Technological Aspects of New Martensitic Nitrogen Steels

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Introduction:

The martensitic transformation of carbon steels is used in three different ways. Firstly to raise the hardness of tool, carburizing, flame hardening and roller bearings steels by carbon in solid solution. Secondly to initiate a homogeneous carbid precipitation promoting either a precipitation hardening by fine precipitates (secondary hardening of tool steels) or a dispersion of coarser spherodized carbides in quenched and tempered steels. This change from lamellar perlitic carbide plates to a globular dispersion in combination with the grain refinement of the matrix greatly improves the toughness. Thirdly the dispersion of hard martensitic grains within a ferritic matrix has a beneficial effect on the strenght and ductility of dual-phase sheet for deep-drawing applications.

The role of nitrogen in the martensitic transformation of steels is similar to that of carbon (1). As nitrogen is volatile it has to be pressed into the melt. The pressurized electroslag remelt process (PESR) developed by Krupp/Klöckner (2) today allows ingots up to 15 Mg in weight. Austenitic CrMn steels with up to 1.2 % nitrogen and more than 850 MPa yield strenght have been developed (3). Looking for possible improvements by nitrogen in martensitic steels one has to consider a solubility increase by alloying elements as the nitrogen pressure is limited. In the sequence of Mn,Cr,Nb,V,Ti (4,5) the nitrogen activity is lowered and its solubility in the melt is raised. However, the nitride solubility upon austenitisation is reduced by these elements in same sequence. From a technological point of view this brings us to the following grades of nitrogen steels:

- Nitrogen in solid solution is raised by chromium rendering hard stainless steels for tooling or roller bearings tempered at ≈ 200° C.
- Nitrogen is precipitated in form of a fine nitride dipersion by tempering tool or bearing steels at 500 to 600° C.
- Nitrogen is precipitated in form of a coarse nitride dispersion by tempering of creep resistant steels at 650 to 750° C.

As in austenitic steels nitrogen in solution might raise the corrosion resistance of martensitic chromium steels. The precipitation of the coherent CrN-nitride may improve the dispersion and thereby the strenght und toughness of creep resistant steels. An improvement of either corrosion or creep resistance would justify the moderatly higher cost of PESR against the ESR process.

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2. Stainless Cold-Work Tool Steels

In preceding work, steels with up to 20% chromium and 0.8 % nitrogen were investigated(6). As a result, alloys with 15 % chromium and 1 % molybdenum containing about 0.5 carbon and/or nitrogen were chosen for comparision (table 1).

alloy	wt %	C	N	Cr	Mo	V	others
X 50 CrMo 15		0,50	-	15,0	1,0	-	-
X 0+50 CrMo 15		-	0,50	15,0	1,0	-	-
X 35 CrMo 17		0,38	-	16,0	1,0	-	-
X 45 CrMoV 15		0,47	-	14,75	0,5	0,15	-
X 12+30 CrMo 15		0,12	0,30	14,70	0,95	0,02	-
X 20+32 CrMo 15		0,20	0,32	15,0	0,97	0,02	
X 40 CrMoV 51		0,40	-	5,19	1,30	0,95	1,08 Si
X 14+30 CrMo 51		0,14	0,30	5,09	1,41	0,09	0,73 Si
X 22+4 CrMoV 12 1		0,22	0,04	11,90	0,93	0,28	
X 7+20 CrMoV 12 1		0,07	0,20	10,20	1,40	0,21	0,04 Nb
X 1+25 CrMoV 12 1		0,01	0,25	11,40	1,07	0,29	
13 CrMo 44		0,195	0,007	0,92	0,42	-	-
4+15 CrMo 44		0,04	0,15	1,01	0,45	0,03	-

Table 1 Chemical composition of the alloys investigated

In figure 1 the hardening behaviour is shown. An increase by about 100° C in hardening temperature is required for the nitrogen steel to give equivalent hardness. This is due to a lower solubility product of M_2N nitrides as compared M_7C_3 carbides (7) and the lower atomic concentration of nitrogen. Chromium nitrides dissolve carbon but chromium carbides little nitrogen (8). Therefore $M_2(N,C)$ undissolved carbonitrides are encountered in the nitrogen and carbon containing steels after quenching from moderate hardening temperatures. The amount of carbon and nitrogen in solution is expressed by the lattice spacing of the martensite. At equal solute contents there is little difference in the M_s temperature and the as-quenched hardness. The tempering characteristics are given in figure 2. The secondary hardening is more pronounced in nitrogen steels.

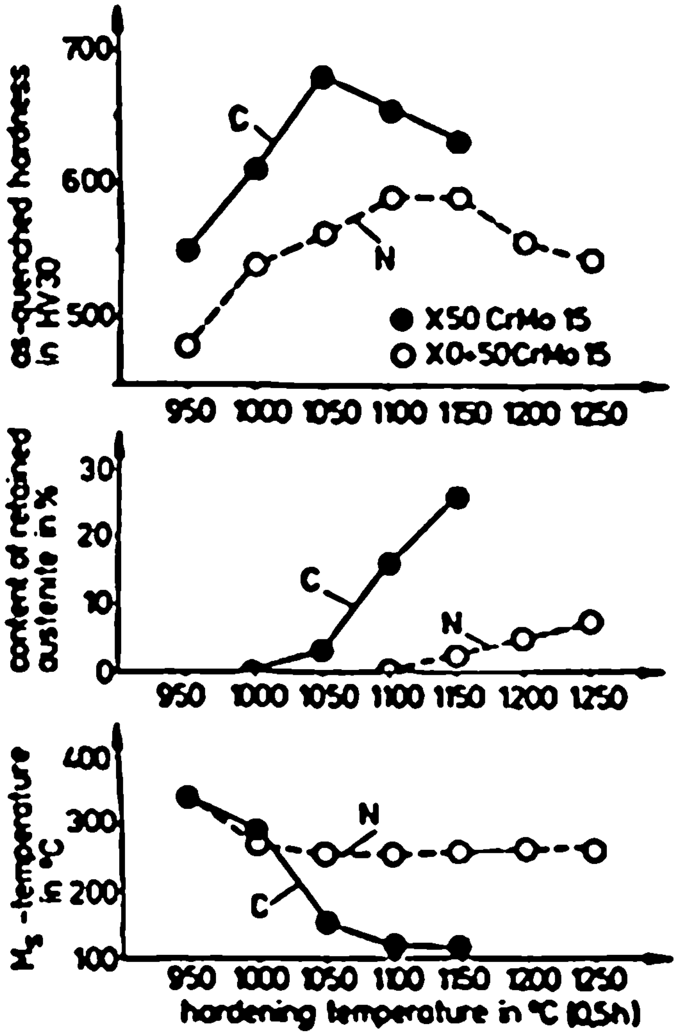

Fig. 1 Hardening of stainless martensite containing C or N.

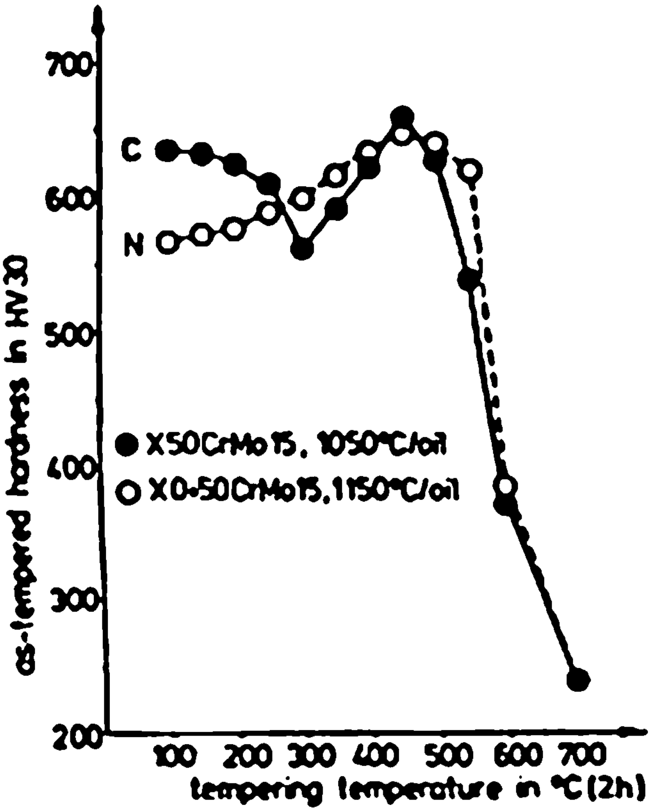

Fig. 2 Tempering of stainless martensite containing C or N.

The corrosive weight loss rates in aqueous 10 % H_2SO_4 or HCl are given in table 2. The current density/potential curves in 10 % H_2SO_4 reveal a drop in passive current density by an order of magnitude as the nitrogen content is raised (6). In an aqueous 3 % NaCl solution the pitting poontential U_p of nitrogen steels is up to 1.5 V higher than in carbon steels. Even after a tempering treatment at 500° C. When U_p is plotted over the efficiency sum S_p a linear relation similar to that known from austenitic steels is found (figure 3).

	weight loss rate	(g/m²h)
alloy	10% H_2SO_4	10% HCl
X 35 CrMo 17	4310	2320
X 45 CrMoV 15	9440	3670
X 12+30 CrMo 15	1030	420
X 20+32 CrMo 15	1210	740

Table 2 Weight loss rate after 90 hours in aqueous solutions at room temperature.
Heat treatment of the specimens: 1050°C, 30 min/oil

3. Hot-Work Tool Steels

The exchange of carbon by nitrogen in H 13 type CrMoV steels leads to undissolvable vanadium nitrides and poor hardenability. After reducing the vanadium content (9) the nitrogen steels display an improved hot strenght and toughness in the quenched and tempered condition (table 1, figure 4). This is due to the finer and more stable nitride dispersion as compared to carbides. Martensite is a prerequisite to generate this microstructure upon tempering.

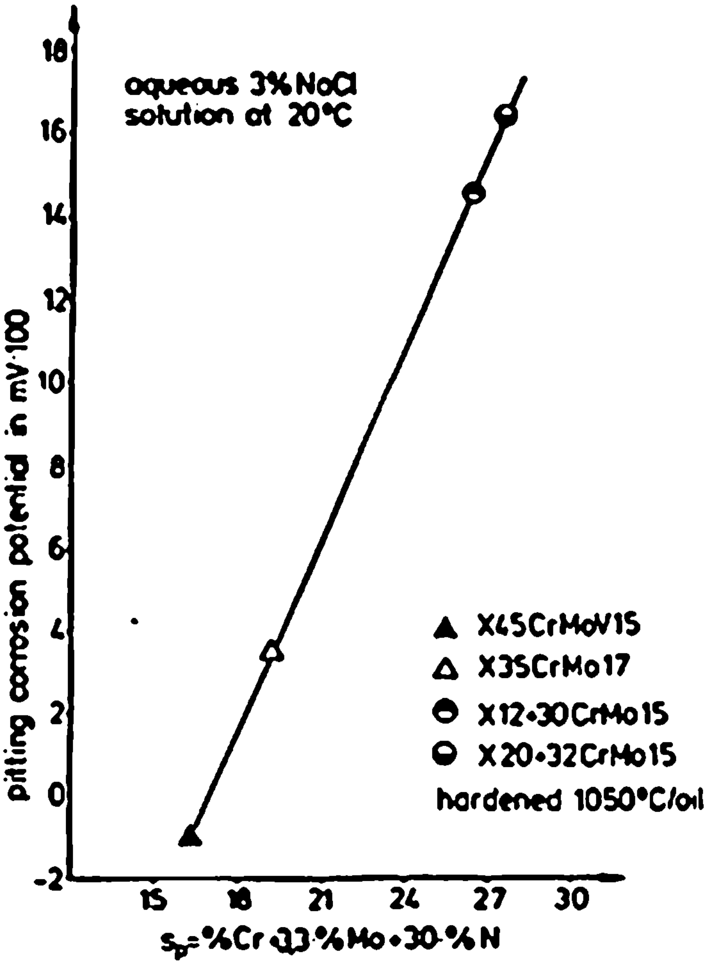

Fig. 3 Influence of nitrogen of the efficiency sum in preventing pitting corrosion of stainless martensitic steels.

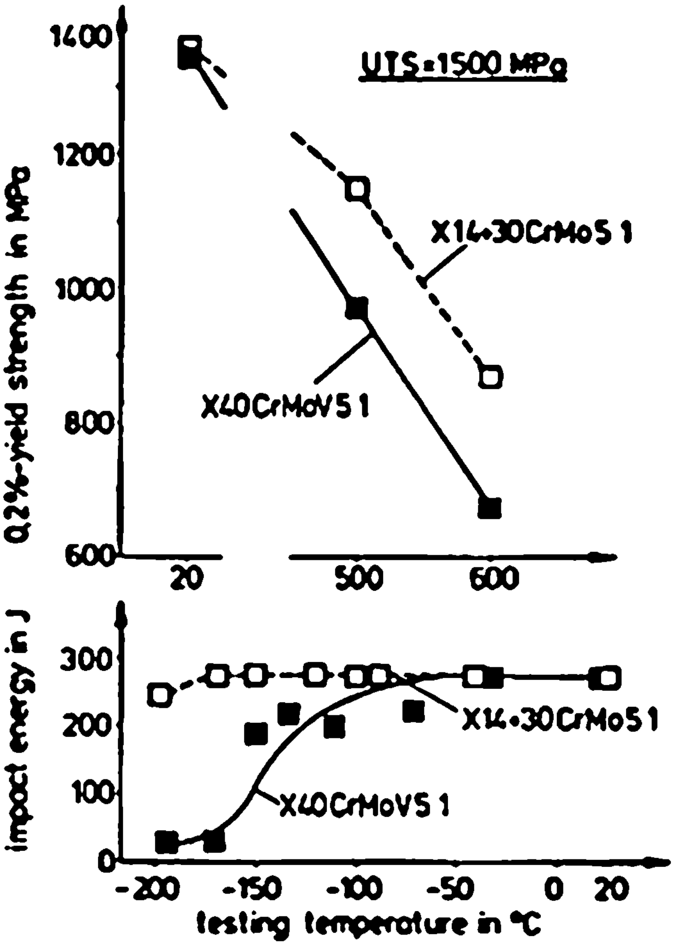

Fig. 4 Influence of nitrogen and hot strength and toughness of precipitation hardened martensite
(hot work tool steel),
unnotched 7 x 10 x 55 mm impact samples,
no fracture at 280 J.

4. Creep Resistance Steels

Creep resistant steels with 12 % chromium are similar to hot-work steels. As seen above the introduction of nitrogen requires a higher hardening temperature which eventually provokes austenite graingrowth (10). A thermo-mechanical treatment by hot-working prior to martensitic transformation removes the embrittlement connected with coarse martensite. After tempering to equivalent UTS the difference in microstructure brought about by carbon or nitrogen is clearly depicted in figure 5. The nitrides are an order of magnitude smaller than the carbides. While the nitrides are dispersed within the martensite plates, the carbides decorate the plate boundaries i.e. the sites of easier nucleation. The coherent MN, however, may well nucleate at dislocations within the plates. The resulting difference in toughness is shown in figure 6. The short time creep properties are improved if molybdenum and niobium are added (fig. 7).

A similar combination of improved toughness and hot strength (11) is found in low alloy CrMo creep resistant steel with 1 % Cr (fig. 8).

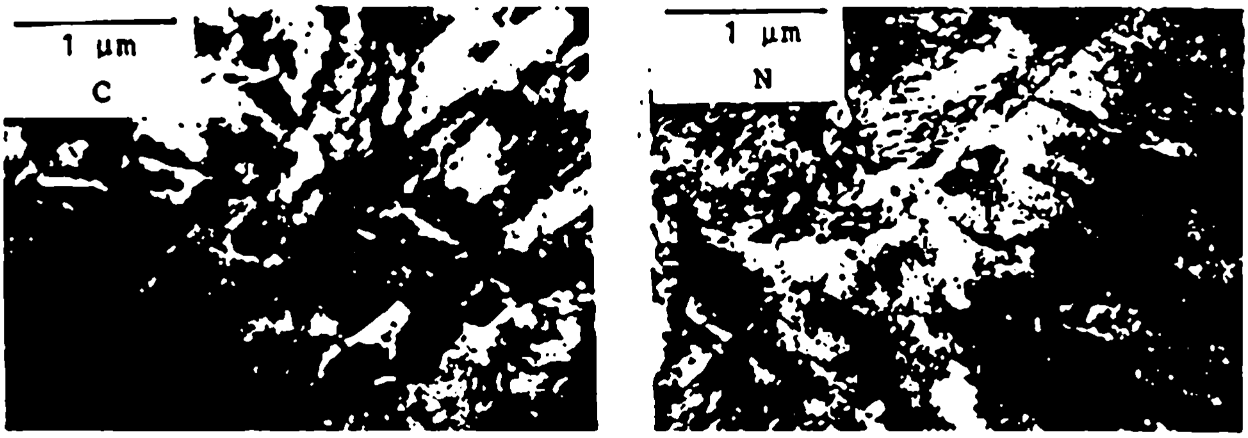

Fig. 5 Microstructure of C- and N-alloyed creep resistant steels with 12 % Cr in comparison
(hardened and tempered to 1000 MPa, TEM).

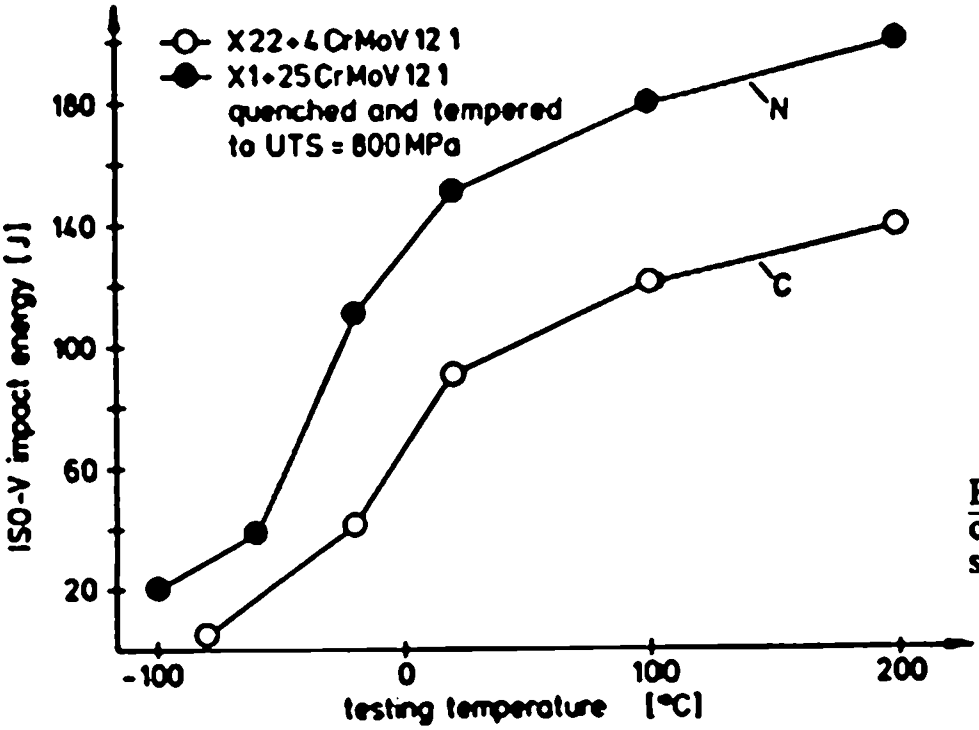

Fig. 6 Toughness of high chromium creep resistant steels containing C or N.

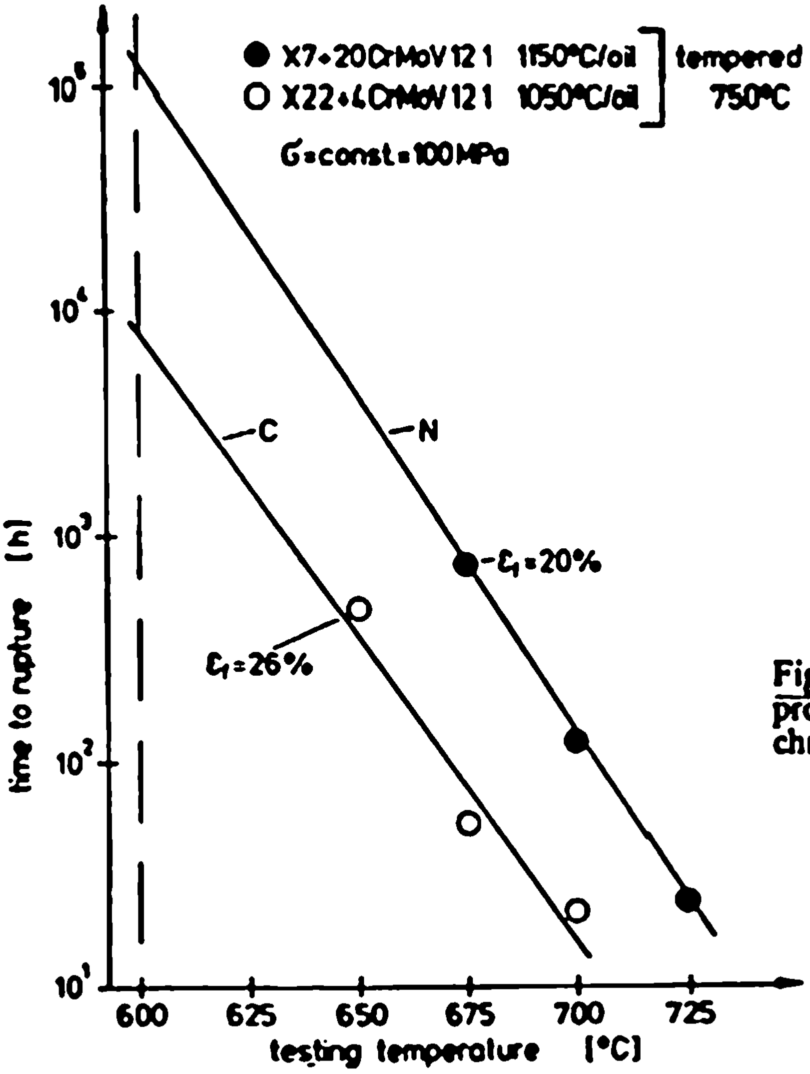

Fig. 7 Comparison of short time creep properties in iso-stress tests. High chromium steels containing C and N.

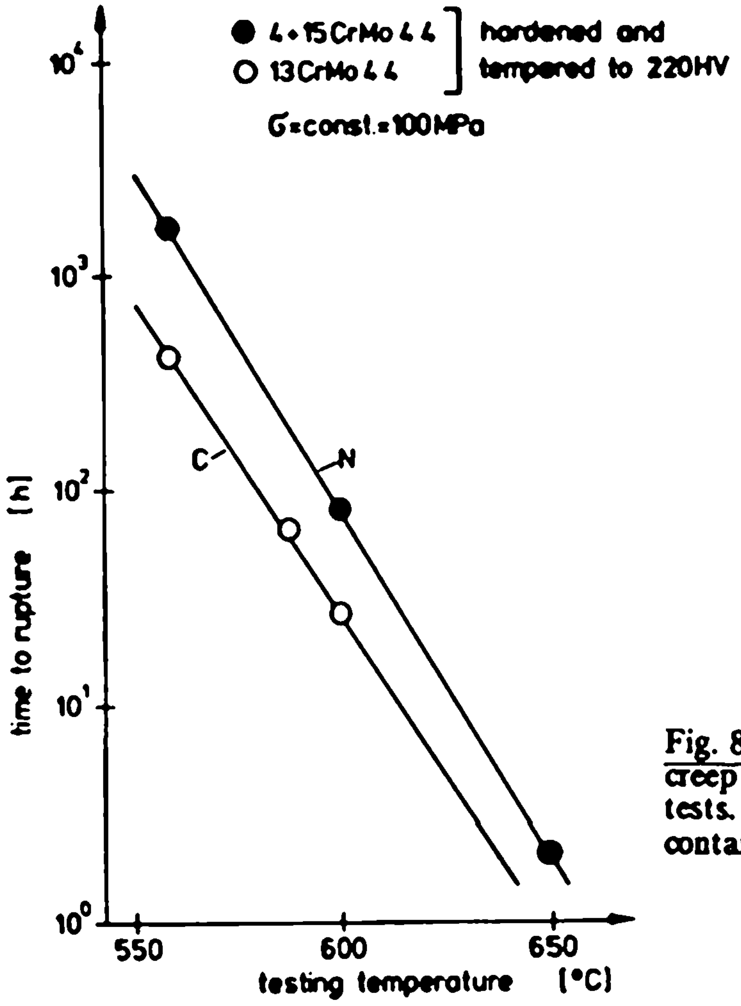

Fig. 8 Comparison of short time creep properties in iso-stress tests. Low chromium steels containing C or N.

5. Conclusions

The lower solubility product of alloy nitrides as compared to carbides requires a reduction of alloy content or a higher hardening temperature. The detrimental effect of the latter on toughness may be overcome by a thermo-mechanical treatment followed by quenching.

The lattice spacing and hardness of the as-quenched martensite is raised by dissolved nitrogen. Precipitation hardening upon tempering is more pronounced in alloyed nitrogen steels as compared to the aquivalent carbon steel.

The nitride precipitates are finer and more stable than the carbides rendering higher impact toughness and hot strenght.

High chromium contents allow high nitrogen levels resulting in stainless martensitic steels for tools and bearings with improved corrosion resistance. After precipitating alloy nitrides by tempering an improved product of hot strength and toughness is gained in hot-work tool and creep resistant steels.

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