### NIOBIUM IN TOOL STEELS

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#### Summary

This review initially outlines the possible roles of niobium, as an alloying element in tool and high speed steels, on hardenability, toughness, dimensional stability, resistance to softening and wear resistance. Then the anticipated or known effects of niobium in cold work, hot work and high speed tool steels are discussed, taking into account its characteristics as a grain refining and carbide forming element. Emphasis, is placed upon the development work already performed, particularly, in relation to high speed tool steels.

### Introduction

Tool steels include a large range of compositions from carbon steels to complex steels containing five or six alloying elements, whose percentages can add up to more than 30 percent of the total composition.

The compositions most used at present are a result, first, of a tradition based on approximately one century of industrial experience, and second, on scientific expertise which arose mainly after World War Two. Almost always tradition imposed itself slowly. Exceptions appeared either when additions such as vanadium or cobalt to certain compositions brought effects of greater or lesser magnitude or when the scarcity of some alloying elements made changes mandatory, as in the substitution of tungsten by molybdenum.

The main reason for this slow evolutionary process is the complexity of working conditions for tool steels. Tensile strength, hardness, toughness, wear resistance, hardenability, machinability and dimensional stability are the important physical properties to be considered for a tool steel material. For hot working and cutting tools the following other properties ought also to be taken into account: resistance to thermal shock, resistance to softening, resistance to heat checking and resistance to erosion at the working temperature. The last two properties are of significance in the case of hot working tools. These properties almost always require high percentages of carbon and of alloying elements. The simultaneous need of two or more of these requirements implies some kind of compromise. This situation becomes more complex because the performance of a tool is not just a function of the steel composition. The aim of the steel manufacturer is to produce steels which cover a broad range of uses, sizes, types and geometry of tools and which could be used for cutting or shaping different materials.

This review discusses the use of niobium in tool and high speed steels. This alloying element is new in the field, but it could represent an important option, due to the known ore reserve levels and the competitive price of niobium.

Initially the text presents the main useful properties of niobium in tool steels, mentioning possible or available uses. Further on, the different steel groups for cold work, hot work, and high speed tool steels are discussed separately, considering those points where there already is commercial or laboratory experience referring to the addition of niobium.

## Characteristics of Tool Steels - The Role of Niobium

## Hardenability

Hardenability is a function of the alloying elements only when they are in solid solution in austenite. Niobium, in the presence of high percentages of C existing in tool steels appears as a carbide (or as a carbonitride) which is less soluble than the carbides of chromium, molybdenum, tungsten and vanadium (1, 2). In this condition the possibilities of using niobium to increase the martensite hardenability are unknown. Increasing the quenching temperature could be tried, but this procedure brings known heat treatment inconveniences.

#### Toughness

The relationship between toughness and composition is still very empirical, and for a given composition different microstructures show different levels of toughness. Normally a small grain size is sought after for tool steels to improve the toughness.

In steels a usual procedure for controlling austenitic grain size is to add small percentages of elements which form low soluble particles that anchor the austenite grain boundaries; it is well established that this effect is more pronounced the larger the volume fraction and the finer the particle distribution.

The elements most commonly used for controlling grain size in steels are: aluminum, vanadium, titanium and niobium, which form low solubility nitrides, carbonitrides or carbides. The study of these additions and the comparisons among them are well known for low carbon steels and for high strength low alloy (HSLA) steels (3 to 5). In the case of HSLA steels niobium is known to be very effective in retarding recrystallization during hot working, which contributes to ferrite grain refinement (6 to 9).

Coladas et al (10) verified the effect of niobium as an austenite grain size controlling element in medium- and high- carbon steels. In conventional tool steels, vanadium is the element usually added in amounts up to 0.25 percent to inhibit grain growth during the austenitizing treatment.

Mori et al (11) prepared a comparative study of grain growth control through addition of niobium or vanadium to a hot working steel similar to DIN 56N1CrMoV7 (the closest U.S. steel type would be 6F3). The composition of the steel used was basically 0.57 percent C, 0.70 percent Mn, 0.90 percent Cr, 1.55 percent Ni, 0.45 percent Mo. The Nb-steel contained 0.13 percent Nb, and the V-steel 0.08 percent V. Figure 1 shows the grain sizes obtained from steel bars of 19 mm, rolled from 900 kg ingots, after being austenitized for periods of less than 2 hours, at temperatures in the range of 850 C to 1200 C. These results show that at the lower temperatures (up to 950°C), grain size and resistance to grain growth given by niobium or vanadium are equivalent. At higher temperatures, however, (above 1050°C) niobium steel has better resistance to grain growth than vanadium steel.

In the field of high speed tool steel, Russian literature (12) mentions niobium, together with the alternatives of zirconium and titanium, as grain size controlling elements in a steel similar to AISI M2. Additions were in the order of 0.2 percent and their effect appeared to be twofold to refine the as-cast structure, and to restrain grain growth during heat treatment.

#### Dimensional Stability

Dimensional stability is mainly related to two factors, the compatibility between composition, tool geometry and quenching procedure, and the difference in thermal expansion coefficients between the carbides and the matrix, particularly when the carbides are of large in size (13). The effect of niobium on composition and quenching procedures will, therefore, depend on the amount of niobium in solution, and the total amount of niobium will be one of the carbide size determining factors.

The actual practical dimensional stability results from the microstructural stability, but the effect of niobium in relation to this property is unknown.



Figure 1(b). Austenitized at 950 C.

Figure 1. Comparison of the grain controlling influence of vanadium and niobium additions to a hot work tool steel (11).



Figure 1(d). Austenitized at 1200 C.

Figure 1. Comparison of the grain controlling influence of vanadium and niobium additions to a hot work tool steel (11).

#### Resistance to Softening at High Temperatures

Resistance to softening at high temperatures in hot working steels depends on the stability of the dislocation and grain boundary structure of the matrix and of the fine carbides precipitated during tempering. The greater the stability of the resulting microstructure, the greater the resistance to softening. For identical carbide distributions, the stability depends on the type of precipitated carbide, on its degree of coherency to the matrix, and on the diffusion coefficients of the carbide components. Experience shows that additions of vanadium and molybdenum and/or tungsten are useful to tempering resistance. It has to be born in mind, however, that niobium has a limited solubility in austenite when compared to the previously mentioned elements. Nevertheless, synergistic effects of secondary hardening are at least known in some steels alloved with molvbdenum and niobium, or with vanadium and niobium (14). Secondary hardening on tempering and improved creep resistance are well established for martensitic stainless steels containing niobium (14a) which are similar in composition to several tool grades.

#### Wear Resistance

Being a complex property, it is difficult to make general assumptions on wear resistance. In tool steels with fixed composition, microstructure and working conditions, an increase of wear resistance can be expected with an increase in the steel hardness and in the amount of hard carbides dispersed in the matrix (the effect of carbide size is not clear). Niobium ought to be explored in connection to this matter, because the low solubility of its extremely hard carbides allows independent variation of matrix composition and of the quantity of existing carbides.

### Cold Work Tool Steels

In this steel group the most important properties are: hardenability, toughness, dimensional stability and wear resistance.

In these steels, the probability of niobium succeeding as a new addition or as a substitute for other alloying elements is based mainly on its use as grain size controlling, or as a carbide-forming element to increase wear resistance.

The authors are unaware of the use of niobium in cold work tool steels in an industrial scale. U.S. Patent no. 3,901,690 (15) employs around 2.6 percent of niobium to increase wear resistance of steel type AISI-A6.

The addition of niobium to cold work steel to improve its wear resistance is also supported by the British Patent no. **637,222** from Carpenter Steel Company **(16)**. This patent shows that in carbon tool steels, the effect of increasing wear resistance can be obtained by the addition of niobium, tungsten or vanadium. In all these cases, an excess of carbon is added to form carbides with the alloying elements without modifying the matrix.

It could also be noted, in reference to wear resistance, that the efficiency of niobium added to cold work steels containing other alloying elements is larger than the efficiency of vanadium or tungsten. The proposed reason for this effect would be the higher dilution of vanadium or tungsten

carbides by the other alloying elements. Niobium carbides are reasonably immune to this effect, since they tend not to alter their identity in the presence of other elements. This means that the solubility of these elements in the niobium carbide is lower than in the vanadium or tungsten carbides.

## Hot Work Tool Steels

Desired characteristics for hot work steels are the same as for cold work steels, plus the requirement of resistance to softening at high temperatures. In the usual compositions, hardenability is high enough not to be a limiting factor even for large-sized forging dies.

Toughness, cold and hot, is one of the main factors determining the performance of hot work tools. The use of niobium as a grain size controlling element should be tried. In relation to this point it is worth mentioning that some forging plants in Brazil are making use of a steel approximately equivalent to DIN 56NiCrMoV7, as a result of the study already mentioned (11). This steel is now being sold commercially with 0.06 percent of niobium in substitution for vanadium used originally as a grain size controlling element. The performance of this niobium steel is at least equal to the vanadium steel.

Improved wear resistance of conventional hot work steels is conferred by the addition of vanadium, tungsten or molybdenum, which promotes an increase in the volume fraction of carbides. Sometimes surface treatments, like carburizing and nitriding, are carried out to further improve the wear resistance of some hot working tools.

The addition of niobium might be an interesting alternative. U.S. Patent no. 3,901,690 (15) presents modifications of steels AISI 11 and H13 with niobium to increase wear resistance. Possibly, as a consequence of this patent a new steel called Thermowear (17) was introduced commercially in the United States; its composition is 0.58 percent C, 0.50 percent Mn, 1.0 percent S1, 4.0 percent Cr, 25 percent Mo, 10 percent V, 3.0 percent Co, 1.5 percent Nb and 0.1 percent Ti.

Field tests showed that automobile valve extrusion dies with Thermowear gives 10 percent better life over H19; as die blocks for forging compressor blades, Thermowear significantly out performed H11 steel. Another field trial as a weld bead roller has shown to have many times the life of H13.

A comparison of the room temperature abrasive wear resistance of Thermowear and of several other steels is given in Table I.

### High Speed Tool Steels

Conventional high speed steels are complex iron-base alloys containing carbon, chromium, tungsten, molybdenum and vanadium amounting to a minimum 15 percent of the steel composition. Cobalt is sometimes added when higher resistance to tempering is required. These steels are used primarily for the manufacture of cutting tools. Table II gives the nominal composition, according to the AISI classification of the most important high speed steels.

All the steels listed in Table II are classified as standard high speed steels according to the American Society for Testing and Material Standard Specification A 600. There are, however, many leaner alloyed high speed steels, classified as intermediate high speed steels, claimed to exhibit the same performance as some of the established grades (18).

STEEL	HARDNESS, ROCKWELL C	AVG. WT. LOSS, g	ABRASIVE WEAR RESISTANCE FACTOR * <u>(1/WT LOSS), g</u> <sup>-1</sup>
H 12	46	0.374	2.67
H 13	48 48	0.266 0.322	3.76 3.11
Н 19	56	0.218	4.59
Н 21	48	0.291	3.44
THERMOWEAR	46 55 58	0.193 0.067 0.027	5.18 14.92 37.04

Table I. Abrasive Wear Resistance of Tool Steels.

\* The abrasive wear resistance is expressed as the inverse of the average weight loss in grams on several test specimens 22 mm (0.875 in) round by 38 mm (1.5 in) long abraded against a graded 120 grit alumina paper for 250 revolutions under a 22.5N (51b) load.

ATCT	c	C ~	V	1.7	Мо	Co
AISI	<u><u> </u></u>	<u></u>	<u> </u>	<u>w</u>	<u>H0</u>	00
Τ1	0.75	4.00	1.00	18.00	0.70(op)	-
т2	0.80	4.00	2.00	18.00	0.60(op)	-
т4	0.75	4.00	1.00	18.00	0.70(op)	5.00
T5	0.80	4.00	2.00	18.00	0.80(op)	8.00
Т6	0.80	4.50	1.80	20.00	0.70	12.00
T15	1.50	4.00	5.00	12.00	0.50(op)	5.00
M1	0.85	4.00	1.00	1.50	8.50	-
M2	0.85	4.00	2.00	6.00	5.00	-
М3	1.05	4.00	2.50	6.00	5.00	-
М3	1.20	4.00	3.00	6.00	5.00	
M4	1.30	4.00	4.00	5.50	4.50	
M10	0.90	4.00	2.00	-	8.00	-

Table II, Nominal Composition, in wt%, of some High Speed Steels.

op = optional element

It can be seen that the composition ranges for high speed steels are wide and varied:

Element	Composition r	ange (wt%)
Careban	0.75 -	1 50
Carbon	0.75	1.50
Chromium	4.00 -	4.50
Molybdenum	0.50 -	8.50
Tungsten	0 - 2	20.0
Vanadium	1.0 -	4.0
Cobalt	0 - 1	12.0

The ability to retain hardness levels of up to Rockwell C50 at about 550 C is probably the single most important physical properties common to all high speed steels (19). The two other properties considered to have an outstanding effect on the cutting ability are wear resistance and toughness.

The steels are normally supplied **as** bars in the annealed state and the final heat treatment is to quench and temper to a minimum hardness of Rock-well **C63**. The as-cast microstructure is characterized by the presence of transformed and markedly cored dendrites of austenite surrounded by an eutectic constituent of transformed austenite and carbides. The eutectic carbides appear in two different morphologies: fan- and fishbone-shaped as illustrated in Figure 2(a) and 2(b) respectively. The type of eutectic carbide and its shape is strongly dependent upon the chemical composition of the steel (20). Niobium alters markedly the as-cast structures as can be seen in Figure 2(c) and 3(a) (b) and (c).

In the deformed and annealed state, the microstructure is composed of a mixture of complex carbides of types  $M_{23}C_6$ ,  $M_2C$ ,  $M_6C$ , and MC in a ferritic matrix. Carbide phases in an annealed M2 high speed steels have been identified metallographically by Blickwede et al (21). The volume percentages of these carbides have been determined by lineal analysis in several high speed steels in both annealed and quenched condition (22 to 24).

Quenching treatment is conducted at temperatures within 80 C of the melting point of the particular high speed steel to assure enough carbon and alloying elements in solid solution in the austenite. Care should be exercised in order to avoid the risk of liquation or excessive grain growth. Hardened high speed steel is constituted of 55 to 80 percent of highly alloyed tetragonal martensite, retained austenite (up to 30%) and undissolved carbides of the types  $M_2C$ ,  $M_6C$  and MC, whose volume fraction varies from 5 to 12 percent.

During the tempering treatment, two important solid state reactions occur: the precipitation of carbides of W, Mo and V responsible for the observed secondary hardening and the transformation of the retained austenite on cooling from the tempering temperature. Thus the microstructure resulting from quench and tempering consists of a tempered martensite matrix bearing large primary non-dissolved carbides and finely dispersed secondary carbides. Usually some retained austenite exists even after multiple tempering.

Niobium has been considered for a long time a potentially useful alloying element for high speed tool steels (24 to 26). However, its widespread utilization never occurred since almost all the most important high speed steels were developed over 30 years ago. It is worth mentioning that Nb became a popular alloying element only after the development of an economical





Figure 2(a). "Fan shaped" eutectic Optical micrograph, unetched, X 200.

Figure 2(b). "Fish bone" eutectic Optical micrograph, Murakami etch, X 1000.



Figure 2(c). "Chinese-script" eutectic and Primary NbC Optical micrograph, unetched, X 200.

Figure 2. As cast microstructure of a high speed tool steel similar to Werkstoff No. 13207.



Figure 3(a). 6 Nb, 5 Mo, 4 Cr, 1 V steel. Eutectic containing W, Mo and V; also primary NbC Scanning Electron Micrograph X 500.



Figure 3(b). 2 W, 4 Nb, 5 Mo, 4 Cr, 1 V steel M<sub>6</sub>C eutectic eutectic, finely-dispersed M<sub>6</sub>C carbides and primary NbC. Scanning Electron Micrograph X 500.

Figure 3. Carbide distributions in as cast high speed steels of the M2 type containing niobium.



Figure 3(c). 2 W, 3 Nb, 5 Mo, 4 Cr, 1 V steel. Small amount of M<sub>6</sub>C and predominant NbC in "lamellar" morphology. Scanning Electron Micrograph X 500.

Figure 3. Carbide distributions in as cast high speed steels of the M2 type containing niobium.

process for the production of Fe-Nb from pyrochlore. In the last decade, particularly in the last five years, research work on use of niobium for high speed steels has increased significantly (12, 27 to 36). Research programs have been specially designed to independently substitute Nb for V, Mb and W in M2 type high speed steel. The results obtained in these programs in terms of response to secondary hardening are shown in Figure 4 and in Tables III and IV. Several points deserve special attention in relation to these results (1):

- 1. The complete substitution of 2 percent V by 2 percent Nb did not quite reach the same maximum hardness attained in the M2 high speed steel;
- The complete substitution of Mo and W by equal amounts of Nb, that is 5 percent Mo and 6 percent W for 5 and 6 percent Nb, respectively, rendered the steels fully ferritic;
- 3. Peak hardness in Nb-containing steels tends to occur at lower tempering temperatures;
- 4. The program designed to study the replacement of Mo by Nb indicated that austenitizing temperature of 1220 C might not have been the optimum solution treating temperature for this series of alloys;
- No containing steels can be solution treated at higher temperatures than M2 witout the danger of liquation or undesirable grain growth;
- 6. The carbon content was kept at the same level as for M2.

Detailed microprobe analysis performed in all of these single-element substitution programs did not detect the presence of niobium in the matrix, but rather in the primary carbides of the MC type indicating that niobium is a stronger carbide forming element than molybdenum, tungsten and vanadium. It was also observed that niobium carbide dissolves less molybdenum, tungsten and iron than vanadium carbide (30, 37) as can be inferred by comparing



Figure 4. Secondary hardening response of modified M2 grades (49).

Table III. Data on molybdenum substitution steels (29).

STEEL	CHEMICAL COMPOSITION (wt%)						HARDN	IESS (ROCKWELL	C)
	С	Cr	V	W	Мо	Nb	As-Quenched from 12200	Q&T at 540P	Q&T at 5609
5Mo-ONb	0.90	4.41	1.93	5.79	5.19	-	63	64	63
OMo-5Nb	0.84	3.95	1.92	6.19	-	5.59	25*	-	-
2Mo-3Nb	0.90	4.34	1.74	6.10	2.34	2.98	62	60	60
2Mo-3Nb	0.88	4.26	1.98	6.12	1.28	2.90	62	59	58

\* fully ferritic matrix

STEEL		CHEM	ICAL COMP	OSITION	(wt%)		HARDNESS (ROCKWELL C)			
	С	C r	V	W	Mb	Nb	As-Quenched(1) from 12409C	Q & T at 5009C	Q & T at 5509C	Q & T at 6009C
OW-6Nb	0.84	4.11	1.04	0.12	5.33	6.10	(96) <sup>(2)</sup>	-	-	-
2W-4Nb	0.82	4.03	0.98	1.96	5.25	4.03	41.5	44.0	42.7	43.9
3W-3Nb	0.80	4.01	0.91	3.04	5.25	3.04	57.3	59.1	57.9	53.6
3W-2Nb	0.83	4.42	1,08	3.00	5.07	1.94	63.6	60.1	57.6	54.9
2W-2Nb	0.72	4.03	1.06	2.08	4.94	2.00	57.4	63.0	63.2	60.0
2W-3Nb	0.83	4.00	1.21	2.10	4.90	2.91	60.7	61.9	61.4	57.5
6W-ONb	0.80	3.91	2.11	6.20	4.88	-		(3)		
	1									

Table IV. Data on tungsten substitution steels (42).

 Samples were austenitized at 11809c, 12409C and 12809C. 12409C was selected since it represented the best compromise for the compositions studied.

(2) - The value in parenthesis represents the hardness in the Rockwell B scale; The sample evidenced ferritic matrix.

(3) - The conventional M2 high speed steel (6W-ONb) quenched from 12009C and double tempered at 5509C gave the following results: 64.5 and 65.5 Rockwell C, respectively.

Figures 5(a) and 5(b). This fact probably explains the decrease in hardness of vanadium carbide from 2800-2950HV, when pure, to some value in the range of 1800 to 2520HV (38 to 41). Niobium carbide hardness of 2400HV (38, 39) is probably less affected.

Taking this fact and solubility/stoichiometric reasoning into account, Nb containing steels have to be designed with higher C content provided the other alloying elements are kept constant. Figure 6 shows the striking effect caused by a 0.2 percent C increase in a steel with the following nominal composition: 2W-5Mo-4Cr-1V-4Nb (42).

These results strongly suggest the possibility of producing a steel where W, Mb and V appear in smaller quantities without losing the well known effect on the secondary hardening.

Research in this direction has been conducted by Cescon (2) who, by performing very careful microprobe analysis of the matrices of several modified M2 type high speed steels, confirmed previous findings of Roberts et al (43). These authors have shown that the matrix composition of M2 high speed stels quenched from 1200 C was 2 percent W = 2.8 percent Mb = 1 percent V = 4.5 percent Cr = 0.5 percent C. Thompson et al (44) have used the





Figure 5. X-ray energy analysis traces (37).





concepts of stoichiometry of alloy carbides (45) and of the matrix composition to design a less expensive high speed steel of the following nominal composition **3** percent W = 3 percent Nb = 1 percent V = 3 percent Nb = 4percent Cr = 1 percent C. Moreover, since Nb is only sparingly soluble in the austenite, the majority of the excess carbides appear as Nb<sub>4</sub>C<sub>3</sub> or NbC

available for wear resistance. The new steel reached a secondary hardness of 933 VPN on double tempering at 540 C (Figure 7) and produced a fine austenite grain size of 20 Snyder-Graff at the optimum hardening temperature.

Souza et al (46, 47) developed a high steel composition for lathe cutting tools, which has been in production industrially since 1980, by a Brazilian manufacturer (Aços Villares SA). Starting from a nominal composition of 1.30 percent C, 4.25 percent Cr, 4.5 percent Mo, 8.0 percent W, 2.70 percent V, 10 percent Co (similar to German steel W. Nr. 1.3207) largely used in Europe and Brazil, the partial and total substitution of vanadium by niobium was made, rebalancing the carbon content. Carbon content was readjusted empirically taking into account forgeability, response to heat treatment and amount of non-dissolved carbides.

In the as-cast structure, conventional steels present a fan-shaped eutectic rich in vanadium, tungsten and molybdenum. The addition of niobium gives rise, depending on composition, to idiomorphic niobium carbides formed in the liquid state and eutectic niobium carbides with "chinese script" – type morphology as already seen in Figure 2(c). The resulting rolled structure is shown in Figure 8. In this figure niobium carbides are emphasized to show their distribution in rolled bar, which has a reduction of 50 times. Hardness values after tempering were in general higher in steel containing both vanadium and niobium, than in steels containing only niobium or vanadium (Figures 9(a) and (b)). However, vanadium-containing steel presents higher hardness values than niobium-containing steel, which suggests that vanadium is important in secondary hardening as could have been inferred from previous results (27, 48, 49). The tool performance of similar steels under con-



Figure 7. Secondary hardening curves after double tempering for 3W-3Mo-V-3Nb high speed steel showing effects of hardening temperature and comparison with standard M2 (44).

tinuous cutting conditions, was evaluated for different compositions quenched and tempered to the same hardness value: 66f 0.5 HRC. The machined material was the steel SAE 4340 quenched and tempered to 300 BHN. Coolant fluid was used, with a feed of 0.202 mm per revolution and a depth of cut of 2 mm. The life curve was prepared, corresponding to a wear width of 0.600 mm. Results are in Figure 10 for three compositions: the conventional one, a composition containing just niobium, and the third one with niobium and vanadium. It can be observed that the Nb plus V steel exhibited the best performance, and that the niobium-containing steel is superior to the vanadium-containing steel.

# Conclusion

The results **so** far obtained on laboratory, pilot plant and industrial scales, although limited in extent, are indicating that niobium truly represents a viable alternative to the more traditional strong carbide forming elements. Niobium utilization in tool steels will probably expand in the near future as more technical data generated from the on-going research work become available.



Figure 8. Rolled (50 times reduction of area) and annealed microstructure of the same steel as Figure 2(c), showing the distribution of niobium carbides. Lighter carbides, containing, mainly W, Mo and Cr are also visable. Optical, micrograph, unetched X 100.







Figure 9. Tempering curves for Nb-HSS with nominal composition 4,25 Cr - 4,5 Mo - 8,0 W - 10,0 Co (the chemical composition for C, Nb and V is inserted in the figures).





#### References

- 1. F. Heisterkamp, and S. R. Keown, "Columbium in High Speed Tool Steels", paper presented at AIME Annual Meeting, Las Vegas, Nov., Feb. 1980.
- T. Cescon, "Substituição do Tungstanio por Nióbio em Aços Rápidos", IPT, São Paulo, 1980 (IPT Report no. 13.379).
- K. J. Irvine, F. B. Pickering and T. Gladman, "Grain Refined C-Mn Steels", <u>JISI</u>, (205) (1967) pp. 161-182.
- L. Meyer, F. Schmidt and C. Strasburger, "Einflug von Niob und Vanadin auf das Gefüge und die Eigenschaften Perlitarmer Aluminium-Beruhigter Srahle", <u>Stahl und Eisen</u>, 89 (22) (1969) pp. 1235-1249.
- L. Meyer, F. Heisterkamp and W. Muschenborn, "Columbium, Titanium and Vanadium in Normalized, Thenno-Mechanically Treated and Cold-Rolled Steels", pp. 153-167 in <u>Microalloying 75</u>, Union Carbide Corporaion, New York, N.Y., 1977.
- A. LeBon, J. Rofes-Vernis and C. Rossard, "Recristallisation et Précipitation Provoquées par la Déformation d'Chaud: Cas d'un Acier de Construction Soudable au Niobium", <u>Memoires Scientifiques de la Revue de</u> Metallurgie, 70 (718) (1973) pp. 577-588.
- J. J. Jonas and I. Weiss, "Effect of Precipitation on Recrystallization in Microalloyed Steels", <u>Metal Science</u>, 13 (1979) pp. 238-246.
- H. Sekine and T. Maruyama, "Retardation of Recrystallization of Austenite During Hot-Rolling in Nb Containing Low-Carbon Steels", <u>Trans.</u> IronSteel Inst. Japan, 16 (1976) pp. 427-436.
- A. T. Davenport, R. E. Miner and R. A. Kot, "The Recrystallization of Austenite During the Hot Rolling of a Cb-Bearing HSLA Steels", pp. 186-203 in <u>The Hot Deformation of Austenite</u>, John B. Ballance, ed.; AIME, New York, N.Y., 1977.
- R. Coladas, J. Masounave and J. P. Bailon, "The Influence of Niobium on the Austenite Processing of Medium and High Carbon Steels", pp. 341-388 in <u>The Hot Deformation of Austenite</u>, John B. Ballance, ed.: AIME, New York, New York, 1977.
- F. Y. Mori, C. A. Barbosa, M. H. C. Souze and I. G. S. Falleiros, "Controle do Tamanho de Grão Austemítico de um Aco para Trabalho a Quente Através de Adição de Nb", <u>Metalurgia ABM</u>, 33 (241) (1977) pp. 743-748.
- 12. Y. A. Geller and Y. L. Grishina, Machine and Tooling, (1976) 47, p. 30.
- J. Frehser "Anisotrope Mæ'anderunger bei der Warmebehandlung Ledeberitischer Chrom-Werkzeugsrahle", <u>Archiv fur das Eisenhuttenwesen</u>, 24 (11/12) (1953) pp. 483-495.
- A. K. Seal and R. W. K. Honeycombe, "The Effect of Tantalum and Niobium on the Tempering of Certain Vanadium and Molybdenum Steels", <u>Journal of</u> <u>the Iron and Steel Inst.</u>, 188 (4) (1958) pp. 343-350.

- 14a. E. A. Little, D. R. Harries, F. B. Pickering and S. R. Keown, "Effects of Heat Treatment on Structure and Properties of 12% Cr Steels'., <u>Metals</u> Technology, 205 (1977) pp. 205-217.
- T. V. Philip and D. W. Dietrich, 'Wear Resistant Alloy Steels Containing Cb and one of Ti, Hf or Zt", U.S. Patent 3,901,690. Aug. 26, 1975.
- C. B. Post and M. C. Fetzer, 'Wear Resistant Steel", British Patent 637,222 1950.
- T. V. Philip, "A New Bearing Steel; A New Hot Work Die Steel", <u>Metal</u> Progress, 117 (2) (1980) pp. 52-56.
- S. Ekelund, "Trends in High-speed Steel Development 1975-1980", paper presented at the Fagersta 1981 High Speed Steel Symposium, Långshryttan, Sweden, Sept. 1981.
- G. A. Roberts and R. A. Cary, Tool Steels, 4th ed., p. 628; American Society for Metals, Metals Park, Ohio, 1980.
- Y. A. Geller and R. D. Mininzon, "Eutectics in High-speed Steels", Stal in English, 6 (1970) pp. 475-478.
- D. J. Blickwede. M. Cohen and G. A. Roberts. "The Effect of Vanadium and Carbon on the Constitution of High Speed Steel", <u>Transactions of the ASM</u>, 42 (1950) pp. 1161-1196.
- F. Kayser and M. Cohen, "Carbides in High Speed Steel: Their Nature and Quality", <u>Metal Progress</u>, 6 (6) (1952) pp. 79-85.
- R. T. Howard and M. Cohen, "Quantitative Metallography by Point-Counting and Linear Analysis", <u>Trans. AIME</u>, 172 (1947) pp. 413-426.
- G. Hoyle, "Recent Developments in High-speed Steels", <u>Metallurgical</u> <u>Reviews</u>, 9 (33) (1964) pp. 49-91.
- G. A. Roberts, J. C. Hamaker and R. Johnson, Tool Steels, 3rd ed., p. 718; American Society for Metals, Metals Park, Ohio, 1962.
- E. Houdremont, Handbuch der Sonderstahlkunde, 3rd ed., p. 1449, Springer Verlag, Berlin, 1956.
- 27. G. B. Brook, J. M. G. Crompton, "Niobium in High Speed Tool Steels", Fulmer Research Institute, Buckinghamshire, Progress Reports R 319 (1-5) (1969-1972).
- R. Mitsche and E. Kudielka, "Qualitative und Halbquantitative Carbidanalysen als Hilfsmittel in der Schnellstahlforschung", <u>Mikrochimica</u> Acta, Suppl. 8 (1979) pp. 569-578.
- 29. R. Wittenberg, University of Sheffield, M.Met. Thesis, 1979.
- 30. E. Haberline and P. Gumpel, "Ueber den Einfluss von Niob auf die Gefuegeausbildung und Haerteannahme von Schnellarbeitsstahlen", <u>Thyssen</u> Edelstahl Technische Berichte, 6 (2) (1980) pp. 127-131.

- S. Karagoz, E. Kudielka and H. Fischmeister, "Menge und Zusammensetzung der Karbide in Einen Niobhaltigen Schnellarbeitsstahl von Typ M7", <u>Mikrochimica Acta</u>, (5-6) (1981) p. 391.
- 32. H. Kudielka, "Roentgenbeugungsuntersuchungen Ueber Phasenumwandlunpen in Niobhaltigen Schnellarbeitsstachlen Vom Typ 6-5-2", <u>Radex-Rundschau</u>, (1/2) (1980) pp. 91-97.
- H. Kudielka, "Rontgenberegungsuntersuchungen Uber Phasenumwandlungen in Vanadium und Niobhaltigen Schnellarbeitsstahlen", <u>Arch. Eisenhuttenwes</u> 51 (9) (1980) pp. 389-392.
- 34. J. Puber, J. Koragöz, E. Kudielka, A. Kulmburg and H. Fischmeister, "Einfluß von Niob und Kohlenstoff auf Gefüge und Standzeit von Schnellarbeitsstählen des Types S 6-5-2 (M2)" <u>Osterreichische Ingenieurzeitung</u>, 24 (1981), 11/12, p. 397.
- 35. T. Cescon, and R. Papalëo, "Estudo Preliminar da Forjabilidade e Resposta ao Tratamento Térmico de Agos Ferramenta contendo Nióbio/Preliminary Study on the Forpeability and Heat Treatment Response of Niobium-Containing Tool Steels Materials", paper presented at ABM Annual Conference, Recife, Pe., Jul. 1981.
- 36. T. Cescon and R. Papal≷o, "Estudo da Estrutura Bruta de Fusão de Materials para Aqos - Ferramenta Contendo Nibbio", paper presented at ABM Annual Conference, Recife, Pe, Jul, 1981.
- 37. T. Cescon, "Desenvolvimento de Agos Rápidos Contendo Nióbio Baseados no Conceito de 'Matrix Steel'", to be presented at ABM Annual Cong., Rio de Janeiro, RJ, Jul. 1982.
- 38. H. S. Kalish. "Some Plain Talk About Carbides". cited in Metals Handbook, 9th ed., p. 453; American Society for Metals, Metals Park, Ohio, 1980.
- S. R. Keown, "The Physical Metallurgy of High Speed Tool Steels", paper presented at the Fagersta 1981 High Speed Steel Symposium, Långshyttan, Sweden, Sept. 1981.
- L. P. Tarasov, "The Microhardness Carbides in Tool Steels", <u>Metal</u> <u>Progress</u>, 54 (6) (1948) pp. 846-847.
- Leckie P. Ewing, "A Study of the Micro-Hardness of the Major Carbides in Some High Speed Steels", <u>Transactions of the ASM</u>, 44 (1952) pp. 348-366.
- T. Cescon, "Resposta ao Tratamento Termico de Agos Rapidos com Parcial Substituição do Tungstênio por Nibbio", IPT, Seo Paulo, 1980 (IPT Report no. 13.816).
- 43. G. A. Roberts and J. C. Hamaker, U. S. Patent 3,117,863 1964.
- 44. J. Thompson, T. Cescon and S. R. Keown, "Alloy Substitution in M2 High-Speed Steel", pp. 37-42 in <u>Towards Improved Performance of Tool Mater-</u> ials, R. S. Irany et al., ed.; The Metals Society, London, 1982.
- 45. G. Steven, A. E. Nehrenberg and T. V. Philip, "High-Performance High-Speed Steels by Design", <u>Transactions Ouarterly of the ASM</u>, 57 (4) (1964) pp. 925-948.

- M. H. C. Souza, C. A. Barbosa, I. G. S. Falleiros, F. Y. Mori and W. Viertler, "Hard Alloys", U. S. Patent 4,224,060, Sept. 23, 1980.
- 47. M. H. C. Souza, I. G. S. Falleiros, C. A. Barbosa and F. Y. Mori, "Uso de Niobio como Substituto ao Vanadio em Aços Rapidos", paper presented at ABM Annual Conference, Recife, Pe, 1981.
- F. Heisterkamp and S. R. Keown, "Niobium Moves into High-speed Tool Steels", <u>Metals and Materials</u> (1980) pp. 35-36.
- S. R. Keown, E. Kudielka and F. Heisterkamp, "Replacement of Vanadium by Niobium in S6-5-2 High Speed Tool Steels", <u>Metals Technology</u>, 7 (2) (1980) pp. 50-57.