

STAINLESS AUSTENITIC STEEL OF SUPERIOR STRENGTH

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ABSTRACT

Solid solution hardening by interstitial elements is a promising way to raise $R_{p0.2}$. The solubility of nitrogen is low in the melt though, and that of carbon low in the stainless austenite. Therefore C+N were combined and raised to about 1 mass% in a steel with 18 mass% of Cr and Mn each. An exceptionally high concentration of free electrons in the solution annealed austenitic lattice entails a very ductile metallic character of the alloy. Tensile tests revealed $R_{p0.2} > 600$ MPa, $R_m > 1000$ MPa, $R > 2500$ MPa, $A_5 > 70$ % and Charpy V-notch specimens a transition temperature of -90 °C for 100 J. The resistance to impact wear lived up to Hadfield manganese steel and the deformed wear surface remained non magnetic with $\mu_{rel} = 1.0012$. The break-through potential in 3 % NaCl and 1nH₂SO₄ was better, respectively as good as of standard steel X5CrNi18-10. The application is seen in corrosion and wear resistant, non-magnetic machine components requiring high strength.

KEYWORDS

Stainless, non-magnetic, austenitic, high-strength steel, carbon + nitrogen, cold work hardening.

INTRODUCTION

The strength of austenitic stainless steels is considerably enhanced by interstitial atoms. The low solubility of nitrogen in the melt and of carbon in the high-chromium austenite suggests a combination of both alloying elements. As nickel lowers the interstitial solubility a chromium-manganese steel is to be preferred. It is the aim of the present study to describe the development of a CrMnCN steel with about 1 mass% of C+N melted under ambient air pressure.

1. EXPERIMENTAL

The ThermoCalc programme [1] was used to derive suitable CrMnCN alloys. The chemical composition of the three alloys investigated is given in Table 1. They were melted in induction furnaces and forged to rods. The standard steel X5CrNi18-10 (CrNi) was taken for reference from rolled stock. Specimens were cut by electro-spark erosion, solution annealed (see Table 1) and machined by turning or grinding. The conduction electron spin resonance (CESR) was measured between 4.2 and 300 K to derive the concentration of free electrons in the paramagnetic austenite [2]. The microstructure was examined by light optical microscopy (LOM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Mössbauer spectroscopy (MOS) [3] and by testing the relative magnetic permeability μ_{rel} . Tensile and ISO-V impact tests were performed at room and lower temperatures. Current-density/potential curves were taken at a rate of 0.6 V/h in aqueous solutions of 3 % NaCl or 1nH₂SO₄ at room temperature to characterize the corrosion resistance. The mass loss by impact wear was measured after 1000 impacts each, caused by mineral

particles of greywacke (760 HV0.1), 11 to 8 mm in grid size, which perpendicularly hit the surface of a 50 x 35 x 10 mm wear plate at a speed of $\bar{v} = 25$ m/s.

Table 1: Chemical composition of the steels investigated (mass%)

steel	C	N	P	S	Si	Cr	Mn	Ni
CN0.82	0,387	0,431	0,044	0,007	0,48	14,7	17,2	<0,1
CN0.96	0,344	0,614	0,021	0,002	0,30	18,2	18,9	0,3
CN1.07	0,489	0,578	0,026	< 0,001	0,43	18,8	18,9	0,4
CrNi	<0,004	0,053	0,028	0,021	0,57	18,7	1,9	9,0

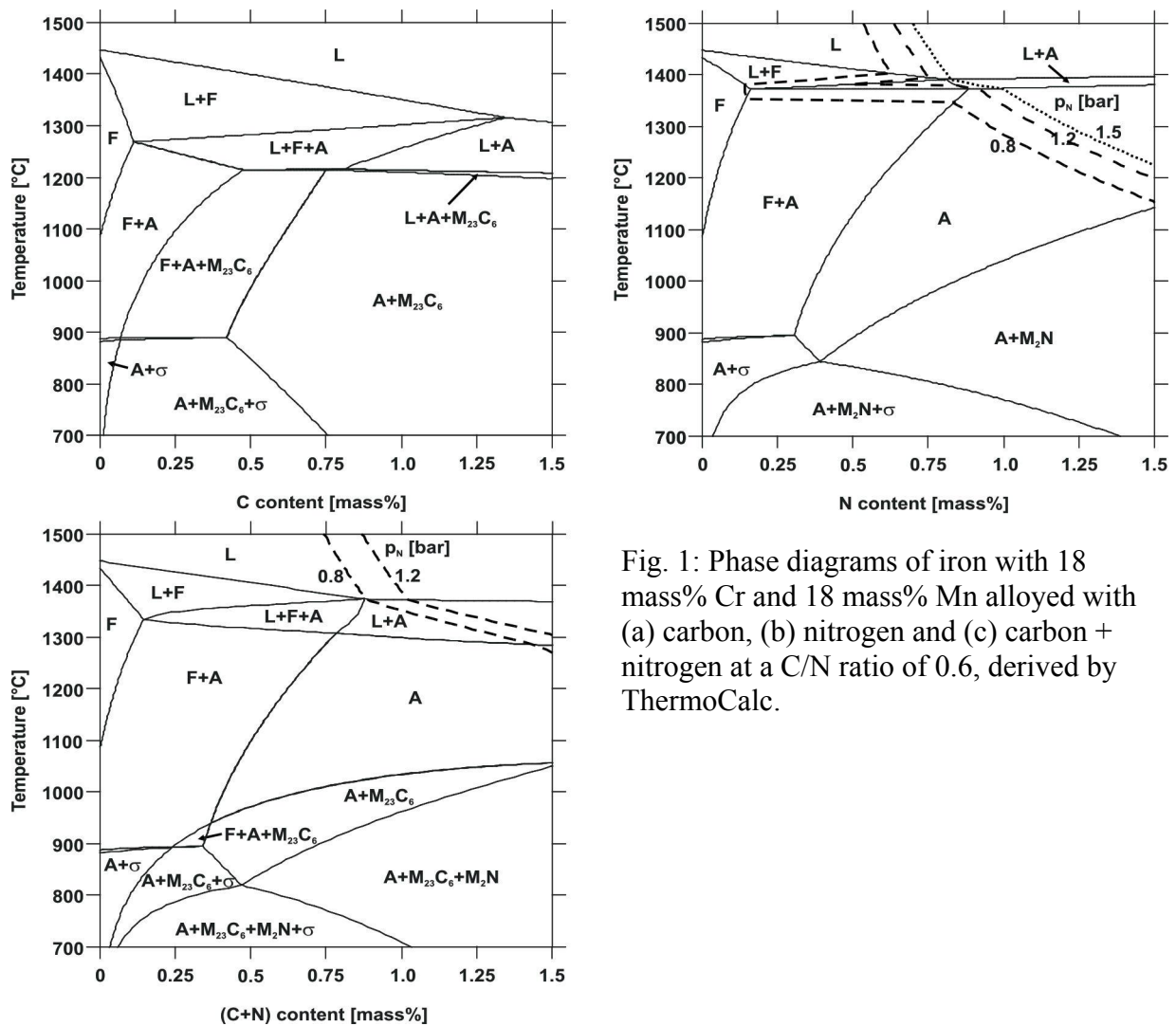


Fig. 1: Phase diagrams of iron with 18 mass% Cr and 18 mass% Mn alloyed with (a) carbon, (b) nitrogen and (c) carbon + nitrogen at a C/N ratio of 0.6, derived by ThermoCalc.

2. RESULTS

The thermodynamic calculations of the constitution revealed a promising range between 15 and 20 mass% of Cr and Mn each to reach a high concentration of C+N in the melt and in the austenite, if the C/N mass ratio stayed between 0.5 and 1. For example, at 18 mass% of Cr and Mn each, there is no phase field of homogeneous austenite available in the FeCrMnC system, while it is well developed in the FeCrMnN system, however at the expense of the nitrogen solubility in the melt (Fig. 1). At C/N = 0.6 the solubilities in melt and austenite are brought in line. This leads to the lean alloy CN 0.82 with C+N = 0.82 mass% and to the alloys CN 0.96 and CN 1.07 of higher strength and corrosion resistance.

The arrows in Fig. 2 show that the concentration of free electrons in the fcc lattice is considerably increased by the combined addition of C+N compared to alloying with C or N alone. In addition the maximum of the N-curve (alloys h) appears to be shifted to a higher interstitial concentration (alloys a to d).

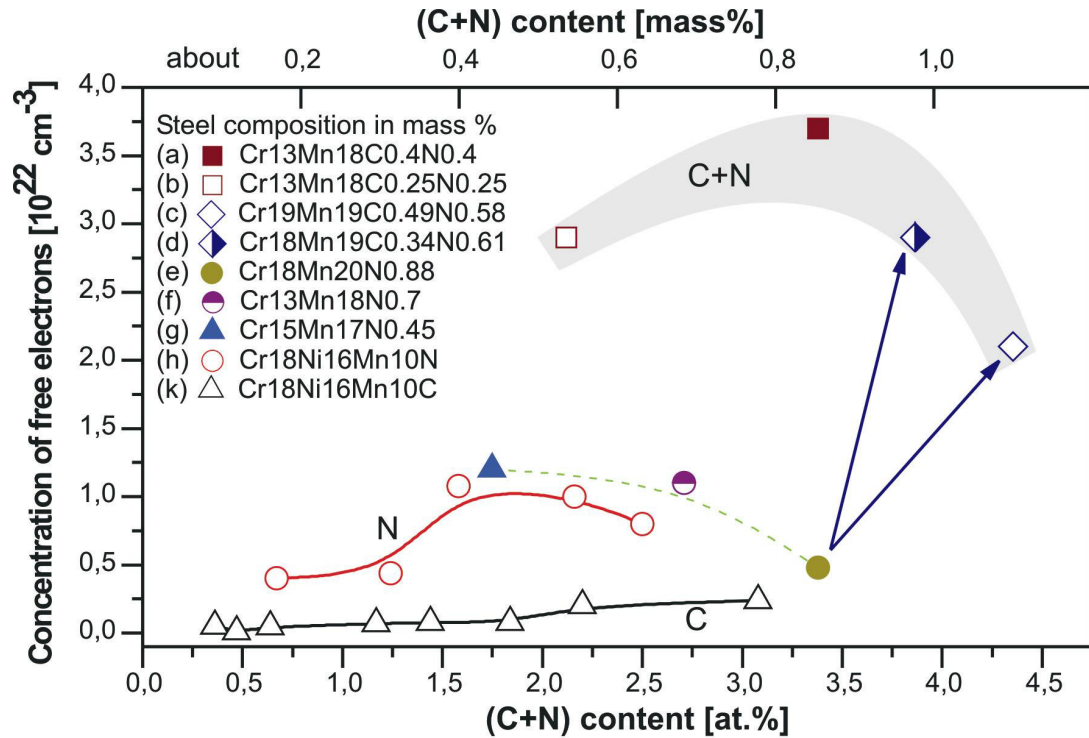


Fig. 2: Concentration of free electrons in austenite derived by CESR, the arrows are indicating the development from a pressure-melted N steel (e) to the new C+N grades CN0.96 (d) and CN 1.07 (c)

Table 2: Properties of the new CN grades compared to the reference CrNi steel

steel	CN0.82	CN0.96	CN1.07	CrNi
$R_{p0.2}$ [MPa]	494	600	604	221
R_m [MPa]	951	1020	1075	592
R [MPa] ¹⁾	2635	2547	2545	1930
A_u [%] ²⁾	68	61	62	70
A_5 [%]	78	73,5	73,5	83
Z [%]	68	68,7	52	86
W_s [J/cm ³]	651	676	694	422
H [HV0.1] ⁴⁾	566	590	630	460
T_T [°C] ⁵⁾	-77	-90	-34	<-150
$\dot{w}$ [g/impact] ⁶⁾	$4.625 \cdot 10^{-6}$	$5.125 \cdot 10^{-6}$	$5 \cdot 10^{-6}$	$9.625 \cdot 10^{-6}$
μ_{rel} ⁷⁾	1.0011	1.0012	1.0012	1.08
E_t [V] ⁸⁾	3%NaCl	-0.032	0.670	1.000
	1n H ₂ SO ₄	1.208	1.050	1.200

¹⁾ true fracture stress, ²⁾ uniform elongation, ³⁾ specific fracture energy, ⁴⁾ hardness on tensile fracture face, ⁵⁾ transition temperature at an ISO-V impact energy of 100 J, ⁶⁾ average wear rate, ⁷⁾ relative magnetic permeability on the impact wear surface, ⁸⁾ transpassivation potential

The mechanical properties are given in Table 2. The proof strength $R_{p0.2}$ increases with the C+N content to a level of almost three times that of the reference CrNi steel. A fracture elongation A_5 above 70 % points to good ductility in spite of intensive cold work hardening, which is characterized by a true fracture strength $R > 2500$ MPa and a high hardness on the fracture surface. As a result a specific work to fracture W_s of almost 700 J/cm^3 is obtained. At room temperature the ISO-V impact specimens are hardly fractured by a 300 J hammer. Below, the impact energy decreases, reaching 100 J at the “transition” temperature T_T given in Table 2. The strength increases as the testing temperature is lowered to the cryogenic range while the ductility remains high (Fig. 3).

The mass loss by impact wear is similar for the three CN steels but about twice as high for the reference CrNi steel (Fig. 4). The hardness increases from the bulk towards the wear surface (Fig. 5). At the very surface a thin amorphous layer was detected by TEM followed by a layer of nanocrystals embedded in an amorphous base [4]. No phase transformation was detected by XRD or permeability tests. However, MOS revealed a magnetic response in the wear surface.

The break-through potential in $1\text{N H}_2\text{SO}_4$ is high for all steels tested (Table 2). In aqueous solution of 3 mass% NaCl the Cr level of about 15 mass% in steel CN 0.82 seems to be insufficient to resist pitting while at 18 to 19 mass% Cr the high C+N content of steel CN 0.96 raises the pitting potential slightly above that of the reference CrNi steel.

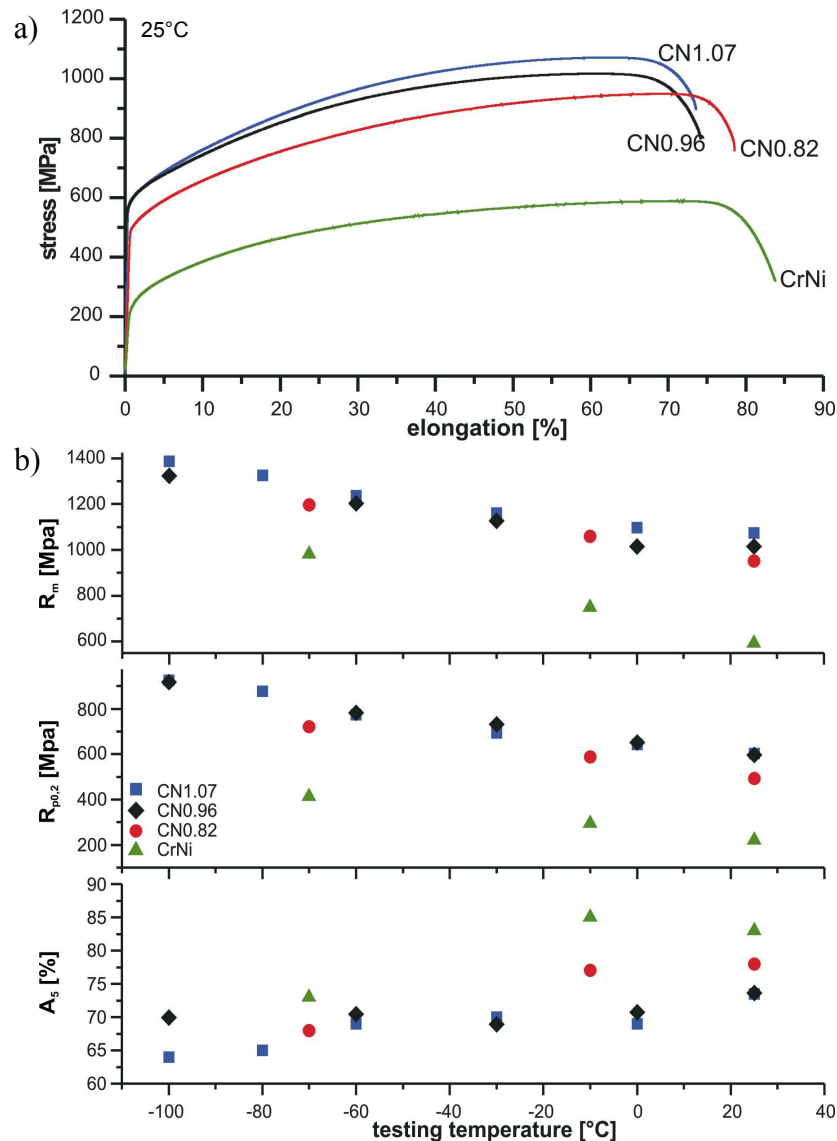


Fig. 3: Results of tensile tests, (a) engineering stress/strain curves, (b) ultimate tensile strength R_m , proof strength $R_{p0.2}$ and elongation at fracture A_5 depending on the testing temperature.

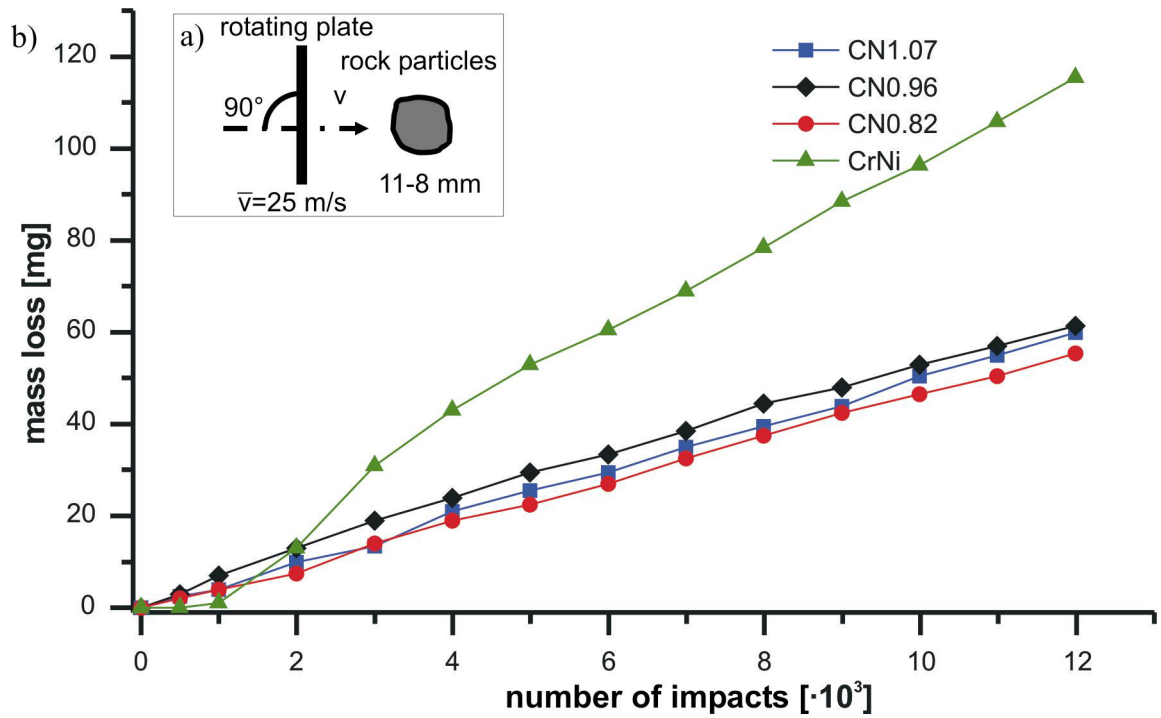


Fig. 4: Impact wear, (a) schematic representation of the impact conditions, (b) mass loss over the number of impacts from which the average wear rate in Table 2 was derived.

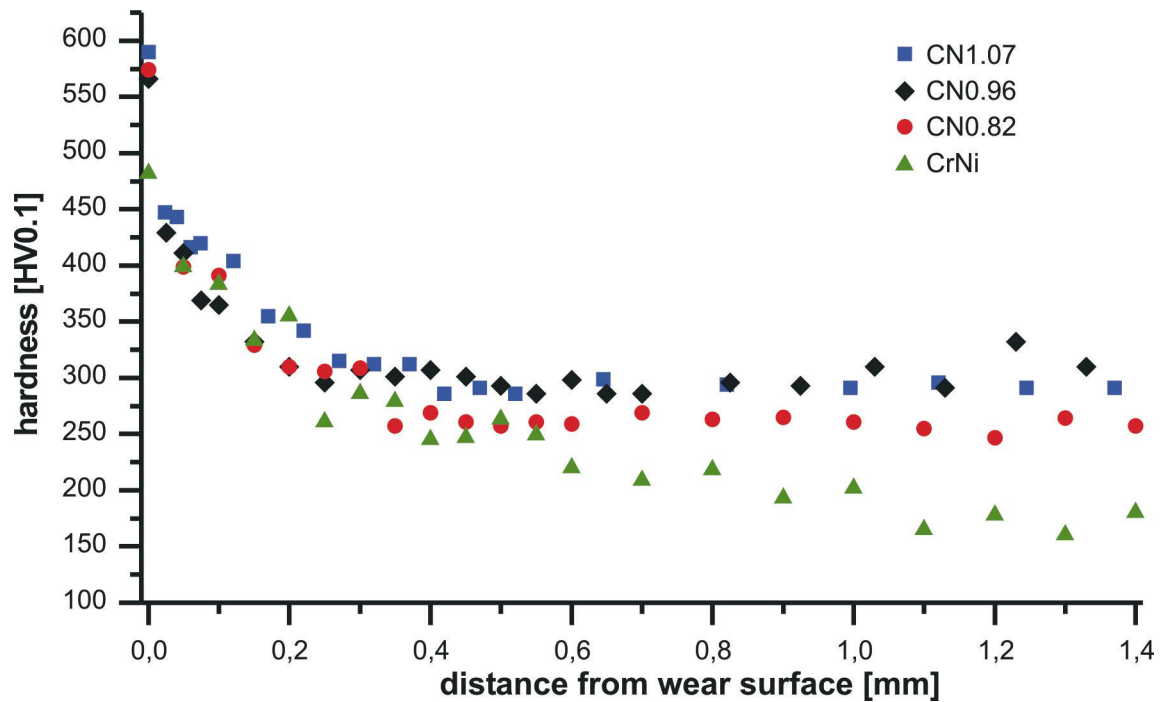


Fig. 5: Hardness profiles below the impact wear surface.

3. DISCUSSION

An isothermal section through the FeCrC system at 1050 °C shows that the solubility limit of C in austenite follows the common solubility product $\% C \cdot \% Cr \approx \text{constant}$, which means that the soluble

C content is inversely proportional to the Cr content while in the FeCrN system the soluble N content is directly proportional to the Cr content. The N-induced concentration of free electrons helps to avoid the clustering of Cr atoms leading to short range atomic ordering which increases the interstitial solubility and thus the stability of austenite [3, 5]. It was shown by MOS that the exchange of 0.6 mass% C by about 0.6 mass% N or 0.3 mass% C + 0.3 mass% N increased ordering in a stainless martensitic steel with 15 mass% Cr and 1 mass% Mo [6]. Besides the different solubilities of C and N in the melt and in austenite, the enhancement of ordering was an incentive to transfer the C+N concept to austenitic steels [7]. The increase of the concentration of free electrons in the order of alloying with C, N or C+N (Fig. 2) and the concurrent rise of ordering observed in martensitic stainless steel suggest that the spherical bond of free s-electrons is the cause of ordering, improved interstitial solubility and austenite stability. In contrast the directional bond of d-electrons leads to interstitial/substitutional clustering in stainless steels alloyed with C only [8]. In binary iron alloys Co and Ni, right to iron in the periodic table, are known to also raise the concentration to free electrons while elements like Cr and Mn to the right decrease it [2]. Compare e.g. steel (a) and (b) with 13 mass% Cr to steel (c) and (d) with 18 or 19 mass% Cr, respectively (Fig. 2). Therefore the C+N concept is the more important for CrMn based stainless steels, because free electrons also support the metallic character of interatomic bonding, i.e. entail ductility.

This is very well documented by the high elongation to fracture. However, the lower reduction of area and the higher impact “transition” temperature of steel CN 1.07 (Table 2) seem to indicate, that the C+N content of this alloy may be already above the optimal level, which holds also true for the concentration of free electrons (Fig. 2).

In contrast to the CrNi reference steel showing a martensitic transformation in the impact wear surface (see μ_{rel} in Table 2), the austenite of the new CN grades proves to be quite stable and not subjected to deformation induced phase transformation. This is well in line with the above – mentioned sequence of free electrons $\rightarrow$ ordering $\rightarrow$ interstitial solubility $\rightarrow$ austenite stability. The ferromagnetic response depicted by MOS seems to be caused by a high concentration of very fine twins in the severely deformed wear surface entailing magnetic ordering within the twins [9].

The beneficial effect of interstitial nitrogen on the resistance to pitting corrosion of stainless steel is well known [10] and effective in the new alloys. Recent work showed that the combined addition of C+N improves the pitting resistance [11]. A further increase is brought about by Mo.

After some initial stage the wear rate of the three CN steels is about equal and quite close to Hadfield manganese steel ($\dot{w} = 4,96 \cdot 10^{-6}$). This offers applications of the new alloys to wear and corrosion resistant castings in off-shore or deep pit mining. Other applications are seen in as-cast pump components, hot worked non-magnetic retaining rings, bearings, injection systems a.s.f.

4. CONCLUSIONS

(a) Thermodynamic calculation led to three stainless austenitic CrMn steel with 0.82, 0.96 or 1.07 % C + N in solid solution, which were produced without pressure metallurgy.

(b) Compared to a standard CrNi steel the yield strength was almost tripled, yet a high ductility was retained.

(c) Due to intensive cold work hardening a C+N grade reached a specific fracture energy in tensile tests of almost 700 J/cm³.

(d) This high strength yet ductile behaviour is based on an exceptional high concentration of free electrons in the C+N austenite, which support the metallic character of interatomic bonding.

(e) Cold work hardening brings the impact wear rate of the C+N grades down to the level of Hadfield manganese steel.

(d) Applications are seen in machine components requiring high strength as well as corrosion resistance impact wear resistance and / or a non-magnetic behaviour.

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