PROGRESS IN NIOBIUM MARKETS AND TECHNOLOGY
1981-2001

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Abstract

The present paper reviews the changes over the past two decades related to niobium deposits and supply, together with the technical advances that have occurred in niobium metallurgy. Also, the significant increase in market applications of niobium-containing steels especially in the field of microalloyed steel and including stainless steel, niobium metal and alloys, superalloys, chemical compounds, and specialty applications of niobium are highlighted. Almost every year since the 1981-82 recession, an increase in the consumption of niobium in steel products, the major market for niobium, has been recorded. The prominent end-users include automobiles, light trucks, oil and gas pipelines, constructional plate and structural shapes. Traditional superalloys such as Alloy 718, modified using higher niobium levels, have been developed for higher temperature applications in jet engines and stationary gas turbines. Other products discussed include niobium-containing intermetallics, thin films, high temperature niobium alloys, capacitors and catalysts.

Introduction

During the two decades since the symposium "Niobium 81" was held in San Francisco, progress over a wide spectrum of niobium technology and applications has been significant.

Although progress has been evolutionary rather than revolutionary, important goals have been met. The technical community has stimulated a steady expansion in the understanding of the science and technology of niobium, which has resulted in new applications, and growth in business activity.

The scientific community had predicted many of today's uses of niobium in 1981. For instance, the manufacture of so-called Interstitial-Free steels using niobium had been attempted in the US ten years prior to 1981 but these attempts were economic failures. Because of progress in steelmaking technology, especially in Japan, the successful large-scale manufacture of millions of tonnes of these steels for the automobile industry is now routine and a major consumer of niobium.

The results of the last two decades of progress are manifest. There has been brisk progress in niobium development and we can be satisfied with sustained growth unlike some segments of the metals industry whose importance has declined over the same time period.

The present paper will illustrate some of this progress and set the stage for the rest of the presenters who will give detailed accounts. It is not the intent to give "chapter and verse" in this presentation but simply to present a prologue of things to come.

Changes in Niobium Supply

As was the case in 1981, Companhia Brasileira de Metalurgia e Mineração (Brazilian Company for Metallurgy and Mining) normally known as CBMM is still the world's most important producer of niobium products.

Historically, CBMM has supplied the majority of the world's niobium from its pyrochlore mine in the carbonatite deposit near Araxá, Brazil. In 1981, CBMM restricted itself to being a producer of standard grade ferroniobium for the world's steel industry after having recently abandoned the export of pyrochlore concentrate. Now, CBMM produces a virtually complete array of niobium products including technical grade niobium oxide, vacuum grade ferroniobium and nickel niobium, electron-beam refined niobium metal and niobium-based alloys as well as special niobium oxides and niobium compounds (Table I).

The "run-of mill" niobium content of the ore being mined by CBMM is 2.5-3.5 percent Nb_2O_5 although regions of the ore body are richer by a factor of two to three times.

The vast majority of CBMM's production is still exported in the form of standard grade ferroniobium because of its widespread use in the production of microalloyed steel. Reserves of pyrochlore at the Araxá complex are 450 million tonnes and with an annual processing rate of 1.5 million tonnes of ore, the supply base will last for centuries. The resources in the fresh carbonatite are one billion tonnes of ore grandine 1.5%Nb_2O_5.

In 1994, CBMM began manufacturing its standard grade ferroniobium using an electric-arc furnace augmented aluminothermic process. Since that time, investment of more than US$80 million has drastically improved the entire manufacturing process. The electric-arc method of manufacture has been improved by the use of a pyrometallurgical process of pre-purification of the feed concentrate. The implementation of this new process was the natural result of CBMM's commitment to improving product quality, minimizing the impact of raw materials cost escalation and also to prevent pollution from its operations. Part of the expansion program was to increase CBMM's production capacity for standard grade ferroniobium from 30,000 tonnes per year to 45,000, its present capacity.

Table I Principal niobium producers

Pyrochlore Ore	Araxá MG-Brazil		Catalão GO-Brazil	St. Honoré Canada
	Residual	Fresh Rock	Residual	Fresh Rock
% Nb2O5	3.0	1.57	1.34	0.67
Reserve (Million Tons)	456	936	18	22
Mining	Open Pit		Open Pit	Underground
Products	FeNb Std Nb Oxides NiNb FeNb VG Nb Metal		FeNb Std	FeNb Std

Since 1981, CBMM has eliminated the use of agents and distributors in the major market areas and today sells through its own subsidiaries. Its products are warehoused at various strategic locations throughout the world ready for distribution on a "just-in-time" delivery basis" to steel makers and alloy producers by Reference Metals Company Inc., based in the US; Niobium Products Company GmbH based in Germany; and CBMM Asia in Tokyo.

Brazil's second largest producer of niobium is Catalao de Goias (Table I), a member of the Anglo American conglomerate, which also operates an open-pit mine in the state of Goias. Catalao processes pyrochlore on-site into standard grade ferroniobium using an aluminothermic process. Apparently, annual production at this company has increased recently from about 3,500 tonnes to about 4,000, which represents slightly more than 15 percent of the peak world market for ferroniobium, as was the case in 1981.

The largest primary production of niobium outside Brazil comes from the underground Niobec mine near to St. Honore in Quebec, Canada (Table I). Cambior Inc. and Mazarin Inc. own this operation equally. Mazarin operates the mine while Cambior markets the product. They are both Quebec-based companies. In 1981, the Teck Corporation owned Mazarin's share and operated the mine and SOQUEM owned Cambior's share. At that time, pyrochlore concentrate was shipped from the mine to independent ferroalloy converters in the United States, Europe and Japan for aluminothermic conversion to standard ferroniobium. Because the disposal of the mildly radioactive by-product slag became increasingly difficult throughout the world, this system became untenable. To solve this difficulty, in 1994 the Niobec mine facilities were expanded to include the aluminothermic manufacture

of standard grade ferroniobium on-site. The by-product slag was returned to the underground mine. The production capability of the Niobec mine has also been increased recently to about 4,600 tonnes, which constitutes slightly less than 15 percent of the peak world market for ferroniobium.

Since 1981, Mamore's subsidiary, Paranapanema, in Brazil has become a participant in the supply of by-product niobium from alluvial tantalite concentrates and tin-slag waste products from its casiterite (SnO_2) operation in Pitinga in northern Brazil. Although still on a limited basis, production of niobium could increase from this source in the future because the Ta/Nb ratio of the mineral in this material is 9/1. Obviously, since the price of tantalum is much higher than that of niobium, this resource is attractive. However, an investment in excess of US$100 million dollars will be needed to develop a new hard rock mine since the alluvial material has limited availability.

In the mid-1990's, Niocan announced the planned production of 4,500 tonnes of ferroniobium annually from the Oka deposit, near Montreal, Quebec. The plan was to develop an underground mine adjacent to the site of the long-defunct St. Lawrence Columbium and Metals Corporation mine. This abandoned mine had been probably the first operating large-scale continuous pyrochlore mining and concentration facility in the world when it began production in 1961, continuing until 1976. Niocan's mine was to be more similar to the Niobec mine and process a niobium mineral with about the same Nb content (0.7%) as that found at the Niobec mine. So far, no production is forthcoming, but development appears to continue.

As was the case in 1981 it is still difficult to perceive of substantial supply of niobium from politically fragile equatorial Africa, or from the Siberian tundra although significant niobium deposits are found in both these regions. In the late 80's and early 90's, Metallurg exported pyrochlore concentrate to Germany sufficient to produce about 500 tonnes of standard grade ferroniobium annually from a small production facility near Lueshe in Zaire. This activity fell victim to civil war but is once again drawing interest. Gabon has a major niobium-containing phosphate deposit near Mabounié, 200 kilometers from the Atlantic. This raw material source is exploitable and could become a significant source of niobium in the fairly near future.

As indicated in Figure 1, additional niobium deposits also exist in Kenya, Uganda, Nigeria, Norway and Greenland among other locations. Nigeria in particular is now once again active in exporting columbite/tantalite materials.

At the time of Niobium 81, the USSR was a net importer of ferroniobium. After the break-up of the Soviet Union, the CIS exported as much as 600 tonnes of ferroniobium annually and remains an exporter but to a much reduced degree. Solikamsk Magnesium has become a producer and exporter of by-product niobium oxide, another change since 1981.

In 1981, limited supplies of by-product niobium were forthcoming from tantalum producers who processed tantalite from Africa, Brazil and Canada and waste tin-slags from Thailand and Malasia for their tantalum values. This situation is largely unchanged although these raw materials are increasingly difficult to come by. Today, the main raw material source for tantalum is primary tantalite raw material from the Sons of Gwalia Ltd. pegmatite mine Greenbushes and Wogina in Western Australia. These mines also produce limited quantities of niobium co-product that is being used as a raw material in the production of high-purity niobium.

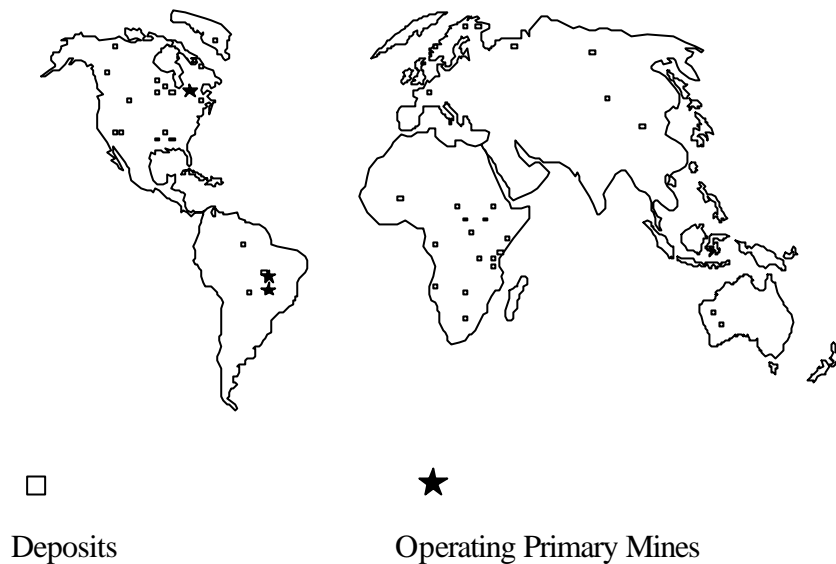Deposits   Operating Primary Mines

Figure 1: Niobium deposits and producing niobium mines.

Even though the realities of the economics of the manufacture and sale of niobium products would not seem to favor new projects, it is probable that significant additional supplies of niobium will be developed at some time in the not too distant future.

Although most of the companies who were involved in niobium in 1981 are still involved to a greater or lesser extent, some players have disappeared. Probably the most notable company to disappear was Fansteel who were a very significant producer of high purity niobium metal and alloys (and tantalum) at their facilities in Chicago and Muskogee, Oklahoma. This company, a subsidiary of the H.K. Porter organization, was acquired by H.C. Starck (a Bayer subsidiary) in the mid 90's. Similarly, Mallinckrodt, a significant processor of columbite/tantalite concentrates and seller of niobium oxide based in St. Louis, ceased business in the mid-1980's when the owners transferred this operation to H.C. Starck's facilities in Germany.

Changes in Niobium Pricing

During most of the 1980's the world market price of ferroniobium decreased by about 15 percent before regaining its 1980 price of about US$14.25 per kg (Nb-contained) in 1992, as illustrated in Figure 2. In fact, in constant dollar terms, the price of standard grade ferroniobium was lowered by more than half during the two decades in question from US$14.25 per kg contained niobium in 1980 to little more than US$6.50 per kg contained niobium today.

Similar behavior has been a feature of the prices of specialty niobium products. For example, niobium metal ingots produced by triple-melt electron-beam melting and refining are marketed at the same price today (about US$45 per kg) as was the case in 1981. Thus, the price of this product has also declined by more than half in constant dollar terms.

Niobium pentoxide (98% minimum purity) the starting material for the manufacture of virtually all high purity niobium metal and alloys cost a little more than US$40 per kg in 1979. When CBMM started production of this material in 1980 their product was priced at just over US$20 per kg as a deliberate

attempt to stimulate consumption and this became the market price by the time of our symposium in 1981. Today the price is close to US$18 per kg, a small decline in current dollars but a steep decline in constant dollars.
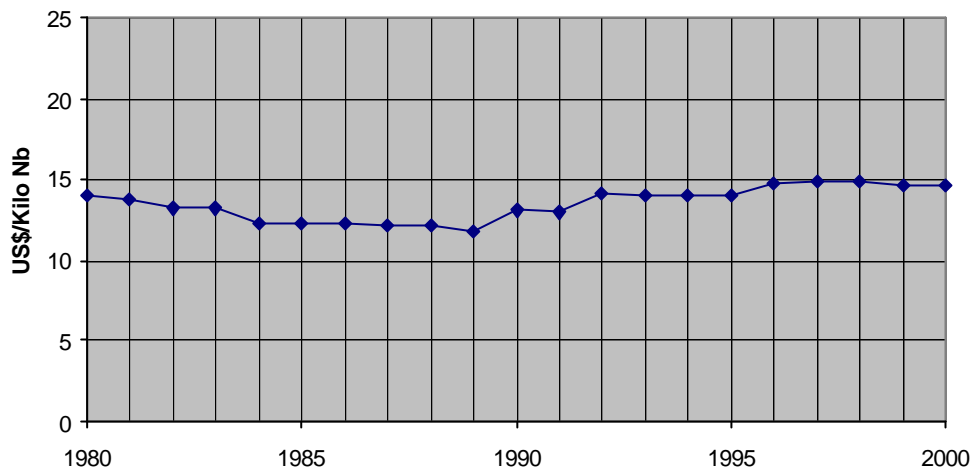

Figure 2: Historical ferroniobium price.

World consumption of niobium had risen rapidly throughout the 1960's and 70's as the steel industry implemented the technology of microalloying in HSLA steel transmission pipelines in response to the OPEC-caused energy crisis. The double-digit inflation that resulted from the rapid escalation in oil price was finally curtailed by drastic increases in interest rates and an inevitable economic recession of major proportion in 1981/82 (just as Niobium 81 was held in San Francisco). This resulted in a significant decrease in steel production and world niobium demand, followed by a somewhat stable world consumption period up until 1993 when a discernable increase in consumption once again could be detected. This stronger demand pattern even intensified in the late 1990's peaking at about 66 million pounds of Nb_2O_5 equivalent in 1998.

There were some exceptions to this "stable consumption" pattern. In North America, for example, sustained growth in the consumption of niobium followed the recession despite a permanent 40 percent reduction in steel production. This occurred because microalloying technology continued to be assimilated strongly by all the major integrated steel producers in North America stimulated by Reference Metals Company's (CBMM subsidiary) determined niobium market development program. This demand pattern has continued up to the present time. The more recent consumption picture shows that "electric furnace" steel producers in the USA (so-called mini-mills) now constitute more than 50 percent of steel production and have also become significant exploiters of niobium microalloying technology.

Since the disastrous North American recession of 1981-82, almost every year has recorded an increase in niobium steel consumption in this geographical area. This increase in "niobium consumption intensity", shown in Figure 3, may be related firstly to an increase in the use of steel in products where much of the steel is niobium containing. The major end-users in this case would be automobiles, light trucks, gas pipelines, and more recently, structural beams.

Secondly, the successful development and implementation of microalloying technology, which has favored the introduction of 'new' niobium containing steels both in the HSLA steel and stainless steel, has also markedly contributed.

This same trend in niobium consumption intensity increase has been seen in the world in general as shown in Figure 3.
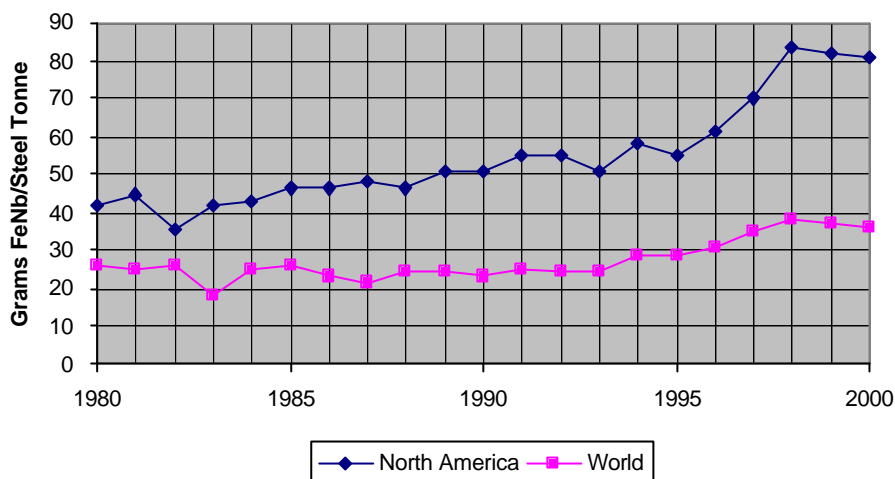

Figure 3: Historical change in niobium consumption intensity.

Niobium Usage in Steel

The predominant use of niobium in 1981 was in steel. This is still the case in 2001 with the production of microalloyed high strength low alloy steel being the most significant use. It is important to note that microalloyed steels consume almost 80 percent of the world's niobium production and constitute over 10 percent of the world's steel production (>80 million tonnes per year).

Niobium strengthens and toughens steel simultaneously by grain refinement, and strengthens by precipitation strengthening and phase transformation control. In addition, with the trend towards lower carbon levels, niobium has become a much more highly effective strengthener in HSLA steels because low carbon content allows increased solid solubility of niobium in the austenite phase. This allows for increased strengthening due to a lowering of the austenite-to-ferrite transformation temperature plus more precipitation strengthening by Nb(CN) particles during and after transformation to ferrite. Lower carbon content also allows steels to accommodate higher niobium content. The relative importance of precipitation strengthening and transformation strengthening is presently being debated and research is showing that the latter may predominate over the former.

The overall ferroniobium consumption picture for the principal applications in North America and Europe is given in Figure 4 and shows that over 75 percent of niobium is consumed in microalloyed steel, not all of which is HSLA steel since a large amount is being consumed in interstitial-free steels for use by the automotive industry. These interstitial-free steels (also known as ultra-low carbon…ULC) are of lower strength but have excellent formability and are typically used to produce difficult-to-form parts such as oil pans. This production of ULC steel is the major change in the niobium consumption picture between 1981 and 2001. Another significant change is the increased consumption of niobium in ferritic stainless steel. This product is being used principally in the manufacture of automobile exhaust systems. Other applications for niobium in 2001 include superalloys and niobium alloys.

Niobium microalloyed steels are produced by virtually every steel company in the world in a variety of

Niobium microalloyed steels are produced by virtually every steel company in the world in a variety of grades. Worldwide, more than 50 million tonnes of steel were niobium-treated in 2001. Of this total, about 80 percent was produced in the US, Europe and Japan. It is estimated that some 8 percent of world steel production is now niobium-treated while this figure is around 12 percent for North America.
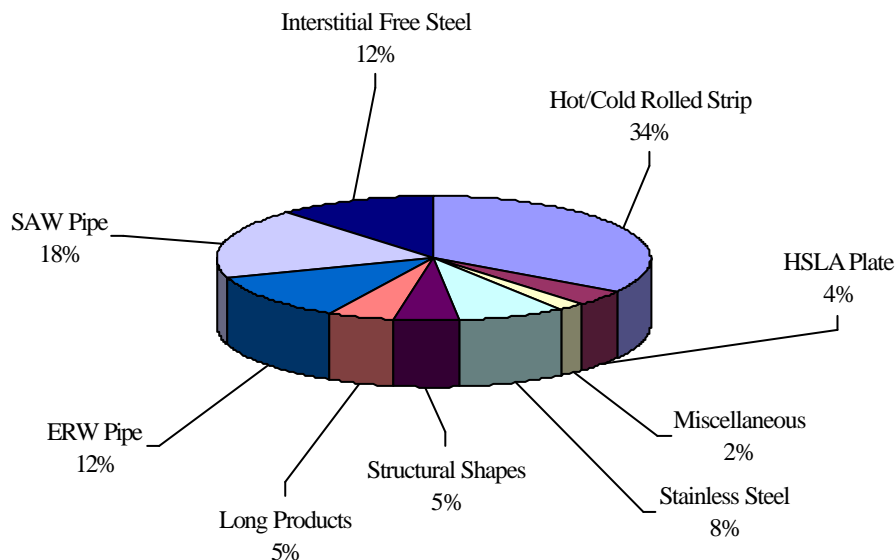

Figure 4: Products utilizing ferroniobium.

Automotive

The largest market area employing niobium containing, microalloyed (MA) steels is now the automotive sector. Niobium is used extensively in both hot and cold rolled sheet/strip, and steels are readily available with yield strengths in excess of 550 MPa. These steels typically contain 0.03%-0.06% niobium with 0.06% carbon and manganese additions between 0.05% and 1.5%. For thehigher strength level an addition of vanadium may be used. In cold rolled thicknesses, titanium (0.04%) and phosphorus (0.05%) may also be employed for additional strengthening.

Since 1981, the automotive industry has switched to a great extent from the use of hot-rolled HSLA steels to the use of thinner gauge, cold-rolled and annealed grades. The effectiveness of niobium as a strengthener is much larger than that of either vanadium or titanium and hence much less alloy addition is necessary to achieve a given strength level.

Titanium, however, is an effective addition (<0.04%) when it is used as a nitrogen getter in Nb-containing microalloyed sheet. The addition of Ti allows increased precipitation strengthening by NbC in ferrite and hence the production of higher yield strength steels.

Titanium, therefore, in combination with niobium, becomes a viable alternative to vanadium in high-strength sheet steels.

With improved cooling systems on hot strip mills, transformation control during processing became feasible and higher-strength bainitic steels have been developed since 1981. These steels exhibit yield strength levels up to, and above, 690 MPa.

Niobium, titanium, boron and molybdenum in solid solution are all instrumental in achieving

bainitic microstructure but not all are required in combination to achieve the desired microstructure, and, hence, mechanical properties. Depending on the capabilities of an individual mill, low levels of microalloying, coupled with fewer alloying elements, may achieve the required steel properties.

Interstitial-free or Ultra Low Carbon steels (ULC) are now used extensively in the construction of automobiles. Although developed in the United States some thirty years ago, these steels have been widely commercialized since 1981, initially in Japan and subsequently in North America and Europe. Two major forces have promoted their developments:

The desire for steels, especially in the automotive industry, which possess excellent stretch formability and deep drawability.

The development of vacuum degassing during steelmaking, which has allowed steels to be produced containing residual carbon and nitrogen levels as low as 10-30 ppm.

It has long been recognized that removal of carbon and nitrogen from solid solution in ferrite contributes markedly to improving formability in cold-rolled and annealed strip. In conjunction with vacuum degassing, small additions of Nb, Ti, or Nb+Ti are used to render these steels "interstitial-free" by "tying-up" the remaining nitrogen and carbon as precipitates. Typical ULC steels have very low carbon contents (0.003%) and contain 0.01%-0.035%Nb and 0.01%-0.06%Ti.

ULC steels are commonly produced using continuous annealing lines (CAL), but can also be produced using batch-annealing processes. Zinc or zinc-alloy coatings are almost universally applied to IF steels for corrosion protection.

Dual-stabilization (Nb+Ti) is of particular importance in the production of hot-dip galvannealed sheet. Ti-only steels are prone to "powdering" (poor coating quality and variability of zinc coating adherence) and the addition of niobium eliminates or minimizes this problem. Also, Ti-only steels are prone to surface defects ("slivers") which for many applications would require a surface grinding operation to produce an acceptable product. Recent work has also shown that a niobium addition improves cold-work embrittlement, and improves formability by promoting a preferred crystallographic texture.

Apart from "gettering" of interstitials, which gives better formability and drawability, a further effect of niobium is related to the formation of a finer grain size prior to cold rolling and annealing which improves planar anisotropy providing greater uniformity of mechanical properties.

Production of Nb-only ULC steels is somewhat more expensive than Ti-only steels but the uniformity of properties coupled with better surface quality and adherence of zinc coatings make the Nb-only steels a viable commercial proposition. However, producers tend to favor the use of a combined addition of Nb+Ti because of cost advantages, ease of production, properties and galvanizing performance.

The excellent formability of these ultra-low-carbon steels is being extensively exploited in the automobile industry, primarily for roof panels, door side panels, oil pans and other similar parts. Consequently, these steels represent an important product in meeting the challenge of other metals and plastics in the automobile industry.

The tonnage of ULC steel that is consumed by the auto industry worldwide is now well in excess of 20 million tonnes per year. The range of ULC steels now extend from low strength, extra deep drawing

quality (EDDQ) to medium strength, bake-hardenable (BH) to higher strength solid solution strengthened steels, or a combination of the latter two types (Table II).

Increasing use of bake-hardenable steels in certain automotive components is being made in order to improve dent resistance. In addition, a higher strength, bake-hardenable steel also allows weight reduction by down gauging.

Table II Compositions (wt%) of some ultra-low-carbon sheet steels

	C	Mn	P	Nb	Ti	B
EDDQ	0.003	0.20	0.003	0.035	0.035	
	0.003	0.20	0.003	0.015	0.040	
	0.003	0.20	0.003	0.020	0.060	
BH	0.0025	0.20	0.001	0.015		
BH-HS	0.0025	0.20	0.070	0.015		0.003m

The advantage of bake-hardenable steel is that a marked increase in strength is achieved after forming by strain aging during the paint baking cycle (170°C for 20 minutes). In other words, ultra-low carbon steel having excellent deep drawability can be easily press-formed prior to strengthening of the final product.

Linepipe/ERW Pipe/Plate

The use of niobium was well established in line pipe steels in 1981 and niobium is still present in the vast majority, if not all, of pipe skelp produced today (Table III). It is added primarily for grain-refinement, which improves both strength and toughness. However, with the implementation of accelerated cooling on present-day plate mills, and with the flexibility provided by Steckel Mill processing, niobium is also benefiting mechanical properties by providing austenite-to-ferrite transformation control and ferrite precipitation strengthening. Yield strengths as high as X80 are common in today's high-pressure gas transmission systems, while X100 should be increasingly applied. In fact, the increasing need to transmit high-pressure gas over long distances, and in severe climatic conditions, could result in the development of X120 linepipe. A low carbon (0.03%) and 0.07% niobium steel with additions of Mo, Ni, Cr, Ti is already under development. Modern-day high strength pipe steel producers are taking full advantage of the threefold benefit of a niobium addition, and reducing or eliminating vanadium.

Further, with the increased application of continuous casting, titanium technology can now be used successfully. A small addition of Ti (0.01-0.02%) can be used to advantage when added to niobium-containing steel. In addition to the precipitation of a fine dispersion of TiN particles, which retain a fine grain size in heat-affected zones of weldments, thereby retaining good toughness properties, the elimination of nitrogen from solid solution precludes the potential for NbN precipitation allowing the precipitation of the more effective NbC(N) particles. The additional precipitation of NbC(N) in ferrite gives a much higher strength product.

Table III Evolution of linepipe compositions (wt%)

Type	C	Mn	Nb	S	P	Other	Comments
Traditional (Pre 1960's)	0.24	0.80	None	0.035	0.030	None	Semi-killed
1972 (X-60 Tough)	0.12	1.20	0.03	0.008	0.020	RE or Ca	Fully-killed
1974 (X-70)	0.06	1.60	0.05	0.003	0.015	V, Mo, RE or Ca	Concast
1982 (X-65 Sour)	0.05	1.10	0.03	0.001	0.010	Cu, Ni, Ca	Concast TMCP**
1985 (X-70)*	0.04	1.50	0.03	0.001	0.010	Ti, V, B, Mo	TMCP** Concast Vacuum Treated
1988 (X-80)*	0.03	1.80	0.05	0.001	0.008	Ti, Mo, B	TMCP** Concast Vacuum Treated
1990's (X80-X100)*	0.03/0.08	1.4/1.8	0.05/.10	0.001	0.010	Ti, Mo, B	
*Produced on both Plate and Steckel Mill **TMPC – Thermomechanical Controlled Processing (Controlled Rolled and Accelerated Cooled Plate)							

Table IV Compositions (wt%) of plates for offshore platforms with yield strength up to 450 MPa

Grade	C	S	P	Si	Mn	Ni	Cu	Nb	Ti
50 N	0.10	0.005	0.007	0.43	1.32	0.19	0.25	0.013	ND
50 AC	0.08	0.003	0.010	0.23	1.45	0.02	0.005	0.010	0.006
50 AC	0.07	0.003	0.008	0.25	1.48	0.16	0.16	0.015	0.008
50 AC	0.10	<0.002	0.011	0.35	1.45	0.04	0.05	0.027	0.019
60 AC	0.07	0.002	0.001	0.13	1.50	0.69	0.28	0.020	0.010

Of note, is the absence of vanadium in many of these steels grades. Perhaps the most striking change in the use of niobium in linepipe is the addition of higher levels of niobium (up to 0.10%). This technology allows greater flexibility of processing and in some cases the elimination of the need for controlled rolling at very low finishing temperatures.

In North America, the predominant steel chemistry for X65/X70 linepipe steel is based on Nb+Ti (Mo)(V) compositions. In other parts of the world, Nb+V chemistries predominate. Over recent years, however, Nb+Ti compositions are now being produced universally. Steckel Mill production in North America does in fact use a variable combination of Nb+Ti+Mo to achieve X80 properties and has done for many years. The level of niobium, between 0.06% and 0.09%, depends on the strength level and pipe wall thickness.

Nb+Ti steel chemistries also dominate the structural plate steel marketplace, especially in applications requiring stringent specifications (Table IV). For example, recent steel chemistries of plates for offshore platforms are basically low niobium (0.010-0.025%), low titanium (0.005-0.020%) steels. Compared with the compositions of 1981, the niobium level has been reduced so as not to impair weldability, and vanadium has been eliminated for the same reason. However, higher strength quenched and tempered steels can contain around 0.05%V.

Even though microalloying levels have been somewhat reduced over recent years, the design of offshore structures to operate under extreme conditions has necessitated higher strength-toughness levels. The latter have been achieved through modified steel processing regimes. Offshore structures now utilize niobium steels modified with 0.5/0.7% nickel having yield strengths of up to 450 MPa and carbon equivalents of around 0.40.

Structural steel plates produced in North America to meet less stringent specification may still be melted to Nb+V chemistries (typically 0.03%Nb - 0.06%V) or higher carbon, V-N chemistries. It would appear, therefore, that there is still much scope for improvement in these chemistries.

Structural Shapes

In 1981, normalizing was usually used to produce structural shapes. In 2001, however, controlled rolling of structural sections is now an accepted practice, as is accelerated cooling after finish rolling. These latter processes, either independently or in combination, have allowed the use of a lower carbon content, which improves both toughness and weldability. The reduced strength ensuing from reduced carbon content is more than compensated for by the addition of Nb (0.01 - 0.05%), or Nb (0.04%) + V (0.06-0.10%) depending on the strength level required.

The technologically progressive accelerated cooling system developed by Arbed (Luxembourg) to produce high strength steel sections (Table V) involves a "selective water cooling system" (WSC) which is designed so as to reduce or eliminate temperature differentials throughout the flange width, and between the flange and the web of thicker sections, thereby producing uniform mechanical properties. A "quench self-temper" accelerated cooling system (QST) has also been developed. Ideally, the superior processing route is a combination of WSC and QST.

For steels containing niobium, this technique provides for both enhanced grain refinement and precipitation strengthening of the ferrite. Using this processing route with steel containing a combined Nb+V addition has achieved yield strength of about 700 MPa. The commercialized lower strength sections typically contain up to 0.05% niobium only, giving yield strength levels of up to 500 MPa minimum. For thicknesses greater than 100 mm, a vanadium addition is usual in order to meet the strength specifications.

Table V Chemical compositions (wt%) and mechanical properties of structural sections (Arbed)

Grade	C	Mn	P max.	S Max.	Nb	V	Ce	YS min. MPa	TS min. MPa	CVN Impact test	
										Temp. (°C)	Min. Absor. Energy (J)
HISTAR 355	0.12	1.40	0.03	0.025	0.05		0.30	355	490		
HISTAR 420	0.12	1.60	0.03	0.025	0.05		0.36	420	530		
HISTAR 460	0.12	1.70	0.03	0.025	0.05	0.05*	0.38	460	560	-20	40
HISTAR 500	0.12	1.70	0.03	0.025	0.05	0.1**	0.41	500	610	-20 / -50	47 / 27
HISTAR 50 TZK Offshore	0.12	1.40	0.02	0.007	0.02		0.30	355	460	-40	68
*, ** Only necessary for thickness above 100mm* and 125mm**											

A major development in the USA since 1981 has been the commercialization of near net shape continuously cast Nb-containing structural steel sections/beams capable of meeting several steel specifications using only one chemical composition. This "multigrade" steel, developed by Chaparral Steel in Texas (Table VI), typically contains only 0.01-0.02% Nb (aim 0.015%) which is sufficient to raise the yield strength of ASTM A36 to above 345 MPa while restricting the tensile strength to below 550 MPa thereby enabling both ASTM A36 and ASTM A572-50 specifications to be met in the same steel.

Table VI Multigrade steel

	Chaparral A36/A572-50 44W/50W	A36	A572-50	44W	50W
Y.S. (Mpa)	345 (min)	250 (min)	345 (min)	305 (min)	345 (min)
S. (MPa)	450-550	400-550	450 (min)	450-621	450-620
El. (%)	23 (min)	21 (min)	21 (min)	23 (min)	22 (min)
C (%)	0.22 (max)	0.26 (max)	0.23 (max)	0.22 (max)	0.23 (max)
Mn (%)	0.50-1.35	-	1.35 (max)	0.50-1.50	0.50-1.50
P (%)	0.04 (max)	0.04 (max)	0.04 (max)	0.04 (max)	0.04 (max)
S (%)	0.05 (max)	0.05 (max)	0.05 (max)	0.05 (max)	0.05 (max)
Si (%)	0.40 (max)	0.40 (max)	0.40 (max)	0.40 (max)	0.40 (max)
Nb (%)	0.005-0.05	-	0.005-0.05	0.10 (max)	0.10 (max)

Niobium is the microalloy of choice in this technology because in order to meet the minimum yield strength requirement of Grade 50 a higher vanadium addition of 0.02-0.03%V (compared with 0.015% Nb) would probably be needed. This would tend to raise the tensile strength of the structurals close to, or greater than 550 MPa, which, while meeting ASTM A572-50 specification, could exceed that allowed by A36.

The use of 0.05 percent niobium is Chaparral's certified maximum when making this multigrade steel. More commonly, the A36/A572-50 grade will contain 0.005 to 0.025 percent niobium.

Other ASTM specifications that are met by the multigrade steel include A572-42, A572-50, A529-42, A5290-50, A709-36 and A709-50.

Constructional Steels

Conventionally, general constructional steels were produced with relatively low strengths to meet minimum yield strength of 355 MPa. A typical use was in heavy truck parts and railroad cars. However, more recently, hot rolled and coiled as well as quenched and tempered higher strength niobium-containing steels (up to 690 MPa yield strength minimum) have found increased application in mobile cranes, off-highway vehicles and mining equipment. In addition to the traditional Nb-V steels, Nb-Ti, Nb-Mo-Ti and Cr-Mo-Nb-Ti chemistries are used to achieve higher strength with a good balance of secondary properties. For example, higher-strength microalloyed constructional steels have been developed recently by LTV to meet a minimum yield strength of 690 MPa (LTV 100XF shown in Table VII).

This 0.09% Nb-Ti-Mo hot-rolled steel achieves its strength through a combination of fine grain size, precipitation strengthening and substructural hardening. This steel has been used in the manufacture of agricultural machinery, rail cars and garbage-removal vehicles. A higher strength version, 110XF, has recently been developed using a slightly higher molybdenum level.

Table VII Chemical composition (in wt%, maximum) and mechanical properties of LTV 100XF steel

C	Mn	S	Si	Al	Nb	Ti	Mo	B
0.08	1.7	0.005	0.3	0.07	0.10	0.10	0.20	0.003

Yield Strength	100 ksi min. (690 MPa)
Tensile Strength	110 ksi min. (760 MPa)
Total Elongation	15% min.
Charpy V-notch Impact Energy at 0°F (-18°C) for gauges over .25 inch. Up to .25-inch thick these specifications apply to -40°F (-40°C)	20 ft-lb min (27 J)

Forging and Cold-Heading Steels

In 1981, microalloyed vanadium-nitrogen, medium carbon, forging steels, developed in the early 70's had become popular, with the primary aim to save on heat-treatment costs. Since then it has been realized that while the strength of these steels could be increased linearly by increasing vanadium content, toughness was adversely affected because of the lack of grain refinement. Safety requirements subsequently imposed by the automotive manufacturers meant that improved toughness soon became a major requirement for many microalloyed forgings.

In the 1990's, the use of Nb-V forging steels popularized by ASCOMETAL (France) took advantage of the triple role of niobium to grain refine, control transformation and precipitation strengthen (Table VIII).

Depending on the grade, the carbon content varies between 0.15% and 0.45%, the lower end of which is an improvement on the more conventional V-N or V-Ti-N steels and provides a major contribution to improved toughness and weldability.

Table VIII Average compositions (wt.%) metasafe steels

	C	Si	Mn	Cu	Ni	Nb+V
Metasafe 800	0.22	0.15	1.5	-	-	0.19
Metasafe 1000	0.43	0.15	1.5	-	-	0.16
Metasafe 1200	0.21	0.55	1.5	1.4	1.5	0.13

Optimal design of the Nb-V steels was determined to be that which contained 0.02%Nb present as precipitate (for grain refinement) and 0.03% Nb in austenite solid solution and available for subsequent precipitation strengthening. The precipitation strengthening effect due to niobium is of the order of 150 MPa, Y.S. at 0.03% soluble Nb. This compares to a strengthening effect of only 50 MPa, Y.S. for the equivalent amount of vanadium.

Applications for microalloyed steel forgings are varied and in addition to the more common such as connecting rods, crankshafts, camshafts, and steering knuckles, other parts such as anti-sway bars, rear swivel axle spindles and reaction rods are being produced.

The most recent development, unique to North America, has centered on the production of low carbon, "multiphase" steels, ferrite + bainite + martensite (shown in Tables IX and X). These steels typically contain around 0.10%C.

Table IX Compositions of two low-carbon, microalloyed multiphase steels (wt%)

Type	C	Mn	Mo	Nb	Ti	B
BHS-1 Freeform™	0.10 0.10/0.15	1.6/2.0 1.4/1.65	0.40/0.50 0.12 max	0.05 0.05/0.12	0.035 max	0.001/ 0.004

Niobium is added (0.05%) for both austenite conditioning during hot processing and to control transformation characteristics during cooling. Manganese (1.4-2.0%) and molybdenum (0.10-0.50%) are also added for transformation control.

The continuous-yielding stress-strain characteristics of the multiphase type of microstructure exhibited by the Mn-Mo-Nb steels are ideal for cold drawing and cold-heading operations.

The spheroidize anneal, reheat, quench and temper operations, necessary for conventional steels, can be eliminated by using multiphase-type steel. It is the elimination of all the costly and time consuming heat treatments, which is by far, the major advantage of switching to microalloyed steels for cold-heading and drawing operations. Uses for Mn-Mo-Nb steel include axle shafts, steering center links, tie-rod ends and bolts.

Table X Tensile test data for cold-drawn freeform™ steel (starting hot-rolled size 0.562-inch)

% Draft	YS MPa	TS MPa	Elongation, %	% Reduction of Area
0	484	690	24.5	66
26	815	877	14.0	59
40	864	932	12.5	57

The properties of bolts made from Mn-Mo-Nb steel were more or less identical to those made from AISI 1335 even though a spheroidize anneal and a subsequent reheat, quench and temper treatment were omitted from the processing schedule of the steel.

During the 1990's, direct quenching of microalloyed forgings (in addition to the multiphase steel) has been used commercially in the USA by Chaparral Steel (Microtuff[R] Table XI). Microtuff is a lower carbon steel containing 0.09%-0.12% Nb.

Table XI Chemical composition (wt%) and mechanical properties of Microtuff[R] (30)

C	Mn	P	S	Si	Cu	Ni	Cr	Mo	Nb	N
0.10 or 0.15	1.65	0.03	0.03	0.50	0.35	0.20	0.25	0.15	0.09	0.012
0.15	0.20 2.00			0.70			0.20	0.12	0.020	

	Y.S. MPa	T.S. MPa	RA%	El%	Hr$_c$	CVN Energy at 0°C Joules
	945	1190	25	8	38	40
	1225	1540	min.	min.	45	min.

Direct quenching produces a martensitic microstructure that is allowed to autotemper. The fine-grained autotempered martensitic forging exhibits exceptionally high yield strength (945-1225 MPa) coupled with good toughness. Applications include hand tools, agricultural components, hardware, digger teeth, conveyor chains and others.

Rod and Bars

The majority of steels in this category are medium carbon (0.20 - 0.50%C) and microalloying elements are added for grain size control. Although Nb is generally a more effective element than V for grain size control there is direct conflict with V because of the latter's effectiveness at higher carbon and higher N levels.

To obtain the highest efficiency in the use of a niobium addition, a billet soaking temperature should be selected to ensure that most, if not all, of the niobium is taken into austenite solid solution prior to rolling. During rolling, some niobium is precipitated as NbC, which retards recrystallization and subsequent grain growth. The result is a fine-grained, room temperature microstructure possessing good ductility and bendability. Niobium remaining in solid solution eventually precipitates during

cooling thereby strengthening the room temperature microstructure.

In general, in higher carbon steel bars, Grade 60 properties can be achieved using a 0.01-0.02% Nb addition which typically compares with the effectiveness of a 0.02-0.03% V addition. Since 1981, the introduction of "walking-beam" soaking furnaces, providing a more uniform soaking of billets, favors the use of niobium, and the elimination of warping of bars which plagued the use of niobium in higher carbon steel bars in the past.

In weldable rebar (lower carbon level of about 0.20%C), the addition of niobium is much more effective than vanadium in raising yield strength and hence it is possible to use a significantly lesser amount of niobium to replace vanadium for a given strength level.

Steel Castings

Since the late 70's, the production of cast steels using niobium microalloying has increased to include many new applications. The effectiveness of niobium in preventing austenite grain coarsening at high temperatures together with its precipitation strengthening capabilities provides high strength, good toughness and increased creep resistance. Consequently, applications that demand stringent property requirements, including offshore and elevated temperature components, are now being found using niobium-containing steels.

Another benefit of steel castings in construction is that the fatigue problems in the critical areas of a fabricated construction associated with weldments are eliminated with overall marked improvements in fatigue resistance.

The lower carbon level of microalloyed steel castings also provides for excellent toughness as well as ensuring good weldability which may preclude preheat and/or a post-heat treatment. Consequently, increased tonnages of Nb-cast steels are now being produced although the logistics of promotion within the foundry industry are compounded by the geographically widespread and smallness of the individual foundries.

A number of recent applications are of note. The addition of niobium in the production of slag pots for use in steel production (Table XII) significantly increases high temperature strength and markedly increased their useful life.

Other applications include Mn-Mo-Nb (±V) steels for housings, drag buckets, connectors, nodes and other offshore components, and railway couplings.

An additional use is in connecting parts weighing 665 kg for the supporting frame of a nuclear reactor (Table XIII).

Welded-in parts for building machinery (Nb+V steel) weighing 120 kg each and rolling mill rolls have both benefited from increased hardness (wear) from Nb (C,N) precipitation.

Table XII Composition (wt%) and typical mechanical properties of Mo-Nb steel cast slag pots

C	Mn	Si	S	P	Ni	Cr	Al	Mo	Nb
0.05	0.50	0.50	0.02 max	0.02max	0.08max	0.40	0.01	0.40	0.03
0.10	0.60	0.60				0.50	0.02	0.50	0.05

Yield strength: 335 Mpa
Tensile strength: 515 MPa
RA%:   65%
El%:   40%
CVN@RT: 70 Joules

Table XIII Mechanical properties of cast 0.4%Mo-0.04%Nb-0.06%V, microalloyed steel connecting parts for the supporting frame of a nuclear reactor

	Y.S. MPa	T.S. MPa	El %	Hardness HB	Impact Energy Absorbed (DVM**)		
					+20°C J	-20°C J	-40°C J
Average	420	540	15	160	92	70	29
Minimum	390	510	11	150	76	49	8

* Specimen taken from center of 350mm (14in.) diameter casting. Heat treatment, 950°C (1750°F)-oil quench +600°C (1110°F) precipitation hardening treatment.

**10mm (0.394 in) square specimen containing a 3mm (0.118) deep, 1mm (0.039 in.) radius notch.

Stainless Steel

While the niobium containing stainless steels that were in use in 1981, such as 20/25 Nb austenitic, AISI 347 and precipitation strengthened 20Nb3, continue to consume niobium, the most significant demand for niobium today is in the manufacture of type 409 derivatives. The use of these nickel-free ferritic stainless steels has increased dramatically in recent years, especially in the automotive industry. Their principal use is engine exhaust systems, where their chemical and mechanical stability allow application in stringent service conditions and permit the auto companies to offer extended warranties on new vehicles. The steel is superior to (and replaces) galvanized or aluminized carbon steel. The automotive industry is mainly using type 409 ferritic stainless steel containing 11.5% Cr. Higher Cr steel (18%Cr - AISI 439) is used in the more demanding "hot-end" of the exhaust system, including manifolds. Niobium levels in stainless steel used in the more stringent applications can be of the order of 0.60%

Traditionally, ferritic and austenitic stainless steels have been stabilized (removal of carbon and nitrogen from solid solution to prevent sensitization and weld-line intergranular corrosion) by the addition of titanium, but research since 1981 showed that several important benefits are found when stabilization is achieved through a combined addition of titanium and niobium (0.10-0.75%Nb), i.e. dual-stabilization. In ferritic stainless steel, these benefits include better surface quality (by allowing a

decrease in the level of Ti), better formability and weldability, better creep resistance, superior thermal fatigue resistance and higher resistance to both aqueous corrosion and high temperature oxidation. Consequently, over the past ten years the consumption of niobium by the stainless steel producers in North America has increased nearly 1000 percent. This corresponds to a more than 50 percent increase in the weight of stainless steel used in a typical family car since 1981.

Another recently developed stainless steel of interest is the anti-bacterial grade being marketed by Nisshin Steel in Japan. This grade was developed jointly with Hitachi. By adding 1.5 % copper and 0.6% niobium to a very low carbon content 17% Cr ferritic grade, resistance to certain bacteria results. A study in Japan found that the steel had a sterilization effect on both E. Coli and Staphylococcus aureus bacteria. Apparently, the copper ions in the steel kill the bacteria by removing their oxygen supply. This steel is being used in clothes dryers, refrigerators, kitchen utensils, and food processing plant as well as medical equipment.

Niobium Usage in Specialty Applications

Superalloys

The story of niobium in superalloys began in the late 1930's when Frank Whittle, an officer in the Royal Air Force, invented the gas turbine. There were no materials in existence at that time that could withstand the very high temperatures created in the turbine's combustion chamber for very long. During WWII jet aircraft saw limited action for this reason. In the 50's, the development of commercial jet aviation provided incentive to solve the materials problems of jet propulsion. Niobium played an important part in solving these materials problems an alloying element in nickel and nickel-iron superalloys. Niobium was added to superalloys to increase strength at high operating temperatures. While several important niobium-containing superalloys of industrial interest were developed in response to this need, by far the most important alloy was the nickel-iron based Alloy 718. Invented by H.L. Eiselstein of the International Nickel Company's Huntington Alloys Division and announced in 1959, this extraordinary alloy (contains up to 5.5% niobium) now accounts for more than 50% of the superalloy content of some of today's high performance gas turbine engines.

Engine builders such as Pratt & Whitney and General Electric quickly recognized the unique utility of Alloy 718 for high temperature applications in aircraft jet engines to replace the limited-utility precipitation strengthened stainless steels such as A286 and the gamma-prime strengthened nickel-based superalloys such as Rene 41 being used in the 50's (Table XIV). By the time of the symposium in San Francisco in 1981 the necessary conservative nature of this industry had fully approved Alloy 718 for use in military engines as well as in critical discs and rotors in commercial gas turbine manufacture. In the twenty years that have passed since then, Alloy 718 has become the workhorse superalloy for high temperature applications up to 650 $^{\circ}$C in gas turbines.

Niobium's primary role in the metallurgy of Alloy 718 is as a solid solution strengthener as well as a precipitation strengthener. Niobium forms both MC-type and M_6C-type carbides during processing and application and it also functions as a gamma double-prime Ni_3Nb former.

Improvements in Alloy 718's purity and cost have encouraged greater application in aircraft engine design both for castings and for forgings. The use of electron-beam and electro-slag melting and modern forging techniques have greatly improved purity and properties and contributed to the greater

use of this alloy. Today, Alloy 718 is still a mainstay of jet engine design.

Table XIV Nominal chemical composition (wt%) of important superalloys containing niobium

Alloy	Ni	Nb	Cr	Co	Mo	W	Ti	Al	Fe	C	Other
Inconel 718	52.5	5.1	19.0		3.0		0.9	0.5	18.5		
Inconel 706	41.5	2.9	16.0				1.8	0.2	37.5	0.03	
Inconel 625	61.0	3.6	21.5		9.0		0.2	0.2	2.5	0.05	
Rene 88DT	56.5	0.7	16.0	13.0	4.0	4.0	3.7	2.1		0.03	0.015B
Rene 95	61.0	3.5	14.0	8.0	3.5	3.5	2.5	3.5	<0.3	0.16	0.01B;0.05Zr
Udimet 630	50.0	6.5	17.0		3.0	3.0	1.0	0.7	18.0	0.04	0.004B
Inconel 751	72.5	1.0	15.5				2.3	1.2	7.0	0.05	0.25max.Cu
Inconel 750	73.0	1.0	15.5				2.5	0.7	7.0	0.04	0.25max.Cu
IN 3C/LC/Hf	74.0	2.0	12.5		4.2		0.8	6.1		0.12	0.012B; 0.10Zr
IN-738	61.0	0.9	16.0	8.5	1.7	2.6	3.4	3.4		0.17	0.010B; 0.10Zr; 1.7Ta
MAR-M 200	60.0	1.0	9.0	10.0		12.0	2.0	5.0		0.15	0.015B; 0.05Zr
Inconel 907	38.0	4.7		13.0			1.5	0.03	42.0		0.15Si
Inconel 909	38.0	4.7		13.0			1.5	0.03	42.0	0.01	0.40Si

Although niobium containing superalloys are mostly used in aircraft engines, a new generation of stationary gas turbines has become an important consumer of niobium in recent years. Starting in the late 90's, niobium superalloys 706 and 718 have been used to produce discs for these stationary land-based turbines. This application is now consuming several hundred tonnes of niobium annually. The shortages of electricity experienced by several regions of the United States in 2001 have ensured that this application for niobium will increase significantly in the future.

With the new requirements for higher operating temperatures in some automotive exhaust systems, and the need to provide extended warranties, the automotive industry is now using the niobium-containing Alloy 625 for the high temperature bellows of the exhaust system. However, a lower niobium content (1%), nickel-based alloy is also being used in this application.

It is also relevant to briefly mention some other factors that contributed to the acceptance of Alloy 718. In the late 70's, competing cobalt-based superalloys such as Waspalloy fell from favor because of rapid cobalt price escalations caused by shortages that resulted from civil strife in the cobalt producing regions of Africa. The ensuing demand for niobium to use in Alloy 718 at the same time

severely tested the ability of the high purity niobium producers to supply sufficient niobium to meet the demand. High purity niobium at the time was produced exclusively as a by-product of tantalum production. The tantalum producers were processing columbite-tantalite concentrates and tin slag for their tantalum value and tantalum demand thus dictated the availability of niobium.

In 1979 the new demand for vacuum grade (high purity) ferroniobium and nickel niobium drove the ferroniobium price upwards very quickly from less than US$4 per kg to more than US$40 per kg. Fortunately, CBMM in Brazil inaugurated its process to produce high purity ferroniobium from primary pyrochlore minerals at its mine in Araxá and priced its product at less than half the market price. The availability of vacuum grade masteralloys at reasonable prices was thus assured at a time when demand for them increased.

Niobium and Niobium Based Alloys

Niobium-based alloys have been established as high-temperature materials since the late 50's. The most important alloy in this case is C103 (Nb-10wt%Hf-1wt%Ti). This alloy is currently used in rocket thruster cones, high-temperature valves and thrust augmenter flaps of turbine engines. Niobium corrosion properties resemble those of tantalum and therefore make the element and its alloys an excellent choice for applications requiring resistance to aggressive environments. Pure niobium, niobium-1wt%zirconium, niobium-40wt%tantalum and niobium-55wt%titanium are examples of materials currently used to resist varying corrosive environments.

Most of these niobium-based alloys were already developed in 1981, but some changes since then are worthy of mention. Superconductor applications have moved beyond high-energy physics research uses to the commercial arena. Niobium-47%titanium alloy wires have become the basis for the manufacture of superconducting magnets for NMR Spectrometers and for MRI medical diagnostic equipment. These alloys are conventionally produced using electron beam furnace melting and refining and vacuum arc melting to produce the alloy.

In 1993, Reference Metals Company's development team proved, on a commercial basis, the viability of a process based on plasma-arc melting (using the melting equipment installed at H.C.Starck, Inc, in Newton, MA.) as an alternative method to produce these alloys. Reference Metals demonstrated that plasma-arc melting technology associated with optimized thermomechanical processing can be used to obtain niobium-titanium products which match the highest quality product available in the market produced via vacuum-arc remelting. The technology allows highly consistent quality, manufacturing flexibility and potential for cost saving for the superconducting industry.

Ternary niobium-titanium-tantalum alloys that are being investigated, as potential substitutes for niobium-titanium simply cannot be produced on a large scale with acceptable homogeneity using vacuum-arc remelting and/or electron-beam melting. RMCI used plasma-melting techniques to successfully produce these ternary alloys for research purposes with very high homogeneity.

Since 1981, Niobium-1% zirconium alloys have become the standard basis for the manufacture of high-intensity sodium vapor lamps for street lighting.

Pure niobium sheet has been developed for RF (radio frequency) cavities for particle accelerators for high-energy physics research.

Niobium Compounds

Niobium-tin intermetallics have become the standard material used in the manufacture of high-magnetic-field conductors for superconducting magnets where niobium-titanium technology is inadequate.

Titanium-aluminum intermetallics (gamma titanium aluminide) containing much more niobium than superalloys are being developed rapidly to strengthen high strength titanium alloys for both structural and high temperature applications in aerospace. With density in the range of 3.7 to 3.9 g/cm^3, which is less than half of that of superalloys (8.3 g/cm^3), and more than 10% lower than titanium (4.5g/cm^3), gamma titanium aluminides have an enormous potential for aerospace applications. 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 believed that gamma titanium aluminides have temperature capability of 700^{0}C with limited prospects to reach 900^{0}C for structural uses. The main problem with these alloys is their poor ductility and fracture toughness.

Miscellaneous Specialty Applications of Niobium

Thin Films

Since 1981, 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 produced from one of several niobium oxides.

Niobium oxide films can be formed with different stoichiometry 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. NbO_2 is used in microelectronics for switching devices. 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).

 In addition, niobium films can also be used as a barrier layer in Josephson junctions and also for decoratative purposes since the whole spectrum of colors can be achieved by varying the thickness of the oxide layer.

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 as anti-reflection coatings. Anti-reflection is achieved as a direct result of light reflections from interfaces between very thin films that destructively interfere, 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.

The high refractive index of niobium pentoxide makes this material an option in every application 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 is

architectural glass and the use of solar control and low-emissivity coatings to improve the energy balance of buildings. Another application is in the automotive industry and the application of reflecting glass for sunroof and side window glass, solar control for windshields and electrically conductive glass for heated windshields.

In addition to its optical and dielectric properties, niobium is also found to be an important interlayer material to improve the adhesion of diamond-like-carbon (DLC) coatings on stainless steel substrates, such as that used in razor blades. 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. The literature suggests 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. The diamond-like-carbon layer is approximately 20 nm thick and the niobium interlayer is approximately 10 nm thick. There is also a 30 to 100 nm thick layer in the substrate that shows a nano-polycrystalline grain layer, probably as a result of the deposition process. Analysis of the microstructure showed very good and continuous adherence at the interface between DLC and the niobium layer.

The use of niobium as a coating material in cutting blades is also mentioned in more recent patents assigned to the Warner-Lambert Company and to Advanced Refractory Technologies, Inc.

Capacitors

At the time of Niobium 81, the electronics industry's need for capacitors was satisfied largely by the use of aluminum and very fine particle size tantalum powder-based devices. Since that time, high-purity layered ceramic capacitors have become common, depending on the application. More than 600 billion capacitors are presently consumed annually by the electronics industry and the annual growth rate in consumption has been more than 10 percent over the last few years. This high growth rate is largely a consequence of the emergence of the use of personal computers, mobile telephones, pagers, automobile electronics and electronic games.

More recently, interest has turned to the potential use of niobium powder as a substitute for the more expensive tantalum powder, especially where cost and/or weight is of paramount importance. Reportedly, tantalum powder can cost more than 350 dollars per pound, whereas niobium powder would potentially be much less costly than this. Niobium is also much less dense than tantalum (8.57 g/cc v 16.6 g/cc), a distinct advantage in mobile devices.

The development of niobium-powder capacitors was pioneered in the former Soviet Union, probably because of its lack of available tantalum resources. This technology has recently become of wider interest where need for cost reduction in the capacitor user industry has created an incentive for capacitor manufacturers to develop technology based on niobium powder. In turn, this interest has caused niobium producers to develop a suitable process of manufacturing very fine particle size niobium powder. This is not a trivial problem although conventional hydriding-dehydriding appears to be promising and relatively cheap as a candidate, especially since flake-shaped particles can readily be used in capacitors and show an acceptably high capacitance. Direct reduction of niobium oxides and chlorides is also being evaluated.

Catalysis

The attractiveness of niobium as a catalytic material did not become apparent until the 1950's and limited research activity occurred during the next two decades. However, as niobium pre-cursers became available in the late 1960's, many catalytic applications of niobium materials were subsequently discovered during the 70's and early 80's. Over this period, literally hundreds of papers on niobium catalysis were published in the world's scientific literature. Partly stimulated by CBMM's technical market development activities, research continues with niobium materials in the form of compounds/complexes, mixed bulk oxides, oxide supports and surface niobium oxide phases.

A review of the catalyst literature reveals that:

- Niobium reacts with many elements of the periodic table to form a wide range of compounds and complexes, which are active for numerous catalytic applications. Examples of these include $NbCL_5$, NbF_5, NbH, NbS_2, NbN, NbC, NbO_x, and Nb organometallics.
- Niobium oxide is extremely acidic which is very important for various hydrocarbon conversion reactions. $Nb_2O_5.nH_2O$ is a newer type of strong solid acid exhibiting high catalytic activity and selectivity for hydration, esterification and condensation reactions. For example, niobic acid catalyzes the hydration of ethylene to ethanol with 97 percent selectivity, high activity and long catalyst life. Remarkably, the esterification of ethyl alcohol with acetic acid occurs over niobium acid with 100 percent selectivity.
- The versatile solid-state chemistry of niobium oxide has allowed the synthesis of novel mixed metal oxide catalysts. Niobium oxide readily reacts with many other oxides to form mixed oxide phases with complex structures. The major application of these niobium mixed oxides has been in the area of selective oxidation, especially as partial oxidation catalysts and pollution control catalysts.
- Nb_2O_5 is a highly effective oxide support material for metallic catalysts, such as ruthenium, used in carbon monoxide hydrogenation to synthetic fuels and chemicals. As a support material for ruthenium, the niobium oxide support better promotes carbon monoxide hydrogenation over the metal catalyst compared to alumina, silica or carbon.
- When niobium is deposited on oxide supports, such as Al_2O_3, TiO_2 or SiO_2, it forms a dispersed niobium oxide surface phase. Markedly different from bulk Nb_2O_5, the surface niobium oxide phase has a pronounced effect on the physical and chemical properties of these oxide supports (e.g., acidity and thermal stability). This characteristic of niobium oxide has been utilized in many catalytic applications.

Because of commercial implications, catalyst work is closely guarded. However, practical applications of niobium materials appear to have included pollution abatement, selective oxidation, hydrocarbon conversion reactions, hydrogenation/dehydrogenation, hydrotreating (removal of sulfur), carbon monoxide hydrogenation for synthetic fuels and chemicals, polymerization, hydration/dehydration and photochemistry/electrochemistry.

Postscript

It is hoped that this brief introductory paper has demonstrated that progress in the use of niobium as an industrial metal during the two decades that have elapsed since the symposium "Niobium 81" has been significant and justifies the need for "Niobium 2001".

It is also perhaps fitting that this present symposium is being held in the United States, almost two hundred years to the day since an Englishman, Charles Hatchett, discovered and named the element

and gave it the name "columbium" in honor of the Massachusetts source of the raw material that was the object of his research.

Hatchett presented his findings to the members of the Royal Society at their gathering in London on November 26, 1801. In 1802 he published the details of his research under the title "*An Analysis of a mineral Substance from* North America, *containing a Metal hitherto unknown*" with the following final comments:

"Considering, therefore, that the metal which has been examined is so very different from those hitherto discovered, it appeared proper that it should be distinguished by a peculiar name, and having consulted with several of the eminent and ingenious chemists of this country, I have been induced to give it the name columbium."

Charles Hatchett Esq., FRS, Philosophical Transactions of the Royal Society, London, Part1, 1802, 92, 49-66