Niobium Bearing Structural Steels
Edited by: Steven G. Jansto and Jitendra Patel
TMS (The Minerals, Metals & Materials Society), 2010

HIGH-PERFORMANCE STEELS FOR PRESSURE VESSELS

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Keywords: Pressure Vessel Steels, Standards, Microalloying, Multigrade

Abstract

While consumption of energy in the world is rising there is growing interest in the building of pressure vessels as well in apparatus engineering and equipment construction for the storage of gases or technical liquids. For these applications, unalloyed or Nb-microalloyed steels with a minimum yield strength of up to 460MPa have been used and produced as heavy plates according to rules and standards and specifications (i.e. DIN EN 10028, ASTM, ASME).

This paper discusses the production and properties of modern steels for welded pressure vessels, which fit the actual requirements very well. Due to purposeful Nb-microalloying, innovative rolling strategies and (if necessary) optimised heat treatment conditions are possible to produce a fine grained microstructure in order to cover the highest material property requirements, in particular the toughness and the resistance against brittle failure. Additionally, important aspects regarding the processing behaviour of modern steels for pressure vessels are highlighted.

Introduction

Due to its load-bearing capacity, its favourable processing behaviour and its high cost effectiveness, steel is the most important construction material in the heavy machinery construction industry. Its exceeding importance is owed to the fact that its properties can be adjusted to even the most demanding technical requirements. In particular, heavy plates made of higher-strength steel with tailored properties are indispensable for a multitude of industries. While consumption of energy in the world is rising there is growing interest in the building of pressure vessels as well in apparatus engineering and equipment construction for the storage of gases or technical liquids. In addition, such tailored steels are used for highly strained components in offshore engineering, in wind power plants and for special pipe steel grades for the manufacture of long-distance pipelines. In all these markets the demand for heavy plates made of tailored steels has been rapidly growing in recent years. The following is to show a survey of advanced steels for the vessel construction sector. Here, the positive effect of micro-alloying with Nb is particularly emphasised, which facilitates to meet the utmost toughness requirements even with deep input temperatures.

Characterisation of vessels and boilers

Modern containers and boilers and vessels are divided into many types:

- Thin walled
- Thick walled

- Storage tanks
- Transportable containers
- Propane bottles
- Gas cylinders

Reactors, columns, heat exchangers etc are common examples of (pressure) vessels (Figure 1). They are usually cylindrical forming the dangerous partnership of low temperatures and welding which always requires special precautions in design and construction. Pressure vessel cylinders are usually made from flat plates which are rolled then welded along longitudinal joints. On the other hand, circumferential joints are used to attach end closures (dished ends or heads) to the cylinder, and to weld together rolled plates for a long vessel if plate size availability or rolling machine capacity is restricted. Today, advanced vessels are mostly dimensioned and designed according to comprehensive codes of regulations. Here, the ASME code is of particular relevance. The ASME code published by the American Society of Mechanical Engineers for boilers and pressure vessels comprises several sections furnishing information required for material specifications, construction/design specifications, and the manufacture and testing of boilers and pressure vessels including components for nuclear facilities. The ASME code today stands for a sophisticated safety concept. Originating from North America, the ASME code today is recognised in about 90 countries. It is regularly updated and thus adapted to any new requirements. Furthermore, there are a great number of nationally applicable regulations for the design of (pressure) vessels such as the AD code which is to be applied in Germany and complies with the EU's Pressure Equipment Directive PED97/23[1].

Figure 1. Fields of application for pressure vessel steels.

Manufacturing of plates for pressure vessels

Heavy plates used in (pressure) vessel construction are made of low-alloy steel grades with minimum yield strength of up to 460MPa. The thicknesses of such plates range from 10mm to 50mm. The steel grades used for the construction of vessels are characterised not only by the required strength but also by a high toughness, good cold forming characteristics, a high fatigue strength and a favourable weldability. In particular, the construction of pressure vessels makes high demands on the properties of the steel.

The supply of modern heavy plate steel with apparent yielding strength requires an exact adaptation of the chemical composition and the assigned rolling and heat treatment procedures. In the steel works of ThyssenKrupp steel is produced according to the TBM (Thyssen Blowing-Metallurgy) procedure. The liquid steel is stirred in this case when one blows gas through the converter bottom. Thereby a better mixing of metal and slag is achieved. The (TBM) process allows lower contents of phosphorus and sulphur as well as a better degree of purity [2-4]. The ladle metallurgy [4] is in the same way important (Figure 2). It relieves the converter process and allows a very precise control of the targeted chemical composition as well as a setting of the sulphur content to extremely low values. This is favourable with regard to the degree of purity and results in a high safety against brittle fracture and an outstanding isotropy of the toughness and deformation properties.

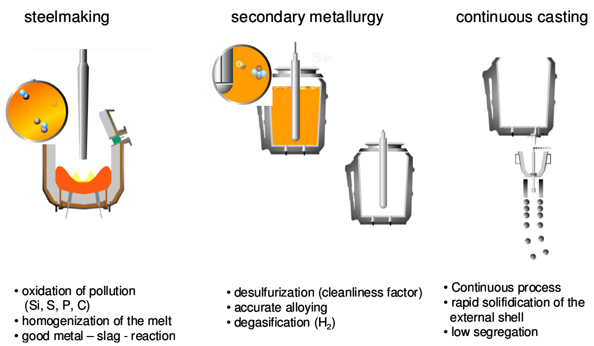


Figure 2. Modern steelmaking.

Next to a balanced chemical composition of the steels, as well as modern steel works metallurgy, the use of modern rolling and heat treatment techniques under consistent use of metallurgical mechanisms is vital. In this case normalised and/or normalised rolled steels, thermomechanically rolled and/or accelerated cooled steels with different chemical compositions are used for vessels and boilers. A general survey of important production methods of (pressure) vessel steels, the typical microstructure, and the resultant yield strength is shown in Figure 3.

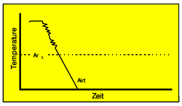
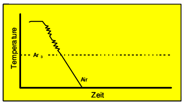
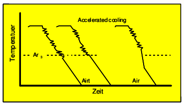
rolling process	Rolling schedule	Particular notes
conventional rolling		High rolling temperature Lower deformation resistance High rolling performance Coarsed and inhomogeneous structure Normalizing / head treatment essential
normalized rolling		Lowered final rolling temperature in range of normalizing-temperature Fine uniform structure No normalizing essential Improved surface condition
thermomechanical rolling (+ accelerated cooling)		Very low final rolling temperature ≈ Ar_3 Multi step rolling schedule Rolling under recrystallisation temp. Straining of the austenite struture Very fine structure Hardening by ML

Figure 3. Modern rolling techniques for high strength steels.

The well-established steels in pressure vessel engineering are low-alloyed steels with a C-content of less than 0.20%. They contain additions of Cr, Mo, Ni and as well as where appropriate a micro-alloying with Nb and V according to the required minimum yield strength and thickness of plate. Common delivery specifications for heavy steel plates for (pressure) vessels are, apart from the DIN EN 10028, material specifications according to ASTM or other, partly national, delivery specifications [5-7].

Figure 4 gives an overview on the variety of steel grades for pressure vessels, chemical composition of the pressure vessel steel as well as the characteristics the yield strength R_e, the tensile strength R_m, and toughness values of the Charpy-V-test.

Standard	Production	Grade		Chemical composition , max (%)				Tensile Test (transverse)			Charpy - V-Test (d=16mm)	
				C	Si	Mn	others*	Re min (MPa)	Rm (MPa)	A min (%)	T (C°)	AV min, J
DIN EN 10025-2	N, AR	S235 S275 S355		.17 .21 .24	/ / .55	1.40 1.50 1.60	Cu, Ni, Nb	235 275 355	360-510 410-560 470-630	26 23 22	20 to -20	27 27 27
DIN EN 10028-2	N	P235 P265 P285		.16 .20 .20	.35 .40 .40	1.20 1.40 1.50	Cu, Ni, Nb	235 265 295	360-480 410-530 460-580	24 22 21	-20	27
DIN EN 10028-3/-5	N / TM	P275 P355 P420 P460		.16 / - .18 /.14 - /.16 .20 /.16	.40 / - .50 - / .50 .60	1.50 / - 1.70 / 1.60 - / 1.70 1.70	Cu, Ni, Nb	275 355 420 460	390-510 450-630 520-660 530-720	24 22 19 17	-20 to -50	27
ASTM	N	A516	60	.21	.40	.90	Cu, Ni, Nb	220	415-550	25	-51	18
			70	.27	.40	1.2	Cu, Ni, Nb	260	485-620	21	-46	20
	N	A537	1	.24	.15 / .50	.70 / 1.35	Cu, Ni, Nb	345	485-620	22	-62	20
	N	A633	A	.18	.15 / .51	1.00/ 1.35	Cu, Ni, Nb	290	430-570	23	-60	20
			C,D	.20	.15 / .50	1.15 / 1.50		345	485-620	23	-40	27
			E	.22	.15 / .50	1.15 / 1.50		415	550-690	23	-20	41
	N	A662	A	.14	.15 / .40	.90 / 1.35	Cu, Ni, Nb	275	400-540	23	-60	20
			B	.19	.15 / .40	.85 / 1.50		275	440-585	23	-45	20
			C	.20	.15 / 50	1.00 /1.60		295	485-620	22	-32	34
	N	A738	A	.24	.15 / .50	1.50	Cu, Ni, Nb	310	515-655	20	30	27
			B	.20	.15 / .55	.90 / 1.50		415	585-705	20		
			C	.20	.15 / .50	1.50		415	550-690	22		
			D	.10	.15 / .50	1.00 / 1.60		485	585-724	20		
			E	.12	.15 / .50	1.10 / 1.60		515	620-760	20		

* if required

Figure 4. Standards for pressure vessel steels.

Apart from the mechanical properties at ambient temperature, pressure vessel steels frequently fulfil ambitious demands on the tensile properties at higher temperatures up to 450°C and they must exhibit optionally the suitability to enamelling/surface coating (e.g. liquid manure container). As a result, the effort for the material testing with these pressure vessel steels is comparatively high.

Because of the high safety relevance of the (pressure) vessel, engineering orders are usually subject to the third party inspection for the supply of the heavy plates by different world-wide external third party inspection agencies, like:

- Germanischer Lloyd
- Lloyds Register
- TÜV Nord GmbH
- Det Norske Veritas
- Bureau Veritas.

A pre-condition for the supply of the (pressure) vessel steels is always an approval by such third party inspection agencies. The basis for it all is a functioning quality management system according to DIN ISO 9001 and the proof of sufficient security with manufacturing. Appropriate approvals are given and examined in fixed time cycles for product and system audits by third party inspection agencies. TKS is an approved supplier of plates to be used in vessel construction in accordance with the above-mentioned regulations.

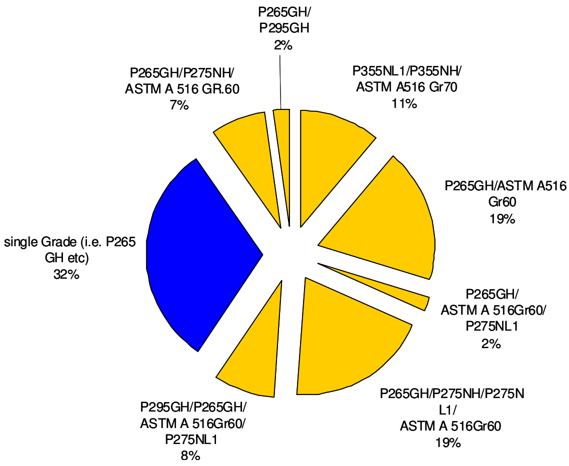


Figure 5: Distribution of steel grades for pressure vessels.

In the preceding financial year TKS manufactured some ten thousand tonnes of plates of various ranges of thickness. Depending on the respective specification, the plate thickness and the demanded property profile, in many cases the plates need to be subjected to a normalising process after rolling.

When providing boiler plates, frequently, an important aspect is striving to simultaneously meet different quality requirements in the delivered plates in order to facilitate the most flexible use of the material for boiler construction projects. Figure 5 shows which quality combinations are usually provided in practice. About 70% of the volumes supplied by ThyssenKrupp Steel for pressure vessels are delivered with multiple certificates. Here, it is important that for such multi-grade or multiple-certificate steels the specifications, which might have a confining effect towards each other, are observed for strength and toughness properties with a narrow scatter range. An example for this is given in Figure 6. The Figure shows a list of the strength properties of plates of different thickness for the (pressure) vessel construction, which *simultaneously* cover the qualities S355J2+N, P355N(L) according to DIN EN 10028 and the ASTM A516 Gr. 70. It is evident here that particularly regarding the tensile strength there is just a comparably narrow scatter width for acceptable values.

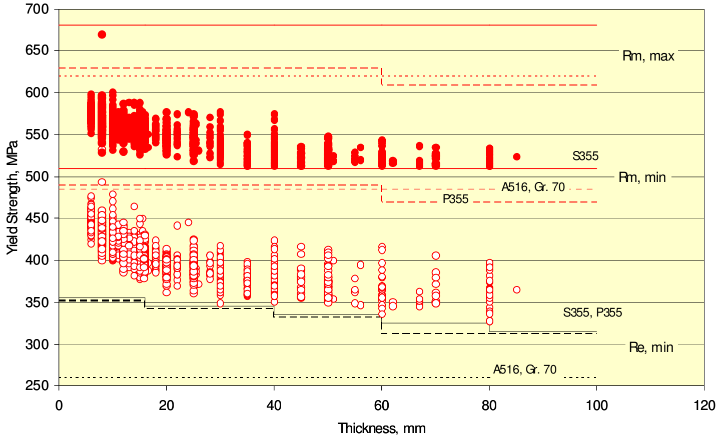


Figure 6. Strength properties of multi-grade S355N/P355N/ASTM516Gr.70.

A precise adaptation of the steel composition and the rolling and heat treatment conditions is required to reliably adjust the complex property requirements for pressure vessel steels. Here, a targeted micro-alloying of the steels with Nb often plays a decisive role to obtain the desired mechanical properties. Above all, this is important to ensure a high toughness with high temperatures and the correspondingly high brittle fracture resistance.

Usage of Nb for improved mechanical properties

Niobium is not a rare element; its content in the Earth's crust is 24g/t and thus it is more widespread than cobalt, lead or molybdenum and even ten times more common than tantalum. Even though it has many interesting applications as a metal and oxide, its dominant role is as a micro-alloying element in the steel industry. While the traditional application of niobium as a stabilising element in stainless steel remained almost constant, the usage as micro-alloying element increased drastically and the technology of thermomechanical rolling, originally developed for large-diameter pipes, spread to other steel products, such as for steel structures and for automobiles. When niobium is used in a micro-alloy, its typical proportion is below 0.10% [8-9].

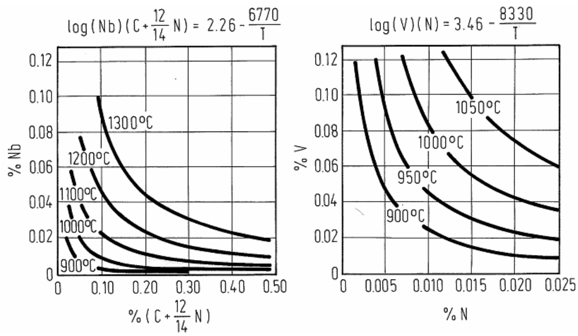


Figure 7. Solubility isotherms in austenite of niobium-carbonitride and vanadium nitride.

The most prominent and outstanding role of niobium in steel in contrast to vanadium is during austenite processing, where usually for the typical carbon level below 0.20%, first the cubic carbonitrides of niobium are dissolved in the upper austenite region and then are re-precipitated in the lower austenite region of 900 to 950°C (Figure 7) [10]. The equally distributed and fine niobium carbonitrides, of typically less than 20nm diameter, successfully control the austenite grain size and thus the microstructure after transformation leading to a significant grain refinement. Grain refinement and precipitation hardening processes in the ferrite add to optimised property combinations, which is consequently used in the fabrication of steels for pressure vessels. In detail, the positive effect of niobium on metallurgical mechanisms, which determine the properties of pressure vessel steels, in comparison to other commonly used micro-alloying elements is given in Figure 8. The studies on the effect of niobium demonstrated that optimised results are already achieved with niobium levels of not more than 0.04%.

Microalloying	Fine precipitates	Retardation of transformation	Grain refinement
Nb	++	+/-	+++
V	+	o	o
Ti	+/- 1)	+	+

+ : positive effect
- : negative effect
o : no significant effect

1) depending on Ti-content

Figure 8. Metallurgical effects of Nb in pressure vessels steels.

Microalloying with Nb in (pressure) vessel steels is an essential part of the alloying concept due to the above-mentioned positive effect on the microstructure and the mechanical properties. In any case, the details specified for the Nb content in the consulted delivery specifications must be observed. Nb micro-alloying is particularly important, when special demands are made on the low-temperature toughness. A toughness certificate for temperatures below -20°C is frequently required for the advanced steels of the (pressure) vessel construction industry. In such cases the criteria of the ASTM for the toughness certificate is particularly high (cf. Figure 4). It often requires a toughness in the notched bar impact test to withstand even -51°C or lower. When striving to cover various qualities within one and the same steel plate, this requirement must be considered. Regarding the commonly used steel grade combination P265GH/ASTM A516 gr.60 as an example, it is found that the minimum toughness with this low testing temperature of 27J at -51°C cannot be reached with sufficient reliability when testing steels without Nb micro-alloying. It is only when Nb is purposefully added, complying with the limit values in the range of up to 0.02% as specified in the standards, that a noticeable toughness enhancement is achieved as a result of the grain refinement (Figure 9). The mean increase of the impact energy due to Nb in these steels at -51°C is then around 60J.

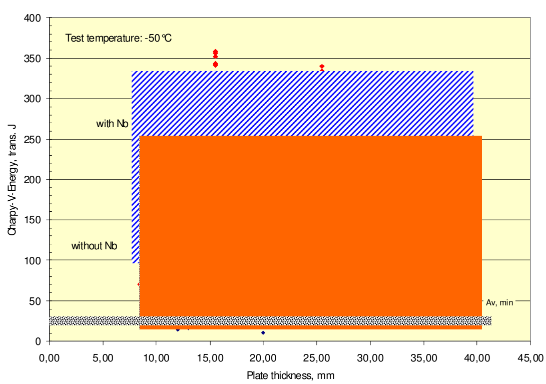


Figure 9: Effect of Nb on low-temperature toughness of grade P2656GH/ASTMA516Gr.60.

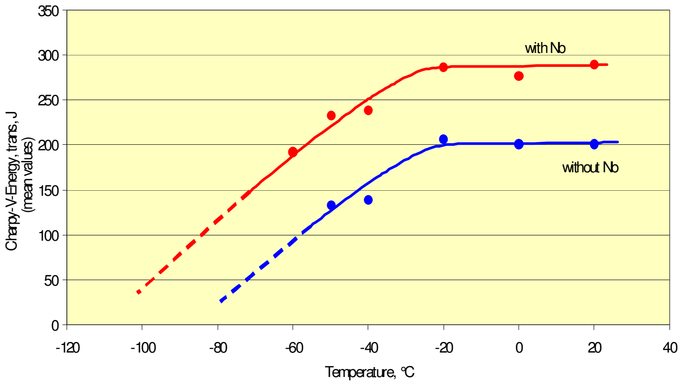


Figure 10. Charpy-V characteristics for Grade P265GH.

Besides the Charpy-V-notch impact energy, the transition temperature T_{27}, which is the temperature where the impact toughness of 27J is obtained and is a characteristic value to describe brittle fracture, is shifted to more favourable values by niobium micro-alloying as shown by the example in Figure 10. According to the brittle fracture concepts of EUROCODE 3, Annex C, a lower transition temperature reduces the growth of cracks and thereby improves the susceptibility of the construction to brittle fracture. Furthermore, this has a simultaneously positive effect on the fatigue properties of welded structures as well as on the acceptable limiting permissible plate thickness.

Processing behaviour of pressure vessel steels

Advanced pressure vessel steels are optimally suited for such subsequent processing methods. During the cold forming process it is required that, depending on the respective yield point, variably high forming forces are applied. At the same time you have to reckon with differing resilience. Owing to the cold forming, the yield strength of the material increases and the toughness decreases. In order to reverse the property changes caused by the forming process and to reduce the involved stresses, the components concerned are subjected to a stress-relief heat treatment within a temperature range of between 550 and 620°C for 4 to 6 hours (Figure 11). A markedly prolonged annealing time is not indicated for the advanced (pressure) vessel steels [11].

The subsequent processing of the pressure vessel steels is mostly done by hot and cold forming processes to manufacture bottoms, spherical segments, pipes, cylinder shells, cones or sections. The forming is possibly followed by a heat treatment. The respective components are then welded together with the usual welding procedures (including submerged-arc welding).

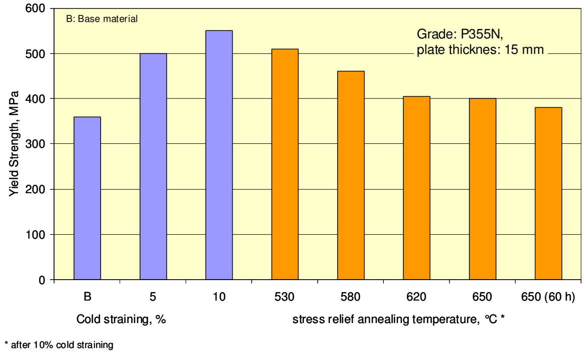


Figure 11. Strength properties of Ps55N after straining and stress relief annealing.

For the hot forming treatment the plates made of (pressure) vessel steels are usually heated to temperatures of about 900 to 1,100°C. Here, you have to reckon with structural changes due to the grain growth of the austenite, which has a detrimental effect on the microstructure produced after the forming and cooling processes thus also affecting the toughness properties. Here, too, micro-alloying with Nb has a positive influence. The grain growth is inhibited due to the formed carbides and carbonitrides and the critical temperature for the initiation of the grain growth is shifted to higher temperatures (Figure 12) [12]. While in CMn steels a considerable loss of toughness is found already above 1,000°C as a result of the austenite grain growth, the Nb-microalloyed vessel steels show yet unchanged toughness properties even after a hot forming at 1,100°C and subsequent cooling. The range of the hot forming temperatures is extended by the Nb micro-alloying. Basically, however, the property profile of the original state, irrespective of the hot forming temperature of between 900 and 1,200°C, in many cases can be restored after a normalising treatment [11].

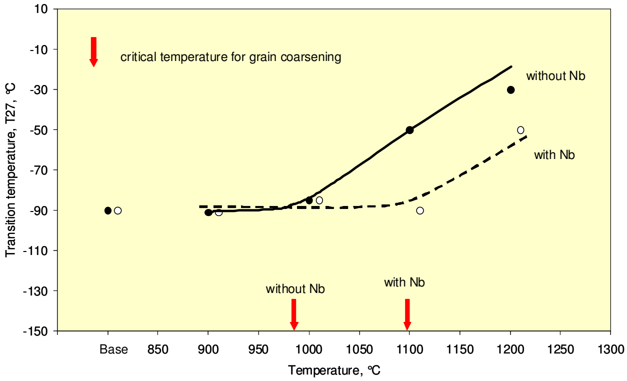


Figure 12. Influence of hot forming temperature on toughness of P355N after hot working.

Pressure vessel steels are very weldable with the usual welding procedures. Welds should preferably not be situated adjacent to anomalies such as stress concentrations or inhomogeneities due to other welds, especially major structural welds. Important aspects during the welding are the cold crack safety and the application-oriented mechanical properties of the welded joints. For both aspects a lot of influencing factors exist (Figure 13) and at ThyssenKrupp systematical basic investigations were carried out in this field. As a result, the highest demands on the load-bearing capacity of welded constructions of pressure vessel steels are able to be fulfilled. The steels show a high cold crack safety through their low carbon equivalent at use of high-quality filler metals with low hydrogen content usual in the case of the shielded gas welding. The considerations represented in EN 1011 to avoid cold cracks (CET-concept) show that at pressure vessel steels a preheating for the hydrogen effusion and delay of the cooling in the welding joint first at thicker heavy plates is necessary.

Avoiding of cold cracks	**Properties in the welded joint**
Influencing factors:	Influencing factors:
Chemical composition - CET*	Chemical composition – CET*
plate thickness d	plate thickness d
hydrogen content of the weld metal HD	pre-heating temperature T_O
heat input Q	heat input Q
pre-heating temperature T_O	geometry of the seam F
residual stresses	

$$* \ CET = C + \frac{Mn + Mo}{10} + \frac{Cr + Cu}{20} + \frac{Ni}{40}$$

Figure 13. Constraints for welding of structural steels.

The welding conditions influence also the mechanical properties of the welded joint of course at the pressure vessel steels (see Figure 13). Important is the suitable determination of the cooling-time $t_{8/5}$ in which the numerous welding-technical actuating variables are combined into a central characteristic. It is proportional to the heat input.

Conclusions

The growing importance of the energy sector leads to an ever increasing significance of the construction of pressure vessels. Advanced pressure vessel steels with minimum yield points from 235MPa fulfil the highest requirements concerning strength and toughness as well as safety against brittle fracture. It is possible to adapt the steel compositions to the manufacturing conditions such that multi-grades can be provided which simultaneously comply with the requirements specified in different, internationally applicable standards for pressure vessel steels. Thereby, the use of niobium as a micro-alloying element is worthwhile. In particular, it refines the grain size and thus improves the toughness of the material guaranteeing a high resistance against brittle fracture. Additionally, the processing behaviour can be improved too.

Actual developments have to consider even higher requirements in toughness at increasingly lower temperatures. To comply with this demand, the use of niobium in pressure vessel steels including Ni-steels for very low temperature applications will further increase in the future.

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