

Development of a high chromium martensitic steel proposed for roller bearing applications

M. Faleschini¹, S. Peissl¹, G. Mori², R. Ebner¹, S. Eglsäer³

¹ Materials Center Leoben, Franz Josef Strasse 13, A-8700 Leoben, Austria.
mario.faleschini@mcl.at

² [Christian Doppler Laboratory of Localized Corrosion](#), Department of General, Analytical and Physical Chemistry, University of Leoben, Franz Josef Strasse 18, A-8700 Leoben, Austria.

³ Boehler Edelstahl GmbH, P.O. box 96, A-8605 Kapfenberg, Austria.

Abstract

High chromium martensitic steels are designed to provide high corrosion resistance in combination with high strength. Some of these steel grades contain primary carbides for improving wear resistance, e. g. the steel 440C. The present paper mainly deals with the effect of chemical composition and microstructure on corrosion and tribological properties of recently developed steels.

Different experimental alloys were produced in form of small ingots. The influence of the alloying elements chromium, molybdenum and cobalt is investigated. The results indicate that corrosion resistance is improved compared to 440C.

Further investigations were focused on heat treatments, especially on tempering temperatures. They are very important for precipitation of secondary carbides, which worsen the corrosion properties. The carbide precipitation and chromium distribution was characterized by means of energy filtered transmission electron microscopy (EFTEM).

To characterize the wear properties of the developed steels, measurements with a Ball on Disc (BOD) tribometer under lubricated conditions were performed. The measured wear rates are comparable to M50, the standard bearing material for aircraft turbine bearings.

Introduction

A common material for applications which require high corrosion resistance and high strength is the martensitic steel quality 440C. This grade contains a high amount of chromium of approx. 17 wt% and a carbon content of 1.05 wt% that is necessary for hardenability.

In the as-quenched condition, the microstructure contains blocky primary carbides. Subsequent tempering leads to precipitation of fine secondary carbides, which strengthen the martensitic matrix.

However, the combination of high contents of chromium and carbon causes an extensive formation of primary carbides, particularly M_7C_3 and $M_{23}C_6$ in 440C [1]. Due to stress concentration and formation of voids in adjacent regions, the micrometer-sized carbides might have a negative effect on durability [2]. Furthermore, the corrosion resistance is poor compared to other stainless steels, because the high carbon content leads to the precipitation of chromium rich carbide phases [3] and thus to depletion of the chromium content in the matrix.

In recent years, new corrosion resistant high-strength steels have been developed. Well known case-hardenable examples are Pyrowear 675 [4,5] and CSS42L [6]. The main difference of material composition compared to 440C, are lower amounts of chromium and higher contents of molybdenum and cobalt after carburization.

The mentioned elements have a considerable influence on corrosion behaviour. It is well known that chromium forms a passivated layer on the surface that protects the bulk material. Molybdenum and cobalt influence the composition of this passivation layer and its stability in corrosive environments [7,8]. With increasing amount of molybdenum, the pitting corrosion resistance of stainless steels is enhanced [8]. However, it is a carbide-forming element and it is still unclear whether molybdenum plays a similar role in high carbon steels.

In literature [9] it has been reported that high cobalt contents of 15 to 20 wt% increase the amount of chromium in the passivated layer, increasing oxide stability and therefore improve corrosion behaviour. At the same time cobalt enforces carbide formation as calculations with Thermo-Calc [10] show and might decrease corrosion resistance. Thus a major effect of cobalt on corrosion properties can be expected, whether it is beneficial or detrimental.

To study the influence of these alloying elements, ingot melts with different amounts of Cr, Mo and Co were produced.

The corrosion behaviour is also affected by the heat treatment, especially the tempering temperature. A significantly reduced corrosion resistance is caused by the precipitation of carbides during tempering [11]. Energy filtered transmission electron microscopy was used to characterize carbides and the chromium distribution in their vicinity in order to clarify the influence of the carbide precipitation and chromium depletion.

Experimental

Four different ingot melted steels (with nominal compositions shown in Tab. 1) were produced to gain information about the influence of alloying elements and their interaction. Samples (40 x 20 x 4mm) were cut from the bars, heat treated and grinded. The specimens were hardened, deep frozen and finally tempered three times using the parameters given in Tab. 2. The chosen temperatures and times assure a hardness of approx. 59 ± 0.5 HRC for all alloys.

For steel No. 2 and No. 3 additional tempering temperatures (as-quenched, 200, 300, 400, 450, 480, 510, 540, 570 and 620°C) were selected to investigate the influence of tempering temperature on pitting potential and hardness.

Anodic polarization curves were measured to study corrosion resistance of the investigated steels in aerated, deionised water with 50ppm of chloride (added as NaCl). These experiments were performed at 50°C using a three electrode electrochemical cell using a saturated calomel electrode (SCE, $E_{SCE} = 241 \text{ mV}_{SHE}$) as reference electrode and a platinum plate as counter electrode. After grinding, all specimens were stored in a desiccator for at least 12 hours to enable passivation. A programmable Jaissle potentiostat-galvanostat IMP 88 PC was used for the electrochemical measurements. The free corrosion potential was measured immediately after immersion for one hour before starting polarization. After polarizing the sample to a cathodic potential of 100mV below the free corrosion potential the potential was increased toward the anodic region with a scan rate of 600 mV/h. Polarization direction was reversed when reaching a current density of 1 mA/cm². All potentials are reported with respect to SCE throughout this work.

EFTEM [12,13] was used to acquire information about the precipitates. For the investigations, a Philips CM20/STEM equipped with a Gatan imaging filter was used.

To study the wear behaviour of the steel grades under pure sliding conditions, Ball on Disc tests (CSM instruments) were performed. The investigated materials were heat treated, ground

and polished and tested at 150°C for a total distance of 1000m. For each run, the sample was completely immersed under a defined amount (7ml, resulting in an oil height of 5mm over the sample) of Mobil Jet II oil. As sliding contact partner, 6mm diameter balls of steel grade M50 were used. The applied load was 15N, resulting in a maximum contact stress of 1634MPa, calculated according to [14]. A white light profilometer (NT1000, Veeco Metrology Group) was used for inspecting the wear tracks. From these data, positive and negative wear volumes, surface roughness, topography and cross section profiles can be determined. The results of the most promising, developed steel quality – steel No. 2 – are compared with standard ball bearing materials M50 and 440C, which were heat treated according to standard specifications.

Results and Discussion

Scanning electron microscopy (SEM) images of the different steel grades are shown in Figure 1. All steels contain one or more types of the primary carbides MC, M₆C and M₇C₃. Qualitative analysis by energy dispersive X-ray spectroscopy (EDX) proved that the MC carbides are rich in vanadium, whereas the M₆C carbides are rich in molybdenum and the M₇C₃ carbides contain a high amount of chromium. Steel No. 1 contains about 1.1 vol.% MC and less than 0.1 vol.% M₆C primary carbides. Steel No. 2 has the lowest concentration of primary carbides of type MC but contains about 0.3 vol.% M₇C₃. Highest volume fraction of carbides is found in steel No. 3, which contains all three types of primary carbides and steel No. 4 has a rather high amount of M₇C₃ type carbides (Table 3).

Results of electrochemical tests of steels No. 1 to No. 4, heat-treated according to conditions as listed in Table 2, are shown in Figure 2. Steel No. 1, which has the lowest amount of alloying elements, shows the most negative free corrosion potential (FCP) followed by the cobalt-alloyed steel No. 4. The alloys with the highest Cr and/or Mo content, steels No. 2 and No. 3, which are both free of cobalt, exhibit the most noble FCP. The pitting potentials show the same trend. In case of steel No. 1 pitting starts already close to FCP, whereas steel No. 2 shows the highest resistance to pitting. Further, steel No. 4 shows a lower pitting potential than steel No. 3.

Steels No. 2 and No. 3 show a passive behaviour, whereas current density steadily increases from FCP to pitting potential for steels No. 1 and No. 4. The latter two steels have no typical passive range under tested conditions.

To investigate the influence of secondary hardening carbides on corrosion properties steel No. 2 was tempered at various temperatures followed by polarization and hardness measurements. If steel No. 2 is tempered at a temperature of 560 °C corrosion resistance decreases significantly. Not only FCP, also pitting and repassivation potentials become more negative (Figure 3). The decrease of pitting potential can only be caused by precipitation of chromium and/or molybdenum rich phases. By comparing hardness and pitting potential as a function of tempering temperature it can be concluded that the beginning of secondary hardening carbide precipitation, which is indicated by increase of the hardness, correlates well with the decrease of pitting potential.

The microstructure of two differently tempered specimens of steel No. 2 was investigated by means of TEM and it could be shown that after tempering at 400 °C there was no evidence of the precipitation of secondary hardening carbides, while after tempering at 570 °C a large number of fine chromium containing secondary hardening carbides were present indicated as carbides of type Cr₂₃C₆ (see Fig. 4).

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These results show that the corrosion properties of high strength steels containing primary carbides and secondary hardening carbides is not corresponding to their nominal chemical composition as described by the pitting resistant equivalent number (PREN, see eq. 1) after [15, 16].

$$\text{PREN} = \% \text{Cr} + 3.3 \cdot \% \text{Mo} + 30 \cdot \% \text{N} \quad (1).$$

According to eq. 1 Steel No. 2 shows improved corrosion behaviour compared to that of steel No. 1 because of the higher chromium content (10 % instead of 4 %). A further increase in the corrosion behaviour should be expected for steel No. 3, which contains more molybdenum at the same chromium content than steel No. 2. Because of a significantly higher amount of Mo- and Cr-rich carbides this steel has a lower pitting potential with a steeper increase of corrosion current density during polarization tests than steel No. 2.

Cobalt, which is not taken into account in eq. 1 and should therefore not influence the corrosion behaviour, clearly decreases the corrosion resistance of such alloys. Cobalt has a low solubility for carbon and decreases C solubility in the steel matrix as well. Thermodynamic calculations show that increased cobalt content in the steel favours carbide precipitation and therefore reduces corrosion resistance.

Corrosion resistance in chloride containing aqueous solutions is mainly dependent on passivation and therefore determined by chromium and molybdenum content in the martensitic matrix. Carbides containing these elements lead to a decrease of the concentration of chromium and/or molybdenum in the matrix and thus to a lower corrosion resistance. These findings explain also, why steel No. 2 with a chromium content of only 10% supersedes the alloy 440C with a chromium content of 17% (see Fig. 3). In addition steel No. 2 contains much more molybdenum and vanadium than steel 440C. The latter forms rather stable carbides which further reduce the already lower carbon content of the material.

Tempering at elevated temperatures also decreases the corrosion resistance significantly. Secondary hardening carbides are rich in chromium, leaving a Cr depleted matrix. Thus a corrosion resistant material should be tempered at lower temperatures. In case of high operation temperatures the selected tempering temperature must be higher to prevent further carbide precipitation and changing of steel properties during service.

The BOD tests give information about the material's behaviour under pure sliding conditions, which is relevant in aircraft turbine bearings where gliding can occur due to a high number of revolutions at low load levels. Results of the BOD wear tests have shown that the developed steel No. 2b seems very promising, not only in terms of corrosion properties. Fig. 5 shows the wear volumes after these tests (1000m at 150°C, immersed in Mobil Jet II oil) after austenitization at 1140°C and different tempering temperatures (150, 350, 560°C). Both reference materials (440 C is the reference in terms of corrosion properties and M50 is the reference in terms of mechanical and wear properties) show greater wear than steel No. 2b after the same test procedure. Previous investigations of the tribological behaviour of different steels [17] have shown that the formation of reaction layers at the surfaces of both materials in contact can play a major role in contact wear. The special oil used in aircraft engines (Mobil Jet II) contains an additive (TCP – tricresyl phosphate) that forms a reaction layer at elevated temperatures, especially on surfaces containing iron. Chromium rich surfaces (as on stainless steels) are not that susceptible to the lubricant additive, leading to more wear especially under sliding conditions. Due to that, increased wear of 440C seems understandable, while the Fe-rich surface of M50 is protected by the phosphates of the reaction layer. The developed steel No. 2b seems to take a position between M50 and 440C, on one hand enough Cr is present to form a passivated layer, on the other hand enough Fe remains at the surface to allow the formation of a reaction layer. It is thus a good compromise between corrosion resistance and mechanical properties.

Conclusion

The influence of Cr, Mo and Co on the corrosion behaviour of chromium martensitic steels was investigated by using anodic polarization curves and EFTEM. Mechanical and corrosion properties of these steels are closely related to each other. Corrosion properties are not only linked to chemical composition but to a high extent to the applied heat treatment.

Cr and Mo generally improve corrosion resistance. However, portions of these elements are precipitated as carbides and only the dissolved content in the matrix is effective.

Cobalt and carbon decrease the corrosion resistance. Cobalt favours carbide precipitation due to lower carbon solubility, while carbon removes Cr and Mo from the matrix.

A higher tempering temperature lowers the corrosion resistance. Secondary carbides are rich in Cr resulting in a decrease of the corrosion resistance.

Tribometric tests of the developed steels have shown that grade No. 2 shows wear properties comparable to M50 with superior corrosion resistance. It seems to be a good compromise between mechanical/wear properties and corrosion resistance. Steel grade No. 2 has been applied for patent (Nr. A 456-2006).

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Tables

Tab. 1: Chemical compositions of the steels investigated [wt%] and the commercial grades 440 C and M50.

Steel No.	C	Cr	Mo	V	Co	Fe
1	0.66	3.9	3.0	1.5	-	bal.
2	0.60	10.1	2.9	2.0	-	bal.
2b	0.64	9.9	2.9	1.9	-	bal.
3	0.69	9.6	4.2	1.9	-	bal.
4	0.71	10.0	2.9	1.6	14.9	bal.
440 C	0.98	17.2	0.5	-		bal.
M50	0.84	4.1	4.3	1.1		bal.

Tab. 2: Heat treatments of the steels investigated.

Steel No.	Austenitization temperature [°C]	Deep-freezing temperature [°C]	Tempering temperature and time [°C; h]
1	1140	-70	560; 3x2h
2	1140	-70	560; 3x2h
3	1130	-70	570; 3x2h
4	1150	-70	570; 3x2h

Tab. 3: Types and amounts of carbides (± 0.1 vol.%) present in the steels investigated.

Steel No.	MC [vol.%]	M7C3 [vol.%]	M6C [vol.%]
1	1.1	-	<0.1
2	0.9	0.3	-
3	2.3	0.8	1.0
4	0.3	2.5	<0.1

Figures

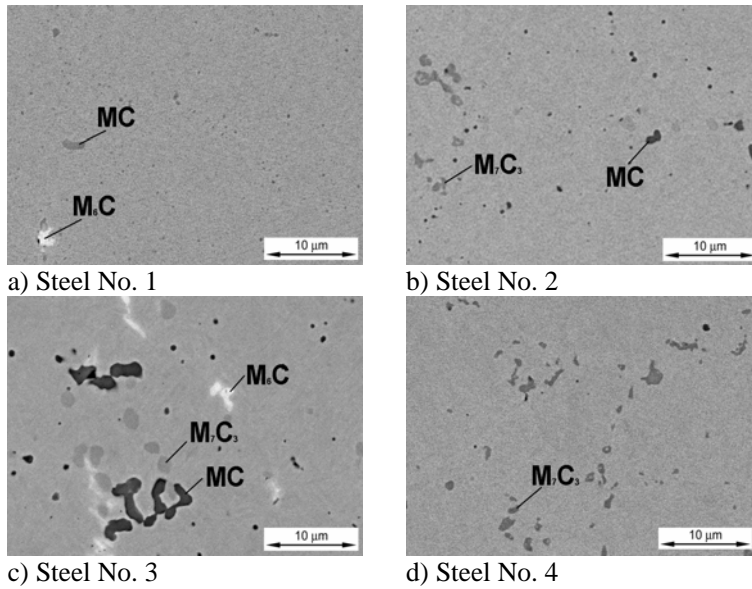


Fig. 1: Microstructure of the investigated steels No. 1-4 (SEM) indicating the differences in the content of primary carbides.

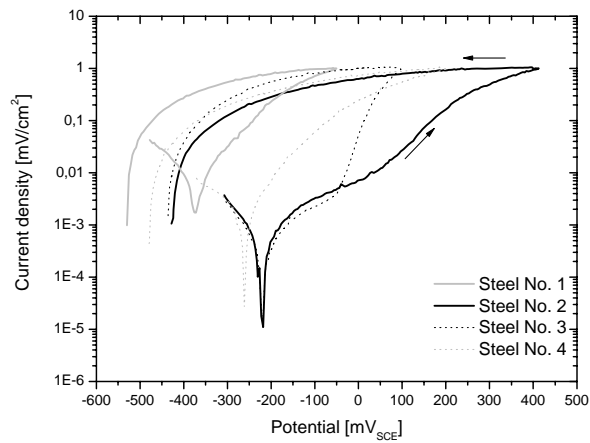


Fig. 2: Polarization curves for steels No. 1-4 in aerated deionised water containing 50 ppm Cl⁻, 50 °C, 600 mV/h.

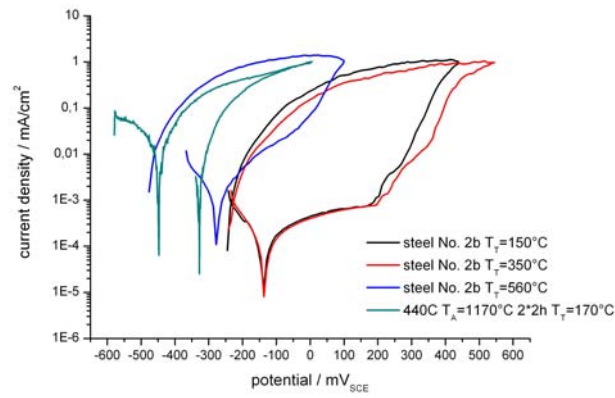


Fig. 3: Polarization curves for steels No. 2 in aerated deionised water containing 50 ppm Cl⁻, 50 °C, 600 mV/h₂ tempered at different temperatures compared to 440C (T_A=1170_°C and T_T=170_°C 2*2h)

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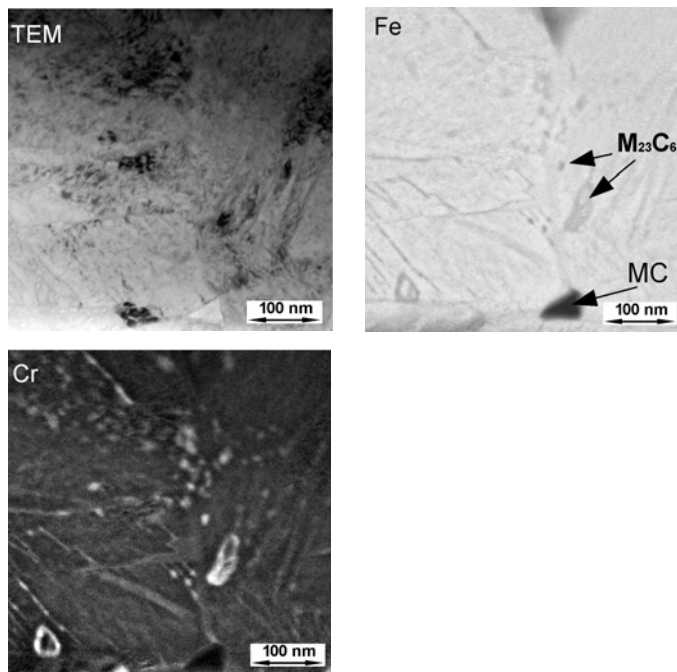


Fig. 4: TEM micrograph, together with mappings of Fe and Cr in steel No. 2 after tempering at 570_°C.

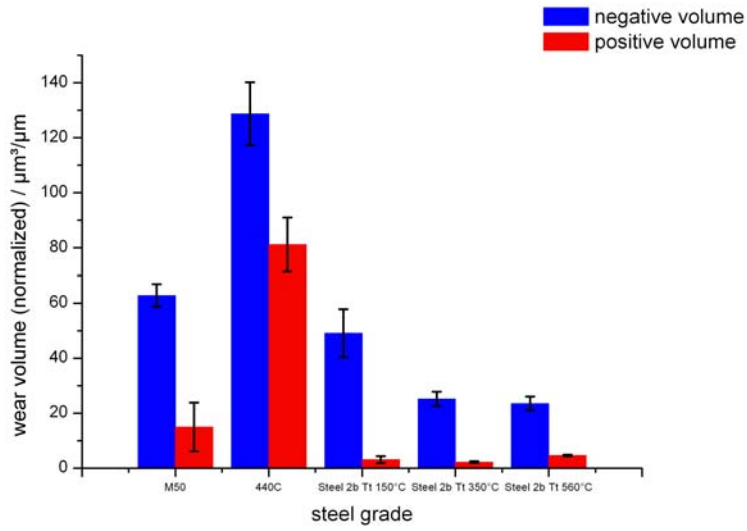


Fig. 5: Normalized wear volumes of the most promising steel No. 2b compared to steel grades M50 and 440C.