A Comparative Study on the Tribological Properties of a Cobalt-Free Superaustenitic Stainless Steel at Elevated Temperature

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Abstract: The properties of a cobalt-free cast superaustenitic stainless steel (SASS) is investigated comparatively to the commercial high-cobalt alloyed GX15CrNiCo21-20-20 (1.4957, N-155) steel regarding its global hardness and wear resistance at elevated temperature by means of in situ hot hardness tests and cyclic abrasive sliding wear tests against an Al2O3 (corundum) counter-body at 600 °C. In the aged condition, results show that the 1.4957 steel suffers a higher material loss due to brittle failure initiated by coarse eutectic Cr-rich carbides which are incorporated into a mechanically mixed layer during abrasive loading. In contrast, within the Co-free steel eutectic M6(C,N) carbonitrides are distributed more homogeneously showing less tendency to form network structures. Due to the combination of primary Nb-rich globular-blocky MX-type carbonitrides and eutectic M6(C,N) carbonitrides dispersed within an Laves phase strengthened austenitic matrix, this steel provides comparable hardness and significantly improved wear resistance at elevated temperature. Thus, it may be an adequate alternative material to commercial SASS and offers the possibility to save cobalt for future applications.

Keywords: cobalt; elevated temperature; heat-resistant steel; hot hardness; hot wear; precipitation strengthening; superaustenitic stainless steel; wear; wear resistance

1. Introduction

Superaustenitic stainless steels (SASS) are widely known as wear-resistant material for technical applications involving high stress at service temperatures exceeding 550 °C. The combination of excellent mechanical properties and good resistance to oxidation makes them suitable for many application areas such as the aircraft and chemical industries, where they can be found in tailpipes, afterburner parts or as buckets, and nozzles [1,2]. Cast SASS are compositionally related to their wrought grade but usually contain higher amounts of carbon (up to 0.6 wt.%) [1]. They are typically used for parts with bigger dimensions such as tubes, retorts, or hangers [1]. In general, SASS gain their high-temperature properties by a stable face-centered cubic (fcc) γ-matrix combined with either precipitation strengthening and/or solid-solution hardening. The most common second phases are carbides, nitrides, and carbonitrides as well as intermetallic phases which form during an isothermal aging treatment within the supersaturated matrix [1]. While precipitation of those hard phases generates an increase in hardness and strength, a sufficient amount of chromium (≥12 wt.%) and silicon (≥0.6 wt.%) must be remain within the austenite to form protective passive films such as Cr2O3 and SiO2 which inhibit excessive oxidation at high temperatures [1].
An example for a highly stress- and heat-resistant SASS is the steel X12CrCoNi21-20 (1.4971, N-155/Multimet®) that has proven to be an economical material of construction for use in heat-treatment equipment where strength at high temperatures is required [2]. From the ecological point of view, though, its use is associated with high consumption of raw elements such as cobalt and tungsten which are extremely critical from the perspective of the European Union [3,4]. It is hence the aim of material scientists to design novel SASS concepts having no, or less critical elements involved but provide adequate properties to currently applied steels. The reduction of cobalt in heat-resistant materials, however, has been part of many studies in the last decades. In 1986, Harf studied the effect of Ni as a substitutional element for Co in the Ni-based alloy Udimet 700 and proposed that the Co-free alloy may achieve comparable creep properties to the standard Udimet 700 alloy type with 17 wt.% Co [5]. Regarding cast SASS, novel alloy concepts based on the system Fe-(18)20Cr-(9)10Ni and Fe-25Cr-35Ni (HP grade) have been investigated [6–10]. One example for a low Co-alloyed SASS is UNS S31035 (EN 1.4990, X7NiCrWCuCoNb25-23-3-3-2) also known as Sanicro®25 from Sandvik (Sandviken, Sweden) which is used in super-heaters and reheaters in ultra super critical (USC) power plants [11]. Its excellent creep resistance at service temperatures up to 700 °C and its small amount of Co (1.5 wt.%) helps improve the energy and resource efficiency of coal-fired power plants by reducing CO₂ emission [11]. The same applies to the modified HR3C heat-resistant austenitic steel with a Co content below 5 wt.% that has been presented by Zhu et al. in 2018 [12]. Compared to the commercial Co-free HR3C, the modified steel exhibits higher impact toughness and creep rupture strength at temperatures beyond 650 °C [12]. As previous studies have mainly focused on the microstructural evolution and/or its impact on mechanical properties such as strength or creep resistance, the wear performance at higher temperatures has also gained more interest in the last years [13]. For instance, Krell et al. recently studied the effect of the aging temperature on the sliding wear behavior of AFA-steels (Alumina-Forming Austenitic Steel) at elevated temperature considering different amounts of aluminum (0–3 wt.%) [14]. The authors showed that with increasing Al-content, very fine NiAl precipitates form within the austenitic matrix provided a strong precipitation strengthening effect that may improve the hot wear resistance at high temperatures [14].

However, since the hot wear behavior of Al- and Co-free cast SASS has not been studied yet in detail, it is the aim of this work to investigate the abrasive wear resistance of a newly developed cast SASS comparatively to the commercial high Co-alloyed GX15CrNiCo21-20-20 (EN 1.4957, N-155) steel by systematic sliding wear tests at 600 °C accompanied by hot hardness measurements at different temperatures (RT-800 °C). In addition, the mechanical properties are linked with a comprehensive microstructural characterization to gain deeper understanding of the microstructure/wear-relation of both alloys at elevated temperature. This work thereby addresses the question, whether Co-free SASS show comparable wear performance as high cobalt-alloyed commercial SASS and cobalt may be used more efficiently for future applications.

2. Materials and Methods

2.1. Materials and Heat Treatment

Experiments were performed comparatively on the commercial cast SASS GX15CrNiCo21-20-20 (1.4957) and the novel alloy concept named 5Mo-2W. Both steels have been industrially produced by centrifugal casting to a seamless tube (Ø140/80 × 1300 mm) from which six specimens in 10 × 10 × 4 mm dimension were cut out from the center of a precut tube segment. The global chemical composition of the steels given in Table 1 was measured in the as-cast condition via optical emission spectrometry (OES) using a QSG750 spectrometer (OBLF Spektrometrie, Witten, Germany). After casting, specimens were applied to a conventional solution-annealing treatment at 1200 °C for 1 h followed by water quenching and an isothermal aging treatment at 820 °C for 4 h (air cool) according to [1]. To avoid an excessive oxidation of the specimen’s surface, both treatments were carried out under vacuum condition (p = 0.45 Pa) in a standard horizontal ROF 7/75 type vacuum tube furnace (Heraeus, Hanau, Germany).
Table 1. Chemical composition of the investigated steels 1.4957 and 5Mo-2W (in wt.%) measured via OES.

| Steel      | C   | Cr | Ni | Co  | Mo | Nb | W  | Mn | Si | P  | S  | N  | Fe |
|------------|-----|----|----|-----|----|----|----|----|----|----|----|----|----|
| 1.4957     | 0.22| 19.8| 19.1| 18.8| 2.7| 0.8| 2.4| 1.2| 1.3| 0.02| 0.01| 0.14| bal.|
| 5Mo-2W     | 0.21| 21.1| 25.0| 0.1 | 5.5| 1.8| 1.8| 1.9 | 1.3| 0.02| 0.01| 0.23| bal.|

2.2. Microstructural Characterization

Microstructural characteristics were investigated via optical microscopy (OM) and scanning electron microscopy (SEM) using a DM2700 light optical microscope (Leica, Wetzlar, Germany) and a Vega3 scanning electron microscope (TESCAN, Brno, Czech Republic). To prevent the investigation of the potentially decarburized surface zone, at least 0.5 mm of the specimen’s surface were removed by mechanically grinding. Then, the surface was polished down to a grit size of 1 µm using diamond polishing suspension and etched with V2A-etchant (200 mL distilled water, 200 mL HCl (32%), 20 mL HNO₃ (65%) and 0.6 mL Vogels Sparbeize) to visualize the steels’ microstructure. OM-micrographs were taken at a magnification of 200× and 1000× whereas high-resolution images have been recorded by SEM using a secondary (SE) and backscattering electron (BSE) detector at 10,000-fold magnification with an acceleration voltage of 20 kV, a working distance of 15 mm and a beam diameter of 150 nm. Phase analysis was performed by X-ray diffraction (XRD) using a D2 Phaser diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) on powder specimens which were produced manually by filing the bulk material in the as-cast condition. For this, the powder was firstly filled into SiO₂ glass capsules that were put under vacuum condition (p = 0.001 Pa). Secondly, the capsules were heat-treated according to the heat-treatment parameters described above. After cooling down to room temperature, the powder was extracted from the capsule and fixed on an amorphous carbon tape for XRD analysis. XRD measurements were performed under rotation of the sample holder with a speed of 10 rpm considering an angle range of 30–55 °2θ, a step size of 0.002 °2θ, and a scan time per step of 8 s. Evaluation of crystallographic structures has been done qualitatively using the software DIFFRAC.EVA from Bruker and the PDF-02-2016 database.

In addition, the chemical composition of phases within the bulk material was measured in the solution-annealed condition via energy dispersive X-ray spectroscopy (EDS) using a XFlash 5030 detector (SDD, Bruker AXS GmbH, Karlsruhe, Germany) and the described SEM settings. Determination of the elemental composition of single phases was given after applying a ZAF correction wherein interstitial alloying elements such as C and N were only considered within the EDS spectra and not for the quantification.

2.3. Hot Hardness Testing

The macrohardness of both steels has been measured by in situ hot hardness tests on one specimen using a SRV®4 high temperature tribometer (Optimol Instruments Prüftechnik GmbH, München, Germany). Therefore, the setup has been equipped with an unheated Vickers diamond indenter and a high-temperature heating module. The hardness was measured with a force of 98.97 N, which corresponds to HV10. The measurement took place in 100 K temperature intervals starting from room temperature (RT) up to 800 °C. A schematic time-temperature profile of the hot hardness tests is displayed in Figure 1.
At each temperature step, four indentations were made under an inert argon atmosphere to prevent any undesired surface oxidation effects on the hardness. After testing, the mean diameter of the indents was measured manually at RT by OM and implemented into Equation (1) [15] to obtain an averaged Vickers hardness value for each temperature step.

\[ HV = 0.1891 \cdot \frac{F_N}{d^2} \quad (1) \]

2.4. Hot Wear Testing

Wear tests at elevated temperature were carried out on the tribometer SRV@4 from Optimol Instruments with a ball-on-disc setup according to Figure 2a. The ball made of Al₂O₃ (corundum, 2100 HV0.05 [16]) with a diameter of 10 mm acted as counter-body. It was applied on the polished surface of specimen with a normal force \(F_N\) of 10 N together with an oscillating movement with an amplitude of 1.5 mm (stroke-length: 3 mm) along the surface and a frequency of 1 Hz (number of loading cycles \(N\) of 2000) without using any lubrication. The surface roughness of the ball was measured via confocal laser scanning microscopy (CLSM) using a VK-X200 microscope (Keyence, Neu-Isenburg, Germany) to a Sa value of 1.7 \(\mu\)m.

For the hot wear test, a single specimen was heated by a resistance heater under an inert Argon atmosphere to 600 °C (Figure 2a) which represents a conventional service temperature of SASS.
The heater was controlled by a thermocouple whereby a constant surface temperature could be ensured. Prior to the tests, the temperature was applied for 50 min to reach isothermal conditions on one hand and to eliminate any influence of thermal expansion of the specimen on the wear performance on the other. Examination of the wear loss has been performed on three specimens in the as-tested condition (see Figure 2b) via CLSM at a magnification of 100x with a vertical scan step size of 0.1 µm using the Keyence VK-X200 microscope. Thereby, the concave and convex wear volume of the wear tracks, meaning the wear-related material loss of the worn surface \( V_1 \) and the brought-out material volume on the surface \( V_2 \) was quantified using the evaluation software MultiFileAnalyzer in the version 1.3.0.116 from Keyence. The ultimate wear loss was finally obtained by subtracting \( V_2 \) from \( V_1 \) according to Figure 2c.

### 3. Results

#### 3.1. Microstructural Characterization

The microstructure of the steels in the aged condition is displayed in Figure 3. Both alloys show a typical dendritic cast microstructure with primary and eutectic carbides that are embedded in an austenitic \( \gamma \)-matrix. As shown in Figure 3b, three different kind of carbides exist in the 1.4957 steel such as eutectic \( M_23C_6 \), “fishbone-like” \( M_6C \) and some MX monocarbonitrides with a morphology typical for this type.

![Figure 3. Optical micrographs of the steel 1.4957 (a,b) and 5Mo-2W (c,d) in different magnifications.](image)

The 5Mo-2W steel shows a nearly identical microstructure (see Figure 3c,d) but the eutectic carbide network is less pronounced and carbides of \( M_6C \) type remain mostly dispersed in the interdendritic regions. MX carbide types also show a more blocky-like morphology and differences in their color appearance which indicates differences of the carbide stoichiometry (see Figure 3d). The chemical composition of these precipitates is shown in Figure 4. In the steel 1.4957, MX carbonitrides exhibit different amounts of Nb which implies that actually not only Nb(C,N) but NbC and Nb(C,N) co-exist (see Figure 4a) within the microstructure. In the \( M_{23}C_6 \) carbide type, though, mainly Cr, Mo, W and C are bonded while \( M_6C \) carbides are primarily made up of Mo, W and C.
In the steel 5Mo-2W, Nb and N are the predominant alloying elements in the MX precipitates whereas C is mostly bonded in the eutectic CrMo-rich carbides of M₆C type that have nucleated at primary Nb-rich MX. As it can be observed in Figure 4b, some Nb and N is also dissolved within the M₆C so that it is actually a carbonitride of M₆(C,N) type, where “M” stands for Cr, Mo, W, Si and Nb. Apart from the described hard phases, the chemical composition of both metallic matrices consists mainly of Fe, Cr and Ni while in the steel 1.4957, high proportion of Co is also dissolved within the matrix.

![Figure 4](image-url) Local distribution of alloying elements within the steel 1.4957 (a) and 5Mo-2W (b) after solution-annealing measured via EDS.

The presence of two different MX stoichiometries in the 1.4957 steel is confirmed by the XRD pattern given in Figure 5a where reflection peaks of the phase Nb₂(C,N) and hypo-stoichiometric NbC₀.₆ can be identified. Likewise, carbide types of W-rich M₆C and Fe-Cr-rich M₂₃C₆ as well as Cr-rich nitrides of Cr₂N type can be found via XRD, whereby the latter cannot be confirmed by EDS, though. Regarding the steel 5Mo-2W, XRD analysis confirms the existence of MX and M₆C in the solution-annealed condition while the presence of any nitride types is not indicated (see Figure 5b).

![Figure 5](image-url) XRD pattern of the steel 1.4957 (a) and 5Mo-2W (b) in the solution-annealed (SA) and aged condition (PH) measured via XRD.
In addition to the hard phases described so far, the recorded SEM micrographs in Figure 6 reveal the presence of small precipitates that precipitated out of the matrix during aging at 820 °C for 4 h. In the steel 1.4957, very fine globular-shaped precipitates can be observed in the center of matrix as well as near eutectic M\textsubscript{23}C\textsubscript{6} carbides, where they appear to coagulate, as displayed in Figure 6a. In contrast, fine vermicular and globular precipitates appear brighter and are homogeneously distributed in the matrix without showing such coagulation effects in the 5Mo-2W steel. However, they seem to be significantly larger than those formed in the steel 1.4957.

Figure 6. High magnification SEM-micrographs (SE) of the steel 1.4957 (a) and 5Mo-2W (b) in the aged condition.

According to the XRD pattern given in Figure 5a, precipitates that can be observed in the 1.4957 steel correspond to the intermetallic Laves-Phase of C14-type with a composition of Fe\textsubscript{2}W, W\textsubscript{2}(Fe,\text{Si}), Cr\textsubscript{2}Si and Si\textsubscript{2}Mo. Furthermore, the intermetallic χ-Phase (Fe\textsubscript{18}Cr\textsubscript{6}Mo\textsubscript{5}) may exist but cannot be confirmed due to overlapping of certain reflection peaks. The presence of the Laves-phases Cr\textsubscript{2}Si and Si\textsubscript{2}Mo together with the χ-Phase is also indicated in the XRD pattern of the steel 5Mo-2W, although there is some possibility for the σ-phase type (Fe\textsubscript{13}Cr\textsubscript{11}Ni\textsubscript{3}Mo\textsubscript{6}) to be in the microstructure as well (see Figure 5b). The same applies to Cr-rich carbides of M\textsubscript{23}C\textsubscript{6} type that is not clearly confirmed by the XRD pattern.

3.2. Hot Hardness

Figure 7 illustrates the result of the hot hardness tests. At room temperature, both steels exhibit nearly same hardness of 265 ± 5 HV10 (5Mo-2W) and 261 ± 8 HV10 (1.4957). With increasing temperature, the mean hardness of both alloys drops almost linearly until 300 °C. When reaching a temperature of 400 °C, the hardness loss decelerates leading to similar hardness values between 600 °C and 800 °C. In this temperature range, the hardness decreases from 202 ± 5 HV10 to 193 ± 9 HV10 (1.4957) and 193 ± 3 HV10 (5Mo-2W).
3.3. Sliding Wear

In Figure 8, a representative wear scar of the steel 1.4957 and 5Mo-2W is depicted in different perspectives. It is obvious that both wear tracks are elliptical in their shape but they differ substantially regarding their width and depth. As the wear track of the 5Mo-2W steel appears to be smooth and slightly grooved in the sliding direction, that of the 1.4957 steel appears fractured with deep brittle breakups in the center of the sliding scar. Accordingly, the wear loss of the 1.4957 steel is about six times higher than that of the 5Mo-2W steel, as shown in Table 2.

![Figure 7. Hot hardness of the steel 1.4957 and 5Mo-2W in the aged condition.](image)

**Figure 7.** Hot hardness of the steel 1.4957 and 5Mo-2W in the aged condition.

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**Figure 8.** Wear track of the steel 1.4957 (a–c) and 5Mo-2W (d–f) in the top view (a,b; CLSM) and in the longitudinal section view (b,e; SEM-SE) according to Figure 2b,c including close-up views of certain subsurface areas (c,f); The arrows mark the sliding direction (SD).
Table 2. Volume loss ($\Delta V$) of the wear tracks shown in Figure 8 measured by CLSM (in $10^{-3}$ mm$^3$).

| Steel     | $V_1$        | $V_2$        | $\Delta V_{(V_1-V_2)}$ |
|-----------|--------------|--------------|------------------------|
| 1.4957    | 194.6 ± 31.9 | 15.2 ± 1.5   | 179.4                  |
| 5Mo-2W    | 40.4 ± 9.4   | 11.1 ± 0.8   | 29.3                   |

Moreover, microstructural differences in the subzone below the worn surface are revealed by close-up views of the longitudinal section. As seen in Figure 8c, the eutectic network of $M_{23}C_6$ carbides in the steel 1.4957 has been broken due to the tribo-mechanical loading. It can be observed that due to the cyclic motion of the counter-body, eutectic carbides are getting incorporated into the severely deformed matrix. The carbides thereby follow the plastic flow of the deformed matrix which lead to a so-called mechanically mixed layer (MML) as proposed by Rigney [17]. In contrast, no MML but a partially damaged but more homogenous severely deformed layer (SDL) of the matrix has formed in the subsurface region near the worn surface of the 5Mo-2W steel as can be seen in Figure 8d in which cracks propagate along the sliding direction. Interestingly, these cracks seem to rapidly stop when reaching the interface of the SDL and the unaffected matrix underneath, indicating a strong in between bonding within this region.

4. Discussion

4.1. Microstructural Evolution

From the microstructural investigation presented in Section 3.1, several differences regarding the microstructural evolution of the steels could be noticed that shall be discussed in detail in this section.

At first glance, it became apparent that in the steel 1.4957 eutectic Cr-rich carbides of $M_{23}C_6$ and $M_6C$ type show greater tendency towards network formation, whereas in the steel 5Mo-2W eutectic $M_6C$ are mainly located in the interdendritic region and seem to be homogenously distributed in the microstructure (see Figure 3). Furthermore, the observed typical morphology of Nb-rich MX precipitates in the steel 1.4957 indicates that these predominantly form at the end of solidification while the globular-blocky shape of MX in the steel 5Mo-2W is typically related to a primary formation in the liquid [18]. The appearance of hard phases is mainly dependent on the differences in the amount of Nb and N of both steels. As shown in Table 1, the global Nb and N content of the 5Mo-2W steel is about 1 wt.% Nb and 0.1 N wt.% higher compared to that of 1.4957. Therefore, carbon and nitrogen will be consumed by the formation of Nb(C,N) more effectively in the steel 5Mo-2W whereby less carbon is available in the liquid to form eutectic Cr-rich carbides. The fact that MX tend to be rich in Nb and N in the steel 5Mo-2W is due to the high affinity of N to Nb. As Nb reduces the activity coefficient of N by about a factor of 2.5 more than that of C [19], it becomes clear that in the presence of both nitrogen and carbon, N-rich Nb(C,N) are more likely to form than NbC. That MX carbonitrides may have a deficit in the metalloid fraction in both steels agrees with findings of previous studies where stoichiometries of Nb$_2$C, Nb$_4$C$_3$ and Nb$_6$C$_3$ are reported for NbC in SASS [20–23]. Hence, the results of this work support the claim that a metal/metalloid ratio of 1:1 is not necessarily needed in order to form NbC and Nb(C,N), respectively. However, for a reliable quantification of the MX stoichiometry, further investigation is necessary using enhanced characterization techniques such as wavelength dispersive X-ray spectrometry (WDS) which have not been in the scope of this study.

Based on the qualitative distribution of N according to Figure 4b it is clear, though, that N is not only dissolved within MX carbonitrides but also in $M_6C$ carbides so that it can be actually written as carbonitride type $M_6C(N)$. This can be traced back to the solubility for N in $M_6C$ that is proposed in [24]. This was also found to be the reason why in CrMnCN steels, $M_6C$ progressively substitutes $M_{23}C_6$ as the amount of nitrogen increases [24]. Nb acts in a similar way to N in terms of favoring the formation of $M_6C$ since it exhibits some solubility in $M_6C$ and is further able to form $M_4C$ in the composition Fe$_3$Nb$_3$C [20]. Thus, higher amount of Nb and N does not only lead to higher fraction of
MX-type carbonitrides and less eutectic Cr-rich carbides. It also shifts the desired carbide composition from $M_{23}C_6$ towards $M_6(C,N)$.

Regarding the effect of the aging treatment on the formation of precipitates within the austenitic matrix, SEM-micrographs in Figure 6 revealed that in the 1.4957 steel, very fine-globular shaped precipitates predominantly nucleate near eutectic $M_{23}C_6$ carbides in the interdendritic region and less in the center of the dendrite while in the 5Mo-2W steel, very fine precipitates with a vermicular morphology appear to be bigger in their size and are more randomly distributed within the matrix.

The fact that precipitates in the 1.4957 preferably form near eutectic CrMo-containing carbides can be explained by the presence of solidification-related microsegregations of Cr and Mo in the interdendritic regions. As the melt enriches with these alloying elements during solidification, CrMo-rich phases such as the intermetallic Laves phases $Cr_2Si$ and $Si_2Mo$ or the $\chi$-Phase $(Fe_{18}Cr_6Mo_5)$ tend to form in these areas. Nevertheless, some precipitates do form in the dendrite core as seen in Figure 6a. These are expected to refer to the intermetallic Laves-phase of $Fe_2W$ or $W_2(Fe, Si)$ type, the presence of which in the 1.4957 steel is described in [25,26]. As tungsten, contrary to chromium and molybdenum, enriches in the solid and not in the liquid during solidification (partition coefficient $k > 1$ [27]), precipitation of W-containing phases is likely to occur in the center of the dendrite. Due to the low diffusivity of W, these precipitates grow slowly and show less tendency to coarsen according to Ostwald ripening [27] being the reason for their very smaller size compared to those in the steel 5Mo-2W. However, the impact of Co on precipitation kinetics must also be considered. From high speed steels (HSS) it is known that Co does not only raise the martensite-start-temperature, it may also suppress the precipitation of carbides such as $M_6C$ and $W_2C$ whereby it shifts the secondary hardness maximum towards higher tempering temperatures [21]. For heat-resistant steels, it is reported that Co increases the stability of the supersaturated solid solution and delays the beginning of decomposition of the solid solution and precipitation of $\sigma$-phase or carbides such as $M_{23}C_6$ type [22]. It is also believed that Co reduces the diffusion mobility of alloying elements such as carbon and tungsten since it shifts the Curie temperature to higher temperatures [22]. Against this background, it becomes clear why precipitates in the steel 1.4957 seems to be smaller in their size and fraction compared to those formed in the steel 5Mo-2W. This difference can be traced back to the effect of Co which stabilizes the solid solution and therefore counteracts precipitation processes during aging. Conversely, the absence of Co in the matrix must lead to bigger precipitates of intermetallic phases in the steel 5Mo-2W as it can be seen in Figure 6b. That these correspond to Laves phases instead of the $\sigma$-phase is indicated by the precipitates’ lamellar respectively vermicular morphology as the $\sigma$-phase typically shows a sharp needle-like shape or Widmannstätten type morphology [28]. Hence, it seems reasonable to assume that these precipitates predominantly belong to the Laves phase ($Cr_2Si$, $Si_2Mo$) and/or the $\chi$-Phase.

4.2. Effect of the Microstructural Properties on the Hot Hardness

As described in Section 3.2, both steels achieve similar hardness values in the temperature range between room temperature and 800 °C although Co is not involved in the alloy concept of the steel 5Mo-2W. This can be explained by the atomic radii of the alloying elements in the $\gamma$-matrix. Besides iron as base metal, the matrix consists primarily of Ni, Cr and Co but the latter is only present in the steel 1.4957 (see Figure 4). Since the atomic radii of these elements are not very different from that of iron [29], solid solution strengthening caused by the parelastic effect within the fcc lattice are quite small. It can therefore be assumed that the hot hardness is rather influenced by the fraction of carbides and intermetallic phases and less by the matrix composition. In this case, the hardness of the steel 1.4957 is supposed to be higher compared to that of the steel 5Mo-2W due to the pronounced eutectic network of hard Cr-rich carbides that should increase the global hardness. The fact that the steel 5Mo-2W shows a comparable hardness at room and elevated temperature despite the absence of such a carbide network can be traced back to higher particle strengthening effects resulting from the higher amount of Laves phase precipitates. As proposed by Takeyama et al., the Laves phase of $Fe_2Nb$ type for example is known to improve the strength of SASS [30] and should therefore have a positive
impact on the global hardness at elevated temperature. In other words, the Laves-phase-strengthening effect of the matrix may compensate a lower hardness resulting from smaller amounts of hard Cr-rich carbides so that in this case specifically both, the 1.4957 and the 5Mo-2W steel, provide a comparable hot hardness at elevated temperature.

4.3. Correlation between the Hot Hardness and the Hot Wear Behavior

Considering the wear behavior of both steels as described in the Section 3.3, a direct correlation between the macroscopic hardness and resistance against abrasive wear at elevated temperature cannot be stated. Instead, the wear properties of the steels differ substantially. As displayed in Table 2, the volume loss of the steel 1.4957 due to the tribological loading is about six times higher than that of the steel 5Mo-2W. A possible explanation for the worse wear performance of the steel 1.4957 is the presence of the pronounced eutectic carbide network. As eutectic carbides are predominantly located along grain boundaries, they deteriorate the cohesion energy between the grains and, thus, tend to brittle fracture under impact loading or to initiate intergranular cracking when the matrix generates a shear band during mechanical loading. At high temperature, this effect increases as the thermal softening of the metal matrix increases. As proposed by previous authors [31,32] it is known that when the matrix softens it may not be able to provide sufficient support for hard phases, whereby they will be torn off the surface during the abrasive cyclic loading rendering additional abrasion and adhesion in the unprotected matrix, which ultimately raises the wear rate [31,32]. In this case, hard phases may promote further surface damaging by initiating submechanisms of abrasion such as micro-cutting or micro-ploughing which were described by Zum Gahr [33].

Apart from this, it becomes clear that carbide debris will be also incorporated into the severely deformed matrix and form a MML as seen in Figure 8c. Since the carbides in the MML are significantly smaller than those in the unaffected base material (compare Figure 8b,c), it seems reasonable that eutectic carbides fractured during wear due to fatigue, indicating that they do not provide any strengthening effect at high temperature but rather weaken the wear resistance of the 1.4957 as the MML formation apparently promotes brittle failure and strong cratering. This, however, stands in contrast to the general believe that MMLs enhance the wear resistance. As proposed by Varga et al., the formation of tribolayers with the abrasive on the worn surface of austenitic steel can overcome the degradation of the matrix at high temperatures and therefore should have a more protective character [32]. The authors found that work hardening effects that occur due to cyclic impact loading combined with massive tribolayer formation at elevated temperature provide superior wear resistance [32]. A hypothetical explanation for the opposite effect of the MML on the wear behavior of the 1.4957 might be the very limited flow ability of the MML. Since broken fragments of hard phases elevate the hardness of the severely deformed matrix locally, the MML counteracts the thermal softening of the matrix at 600 °C. The MML thereby maintains a comparably higher hardness compared to the base material during cyclic loading. As an increasing hardness goes along with a loss of ductility and plasticity, the ability for stress compensation by the plastic flow of the MML decreases. Consequently, the critical level of internal stress that leads to microcracking will be reached earlier than in the less carbide containing 5Mo-2W steel. The latter, conversely, forms the adherent SDL which has the chemical composition of the base material and does not show any incorporated carbide fragments which allows it to be assumed that it is mostly built from worn and recompacted matrix material. That in turn implies that neither the present MX and M₆(C,N) carbonitrides nor the Laves phase strengthened matrix favors strong cratering. Additionally, as the volume loss of the steel is much lower despite the brittle failure of severely strengthened surface layer, the unaffected matrix underneath those layers must still have a strong connection to the SDL that works against their detachment under cyclic abrasive loading. Further positive aspects are the globular-blocky morphology and the disperse distribution of MX in the matrix that both benefit the wear resistance as they inhibit rapid crack propagation in the severely deformed matrix. As displayed in Figure 9, MX-type carbonitrides forces cracks to propagate around them and along the severely strengthened subsurface which is accompanied with a much higher energy...
consumption than moving along weakened grain boundaries that are decorated with eutectic carbides. Due to this crack behavior, the stress level lowers in front of the crack tip during propagation so that the crack tends to stop at a certain point in the microstructure before larger fragments are released from the surface (see Figure 9). Thus, the properties of the matrix as well as those of the hard phases benefit the resistance against catastrophic cratering that ultimately results in a much lower wear-related loss of material.

Figure 9. Effect of MX-type precipitates on the crack propagation in the steel 5Mo-2W; the arrow marks the crack stop in the subsurface region.

However, wear at high temperature is a very complex process and cannot be traced back to single factors such as material constituents, since the wear loss is the result of the whole tribological system including environmental effects. Besides the detrimental impact of eutectic hard phases on the wear resistance, further reactions between the environment and the base material during the test must also be considered. As proposed by Fischer [31], effects such as tribooxidation between the abrasive particles and the surface of body and counter-body may contribute to the formation of MML. In contrast, Krell et al. who performed wear tests on the same experimental setup as in this work claim that the occurrence of tribochemical reactions can be ruled out as the tests are conducted under an inert environment atmosphere and the used counter-body (Al₂O₃) is chemically non-reactive [14]. The authors further showed that a metallic layer may deposit on the surface of the Al₂O₃-ball during testing which inhibits the material transfer from the counter-body to the base material. This correlates with the findings of this work as incorporated abrasive particles from the counter-body could not be observed via SEM, meaning that if abrasive particles will torn o the counter-body, their size and amount is expected to be negligible small. Taken this into account, the MML formed on the surface of the 1.4957 steel consists of only fragments of eutectic hard phases and tiny Laves phase precipitates that are still embedded within the plastically deformed matrix. That surprisingly the MML as the weak point within the tribosystem is still visible and has not been fully worn during the test indicates that the formation of MML is somehow a continuous process that is driven by the cyclic loading. Once a certain amount of MML is removed and the counter-body exerts sufficient tension on the subsurface, MML formation resumes until the shear stresses overcome the flow ability and the wear continuous.

That the formation of this kind of MML results in a higher loss of material also agrees with the results of Krell et al. [14] who found that MML forming AFA-steels undergo a higher wear loss than those where no MML could be observed. The authors concluded that MMLs are only beneficial for the wear resistance if abrasive particles take part in their formation which is mostly the case when unconstrained abrasives are conducted. Furthermore, the experimental setup used in this study must be considered as it provides much higher local mechanical stresses and strains compared to other studies where small and loose abrasives has been applied [14]. That MML forming materials may perform worse than complex hardfacings which do not form MMLs has also been shown by
Winkelmann et al. who investigated the wear behavior via a plunger that creates high stress by applying a repetitive impact motion on an abrasive particle flow [34,35]. However, it still must be noted that beside the formation of MML, the thickness of the subsurface strain gradient as well as the hard phase appearance are crucial factors for the overall wear loss and must therefore be considered to find a reliable explanation of wear mechanisms at high temperature.

Another factor that contributes to the wear resistance of austenitic steels are strain hardening effects. It is known that an improved strain hardening will be achieved when cross-slip of dislocations in the fcc lattice becomes more difficult. If dislocations pile up at internal obstacles such as grain boundaries, they increase the internal stress level of the material and strengthen the material locally. It is well established that deformation mechanisms of the matrix are related to its stacking fault energy (SFE) that is influenced by the chemical composition of the matrix. While Ni has a positive effect on the SFE, Cr is believed to decrease it when the Ni content is about 14 to 16 wt.% [36,37]. Lu et al. proposed that Co always reduces the SFE of fcc materials since it stabilizes the hcp lattice and therefore always promotes the formation of stacking faults [38]. Since lower SFEs are responsible to greater strain hardening, it seems reasonable to assume that the matrix of the 1.4957 possesses a lower SFE than that of the 5Mo-2W steel at 600 °C due to its high proportion of Co. It is therefore hypothesized that due to the SFE-lowering effect of Co, crystal defects such as stacking faults or dislocations will induced more easily in the 1.4957 so that the steel exhibits a higher work hardening potential at the beginning of the test (prior to the MML formation) that in turn favors the formation of hard MML. However, further studies on the matrix deformation behavior at high temperature must be conducted to clarify the impact of the SFE on the global wear performance of both investigated steels.

5. Conclusions

The aim of the present work was to study the resistance against abrasive wear of a novel Co-free cast SASS compared to that of the commercial grade 1.4957 (GX15CrNiCo21-20-20) in the conventionally aged condition. Therefore, the hot hardness and wear behavior of both steels have been determined comparatively by means of systematic hot hardness measurements at different temperatures (RT-800 °C) and abrasive sliding wear tests at 600 °C. To gain a deeper understanding on the effect of microstructural characteristics on the wear behavior, these tests were accompanied by a comprehensive microstructural characterization. Based on the presented results, the following conclusions can be drawn:

- The investigated Co-free steel 5Mo-2W provides an equal hot hardness and a significantly improved sliding wear resistance at 600 °C. As a potential alternative material to commercial SASS, it offers the possibility to save cobalt for future applications.
- The good hot hardness and wear resistance of the steel can be traced back to the absence of an eutectic Cr-rich carbide network as well as the presence of fine-dispersed blocky-globular Nb-rich MX-type carbonitrides which are embedded in a primarily Laves phase strengthened γ-matrix.
- Networks of coarse eutectic carbides favor the formation of severely deformed mechanically mixed layers (MML) that worsen the resistance against sliding wear at elevated temperature.
- Cobalt influences the precipitation kinetics of intermetallic phases during aging but has no impact on the global hot hardness of SASS.

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