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Principles of pressurised-electroslag-remelting (P-ESR) and hot forming of high-nitrogen steels

High nitrogen steels are commonly known for their excellent mechanical properties, i.e. strength and corrosion resistance. A state-of-the-art production routine is P-ESR melting (pressurised electro slag remelting). It is possible to manufacture both, austenitic as well as martensitic steels suitable for forging and hot rolling. Some basic knowledge of the material peculiarities is mandatory to avoid any potential issues during plastic deformation.
The following paper provides an overview of the manufacturing of HNS as well as some properties to be considered for plastic deformation.

Nitrogen in steel

Nitrogen as an alloying element has been known and used in technical applications since the 1940s, initially under the premise for nickel substitution in stainless grades.

Nitrogen in low alloy steels is undesirable due to the formation of brittle nitrides. However, the use of nitrogen in high alloy steels has an array of advantages that makes it interesting as alloying element. This was sufficiently investigated as many publications show, so that here only the most important facts need to be summarised [3...5]:

- significant increase in strength without restricting ductility;
- improvement of corrosion resistance;
- increasing the high temperature tensile strength;
- extended/stabilized austenite form;
- no formation of stress-induced martensite with high cold working rates;
- inhibits the discharge of intermetallic phases.

The material group specified as HNS (high nitrogen steels), **table 1,** is characterised through an interesting material profile. Energietechnik Essen GmbH produces a range of pressurised austenites and martensites for many applications.

Table 1: Excerpt from the product portfolio of Energietechnik Essen GmbH with sample applications

Material No.	designation	micro-structure	fields of application
1.4108	X30CrMoN15-1	martensitic	high-performance bearings, medical technology, cutlery, aeronautical, engine components
1.3816	X8CrMnN18-18	austenitic	energy technology defense technology
1.3815	X8CrMnN19-19		energy technology, fastening elements
1.4456	X8CrMnMoN18-18-2		energy technology, fastening elements, offshore technology
1.4452	X13CrMnMo18-14-3		medical technology, engine components, jewelry industry
1.6978	X15CrMoVN 10-1	martensitic	mold design and construction, valves, turbine manufacturing
1.4028 modified	X28CrN13		synthetics
-	X25CrMnMoN18-18-1	austenitic	energy technology, engine parts construction, bushings and bearings

The nitrogen effect on the mechanical properties is positive, especially, as far as offset yield stress $R_{p0.2}$ is concerned. **Figs. 1** and **2** clarify the increase in the tensile strength with the increasing nitrogen content and, accordingly, compare the increase in tensile strength and the effect of different elements.

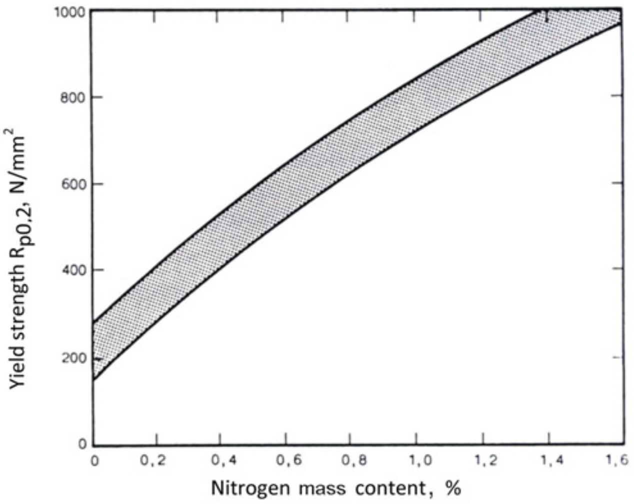

Fig. 1: Influence of N on $R_{p0.2}$ [5]

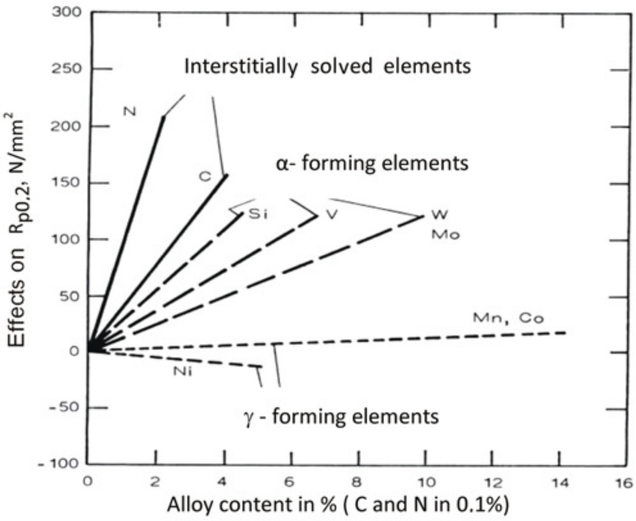

Fig. 2: Tensile strengthening effect of different elements in contrast [5]

The increase in corrosion resistance is due to the support of the short range order of Cr-atoms, **fig. 3.** While carbon supports the formation of Cr-atom clusters on the basis of its electron configuration, nitrogen allows for a uniform allocation of Cr-atoms in the grid, thus reducing the risk of a $M_{23}C_6$-formation. The cluster, **fig. 4,** is to be regarded as local accumulation of approx. 100 atoms.

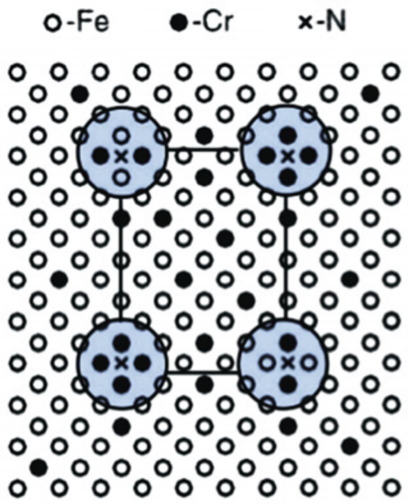

Fig. 3: Schematic of a short range order. Nitrogen increases the concentration of free electrons in austenite, thereby forming a non-directional bonding and a homogeneous distribution of the atom in the crystal lattice [8]

The P-ESR process

All given steels were remelted and pressurised employing the P-ESR-process. To be able to do so, Energietechnik Essen GmbH runs a furnace with an operating pressure of 40 bar maximum designed to remelt ingots of up to 20 t and 1030 mm diameter, **fig. 5.** The functional principle is schematically shown in **fig. 6.**

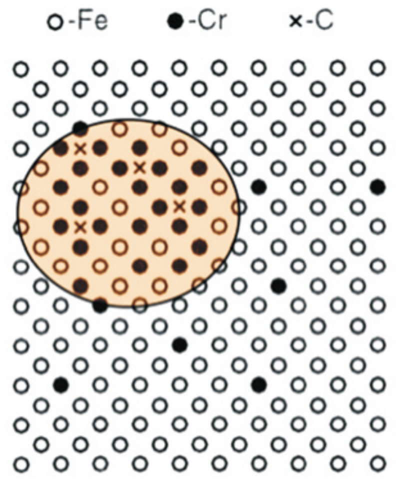

Fig. 4: Scheme of cluster formation. Carbon decreases the concentration of free electrons in austenite, thereby forming a directional bonding of heterogeneous distribution of the atom in the crystal lattice [8]

The physical fundamentals of nitrogen pick-up are specified by Sievert´s law; accordingly, nitrogen solubility is a function of pressure and temperature:

$$[\%\mathrm{N}] = k \cdot \sqrt{p_{\mathrm{N}_2}} \qquad (1)$$

with p_{N2}: nitrogen partial pressure over melt in bar, k: material constant (temperature and alloy dependent).

In real systems, the actual solubility is additionally determined by alloy composition. Thermodynamic activities are used to describe the effect of the individual elements:

$$[\%\mathrm{N}]_{\mathrm{Fe}\text{-}X} = \frac{[\%\mathrm{N}]_{\mathrm{Fe}}}{f_{\mathrm{N}}^{X}} \cdot \sqrt{p_{\mathrm{N}_2}} \qquad (2)$$

with $[\%\mathrm{N}]_{\mathrm{Fe}\text{-}X}$: nitrogen solubility in multi-component systems, $[\%\mathrm{N}]_{\mathrm{Fe}} = 0.044$ % (equilibrium constant in pure Fe at 1600 °C and 1 bar).

Activity coefficient f is, thereby, defined as:

$$\log f_{\mathrm{N}}^{X} = e_{\mathrm{N}}^{X} \cdot [\%X] \qquad (3)$$

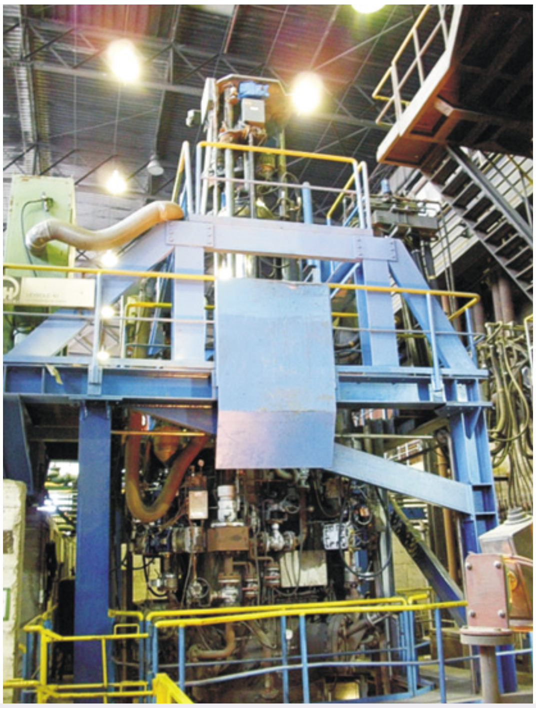

Fig. 5: View of the industrialized P-ESR process for ingot weight up to 20 t und ∅ 1030 mm

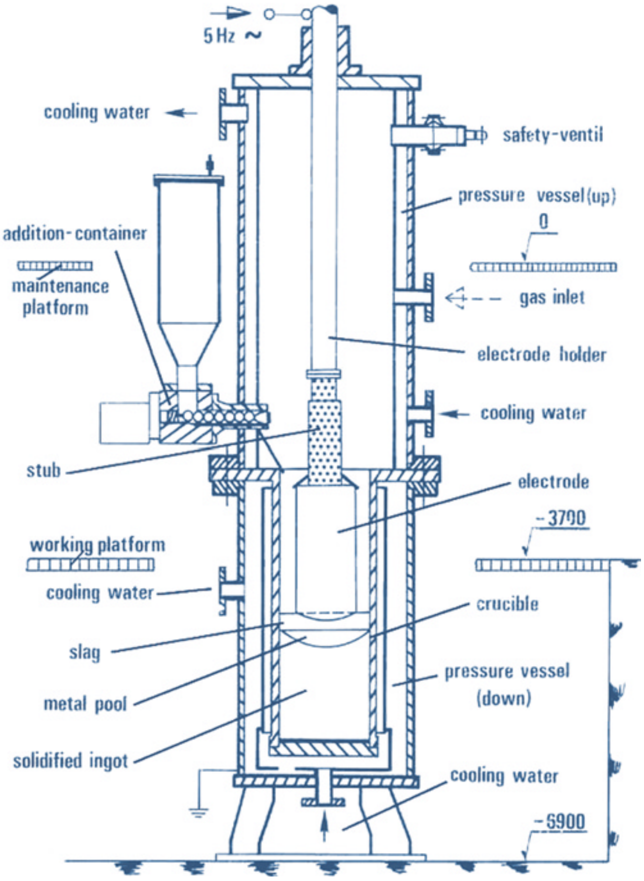

Fig. 6: Schematic design of a pressure electro slag remelting furnace (P-ESR)

e_N^X : interaction coefficient, $[\%X]$: mass contents of elements X in %.

It is obvious that specific elements increase nitrogen solubility (e. g. manganese), while others reduce it (e. g. silicon), **table 2.** This does not only effect the nitrogen pick-up during remelting but also the precipitation of potential intermetallic phases in the solid state. Accordingly, nitrogen solubility is higher in austenitic steels than in ferritic or martensitic grades.

Nitrogen is picked up from the gas phase and also from a solid nitrogen carrier. The choice of a solid-body nitrogen pick-up medium finally depends on the following boundary conditions:

- ♦ nitrogen partial pressure should be high enough to allow dissociation to occur at ~ 40 bar;
- ♦ characteristics of slag and flux may not change (e. g. electrical conductivity, metallurgical properties, etc.).

In practice, standard Si_3N_4 is used, exceptionally CrN as well. In this case, the transfer of silicon, respectively, chromium has to be taken into consideration, too. **Table 3** compares the advantages and disadvantages of Si_3N_4 and gaseous nitrogen.

Selection of the appropriate slag takes place in accordance with the metallurgical characteristics of the respective alloy. Above all, the slag composition is of importance for the nitrogen pick-up of the steel.

Table 2: Activity coefficients of several elements and their effect on nitrogen solubility in steel at 1 bar

Element	coefficient e_N	effect on N solubility
C	+ 0.125	reduction
Si	+ 0.065	
Ni	+ 0.01	
W	- 0.0015	increase
Mo	- 0.01	
Mn	- 0.02	
Cr	- 0.045	
V	- 0.11	
Nb	- 0.06	
Ti	- 0.053	

Table 3: Advantages and disadvantages of different nitriding media

	Advantage	disadvantage
Si_3N_4	nontoxic	very abrasive (joints and gaskets, valves)
	ease of operation and storage	dissociation kinetics of N^{3-}-ion must be considered
	ease of dissociation	non-continiuous allowance on slag
		silicon transfer in melt
N_2 gas	continuous allowance possible	slag composition very important
	simple regulation over the pressure	at high pressures, Sievert's law is not ideally obeyed
	high equal distribution in ingot	diffusions conditions in slag-metal system must be known
	appropriate for Si-critical steel grades	

Microstructural characteristics

At first sight, the considered HNS do not significantly distinguish from the nitrogen-free variants. **Figs. 7** and **8** show exemplary micrographs of an Mn-bearing austenite with approx 0.65 % nitrogen as well as martensite with approx. 0.4 % nitrogen. However, it should be noted that, differing from conventional nitrogen-free alloy variations, HNS show specific precipitation behaviour. This calls for consideration so that potential difficulties with the forming operation or with heat treatment can be avoided.

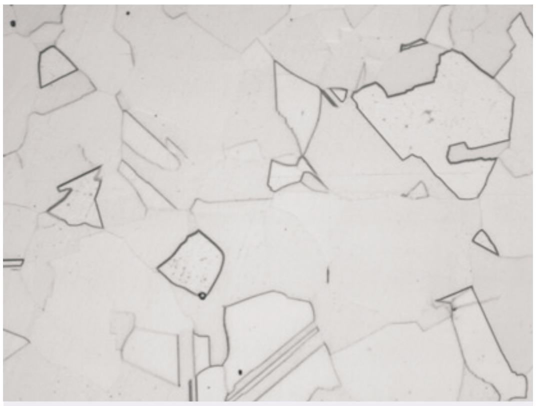

Fig. 7: Microstructure of an undeformed and solution-annealed austenite with ~ 0.6 % N

Fig. 8: Tempered microstructure of nitrogen-alloyed martensitic grade 1.4108 (magnification: 1000:1)

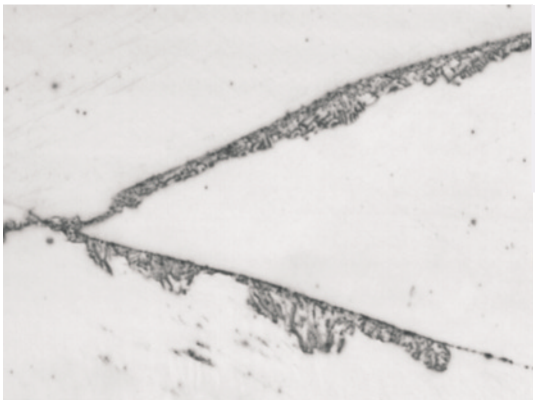

Fig. 9: Beginning of precipitation of nitrogen pearlite cold worked austenitic structure 1.3816 with nitrogen pearlite; 800 °C 15 min

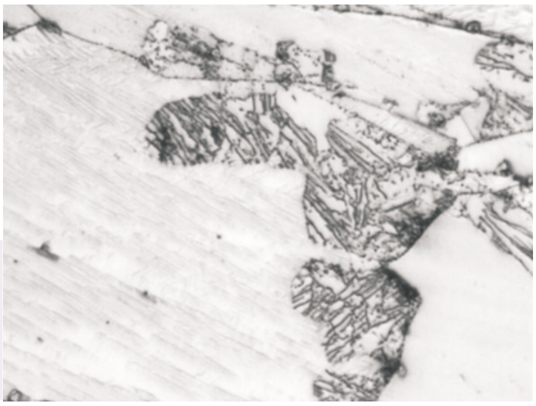

Fig. 10: Advanced precipitation of nitrogen pearlite cold worked austenitic structure 1.3816; 800 °C 30 min

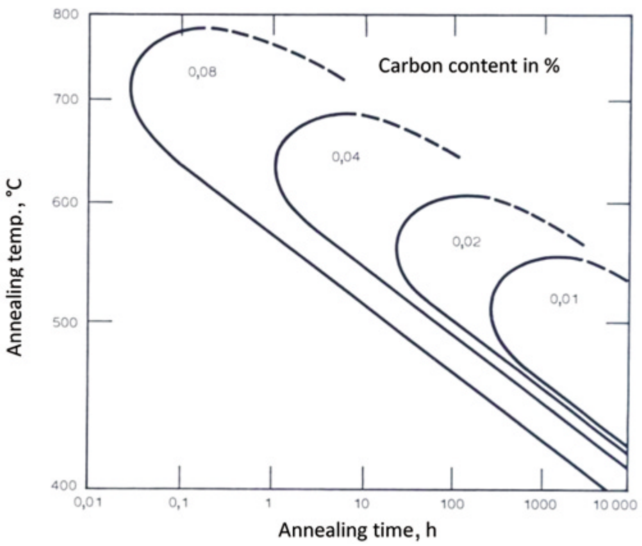

Fig. 11: Influence of carbon content on the occurrence of intergranular attack in unstabilized austentic steels with around 18 % Cr and 8 % Ni. Examination in Strauß test [2]

Precipitation behaviour of nitrogen alloyed steels

Now, a short overview follows over the single microstructural phases and the conditions making their formation happen.

Nitride and nitrogen pearlite. For austenitic steels, it should be considered that in the temperature range of approx. 400 °C - 1000 °C and in connection with the alloy composition, nitrides of type Cr_2N precipitate. This so-called nitrogen pearlite significantly raises the susceptibility to cracking of the steel. Depending on the alloy composition, the precipitation window for nitrogen pearlite or other nitrides is shifted to higher or lower temperatures. **Figs. 9** and **10** exemplarily show an austenitic structure with beginning and advanced precipitation of nitrogen and nitrogen pearlite. Note at which speed precipitation occurs!

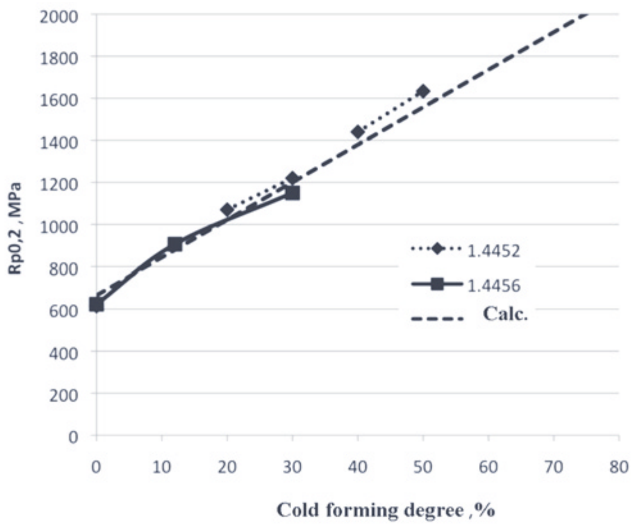

Fig. 12: Influence of cold forming degree, nitrogen content and grain size on the offset yield stress $R_{p0.2}$. Comparison of measured and calculated values

To prevent the occurrence of such brittle phases, it is necessary that during hot forming, this precipitation area is crossed fairly quick.

Carbides. Depending on carbon content and tempering time, austentic steels tend to precipitate $M_{23}C_6$ carbides on the grain boundaries. Thereby, the ductility of the material is significantly decreased without causing any mentionable change in strength properties. The susceptibility to intercrystalline corrosion markedly increases.

Precipitation of this carbide can only be prevented by a quick quench in the critical temperature range. **Fig. 11** shows the occurrence of precipitation for different alloy compositions and annealing time. It is obvious that for a constant temperature, precipitation starts the sooner, the longer the annealing time and the higher the carbon content. Fine carbides are beneficial for corrosion resistance, because the local chrome depletion is lower compared as if it would result from coarser carbides. It is possible to balance Cr-depletion by extending homogenisation (i.e. holding time) within the precipitation area.

High-nitrogen ferritic steels are also characterised by their good high-temperature strength and, accordingly, hot forming behaviour. Under certain conditions, these steels can be subjected to thermomechanical forging and rolling. The last forming step will effectively increase the dislocation density so that adequate nucleation for the desired precipitate exists. For example, the precipitates of carbides, nitrides as well as carbo-nitrides may happen to be finely distributed. This can be of interest as far as high-temperature strength is concerned. The previously mentioned effects of fine carbides concerning the dissolution and corrosion resistance are also valid here.

Influence of nitrogen on the resistance to forming and tensile strength

The significant increase in the resistance to forming caused by nitrogen is due to the avoidance of dynamic recovery. In this respect, the grain boundary strain and yield stress increase accordingly. This increase again depends on alloy composition, grain size and temperature.

The impact of nitrogen on tensile strength can be estimated through the modified Hall-Petch relationship [3]:

$$\sigma_{0.2} = \left(127.6 + 309.9\left(\%\mathrm{N}\right)^{0.5}\right) + \left(7 + 7\left(\%\mathrm{N}\right)d^{0.5}\right) \quad (4)$$

with d: medium grain diameter in µm. The first term describes the influence of nitrogen on friction, while the second describes its influence on grain boundary strength.

In the case of cold-worked microstructures, the deformation degree must be accounted for. An empirical description following the Hall-Petch relationship follows as [4]:

$$\sigma_{0.2} = 145\left(1 + 15\left(\%\mathrm{N}\right)\right)^{0.5} + \left(8 + 38\left(\%\mathrm{N}\right)\right)d^{-0.5} + \left(17 + \left(\%\mathrm{N}\right)\right)KV \quad (5)$$

with KV: cold forming degree in %.

Fig. 12 shows the clear correlation between measurements and calculated tensile strength, so that the formula can be used to estimate the expected tensile strength values.

Hot forming of HNS and material characteristics

Hot forming of HNS alloys puts special requirements on the rolling mill and forge arising from the high deformation resistance. Principally, P-ESR steels show unrestrictive ability for hot deformation, however, the necessary forming force increases with increasing nitrogen content. Further, the temperature range is narrowed with increasing nitrogen content. This relation is pointed out by means of the exemplary hot flow curves for both, the conventional Cr-Ni alloyed steel (1.4301) and the Mn-alloyed austenitic steel (1.4452) produced by P-ESR, **figs. 13** and **14**.

The high-temperature tensile strength of the nitrogen-alloyed Mn-austenite shows a significant increase compared to that of the classic Cr-Ni austenite.

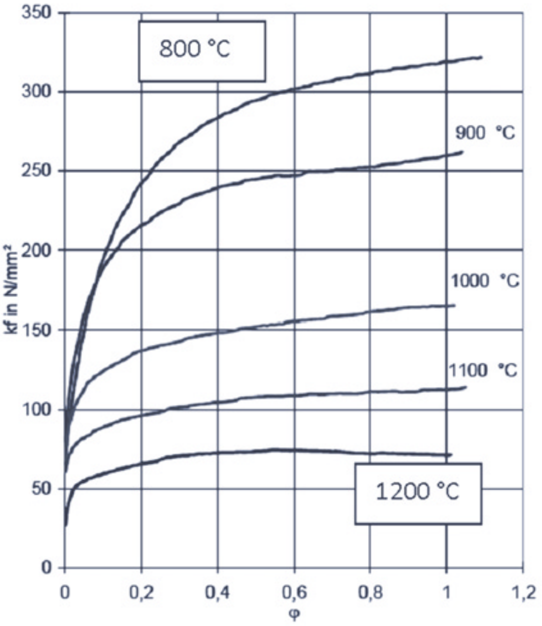

Fig. 13: Hot flow curve of 1.4301 obtained at deformation rate $\dot{\varepsilon} = 1/s$ [5]

Fig. 15: Bar out of 1.4452-material with edge cracks. Root cause: precipitation of nitrogen pearlite due to nitrogen pick-up in the surface area of ~ 1.3 % N

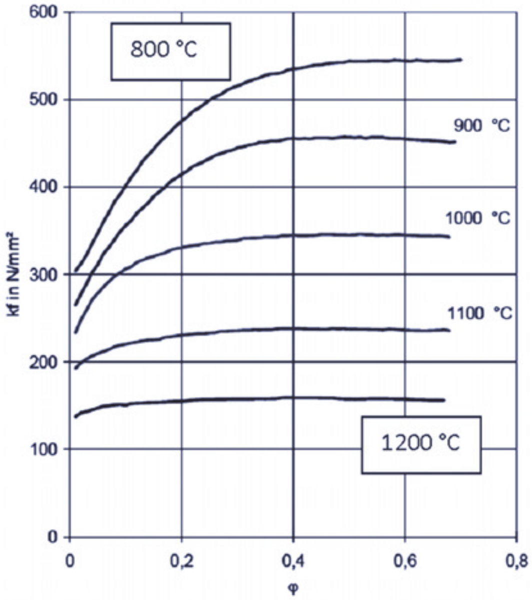

Fig. 14: Hot flow curve of 1.4452 obtained at deformation rate $\dot{\varepsilon} = 1/s$ [5]

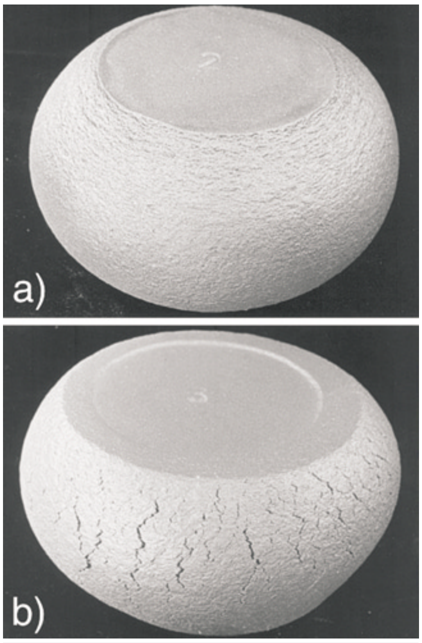

Fig. 16: Compression test performed on a cylinder of 100 mm ∅ and 150 mm length, furnace temperature 1220 °C, $\varphi = 2.2$
forging temperatures of a) 1000 °C and b) 900 °C

Potential problems with forming operations

Besides the previously mentioned high-temperature strength and the precipitation sensitivity of austenitic steels, the usual steel specific forming problems hold for these types of steels as well.

Due to their low ductility, nitrogen alloyed steels exhibit a considerably higher tendency to hot cracking compared to conventional steels, **fig. 15.** The visible hot cracks arose in temperature regions where ductility is reduced, i.e. just below recrystallization temperature. Also known as *ductility-dip cracks* they possibly occur in all processes where the microstructure is subjected to tension at this critical temperature. Both, the location and elongation of these hot cracks is effected by several process parameters, e.g., deformation rate, chemical composition and cooling rate, and are, therefore, not clearly defined.

In addition, increased surface cracking can appear between the contact area of the tool and workpiece during forging, **fig. 16.** The cracks occur in the working area between tool and forging part due to local spot deformation, thus indicating undue high stresses. This is likely to happen in the saddle radius. It is mandatory to prevent any nitrogen pick-up from the furnace atmosphere to avoid surface cracks.

Outlook

Nitrogen alloyed steels are a material group with excellent mechanical properties. Some knowledge of the material peculiarities is mandatory to avoid potential problems during deformation.

The combination of properties, such as, the high strength and ductility, resistance to creep, wear resistance and high corrosion resistance, make nitrogen alloyed steels an important construction material.

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