The Microalloying Industry.

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The theme of this paper is multi-faceted. Firstly, a picture of the geographic framework of the Microalloying Industry is assembled to provide a balanced perspective for the conference. As the world becomes a smaller but much more complex place, such considerations are becoming more and more a part of the strategic planning process, and misconceptions can easily be introduced.

The sources of microalloying elements are indentified and the ability of the various producers to supply the needs of consumers are appraised. Potential new sources are considered.

Historical consumption trends are analysed and the cyclical nature examined. Similarly, the relationship between supply and demand is discussed, and this discussion is extended to include a consideration of the price of microalloys. Also, the effect of price on consumption is examined.

Finally, recent technological developments in microalloyed steels are discussed.

INTRODUCTION

The microalloying industry, comprising producers, suppliers and end users is a relatively new endeavor. Some of the companies involved, such as the Union Carbide Corporation are old established companies whose participation in microalloying (via vanadium) represented a new application for an existing product. At the other extreme, CBMM* in Brazil was founded and prospered principally on the basis of the use of its product, niobium, as a microalloying element.

Probably the first application of microalloying on an industrial scale was the use of niobium in hot rolled strip marketed in 1959 as GLX-W by Great Lakes Steel Corporation in the United States(1). This product was developed on the basis of an empirical "suck it and see" basis rather than an understanding of the science involved and several years elapsed before laboratory research in England(1) explained the mechamisms involved.

The first significant technological conference which addressed the mechamisms of microalloying was held in Harrogate in England in 1963 and was organized jointly by the Iron and Steel Institute (London) and the British Iron and Steel Research Association(2). This conference was called "Metallurgical Developments in Carbon Steels" and contained a number of papers which referred to the effects of microalloying, or, in the words of I.M. Mackenzie in his Foreword "the content of minute percentages of elements such as nitrogen, niobium, aluminum and boron". This conference had been convened because of the recognition that a technology with the potential of upgrading the strength of "carbon steels" or "mild steels" had begun to grow and that the way ahead lay in a better understanding of the metallurgical principles involved.

Subsequent to this "inaugural" conference a series of other milestone conferences were held over the years to review the state-of-the art of microalloyed HSLA steels as they were developed and introduced into the market-place(3-11). From a compositional standpoint, mild steels gave way to C-Mn HSLA steels which gradually were transformed into the microalloyed C-Mb-Nb, C-Mn-V, and C-Mn-Nb-V steels which exist today. In some cases these basic steels also use additional elements such as Mo, Ni, Cr, B etc. From a processing standpoint microalloyed steels are flexible enough to be used in a variety of conditions including the as-rolled state, after normalizing, after quenching and tempering, and after accelerated cooling using water or air directly after processing.

The science and technology of microalloying, used in the production of most high-strength low-alloy steels, has in the last decade become a truly international pursuit. Essentially every country which operates a steel industry recognizes the benefits which microalloying can bring as a means of economically increasing the strength and toughness of structural steels, thereby allowing structures to be build using less steel.

Probably the government which currently recognizes this axion to a greater extent than any other is that of the Peoples Republic of China which has identified the application of micro - alloyed HSLA steels as a national objective(12,13).

Thus has the microalloying industry developed in the space of a couple of decades from the empirical trials of a few pioneering individuals to the establishment of a new technology and industry with an annual turnover of billions of dollars.

It has become clear during this development, that there are essentially three microalloying elements of primary importance - niobium, vanadium and, to a lesser degree, titanium, and this paper will primarily address these metals. However, some attention will be given to other elements because of their peripheral roles in HSLA steels.

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WORLD DISTRIBUTION OF NIOBIUM, VANADIUM AND TITANIUM DEPOSITS

It is clear from a study of the technical literature that mineral deposits of the elements niobium, vanadium and titanium are found in many areas of the world. In fact, not a single continent lacks an exploitable deposit using present-day technology, although some continents dominate production for economic reasons.

Niobium

There are two important mineral forms of niobium containing materials. The first important form, and still the form which provides some of the raw material for the manufacture of high purity niobium is called columbite. Columbite is chemically $FeNb_2O_6$ and is commonly found in solid solution with the isomorphous tantalite mineral $FeTa_2O_6$. The other mineral form of niobium, and by far the more important because of its abundance, is pyrochlore. Chemically, pyrochlore is much more complex than columbite and, in addition to niobium contains sodium, calcium, barium, titanium and fluorite as principle impurities, and a number of minor impurities. The principle rocks in which niobium mineralization is found are called alkaline carbonatites and these occur very extensively. It is estimated that more than 500 carbonatites exist worldwide(14).

There are more than 150 carbonatite occurrences in Africa, with significant niobium mineralization being found in Uganda (Toraro), Zaire (Lueshe), Tanzania (Panda Hill), Zambia (Kalubwe), Kenya (Mrima Hill).

In eastern Canada there are at least 40 carbonatites and a number show significant niobium mineralization. The important ones are St. Honore, Quebec; Oka, Quebec; Manitou Islands, Ontario; and James Bay, Ontario. Also, western Canada shows a niobium containing carbonatite at Thor Lake, Northwest territory and a placer deposit with significant niobium content in the Bugaboo area of British Columbia. It is probable that other carbonatites will be found in western Canada. Carbonatites are less numerous in the United States. However, deposits at Magnet Cove (Arkansas) and Powderhorn (Colorado) show significant niobium mineralization.

Brazil contains a number of very significant carbonatites with respect to their niobium mineralization. The most important are those at Araxá (Minas Gerais) and Catalão (Goias). Others occur at Tapira (Minas Gerais) and Seis Lagos (Amazonas).

Outside the principle carbonatites, other niobium mineralizations occur in Thailand (casiterite) and Nigeria (columbite).

The Peoples Republic of China owns extensive reserves of niobium contained in its extensive iron ore deposits (niobiferous magnetite) in the Pao Tou region of Inner Mongolia. Although a low grade ($0.1\% Nb_2O_5$) this niobium is being extracted from blast furnace iron and converted to ferroniobium.

The Soviet Union is known to contain niobium deposits probably associated with carbonatites in Polar Siberia, the Kola peninsula and several other locations.

Australia is known to shown niobium deposits of significance. For example, a find containing 0.5% niobium was recently reported(15) near Halls Creek, Western Australia.

Vanadium

The predominant sources of vanadium are the vanadiferous magnetites in which vanadium is present in small but recoverable concentrations. In the USA vanadium is also found in association with uranium ores (Carnotite and Roscoelite) and also associated with clays(16).

Vanadium deposits are widely distributed throughout the world. In the USA deposits are found in Colorado, Utah and Wyoming. In Africa, the major source for vanadium, the metal is found in deposits in South West Africa and in South Africa. In Europe deposits are found in Norway and Finland. The USSR has extensive deposits of vanadium as has the

Peoples Republic of China. Additional deposits of lesser importance are located in Australia, Chile and Venezuela (oil residues).

Titanium

Since titanium based alloys are used as structural materials in their own right, the world production and consumption of titanium is almost two orders of magnitude greater than that of either niobium or vanadium. The amount of titanium used for microalloying is also very small compared to the total titanium usage.

The major mineral forms of titanium are Ilmenite and Rutile with Anatase beginning to become more interesting. Major production of titanium minerals comes from Australia, United States and the Soviet Union. Other producing countries include Canada, Finland, Norway, India, South Africa, Sierra Leone and Malaysia. Brazil is developing its anatase resources.

WORLD PRODUCTION

Although resources of niobium vanadium and titanium are all extensively distributed throughout the world, only a relatively few deposits are mined commercially. This is especially the case for niobium but also for vanadium. Three producers* of niobium raw materials dominate the situation whereas four producers** of vanadium are dominant. This is a significant consideration in terms of strategic analyses. By the same token, titanium production is dominated by three producing countries***.

WORLD RESERVES

The reserves of all three microalloying metals of relevance are very extensive. The reserves of niobium currently confirmed are sufficient to last, literally, for several thousand years(20). In the case of vanadium, the reserve base is not so dramatic but there is still sufficient to last all applications for at least 150 years(19). Titanium reserves are obviously sufficient for the foreseeable future.

SUPPLY-CONSUMPTION

The total world consumption of niobium in all applications in recent years has been in the range 10,000-14,000 tonnes of contained niobium. The comparitive figure for vanadium is of the same order of magnitude between 30,000 and 40,000 tonnes of contained vanadium. In the case of niobium approximately ninety percent is used in microalloying whereas a smaller fraction of vanadium is used in this application. The titanium situation is much different. Because of the use of titanium oxide as a paint pigment, the total world consumption of titanium is more than an order of magnitude greater than that of either niobium or vanadium, but a very small percentage is used as ferro-titanium or titanium scrap in HSLA steels. To supply these consumption needs, it is estimated that the niobium producers have approximately 50 percent excess capacity with almost all of this being attributable to the large capacity of CBMM's facilities in Brazil. The vanadium producers also operate with significant excess production capacity most of which is in South Africa and China with South Africa being overwhelmingly the dominant factor in excess production capability(19).

To elaborate on the way that the demands of the microalloying industry have impacted on supply-demand picture, we will use predominantly niobium data to illustrate the various points to be made.

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* CBMM, Mineração Catalão, Niobec

** Union Carbide, Hiveld, USSR, PRC

*** USSR, USA, Australia

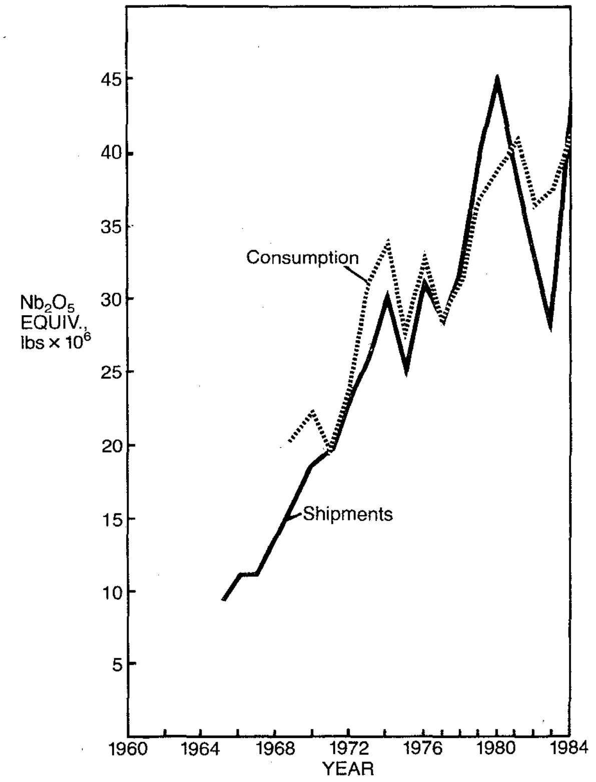

Figure 1 - World niobium shipments and consumption as functions of time.

Figure 1 shows the world shipments and consumption of niobium in terms of pounds of Nb_2O_5 equivalent (this unit is the industry norm for comparative purposes) between 1965 and 1984 and also the corresponding world consumption. It is clear that a good relationship exists between shipments to end-users and distributors and consumption. Clearly, large inventories are not a feature of the niobium industry. The rate of growth in niobium consumption and/or shipments is very difficult to determine. Until about 1980 it appeared that the annual growth rate was quite significant. However, the volatile behaviour of the last five years has made statistical analysis problematical. The world recession centered around 1982 caused a marked disruption in the supply-demand relationship. The record shipment level of 1980 (45 million pounds Nb_2O_5) was followed by successively lower shipments in the following three years, before recovery commenced with the 1984 shipments. However, in real terms there has been no growth in shipments or consumption between 1980 and 1985. Whether or not the future will show growth is not clear from the present vantage point. In the near term the stimulus for new growth would continue to come primarily from the construction industry around the world as they increase the quantities of microalloyed steels in automobiles, trucks, pipelines, etc. Figure 2 shows the change in niobium shipments, niobium consumption and world crude steel production, all as functions of time. There is a close correspondence in the shapes of these relationships, showing the dependence of niobium on steel production. Also, these graphs show that the volatility of niobium consumption in the last six years was caused by a similar volatility in steel production.

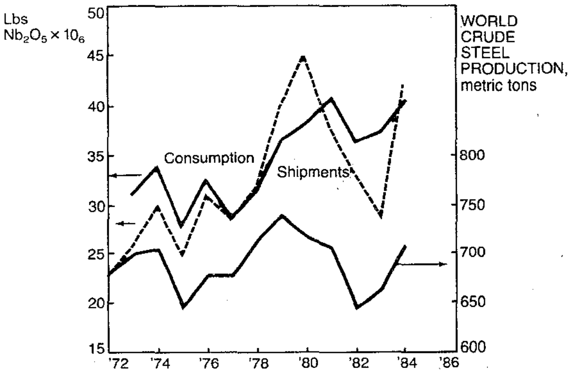

Figure 2 - World niobium shipments and consumption as functions of time compared to world crude steel production.

Figure 2 shows, quite convincingly, that the amount of niobium consumed per tonne of crude steel produced has increased significantly between the early 70's and the early 80's. In 1974 for instance, a world steel production of just over 700 million tonnes consumed about 34 million pounds of Nb_2O_5 equivalent whereas in 1984 the same level of steel production consumed about 41 million pounds of

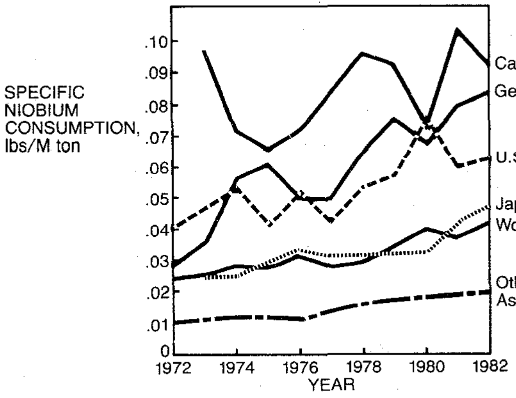

Figure 3 - Specific niobium consumption pounds/M. Ton for selected countries.

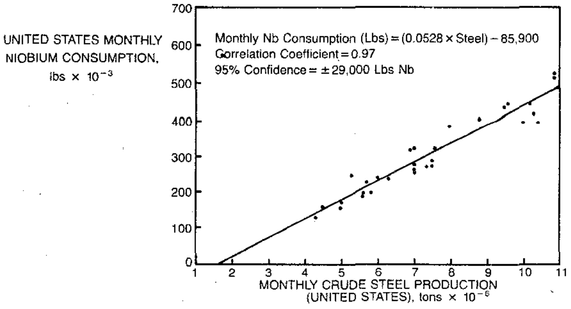

Figure 4 - United States monthly niobium consumption as a function of steel production.

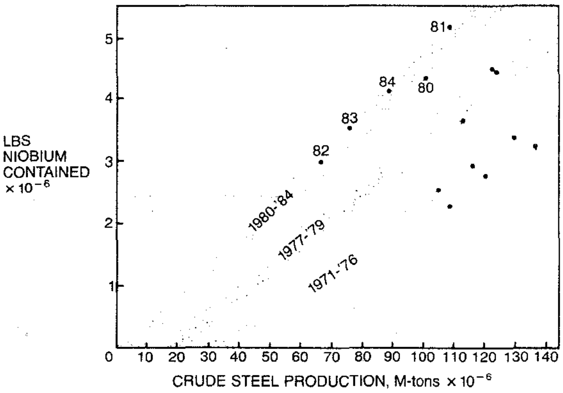

Figure 5 - United States yearly niobium consumption as a function of steel production.

Nb_2O_5 equivalent. This represents a 21 percent increase for the ten year period. In some countries the specific niobium consumption grew at a much faster rate (e.g. USA, Germany) whereas the less developed countries showed a much lower rate of increase (Figure 3). This trend is beginning to reverse itself as the world market-place for steel has changed in character, and the less developed countries produce more microalloyed steels.

Figure 4 confirms the relationship between monthly steel production and niobium consumption on a more quantitative basis for the USA. Although a very exact correlation is shown, it is important to note that such correlations do not exist in other countries such as Germany and Japan. The reason for this is that in these countries, niobium usage is not so widely distributed throughout the steel product spectrum as in the USA. Figure 5 shows the same relationship for the USA but with both variables on an annual basis. This latter relationship is interesting in that it illustrates that the specific niobium consumption (also per tonne) in the USA seems to have increased in a discontinuous fashion in two increments from the early seventies to the later seventies and then to the eighties. These two increments may have resulted in the first case from an increase in pipeline construction caused by the "oil crisis" and in the second place from automobile "downsizing".

Thus it is apparent that without any major technological breakthrough, the future growth in niobium consumption is directly dependent on growth in steel production and the greater implementation of HSLA technology.

ECONOMIC CONSIDERATIONS

One of the most important considerations for a steel producer or a steel user is that of cost. In the present day market-place, which is rapidly becoming a world market, fierce competition exists between the worlds steel companies, and the selling price of many grades of steel continues to decline. In this environment cost considerations are important. The question arises as to what effect microalloying has on the cost of steel, and what differences exist between niobium, vanadium and titanium.

As a general rule when considering a modern HSLA steel with less than 0.1 percent carbon and nitrogen content less than 80 ppm, 0.02/0.03 percent niobium will have the same strengthening effects as .04/.06 percent(28,29) vanadium and .06/.09 percent titanium. This will be elaborated on later. Another important factor in the cost equation is the amount of microalloy which is "lost" when the addition is made to the liquid steel. This recovery is about the same for niobium and vanadium and varies between 75 and 100 percent for fully killed steel. The recovery for titanium, however, is much lower varying between 40 and 60 percent.

The price per kilo of these three microalloys in the USA is currently (March 1986) of the order of 3 US$ per kilo contained for titanium, 13 US$ per kilo contained for vanadium and 12 US$ per kilo contained for niobium. The price on the international market will vary with different freight costs and import duties. Using these prices, and taking into account strengthening effectiveness and typical steelmaking recoveries, the conclusion reached is that a given unit of strength from microalloying costs almost exactly the same for niobium and titanium but costs more for vanadium. To produce, for instance, an 80 Ksi (550 MPa) yield strength hot-rolled strip on a modern strip mill using water cooling, the microalloying cost would be close to 14 US$ per tonne using niobium or titanium and close to 23 US$ per tonne using vanadium. If the nitrogen content of the vanadium steel were raised to 150 ppm, however, then the microalloying cost would be only slightly higher than the niobium or titanium steel at 18 US$. Similarly if a niobium plus vanadium option is chosen, then the cost would be at 18 US$ per tonne. Clearly, for those companies with the facilities to allow titanium recoveries in excess of 50%, then from a cost standpoint, titanium is attractive. However, titanium is much more difficult to use reproducibly. These calculations are illustrated in Table I, which also specifies the compositions referred to in the comparison.

Thus, the price differential between the three microalloys is not a crucial factor in determining which to use, since the cost per unit increase in strength is not widely different. Clearly, the alloy design must be based on purely metallurgical ground not price of microalloys. Factors such as strength level desired, toughness level required, castability, weldability, etc., are those which direct the decision.

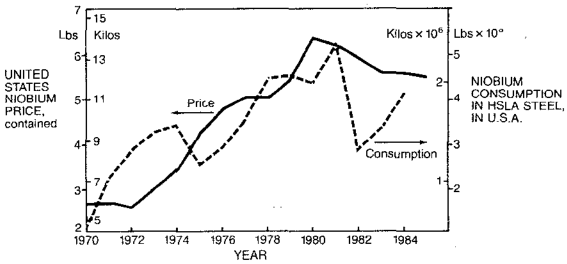

Figure 6 - Change in consumption of niobium and price with time.

TABLE I

COST COMPARISON TO PRODUCE 80 Ksi HOT ROLLED STRIP, TYPICALLY 6mm THICK ON A HOT STRIP MILL WITH CONTROLLED COOLING

	Weight of MA Addition K/Ton				Actual Addition K/Ton			Cost
Grade Options	Nb	V	Ti	Recovery	Nb	V	Ti	US$
Nb Steel								
0.08C, 0.1Nb	0.91	-	-	80%	1.13	-	-	13.60
V Steel								
0.15C, 0.15V	1.36	-	-	80%	-	1.70	-	22.96
Nb-V Steel								
0.1C, 0.03Nb, 0.08V	0.27	0.73	-	80%	0.34	0.91	-	4.08 + 14.41 = 18.49
V-N Steel								
0.1C, 0.12V, 0.015N	-	1.09	-	80%	-	1.36	-	18.37
Ti-Steel								
0.08C, 0.25Ti	-	-	2.27	50%	-	-	4.54	13.62

Price/K, Ctd(US$)

Nb - 12
V - 13.50
Ti - 3

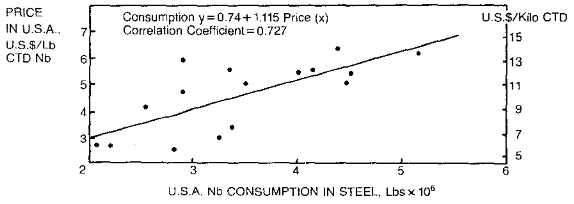

Figure 7 - Apparent correlation between consumption and price of ferroniobium

If the price differential between the microalloying elements is not of significance in determining which element to use, then industry consumption of a microalloying element should similarly not be influenced by its price. To test this postulate, Figure 6 shows the price of niobium (in ferroniobium) in the USA and the consumption of niobium in the steel industry in the USA for the years 1970 through 1984. It is clear that as inflation caused the price of niobium to escalate between 1970 and 1980, the consumption increased at the same time. As the price decreased between 1980 and 1984, the consumption also decreased. Obviously, the conclusion that increased consumption of niobium was caused by an increase in price is untrue. Clearly, price is the dependent variable in Figure 7, and as consumption increased, then prices were raised and vice versa. This is the normal pattern in a free market system. However, we can conclude that the level of niobium consumption is independent of its price. Other factors control the level of consumption. The question then arises as to what these factors are. It is possible that even though the price of niobium escalated between 1970 and 1980, the price of the competing microalloys escalated even faster causing a greater use of niobium rather than, for example, vanadium during this period. To test this hypothesis, Figure 8 shows the price of both niobium (in ferroniobium) and vanadium (in ferrovanadium) between the late 1950's and 1985. It is clear that by the end of the 1960's, the price of vanadium had become more than fifty percent higher

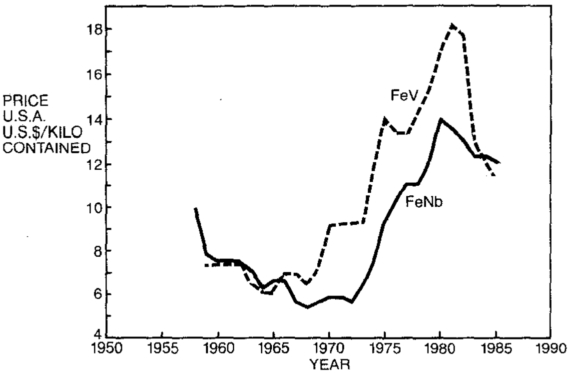

Figure 8 - Price history of ferrovanadium and ferroniobium.

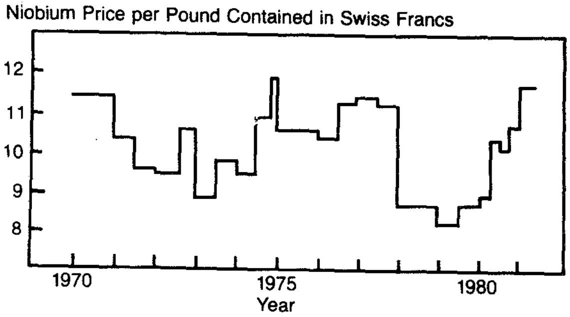

Figure 9 - Niobium price history in Swiss francs.

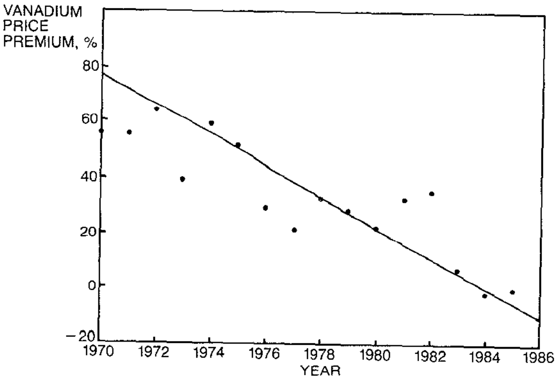

Figure 10 - Change in vanadium price premium with time.

than niobium. During the decade of the 1970's, however, this price differential gradually declined as price of both metals escalated due to inflation (although in Swiss francs the price was stable (Figure 9)). This reduction in the price differential is not clear from Figure 8, but is made obvious in Figure 10 where the price difference expressed as a percentage is plotted as a function of time. Figure 10 shows that, in fact, the premium which vanadium commanded over niobium was continuously reduced over the decade of 1970's, and not increased. Since we saw from Figure 6 that the consumption of niobium increased during this time period (as did that of vanadium), it is clear that reductions in the price differential between niobium and vanadium did not inhibit the growth of niobium consumption.

Consequently, it appears very clear that other influences were responsibly for the growth in consumption of niobium, and that metallurgical considerations have dictated which microalloying element provides the greatest utility in any given application.

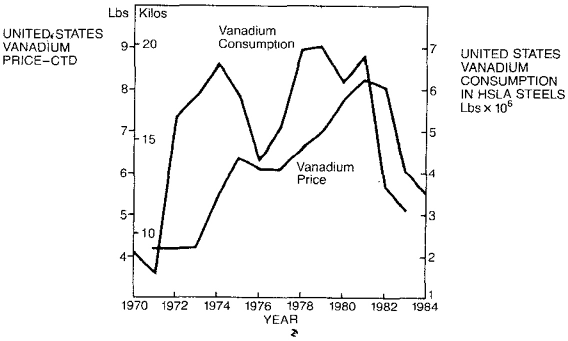

Figure 11 - Relationship between ferrovanadium consumption and price.

However, we have seen that although the consumption of niobium has increased, the consumption of vanadium in microalloying applications has also increased (Figure 11). Clearly, the growth in the use of microalloyed steels in absolute terms and also as a percentage of the steel product mix has been responsible for this growth.

METALLURGICAL CONSIDERATIONS

The foregoing section has presented a strong argument in favour of rejecting the idea that the steelmaker chooses which microalloy to use as a consequence of their relative selling prices, and suggests that in most cases the design of a microalloyed steel is based on using the microalloy which allows him to produce a steel which meets the customers strength and toughness specification and provides the maximum product yield and margin for error during processing. This does not mean that the composition of HSLA steels has been optimised by all steelmakers, but simply that the steelmaker is satisfied with the compromises he has made.

In general, microalloying elements are added to steel to increase strength. The relative strengthening effect of niobium, vanadium and titanium is largely a function of carbon and nitrogen content and the processing scheme. In the case of titanium which reacts very strongly with nitrogen (oxygen and sulphur) some of the addition is wasted since it forms high temperature nitrides (oxides and sulphides) which have little or no effect on strength. With normal residual nitrogen (oxygen and sulphur) content this wasted amount is generally considered to be between .04 and .06 percent. For the case of niobium and vanadium this is not the case since they do not form significant nitrides or sulphides in the liquid phase and the amount wasted is much less. The effectiveness of niobium and vanadium as strengtheners depends rather on carbon content. At carbon contents above about 0.2 percent and normal residual nitrogen content the relative strengthening effects of niobium and vanadium are not very different. Niobium is a more effective grain refiner but vanadium is a more effective precipitation strengthener(34) (Figure 12). This is especially so in the case of normalized

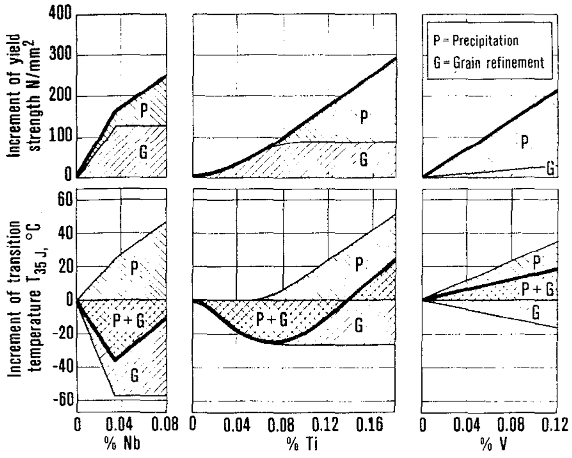

Figure 12 - Metallurgical effects of niobium, vanadium and titanium.

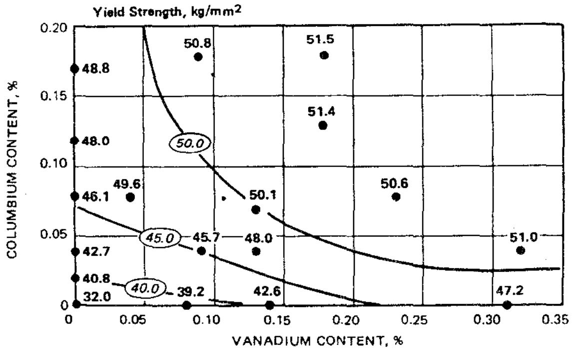

Figure 13 - Isostrength relatioship for vanadium - niobium HSLA steels.

steels. However, as the carbon content is reduced to 0.1 percent and below as in modern HSLA steels and degassing is used to lower the nitrogen content, the situation changes. Because vanadium carbides are ineffective strengtheners compared to niobium carbides, and because less nitrogen is available, niobium becomes the more effective strengthening element(32, 33) (Figure 13).

Thus, modern considerations in HSLA steels are concerning themselves with utilizing micro-alloying elements to their utmost potential and with changing the approach as necessitated by changes in steel production methods.

The most significant recent developments in HSLA steels are concerned both with steelmaking and with steel processing.

Steelmaking Innovations

Although modern developments in the metallurgy of steelmaking are of general utility, they are of special significance where HSLA steels are concerned.

The most significant advance in steelmaking in the last few years has been the ability to produce steels from basic oxygen furnaces with impurity levels unheard of in 1970. Steels are now available commercially with sulphur levels of 10 ppm or less, total oxygen less than 15 ppm, phosphorus and nitrogen less than 20 ppm and hydrogen less than 1.5 ppm. The reduction of sulphur and oxygen to these low levels is beneficial because most of the inclusions in steel are either oxides or sulphides and in order to meet today's demanding service requirements, minimum inclusion content is essential. Because of the embrittlement caused by phosphorus, particularly when the steel is exposed to thermal cycles which promote phosphorus segregation, such as welding, it is important that phosphorus must be reduced to as low a level as possible. Nitrogen in steel is known to reduce the ductility and castability of steel, which significantly reduces product yield. In addition, nitrides formed with niobium, vanadium and aluminum have lower solubility in austenite than carbides leading to premature precipitation and higher rolling loads. Hydrogen in steel causes reduced ductility and flaking, and similarly, it is reduced to the lowest level which is feasible.

A complete system for achieving low levels of sulphur, phosphorus, oxygen, nitrogen and hydrogen is shown schematically in Figure 14, which also shows the reduction in each of the elements in reducing impurity levels, but requires strict operating discipline. Such procedures improve the utility of HSLA steels, but significantly raise the production costs(24).

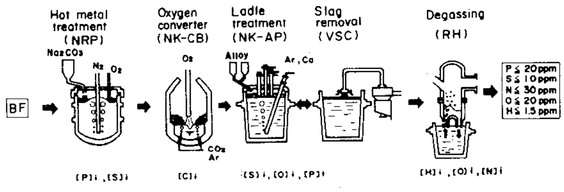

Figure 14 - Modern system for the production of low impurity HSLA steels.

Despite the low levels of sulphur achieved in the system described above, in order to meet the most stringent requirements for impact and HIC resistance of sophisticated HSLA steels, any sulphur remaining in the steel must be of globular form. Calcium additions are the currently favored method for achieving globularization of sulphides. The preferred methods of adding calcium to steel include: calcium silicon injection during the desulphurizing stage, or cored wire containing either calcium metal or calcium silicon added into the ladle after the completing of all other processes, or into the tundish of the continuous casting mould (microalloys are also being added in cored wire).

Because of the greater solubility of rare earth metals in steel, REM has the potential for achieving high impact resistance and HIC resistance at higher sulphur contents than is possible with calcium. At present, REM additions are only made to limited tonnages of steel (in the form of misch metal wire which is added into the continuous casting mould) because of nozzle blockage problems. However, technology is being developed to allow the use of rare-earth elements in continuously cast steel. REM is also still used in ingot casting practice at some companies, but this is rapidly diminishing.

Continuous Casting

Progress in producing continously cast HSLA slabs of such high quality that products rolled from such slabs can meet the most demanding requirement of impact and HIC resistance has progressed as rapidly as the ability to produce steels with low sulphur, phosphorus, etc. The machines being installed in steel plants today are stronger in that they prevent any deformation of the slab in the withdrawal system under the mold. As a result, the incidence of cracking of such slabs is reduced, and bulging, which results in excessive center segregation in slabs is prevented.

An equally significant development is the prevention of reoxidation of continuously cast steels by the use of ceramic shrouds between the ladle and tundish and the tundish and the mold. A further refinement is the injection of argon into these ceramic shrouds to prevent air infiltration.

A further improvement in continuously cast slabs is achieved by the use of electromagnetic stirring (EMS) in the continuous casting mold and just under the mold. Such stirring reduces the segregation at the center line of the slabs. In order to achieve impact and HIC resistance throughout the slab, reduction of center segregation is essential in some HSLA steels.

All continuously cast slabs, particularly those containing micro alloys are subject to transverse cracking. At present the best method of minimizing such cracks is to increase the oscilation rate of the continuous casting machine, but this is not a perfect answer. Also, the use of "mist" cooling as well as raising or reducing the rate of spray cooling have been found to be effective in minimizing slab bending in the critical temperature region where hot ductility is limited. This latter technique is particularly effective for casting HSLA steels. Also, the application of low nitrogen technology and the use of titanium to eliminate free nitrogen is beneficial.

Alloy Design and Processing Innovations

There are a number of innovations in HSLA steels concerning alloy-design, processing and fabrication which are of interest. The following discussion describes these developments.

As referred to previously, dramatic reductions in impurity levels have been achieved at the steelmaking stage. HSLA steels are now being produced in Japan with carbon and nitrogen contents in some cases as low as 30-40 ppm C+N in the case of sheet steels for deep-drawing applications(21) and less than 200 ppm for plate and strip. This means that, in the case of deep drawing steels, they can be made non-ageing (interstitial free) by the use of very small additions of niobium or titanium to tie up the interstitial carbon and nitrogen. This markedly reduces alloying costs compared to the interstitial free steels developed during the 70's in the USA which had interstitial levels more than an order of magnitude higher. These new-generation IF steels can also benefit from the rapid cooling rates available on modern continuous annealing lines. This further enhances freedom from strain-ageing.

Where plate steels are concerned, low carbon and nitrogen contents exert a profound effect on the processing and properties of HSLA steels and magnify the differences in the effects of the microalloying elements niobium, vanadium and titanium.

In conventional HSLA steels where carbon contents are greater than 1000 ppm and nitrogen contents are greater than 100 ppm, vanadium is a weak grain refiner, but powerful precipitation strengthener because of the precipitation at low temperatures of V(CN). However, where interstitials are reduced in modern plate and strip steels, the effectiveness of vanadium as a precipitation strengthener is markedly reduced because little carbon and nitrogen are available for precipitation. On the other hand, the effects of niobium are enhanced by low carbon and nitrogen contents. Firstly, low nitrogen content avoids premature and wasteful precipitation of NbN at high temperatures in austenite and maximizes the precipitation of niobium as a carbide at low temperatures in ferrite. Also, lower interstitials allow maximum solution of niobium during reheating. Thus, the alloying costs of niobium HSLA steels can be reduced without dimunation in strength.

Lower interstitial levels also effect the utility of titanium. Less titanium is needed to tie-up nitrogen to achieve the grain refining benefits of titanium during processing and subsequent welding. Also, titanium becomes easier to handle, especially when low oxygen contents are combined with low carbon and nitrogen levels. Titanium can also be used to increase the effectiveness of niobium as in the work of Repas(22), where the addition of titanium to a hot-rolled strip steel to tie-up nitrogen allowed a reduced level of niobium to be added without loss in toughness and strength (Figure 15). In effect, the titanium combines with nitrogen present in the steel, thereby preventing the formation of niobium nitrides and attendant problems associated with the dissolution of this compound during slab reheating and premature precipitation in austenite. The work also showed that solubility of niobium in austenite was enhanced, roll-separating forces were reduced and substantially increased precipitation strengthening in ferrite was obtained.

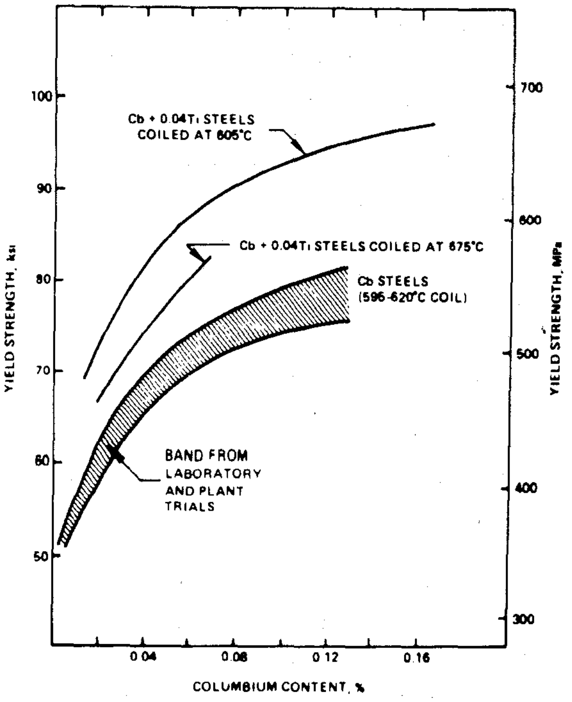

Figure 15 - The effect of titanium additions on the yield strength of niobium HSLA steel.

TABLE II

COMPOSITION OF VERY LOW CARBON
CONTENT BAINITIC HSLA STEELS

STEEL	COMPANY	COMPOSITION								
		C	Si	Mn	P	S	Nb	Ti	B	N
ULCB	NSC	0.02	0.15	1.87	0.022	0.003	0.05	0.02	0.001	0.006
NK STAF 70	NKK	0.02	0.25	1.91	0.021	0.001	0.05	0.027	0.001	0.008

A combination of the use of low interstitials with niobium, titanium and boron is used in the ULCB plate steel from Japan. This steel is marketed by NSC as ULCB(23) and NKK as STAF-70(24). The composition of these grades are shown in Table II where it can be seen that as well as a low carbon content, the steels use niobium for grain refinement during rolling, titanium nitride for grain refinement during reheating and rolling, and in the HAZ of high heat input welds. Also, boron is added to allow the formation of beneficial acicular ferrite during austenite transformation at low temperature.

The rolling regime used for this steel consists of a very low reheating temperature (1000-1150°C) to maximize the grain refining potential of titanium nitride and a finish-rolling temperature of about 700°C to maximize strain accumulation. The ULCB type steels can be processed to give yield strengths between 350 and 470 MPa with excellent toughness for all applications.

The use of boron in the ULCB steel is an example of the resurgence of the use of boron as a microalloying element in HSLA steels. The use of boron dates back to the 50's when Fortyweld was produced in Britain using a combination of molybdenum and boron to suppress the ferrite transformation. However, because steelmaking technology was such that control of carbon, nitrogen and oxygen was difficult, the effect of boron could not be consistently predicted. However, now that very low carbon and nitrogen contents can be achieved consistently (with low oxygen) boron is once again considered as a microalloying element.

The benefits of microalloying have only relatively recently begun to be exploited in two additional product areas: long products and forgings. Long products, generally, start as hot rolled wire, rod or bar and are often used in this condition. More ofter, however, these materials are subjected to further hot or cold forming processes to achieve the requisite final size, shape, strength and/or surface quality.

The use of HSLA steels in applications involving the cold deformation of hot rolled steel has been investigated recently by both Ugine - Aciers(25) and Sumitomo Metals(26). The purpose of both of these studies was to explore the possibility of eliminating the heat treatment step in the fabrication of high strength fasteners and bars for machine and structural use. The Ugine-Aciers study revealed that the cold drawn and cold headed low carbon Mn-Nb-B ferrite-bainite steel could achieve properties that would both match those of Q+T steels and also satisfy the final material specification. Similarly, the Sumitomo work showed that low carbon ferrite-pearlite HSLA steels could exhibit excellent strength, toughness, welding and fatigue properties. These two studies came to the same conclusion, i.e. that there are many important technological areas involving long products where heat treatments are not required and can be avoided by the substitution of the proper microalloyed HSLA hot rolled bar steel.

Perhaps the most exciting new area for the use of HSLA steels is in the forging industry. When done correctly, the hot deformation of forging is used to condition the austenite prior to transformation. This properly conditioned austenite then transforms to a fine grained ferrite which can exhibit both good strength and toughness. The use of HSLA steels in closed-die forging applications has been the subject of several recent investigations. Automobile parts such as crankshafts and connection rods appear to be ideal applications for as-forged HSLA steels. England, Germany, Sweden, Japan and Brazil are currently enjoying the economic benefits of using HSLA forging steels. Once again, the saving in heat treating costs is the reason why the HSLA steels are replacing the traditional Q+T steels.

Microalloyed steels have also been used in heavy, open-die forgings. Researchers in Switzerland have demonstrated(27) that the proper combination of forging practice and steel composition can lead to very exciting properties in sections up to 5 inches (120 mm) thick. Some of the results they obtained with a .12C-1.45Mn-.07Nb-.07V steel are shown in Figure 16.

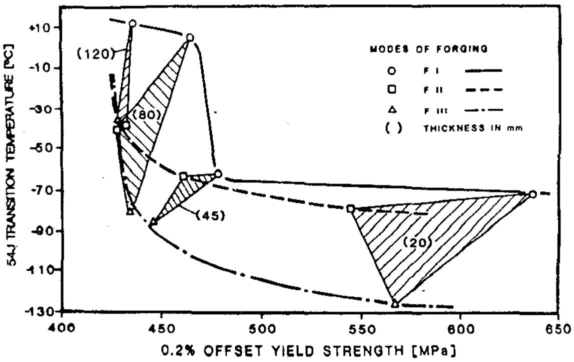

Figure 16 - Mechanical property data for niobium-vanadium open-die forging grade HSLA steel.

Continuous annealing facilities for the production of thin-gage cold-rolled HSLA steels have been installed by a number of companies in recent years. The purpose of this kind of facility is to increase the throughput of steel at the annealing stage and to increase flexibility, such as increasing the cooling rate after annealing. However, it is found that microalloying is still a desired feature in HSLA steels processed via this route. Niobium, vanadium and titanium are used in cold-rolled HSLA steels to provide strengthening by grain refinement and precipitation strenthening, although the level of microalloying elements used is less than in conventional hot-rolled HSLA steels.

Several additional processing innovations have been introduced by various steel companies in recent years to improve the utility of HSLA plate production. Sumitomo have developed a process called the SHT process(28), which emphasizes a combination of controlled rolling and heat treatment during rolling to produce fine-grained niobium containing steels. The processing route depends on an exploitation of grain refinement, precipitation strengthening by niobium carbonitride, work hardening of ferrite and transformation hardening. Sumitomo use de SHT process when toughness requirements below -20ºC are required.

Nippon Kokan introduced the OLAC process (On-Line Accelerated Cooling) for the production of high strength steels using the direct quenching route(29). The use of accelerated cooling to an intermediate temperature (rather than room temperature) was pioneered by Tither et all at BISRA(30) as inter-quenching, but until the advent of the NKK OLAC process, direct cooling had never been commercialized. The OLAC process cools the plate directly after rolling at a carefully controlled rate of not more than 15ºC per second to an intermediate temperature. This cooling rate is carefully matched with composition and thickness to obviate the need for subsequent tempering. Seven other companies in Japan and Europe have subsequently installed plate-accellerated cooling equipment.

For some time, metallurgists from CBMM in Brasil have been publicizing the metallurgical benefits inherent in using a steel with a niobium content in excess of the conventional level. The main benefit of these steels is realized at a niobium content greater than 0.08 percent, at which composition it is found that fine grained structures can be achieved by using a finishing temperature of greater than 800°C (rather than controlled rolling at 700°C). This steel can be rolled with conventional throughput rolling rates, and has been called HTP (High temperature processing).

A similar innovation which attempts to eliminate costly and incovenient controlled rolling is the development called recrystallization controlled rolling. This approach aims at transformation, after rolling from a recrystallized austenite, rather than a "pancake" austenite. The steels examined have used vanadium nitrides as precipitation strengtheners. To achieve a fine recrystallized austenite during reheating and prior to transformation, titanium nitride precipitates are used to pin the austenite grain boundaries. Although this approach shows promise, to be successful a substitute must be found for precipitation strengthening via a nitride, because of the difficulties associated with the castability of high nitrogen steels. Also, difficulties associated with aluminum control(31) lead to yield strength variability in high nitrogen steels.

CLOSURE

It is clear that from a modest beginning in the early 1960's, research and development has advanced the microalloying industry into a world undertaking with many participants and extensive revenues. Because microalloying elements are mined and processed in diverse parts of the world the industry enjoys unlimitated sources of supply and no country need view microalloying elements as critical from reserves standpoint or strategically subject to interruptions in supply. By the same token, the idea of a country needing to hold a stock-pile of microalloys is similarly unnecessary. This follows not only from the fact that supply of the three major microalloys is assumed but from the axiom that there are many different compositional options available to the steelmaker. In an emergency situation, there will always be means available to produce microalloyed steels. Furthermore, it should always be remembered that although HSLA steels allow steel to be used more efficiently, HSLA steels are not absolutely essential to construction in an emergency situation.

From a technology standpoint, microalloying continues to change in nature as different and more effective ways are being found to exploit the unique metallurgical benefits of microalloying elements, singly or in combination with each other.

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