NIOBIUM: FUTURE POSSIBILITIES – TECHNOLOGY AND THE MARKET PLACE

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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 enduses 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 "hightech" 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

<u>General</u>

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 Nb₃Sn 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 interacted areas the energy analysts in the coming decides in order to most the energy analysts areas the energy analysts are set of the energy and the energy analysts are set of the energy and the energy are set of the energy and the energy are set of the energy and the energy are set of the energy are set of the energy and the energy are set of the energy are set of the energy and the energy are set of the en

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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 The progress of the last 20 years in pipe steel development and production applications. 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 microalloved 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.

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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	+	+++

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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)

<u>Microalloyed Steels.</u> 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

	Che	mical cor	nposition	Mechanical properties				
Grade	С	Mn	AI	Nb	Y.S. (MPa)	T.S. (MPa)	EI. (%)	
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.

<u>Multiphase Steels.</u> 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.

<u>Microalloyed Sheet.</u> 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 $170^{\circ}C / 20$ 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 microalloving 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.

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	++	+	

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

* 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 nonmetallic 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.

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

Table V Examples of base composition, 50 mm plate thickness

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 vield strength show microalloving 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.

	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.





(b)

(a) 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
supera	lloys c	containing	niobium						

Allow	Chemical composition (%)										Others
Alloy	Ni	Cr	Co	Nb	Мо	w	Ti	AI	Fe	С	Others
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°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 '' (Ni₃Nb) 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°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 (Nb₂O₅) 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°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°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 Pd₂HfAl 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-S 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



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 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.

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:

<u>High temperature applications.</u> 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.

<u>Superconductivity.</u> 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.

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