium pentoxide makes this material an option in every solution involving a stack of different oxide coatings applied to glass to improve its performance. Several markets have been impacted by the use of these high-performance glasses. A good example involves architectural glasses and the use of solar control and low-emissivity coatings to improve the energy balance of buildings. Another area involves the automotive industry and the application of reflecting glass for sunroofs and side window glass, solar control for windshields and side windows and electrically conductive glass for heated windshields.

On another front, niobium thin-film can be used as an interlayer material to enhance the adhesion of different materials. In the process of improving the performance of razor blades with regard to precision edge degradation, Gillette developed and patented a system that relies on diamond-like-carbon (DLC) for this purpose (76 - 78). The literature suggests (79) that, in the initial years, the application of diamond-like-carbon was restricted to areas involving optical coatings and magnetic storage media because of the difficulty of DLC in gaining good adhesion to metallic substrates, among other reasons. The application of niobium as an interlayer material helps to improve the adhesion of DLC coating to stainless steel substrates. In an actual cross section of a multilayer structure of a razor blade, the diamond-like-carbon layer is approximately 20nm thick and the niobium interlayer is approximately 10nm thick. The use of niobium as a coating material in cutting blades is also mentioned in more recent patents assigned to Warner-Lambert Company (80) and to Advanced Refractory Technologies, Inc (81).

Application of niobium is still small compared to other materials in these markets (such as titanium). Thus, it is possible that the benefit of higher volumes is still not realized for niobium end-users. Higher volumes coupled with standard sizes for niobium products should help in improving the overall cost-structure of niobium targets for this market.

Niobium in Medical Implants

The population ratio of the aged people of main countries is rapidly growing. As a consequence, the number of aged people demanding replacement of failed tissue with metallic implants is growing and pushing the development of better materials for this application. Examples of implants are artificial hip joints, artificial knee joints, bone plates and dental implants.

Two main driving forces are responsible for the presence of niobium in medical implant applications. The need to develop an alloy with low modulus to minimize bone resorption and to avoid alloying elements with potential adverse tissue reactions, i.e. the material should be biocompatible.

Currently, the largest amount of implants are made of 316L stainless steel, Co-Cr-Mo alloy, Ti-6Al-4V or commercially pure titanium. All these materials have significantly higher elastic modulus than bone. Concern has been raised from time to time about the stress shielding phenomenon observed in prostheses, i.e. insufficient loading of bone due to the high modulus of the device. This can potentially lead to bone resorption and eventual failure of the arthrosplasty (82). For example, cementless hips have also been associated with thigh pain. This has been attributed to the high stiffness of the prosthesis, which prevents the bone around it from bending while the part of the femur distal to the prosthesis does bend under load. It has been clinically found that patients with stiffer implants suffer of greater hip pain (82).

The clinical data has also been corroborated by laboratory and animal studies. Both finite element analyses and strain gage analyses have demonstrated that lower modulus hips produce stresses and strains that are closer to those of the intact femur. Canine and sheep implantation studies have shown significantly reduced bone resorption in animals with low modulus hips (82). Thus the development of new alloys aiming at low modulus has driven much of the research in this field of application.

Additionally, certain metal ions such as Al, V and Co released by orthopaedic materials have been associated with potential adverse long-term effects. It has been found to be preferable to eliminate these elements from the implant materials as wear debris can be generated by fretting and abrasion by bone and/or bone cement.

Table X Titanium based alloys containing Nb for biomedical applications (83-85)

	Alloy	**Remarks**
1	Commercially pure Ti	(*)
2	Ti-6Al-4V	(*)
3	Ti-6Al-7Nb	α + β type – *Switzerland*
4	Ti-5Al-2.5Fe	α + β type – *Germany*
5	Ti-6Al-6Nb-1Ta; Ti-6Al-2Nb-1Ta	α + β type – *Japan*
6	Ti-5Al-3Mo-4Zr	α + β type – *Japan*
7	Ti-15Sn-4Nb-2Ta-0.2Pd	α + β type – *Japan*
8	Ti-15Zr-4Nb-2Ta-0.2Pd	α + β type – *Japan*
9	Ti-13Nb-13Zr	Near β type – low modulus – *USA*
10	Ti-12Mo-6Zr-2Fe	β type – low modulus – *USA*
11	Ti-15Mo	β type – low modulus – *USA*
12	Ti-16Nb-10Hf	β type – low modulus – *USA* (*)
13	Ti-15Mo-5Zr-3Al	β type – low modulus – *USA* (*)
14	Ti-15Mo-3Nb	β type – low modulus – *USA* (*)
15	Ti-35.3Nb-5.1Ta-7.1Zr	β type – low modulus – *USA*
16	Ti-29Nb-13Ta-4.6Zr	β type – low modulus – *Japan*

Niobium is one of the five elements which have been identified as being the most biocompatible, the other four being titanium, zirconium, tantalum and platinum. Table X presents the main alloys developed as biomaterials over the years (83). The alloys in this table are listed in the order of their introduction as a biomaterial. Alloys 3 and 4 came as a response to the presence of vanadium. Vanadium has been substituted by another beta stabilizer. Subsequently came the effort of eliminating both, vanadium and aluminum and the alloys 6 and 7 were developed. The elimination of aluminum from the chemical composition of these materials is due to the concern with its association to Alzheimer's disease. The elimination of iron is associated with MRI compatibility. Following this development came the pursue of a low modulus material to avoid bone resorption. The alloy Ti-13Nb-13Zr was the first to answer this additional constraint in the development of implant materials.

In developing the alloy Ti-13Nb-13Zr, Mishra et alli (82) determined that the alloy has a low modulus, excellent wear resistance and corrosion resistance, and superior biocompatibility. Compared to mill-annealed, standard grade Ti-6Al-4V, Ti-13-13 was determined to have equivalent tensile strength (UTS 994MPa, YS 864MPa) and ductility (13% elongation), 30% lower elastic modulus (81GPa), equivalent 10 million cycle unnotched axial fatigue endurance limit (500MPa), higher notched fatigue endurance limit, 20% higher plane strain fracture toughness, 30 to 40% lower flexure and shear moduli, 40% lower corrosion rates in simulated body environments and equivalent wear resistance. Cold working of Ti-13-13 lowered its modulus to below 50GPa while retaining the high strength. The UTS can also be increased to more than 1,100MPa with YS of 980MPa by hot working and heat treatment variations. The alloy was found to have higher osseointegration than CP Ti, and lower inflammation, fibrosis and necrosis, compared to Ti-6Al-4V. It contains only titanium, niobium and zirconium which are the three most biocompatible elements of the periodic table. For comparison purposes, the modulus of elasticity for Co-Cr-Mo alloys is approximately 230GPa, 316L Stainless Steels is 220GPa, Ti-6Al-4V is 120GPa and bones have modulus in the range of 30 and 40GPa.

After the development of the Ti-13Nb-13Zr alloy several others alloys, also containing niobium, were introduced aiming at solving the problem with rigidity compatibility.

Data on cyto-toxicity, biocompatibility and allergy are all important in determining the alloying elements to be used in the development of new alloys. Cyto-toxicity data (83) shows that the most toxic elements are vanadium, copper, zinc, cadmium, mercury, magnesium, strontium, iron, cobalt, bismuth and silver, with molybdenum being a question mark. Allergy data from Europe shows that approximately 20% of young females and 4% of young males suffer from nickel allergy. Other elements found to have a considerable percentage of allergic reaction are mercury, cobalt, tin, palladium, chromium, copper and platinum (83). Therefore, considering all the requirements when designing alloys for medical implants, the safest metallic materials would be titanium alloys containing niobium, zirconium and tantalum.

Pure niobium is also a candidate for developing new implant materials because it has better electrochemical properties and better biocompatibility than titanium and titanium alloys. However pure niobium has lower mechanical strength than titanium and titanium alloys. Recent results have shown that cold work may be sufficient to develop the necessary mechanical properties to introduce pure niobium as an implant material.

Shape memory effect is very important for several implant applications. Although the alloy Ti-Ni has been tried as an implant material, its nickel content restricts its current use. A new family of shape memory alloys containing titanium, niobium and tin are under development for bio-applications. Shape memory effect has been investigated in nickel-free Ti-Nb-Sn alloys for biomedical applications by Nitta et al (86). Ms temperature decreases significantly with increasing Nb or Sn content. The decrease in Ms is about 50°C with 1at% increase of Nb content and about 100°C with 1at% increase of Sn content. Shape memory effect is observed when alloys are deformed below Af in a similar way to shape memory TiNi alloys. The maximum recovered strain is evaluated to be about 3.5% in Ti-18at%Nb-4at%Sn, which is similar to other Ti alloys with the parent phase of bcc, but smaller than TiNi alloys with the parent phase of B2 ordered structure. Another advantage of Ti-Nb-Sn alloys is to have excellent deformability at ambient temperature in comparison with TiNi alloys (86).

Niobium for Electrolytic Capacitors

Niobium oxide is well established as a material for ceramic capacitors. Niobium also has a prominent future as a material for electrolytic capacitors. The idea of having niobium in this field of application is not new. The first electrolytic capacitors made out of niobium were manufactured decades ago. However, the limitation imposed by the poorer stability of the niobium oxide film when compared to the tantalum capacitor has limited its used for all these years. More recently, several technological advances have overcome this limitation and niobium is expected to play a very important role as a material for electrolytic capacitors in the near future.

Niobium has been studied as a potential substitute for tantalum in this application in several occasions over the last decades. In fact, niobium has always presented a theoretical potential of achieving very high capacitances. Table XI shows the relevant properties of niobium for this application as compared to those of tantalum and aluminum. Thus, a tantalum powder of 40,000 µF.V/g is equivalent to a niobium powder of 80,000 µF.V/g.

Table XI Niobium as a potential substitute for tantalum and aluminium in electrolytic capacitors

	Niobium	**Tantalum**	**Aluminium**
Density (g/cm³)	8.57	16.6	2.7
Melting point (°C)	2468	2996	660
Dielectric constant	41	27	9
Oxide formation constant at 20°C (A/V)	25	17	12

However, the main driving force explaining this interest has been the characteristics of the niobium supply as a raw material. Niobium is plentiful, reliable and has demonstrated unique price stability over the years, which was reported by NEC (87) as a very important characteristic to cope with the rapidly increasing demand of electrolytic capacitors imposed by the electronic industry, especially for cellular phones, personal computers and automotive electronic systems. In contrast, tantalum has had price instability in several occasions due to lack of supply. More than once in the past the installed capacity to generate tantalum ores was not in phase with curve of demand for tantalum products, in special tantalum capacitors. The most recent of these circumstances occurred in 1999 and 2000 when the price of tantalum ore escalated and the risk of shortage was evidenced by the long delivery times in the industry.

Although the replacement of niobium for at least some of the tantalum capacitors is the most obvious target in this niobium development, there is a chance to create a new market with niobium electrolytic capacitors when combining the high capacitance of niobium with its volumetric efficiency. Applications such as the ones that cannot afford the high price of tantalum capacitors and the low volumetric efficiency of aluminum capacitors may become feasible with niobium capacitors. In addition, some of the tantalum capacitor could be replaced by the niobium capacitors especially in those applications where high capacitance is more important than low d.c. leakage, which is a characteristic excelled by the tantalum capacitors.

H.C.Starck (88) has developed a new reduction process to obtain very fine niobium powders via direct reduction of its oxide that resulted in reported capacitances as high as 150,000 µF.V/g. They have reported (88) that the two main developments in powder processing to accomplish this success in the niobium powder manufacturing for this application were (i) the reduction of powder oxygen by deoxidation with magnesium or similar alkaline metal, and (ii) the development of treatments that add nitrogen to the surface and bulk of the powder in order to reduce the oxygen concentration and stabilize the metal anodic oxide film interface to oxygen migration. Serjak et al (88) report that the niobium powder manufactured with this new method has physical characteristics very similar to the capacitor grade tantalum powder, which allow it to be processed on the same equipment used for tantalum by the capacitor manufacturers. Moreover, extensive tests have shown that these niobium powders have leakage as low as 0.5nA/μF.V, which is comparable to tantalum tested under the same conditions. Leakage current is the one flowing to reform and repair the oxide layer while a voltage is being applied. It is measured several minutes after the capacitor reaches the rated voltage.

Capacitor grade niobium powders can also be obtained via hydriding and de-hydriding process followed by a particle conditioning known as flake formation. This manufacturing route has been optimized by Cabot Corporation in the past (89). Although this processing route has been thought to result in lower capacitance powders, improvements have been reported to allow for the manufacturing of niobium powder with as much as 70,000 μF.V/g.

The technological solution at NEC (87) for the implementation of their line of niobium capacitors was to adopt a functional polymeric material instead of manganese dioxide as a cathode. NEC was also the first company to commercialize functional polymer-type tantalum capacitors. The use of a functional polymer as a cathode avoids the niobium exposure to a higher temperature (200 to 300°C), which is necessary in the case of the manganese dioxide process to form the cathodic layer, solving the problem associated with the lack of stability of the niobium oxide film at higher temperatures. The formation of a cathodic layer with a conductive polymer occurs at room temperature (25^oC), which allows for no defect to be formed in the niobium oxide film. Furthermore, during the high temperature loading test for reliability evaluation, if a defect is developed in the niobium oxide film the conductive polymer in contact with the defect oxidizes to become an insulator, preventing any increase in leakage current (87).

In June of 2001 NEC reported the successful start up of commercialization for its line of niobium electrolytic capacitors. The other major capacitor manufacturers, e.g. Vishay, AVX, Kemet and EPCOS are expected to also offer niobium capacitors with their own technological solutions.

Copper-niobium

Research studies in the past have demonstrated that heavily cold-worked copper-niobium alloys present attractive combination of properties. These alloys present high strength with good electrical and thermal conductivities and present much easier fabrication characteristics when compared to more complex composite materials.

While developing in-situ fabrication of Cu-Nb_3Sn superconducting material, Bevk et al (90) showed that a Cu-20wt%Nb alloy, highly cold deformed, could reach ultimate tensile strength as high as 2,300MPa. This strength level is higher than that predicted by the rule of mixtures and close to the theoretical strength of metal whiskers. Since pure niobium has a very small solubility in copper and is extremely ductile, a starting material with well dispersed niobium particles in a copper matrix, obtained via melting routes such as vacuum-arc or plasma-arc melting, or via powder route, subsequently cold deformed, will allow a final product (wire or sheet) with the special combination of properties mentioned above.

The favorable copper-niobium properties can be traced to their aligned composite structure formed by mechanical deformation. The homogeneously dispersed niobium particles in the as-cast ingot are transformed into ribbon-shaped filaments in the copper matrix after cold deformation.

Several components for aerospace systems require materials with high strength, enough capacity to dissipate heat fluxes as well as properties stability at temperatures as high as 1,200F. Ames Laboratory and Rockwell International (91) have reported achievements in obtaining Cu-15wt%Nb sheets with 0.25mm thickness and 1,028MPa for the ultimate tensile strength.

In recent developments (92) fostered by NASA the system Cu-Cr-Nb has been studied and the alloy Cu-8Cr-4Nb (at%) identified as a material to replace the conventional NARloy-Z for thrust chamber applications. Figure 27 shows thrust chamber components fabricated with the alloy Cu-8Cr-4Nb (at%). The alloy, which is dispersion strengthened by the intermetallic Cr_2Nb was found to have good thermal conductivity, lower thermal expansion, higher strength especially after brazing, good ductility at all temperatures, superior creep resistance and longer low cycle fatigue lives when compared to NARloy-Z.

Another application with good market potential for copper-niobium alloys is annealing bands. In high-speed resistance annealers the wire to be heat-treated is resistance heated. The most common band material currently used in these annealers is nickel. The erosion of these bands is excessive and translates into increased maintenance and lost production time, in addition to affecting the quality of the final product by generating inclusions in the wire. Copper-niobium annealing bands far outlast standard materials such as nickel and stainless steel due to its much higher conductivity and high strength levels that can be achieved when compared to these materials (93). As an example, the electrical conductivity of copper-niobium alloys is approximately 80% IACS as opposed to 25% IACS for nickel. As a consequence, copper-niobium presents high arc-resistance with decreased material erosion in operation.

Donaldson et al (94) have shown that copper-niobium was the material with the lowest erosion rate among numerous other electrode materials when examining electrode erosion in high current and high-energy spark gaps. In addition to copper-niobium, the authors included in their study materials such as copper, carbon, molybdenum, copper-tungsten, copper-molybdenum, copper-carbon, copper-zirconium and copper-zirconium-chromium. The erosion rate of copper-niobium was half of that for the second best material and it was more than ten times lower than that of copper.

Superconductivity

High RRR (residual resistivity ratio) bulk niobium cavities are the workhorses of all the SRF accelerators that are under construction such as the Spallation Neutron Source in the U.S. and/or in planning to be built such as the RIA in the U.S. and TESLA in Germany. The largest of these projects is TESLA, planned to be built in Germany, which is designed to be more than thirty kilometers long and to consume some 600 tones of high Residual Resistivity Ratio niobium cavities (95). Figure 28 shows a six-cell cavity used in the SNS Project.

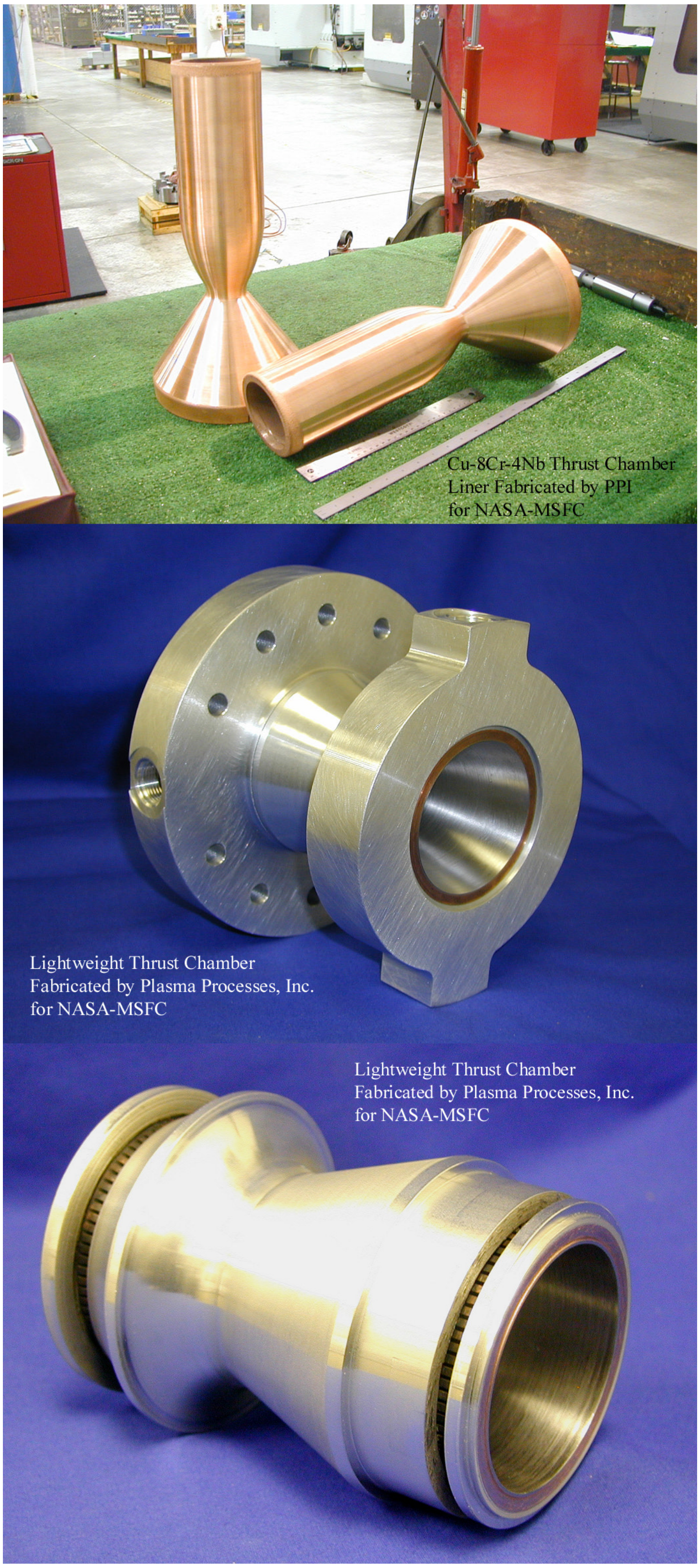


Figure 27: Thrust chamber components manufactured with Cu-8Cr-4Nb alloy. Courtesy of NASA.

Figure 28: Six-cell superconducting RF niobium cavity for the Spallation Neutron Source Accelerator. Courtesy of Thomas Jefferson National Accelerator Facility.

Superconducting niobium-titanium cables still are the largest application of any niobium-based alloy, which the main consumption dictated by the MRI industry. Larger amounts of niobium metal (approximately 400 tonnes) will be consumed in the construction of the Large Hadron Collider Accelerator in Europe. This specific demand has been initiated two years ago and should last until 2004.

The next generation of colliders should demand a superconducting material with enhanced properties when compared to the conventional Nb-46wt%Ti material. Several efforts are taking place to develop affordable superconducting cables using Nb_3Sn. It is reasonable to expect that this material could replace NbTi for MRI applications in the future.

Conclusion

This year the metal niobium is 200 years old. However, its industrial application is only about 70 years old, which compared to other metals, is rather a short period. The industrial breakthrough as an alloying element in steel came even later, in the late 1950’s, when the development and industrial application of microalloyed steels coincided with the emergence and exploitation of the Araxá niobium deposit and other pyrochlore mines. Around this time the cobalt crisis paved the way for niobium in superalloys.

The bulk of niobium still goes into steel and, as it stands, this will remain so in the foreseeable future, because niobium’s present position in the 3 main microalloyed steel domains is unchallenged:

<u>Pipe steels.</u> Niobium will remain a chief microalloying element in all steel grades. Due to the latest technological development the usage can even increase.

<u>Automotive steels.</u> Niobium will remain the most important microalloying element in all hot and cold rolled HSLA steels. There is a good chance that niobium will also penetrate the new and important group of multi-phase steels, because their properties can be further improved.

<u>Structural steels.</u> All thermomechanically processed high strength steels for structural components will contain niobium as the first-choice microalloy in the future. The technical

trend from QT steels towards TM steels will further enhance the application of such steels and hence of niobium.
The penetration of niobium into high carbon tool and engineering steels continues to make progress and will lead to further diversification. Nevertheless, extensive research will be mandatory to maintain and expand these applications.

Besides these standard applications niobium has a bright future as an optional material to be part of advanced solutions in the "high-tech" industries, such as:

High temperature applications. In all important superalloys niobium is an indispensable addition. The latest developments to even higher operating temperatures or lower cost alloys leaves niobium's position unchallenged. This is true also for the niobium-based alloys, where niobium is viewed as contributing to the demanding goals of the aircraft and space industries. The latest development of titanium aluminides includes higher niobium contents as well.

Superconductivity. Due to the high critical temperature of niobium and the good workability of NbTi the position of niobium remains unchallenged despite some progress of ceramic superconductors.

In a variety of new technologies such as in thin films, medical implants, electrolytic capacitors, copper-niobium alloys, special grades of niobium oxide and niobium compounds for catalytic uses, niobium has made substantial inroads for new applications. These do not comprise much tonnage, but have a very high potential for value added products. However, much research and development efforts are needed to make it happen.

References

(1) E.C. Bain, R.H. Aborn and J. J.B. Rutherford, Trans. Am. Soc. for Steel Treating 1933, 21, 481.

(2) See paper of L. Meyer, Proceedings of The International Symposium Niobium 2001, (Orlando, Florida, USA), in particular references 1 and 2.

(3) T.C. Barron, Proceedings of The International Symposium Niobium 81, (San Francisco, California, USA, 1981), 1223-1236.

(4) H. Stuart, Proceedings of "The International Symposium Niobium 81", (San Francisco, California, USA, 1981), 1237-1249

(5) H.G. Hillenbrand and M. Gräf, Proceedings of The International Symposium Niobium 2001, (Orlando, Florida, USA).

(6) H.G. Hillenbrand et al., "Development of Large-Diameter Pipe in Grade X100," Pipeline Technology Conference, (Brugge, Belgium, 2000).

(7) K. Hulka, J. M. Gray and F. Heisterkamp, "Metallurgical concept and full scale testing of a high toughness, H_2S resistant 0.03%C-0.1 %Nb steel," (Niobium Technical Report, NbTr-16/90, 1990).

(8) ULSAB-AVC Consortium (2001) ULSAB-AVC Technical Transfer Dispatch #6 – Body Structure Materials, May 2001.

(9) This chapter includes information from Internal Reports of Niobium Products Company prepared by Dr. Jitendra Patel.

(10) Heller et al., "Thermomechanical rolling of hot-rolled multiphase steels," in Conference Preprints of Thermomechanical Processing of Steels, (London, UK, May 24-26, 2000). The Institute of Materials.

(11) J. Neutjens et al., "Processing and properties of a new hot rolled high strength fine grained multi phase steel," 40th Mechanical Working and Steel Processing Conference Proceedings, The Iron and Steel Society, (Pittsburgh, PA, October 25-28, 1998).

(12) C. Eberle, "New thermomechanical strategies for the realisation of multiphase steels showing a TRIP effect," 40th Mechanical Working and Steel Processing Conference Proceedings The Iron and Steel Society, (Pittsburgh, PA, October 25-28, 1998).

(13) H. Takechi, "Effect of niobium additions on the formation of retained austenite in hot rolled TRIP steels," Proceedings of the fourth international conference on HSLA Steels, Metallurgical Industry Press (Xi'an, China. October 30 – November 2, 2000).

(14) M. Korchinsky and H. Stuart, "The role of strong carbide and sulfide forming elements in the manufacture of formable high strength low alloy steel," Symposium on low alloy high strength steels, The Metallurgy Companies, (Nürnberg, BRD, May 21- 23, 1970).

(15) L. Meyer, W. Bleck and W. Müschenborn, "Physical Metallurgy of IF Steels," ISIJ, (Tokyo, Japan, 1994), 203.

(16) H. Abe and S. Satoh, (Kawasaki Steel Techn. Rep, 22, 1990), 48.

(17) Y. Sakuma, O, Matsumura and H. Takechi, Met. Trans. A, 22 A, (1991), 489.

(18) K. Hulka, W. Bleck and K. Papamantellos, 41st mechanical working and steel processing conference, (Baltimore (MD), Oct. 1999).

(19) W. Bleck, Proceedings of The International Symposium Niobium 2001, (Orlando, Florida, USA).

(20) M. Tsuda, "Soft Stainless Steel, Ferritic Stainless Steel, NAS430DS, NAS436LS," (NipponYakinTechnical Report. 2, 1993), 41-47.

(21) N. Hiramatsu, Proceedings of The International Symposium Niobium 2001, (Orlando, Florida, USA).

(22) P.Charlier and L Bäcker, Proceedings of the 7th International Conference on the Strength of Metals and alloys, (Montreal, 12-16 August, 1986) vol.2, 1019-1024.

(23) P. Charlier, A. Guimier, Proceedings Microalloyed Steel Grades for the Car and Truck Industry, (Moscow, 19.-21 April, 1988).

(24) B. Heritier, Ph Maitrpierre, J.Rofes-Vernis and A.Wyckaert, "HSLA-Steels Technology and Application," (ASM Book, Metals Park Ohio, 1984).

(25) F. Jeglitsch, Proceedings of The International Symposium Niobium 2001, (Orlando, Florida, USA).

(26) Barker, J.F., "The Initial Years of Alloy 718, A GE Perspective," Superalloy 718 Metallurgy and Applications, ed. E.A. Loria, (TMS, Warrendale, PA, 1989), 269-277.

(27) Schafrik, R.E., Ward, D.D. and Groh, J.R., "Application of Alloy 718 in GE Aircraft Engines: Past, Present and Next Five Years," Superalloys 718, 625, 706 and Various Derivatives, ed. Loria, (E.A.. TMS 2001).

(28) Paulonis, D.F. and Schirra, J.J. "Alloy 718 at Pratt & Whitney – Historical Perspective and Future Challenges," Superalloys 718, 625, 706 and Various Derivatives, ed. Loria, (E.A. TMS 2001).

(29) Schwant, R.C. et al., "Large 718 Forgings for Land Based Turbines," Superalloys 718, 625, 706 and Various Derivatives, ed. Loria, (E.A. TMS 1997), 141-152.

(30) Schilke, P.W. and Schwant, R.C., "Alloy 706 Use, Progress Optimization, and Future Directions for GE Gas Turbine Rotor Materials," Superalloys 718, 625, 706 and Various Derivatives, Ed. Loria, (E.A. TMS 2001), 25-34.

(31) Smith, G.D.; Tillack, D.J. and Patel, S.J., "Alloy 625 – Impressive Past, Significant Present, Awesome Future," Superalloys 718, 625, 706 and Various Derivatives, ed. Loria, (E.A. TMS 2001), 35-46.

(32) Fahrmann, M. G. and Smith, G. D., "Capitalizing on Computational Tools in Alloy and Process Development," Advanced Technologies for Superalloys Affordability, ed. Chang, K.-M., Srivastava, S.K., Furrer D.U. and Bain, K.R., (TMS 2000), 73-81.

(33) Fahrmann, M. G. and Smith, G. D., "Capitalizing on Computational Tools in the Development of a New Low-Cost Diesel Truck Exhaust Valve Alloy," (Paper presented at the TMS Fall Meeting, February 2001, New Orleans).

(34) Titran, R.H., "Refractory Metals Forum: Niobium and Its Alloys", Advanced Materials & Processes, 142 (11) (1992), 34-41.

(35) Wojcik, C. C., "High Temperature Niobium Alloys," High Temperature Niobium Alloys, ed. J.J.Stephens, I.Ahmad, (TMS, Warrendale, PA, 1991), 1-12.

(36) Dimiduk, D.M.; Mendiratta, M.G. and Subramanian, P.R. "Development Approaches for Advanced Intermetallic Materials - Historical Perspective and Selected Successes," Structural Intermetallics. ed. R. Darolia et al., (TMS, Warrendale, PA, 1993), 619-630.

(37) Subramanian, P.R.; Mendiratta, M.G.; Dimiduk, D.M. and Stucke, M.A., "Advanced intermetallic alloys - beyond gamma titanium aluminides," Materials Science & Engineering A, 239-240 (1997), 1-13.

(38) Bewlay, B.P.; Jackson, M.R. and Lipsitt, H.A. "The balance of mechanical and environmental properties of a multielement niobium-niobium silicide-based in-situ composite," Metallurgical Materials Transactions A, 27A, (1996), 3801-3808.

(39) Schafrik, R.E. "A Perspective on Intermetallic Commercialization for Aero-Turbine Applications," Third International Symposium on Structural Intermetallics, (TMS 2001).

(40) Davidson, D.E., "Designing with Gamma Titanium CAESAR Program Titanium Aluminide Component Applications," Superalloys 1996, ed. R.D.Kissinger et al., (TMS, Warrendale, PA, 1996), 545-553.

(41) Williams, J.C., "The Effect of a Changing Environment on the Requirements for Engine Materials," Superalloys 1992, ed. S.D.Antolovich et al., (TMS, Warrendale, PA, 1992), 3-11.

(42) Austin, C.M. and Kelly, T.J., "Gas Turbine Engine Implementation of Gamma Titanium Aluminide," Superalloys 1996, ed. R.D.Kissinger et al., (TMS, Warrendale, PA, 1996), 539-543.

(43) Kim, Y-W., "Intermetallic Alloys Based on Gamma Titanium Aluminide," JOM, 41 (7) (1989), 24-30.

(44) Chan, K.S., "Understanding Fracture Toughness in Gamma TiAl," JOM, 44 (5) (1992), 30-38.

(45) Austin, C.M. and Kelly, T.J., "Development and Implementation Status of Cast Gamma Titanium Aluminide," Structural Intermetallics, ed. R. Darolia et al., (TMS, Warrendale, PA, 1993), 143-150.

(46) Huang, S-C., "Alloying Considerations in Gamma-Based Alloys," Structural Intermetallics, ed. R.Darolia et al., (TMS, Warrendale, PA, 1993), 299-307.

(47) Huang, S-C.; McKee, D.W.; Shih, D.S. and Chesnutt, J.C., "TiAl Alloys Containing Cr and Nb," Intermetallic Compounds Structure and Mechanical Properties, The Japan Institute of Metals, (Sendai, Japan 17-20, June 1991), 363-370.

(48) Varma, S. K.; Chan, A. and Mahapatra, R. N., "Static and Cyclic Oxidation of Ti-44Al and Ti-44Al-xNb Alloys," Oxidation of Metals, 55 (5/6) (2001), 423-435.

(49) Zhang, W.; Chen, G. and Sun, Z. "Oxidation of Ternary Ti18Nb48Al and Ti10Nb45Al Alloys," Scripta Metallurgica et Materialia, 28 (1993), 563-567.

(50) Chen, G.L., Zhang, W.J., Liu, Z.C., Li, S.J. and Kim, Y-W., "Microstructure and Properties of High-Nb Containing TiAl-Base Alloys," Second International Symposium on Gamma Titanium Aluminides (ISGTA99), ed. Y-W. Kim et al., (TMS, Warrendale, PA, 1999).

(51) Appel, F.; Lorenz, U.; Paul, J.D.H. and Oehring, M., "The Mechanical Properties of Niobium Alloyed Gamma Titanium Aluminides," Second International Symposium on Gamma Titanium Aluminides (ISGTA99), ed. Y-W. Kim et al., (TMS, Warrendale, PA, 1999).

(52) Appel, F.; Oehring, M. and Wagner, R., "Novel Design Concepts for Gamma-base Titanium Aluminide Alloys," Intermetallics 8, (2000), 1283-1312.

(53) Appel, F. et al., "Recent Progress in the Development of Gamma Titanium Aluminide Alloys," Advanced Engineering Materials, 2 (11) (2000), 699-720.

(54) Woodward, C.; Rao, S.I. and Dimiduk, D.M. "Computational Tools for Alloy Design: Solid Solutions in Gamma Ti-Al," JOM, 50 (7) (1998), 37-41.

(55) Huang, S-C. U.S. Patent 4,879,092, "Titanium Aluminum Alloys Modified by Chromium and Niobium and Method of Preparation," (1989).

(56) Austin, C.M. and Kelly, T.J. "Gas Turbine Engine Implementation of Gamma Titanium Aluminide," Superalloys 1996, ed. R.D.Kissinger et al., (TMS, Warrendale, PA, 1996), 539-543.

(57) Austin, C.M.; Kelly, T.J.; McAllister, K.G. and Chesnutt, J.C. "Aircraft Engine Applications for Gamma Titanium Aluminide," Structural Intermetallics 1997, ed. M.V. Nathal et al., (TMS, Warrendale, PA, 1997), 413-425.

(58) Kampe, S.L.; Christodoulou, L. and Larsen Jr., D.E. U.S. Patent 5,458,701, "Cr and Mn Bearing Gamma Titanium Aluminides Having Second Phase Dispersoids," (1995).

(59) Kim, Y-W. and Dimiduk, D.M. U.S. Patent 5,558,729, "Method to Produce Gamma Titanium Aluminide Articles Having Improved Properties," (1996).

(60) Gouma, P.I.; Subramanian, K.; Kim Y-K. and Mills, M.J. "Precipitation and Creep Strengthening Mechanisms in K5 Series Gamma-TiAl Alloys," High-temperature Ordered Intermetallic Alloys VIII, ed. E.P.George et al., (MRS, Warrendale, PA, 552, 1999), KK2.11, 1-6.

(61) Jain, S.K. and Roessler, J.R. U.S. Patent 5,296,056, "Titanium Aluminide Alloys," (1994).

(62) M. Lu. And J. Barrett, "Investment Casting of Large Gamma Titanium Aluminide for Aircraft Application", (Paper presented at Automat 99, Dayton ASM, June 22, 1999).

(63) Bartoltta, P. NASA, "Aerospace Materials Processing Technology Transfer to Industry," GRC news release 99-79, October 8, 1999.

(64) Tetsui, T.; Higuchi, H. and Takita, K. "Development of TiAl Forged Alloy for High-Temperature High-Speed Rotating Components," Mitsubishi Heavy Industries, Ltd., Technical Review Vol.34, nr.1 (Feb 1997).

(65) Tetsui, T.; Takita, K., Higuchi, H. and Ono, S. "Rotating Strength of Forged TiAl Alloys," Intermetallics, 7 (1999), 193-199.

(66) Tetsui, T. and Ono, S. "Endurance and Composition and Microstructure Effects on Endurance of TiAl Used in Turbochargers," Intermetallics, 7 (1999), 689-697.

(67) Tetsui, T.; Kyoya, M. and Miura, Y. “Development of TiAl Turbocharger for Passenger Vehicles,” Mitsubishi Heavy Industries, Ltd. Technical Review 37 (3), 88-91, (2000).

(68) Wu, X.; Hu,D.; Botten, R. and Loretto, M.H. “Micro-Yield and the Fatigue Limit of TiAl Alloys,” Third International Symposium on Structural Intermetallics, TMS, (2001).

(69) Gerfin, T. and Graetzel, M. “Ellipsometric investigation of metal-organic chemical vapor deposition of niobium oxide films,” Chemical Vapor Deposition of Refractory Metals and Ceramics III, Vol. 363, ed. Gallois, B.M. and Pickering, M.A., (MRS, Pittsburgh, PA), 45-50.

(70) Deutschmann, L.; Suhr, H.; Herrmann, W.A. and Haerter, P. „Thin films of niobium and niobium oxides by PECVD,” Eur. J. Solid State Inorg. Chem., 28 (5) (1991), 1161-1171.

(71) MacLeod, H.A., “Thin Film Optical Filters,” 2 ed., (McGraw-Hill/Adam Hilger, New York, 1989). In: Bohling, D.A.; Diggins, D.R.; Morris, M.A. and Murphy, P. A look at lenses. Vacuum & Thin Film, Nov.-Dec. 1998, p. 22-28.

(72) Bohling, D.A.; Diggins, D.R.; Morris, M.A. and Murphy, P. “A look at lenses”, Vacuum & Thinfilm, (Nov.-Dec. 1998), 22-28.

(73) Southwell, W.H. “Modeling of Optical Thin Films,” Vacuum & Thinfilm, (May 1999), 17-23.

(74) Hill, R.J. “Coated Glasses for the 21st Century,” Vacuum & Thinfilm, (April 1999), 19-23.

(75) Klinger, R.E. and Solberg, S.E., “Absorbing anti-reflection coatings for computer displays,” U.S. Patent Nr. 5,858,519, (January 12, 1999).

(76) Hahn, S.S.; Madeira, J. and Ruth, J.A. “Razor blade technology,” U.S.Patent Nr. 5,295,305, (March 22, 1994).

(77) Hahn, S.S.; Madeira, J., Chou, C.P. and Brooks, L.E., “Razor blade technology,” U.S.Patent Nr. 5,669,144, (September 23, 1997).

(78) Surowiecki, J. “The Billion-Dollar Blade,” The New Yorker, (June 15, 1998), 43-49.

(79) Jethanandani, R. “The development and application of diamond-like carbon films,” JOM, (February 1997), 63-65.

(80) Wexler, F.C. “Multi-blade razor head with improved performance,” U.S.Patent Nr. 5,630,275, (May 20, 1997).

(81) Goel, A. and Bray, D.J. “Method for preserving precision edges using diamond-like nanocomposite film coatings,” U.S.Patent Nr. 5,795,648, (August 18, 1998).

(82) Mishra, A. K.; Davidson, J. A.; Poggie, R. A.; Kovacs, P. and FitzGerald, T. J., “Mechanical and Tribological Properties and Biocompatibility of Diffusion Hardened Ti-13Nb-13Zr – A New Titanium Alloy for Surgical Implants,” Medical Applications of

Titanium and Its Alloys: The Material and Biological Issues, ed. Brown and J. E. Lemons, (American Society for Testing and Materials, ASTM STP 1272, S. A., 1996), 96-113.

(83) Niinomi, M. "Recent Biocompatible Metallic Materials," Structural Biomaterials for the 21st Century, ed. Niinomi, M. et al., (The Minerals, Metals & Materials Society, 2001), 3-14,.

(84) Ikeda, M.; Komatsu, S.; Sowa, I. And Niinomi, M. "Isothermal Aging Behavior of Ti-29Nb-13Ta-4.6Zr New Beta Alloy for Medical Implant," ed. Niinomi, M. et al., (The Minerals, Metals & Materials Society, 2001), 15-23.

(85) Kuroda, D.; Niinomi, M.; Akahori, T.; Fukui, H.; Suzuki, A. and Hasegawa, J. "Mechanical Performance of Newly Developed β-Type Titanium Alloy, Ti-29Nb-13Ta-4.6Zr, for Biomedical Applications," ed. Niinomi, M. et al., (The Minerals, Metals & Materials Society, 2001), 99-106.

(86) Nitta, K.; Watanabe, S.; Masahashi, N.; Hosoda, H. and Hanada, S. "Ni-Free Ti-Nb-Sn Shape Memory Alloys," ed. Niinomi, M et al., (The Minerals, Metals & Materials Society, 2001), 25-34.

(87) Nishiyama, T. and Nakada, T. "Development of Niobium Capacitors," (Proceedings TIC Conference, San Francisco 2000).

(88) Serjak, W.A.; Schechter, L.; Tripp, T.B.; Lanin, L.L.; Reichert, K.; Thomas, O. and Vieregge, J., "A New Material for Capacitors: Niobium," CARTS 2000: 20th Capacitor and Resistor Technology Symposium, 82-85.

(89) Fife, J. Cabot Corporation. World Patent WO 99/57739.

(90) Bevk, J.; Harbison, J. P. and Bell, J. L., J. Appl. Phys., 49 (6031) (1968).

(91) Spitzig, W. A.; Reed, L. K. and Krotz, P. D., J. Mat. Sci. Let., 10 (371) (1991).

(92) Ellis, D.; Keller, D. and Lerch, B. "Thermophysical and Mechanical Properties Database for Extruded GRCop-84," (Paper presented at the TMS 2001 Annual Meeting, February 2001).

(93) Forde, Paul. H.C.Starck, Inc. Private communication.

(94) Donaldson, A.L.; Kristiansen, M.; Watson, A.; Zinsmeyer, K.; Kristiansen, E. and Dethiefsen, R. "Electrode Erosion in High Current, High Energy Transient Arcs," 37-43.

(95) Singer, W.; Kaiser, H. and Proch, H. "Application of High Purity Niobium for Superconducting TESLA Cavities," (Paper presented at the TIC Conference. San Francisco, 2000).