Development of X40CrSiMo10-2 steel series for heavy-duty in hot environment of marine diesel engines

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Keywords: Exhaust Valve, Marine Diesel Engine, Heavy-Duty, Hot Temperature Environment, Induction Melting, Sand Casting, 5-Successive Forging Steps, Scattered Cr-Mo Carbides

Abstract. Different X40CrSiMo10-2 Steel series are developed to serve as a heavy-duty exhaust valve for marine diesel engines. The alloys contain 0.35-0.50 % Carbon combined with 8.5-10.0 % Chrome, 2.0-2.5 % Silicon and 1.0-1.3 % Molybdenum. The steel series were processed in an induction melting furnace and cast as round cylinders with 105 mm mean diameter, and 360 mm height. Melt steel was bottom poured with 27 mm average diameter runner. Each Cast ingot was weighting 26.5 Kg. The thermodynamic calculations ensured formation of strong-stable Cr-Mo carbides containing $Cr_{23}C_6$ and Mo_2C at the specified working temperatures. Cr enhances oxidation resistance of the alloy, while Si besides Cr are working to secure a ferrite phase matrix at room temperature and up to Ac1(855 ºC). On the other hand, Mo beside the strengthening effect, it is fighting against coagulation of carbides within the matrix during working in the hot environment. A microstructure of the as – cast condition exhibits coarse ferrite grains due to slow rate of cooling during solidification in the sand mold. Cr and Mo- carbides are precipitated as thin layers enveloping the solidified ferrite grains, while the majority of carbides are precipitated as clusters scattered over the grains. On heating the steel to a temperature higher than Ac1, considerable portion of the ferrite matrix is transformed to austenite phase and the scattered carbides are then dissoluted. Multi-step hot forging is a complementary process, where the matrix would be finer with homogeneously distributed embedded carbides. Forging would be carried out by 5- successive controlled steps to obtain 50 mm diameter round bars.

Introduction

Carbon-steels containing Chromium -Molybdenum (Cr-Mo) are considered as the most suitable candidates for heavy duty service in hot-temperature environment. The alloy should possess high adhesive wear resistance and hot corrosion. The working environment of exhaust valves of marine diesel engines are typical to hot temperature (300 ºC) and adhesive wear action. Furthermore, the combustion gases contain considerable amount of Sulphur, as the diesel fuel composed of numerous Sulphur compounds. Consequently, the exhaust valve should posse good hot oxidation and corrosion resistance to withstand against the sulfuric acid (H2SO4) formed during combustion stroke.

The behavior of valve alloy at high temperature, and oxidation characteristics should be carefully designed [1]. Due to non-uniform cross-section of the valve, considerable temperature variations and thermal loads are maintained causing excessive stresses, which are considered as one of the reasons for premature valve damage [2, 3].

Materials Research Proceedings 44 (2024) 374-380 https://doi.org/10.21741/9781644903254-40

Considerable microstructure changes and alloy hot oxidation are maintained due to high temperature environment. Sulfidation reaction accelerates the oxidation phenomenon especially in marine internal combustion engines operating with high-sulfur diesel. Hot corrosion attack is characterized by a loosely adhering oxide scale separated from the alloy-affected region. Sodium chloride that forming sodium sulfate at marine environment with the high sulfur contain diesel. is the most aggressive of alkali

Hot corrosion is obviously met with a diesel engine exhaust environment, where an increasing demand for extensive engine output has raised the valve temperature. Diesel fuels contain varying amounts of sulfur so the combustion product can promote sulfidation. Sodium chloride have been recognized as the most potent of alkali salts to accelerate the hot corrosion, where a marine environment is playing very active roles [4].

On crude oil refining, two main desulfurization processes are recently implemented for sulfur compounds removal from the crude oil. Hydrodesulfurization (HDS) is one of the catalytic processes, which aims at turning organic sulfur compounds into H2S using H2 as the reactant in the presence of metal catalysts operating at high temperature and pressure. Furthermore, a recent process is bio desulfurization (BDS), which is a new bio-catalytic desulfurization method, where sulfides in crude oil can be turned into elemental sulfur that can be removed by 3 steps. S-content after the first removal step would be 0.58%, then S is lowered to 0.11% after the second step, and lastly S reaches to 0.09% at the end of the process [5].

Investigating deformation behavior of alloy X45CrSi93, which is not containing Mo, at temperatures between 900 and 1000°C. The microstructural analysis showed a pronounced phase transformation from α-ferrite dissolution to austenite and carbide [6].

In the absence of alloying with Mo at high working temperature, the austenitic matrix is decomposed to form the lamellar structure consisting of $\gamma + Cr_{23}C_6$, where carbides were existed at the grain boundary and within the γ grains. The lamellar structure nucleates at the boundaries and grows at the expense of the parent matrix, and known as cellular decomposition. The separated lamellar structure from the matrix decreases strength, toughness, loading ability of the matrix are leading to early fatigue failure and hot corrosion [7]. The amount of the lamellar structure ($Cr_{23}C_6 + \gamma$) is recommended to be less than 15% [7].

Molybdenum additions improve resistance to pitting and crevice corrosion in chloride containing environments and sulfuric, phosphoric, and hydrochloric acids. Mo Improves toughness and wear resistance of steel, where Mo has a solid solution strengthening effect on Ferrite, in addition to its role of forming stable Mo-carbides (Mo_2). Mo effectively inhibits the accumulation of cementite at 450~600°C and promotes the precipitation of Cr and Mo carbides, and thus becoming the most effective alloy element to improve the thermal strength of steel. The development of high-performance materials for ultra-high temperature applications represents one of the biggest challenges of the last decades. molybdenum-based alloys have been considered as their high temperature strength, and creep resistance [8, 9]. Mo containing steel can be fair forged and rolled. Mo can be dissolved in ferrite, austenite and forming carbide, and is an element to reduce Austenite phase zone.

Recently, a work was dealing with simulation of different forms of carbide precipitation and mechanisms of crack propagation using advanced Finite Element approaches [10, 11]. The work proposed that carbides could be precipitated in the form of any of net, band, cluster, and random structures. Each of these structures could be either coarse or fine. Fig. 1 presents the proposed forms of carbide precipitation [10, 11].

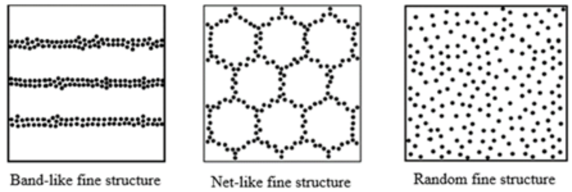


Fig. 1. Forms of carbide precipitation.

Crack propagates in the net-like carbide following the carbide network. However, if the matrix grains are too big, the crack goes through. On the other hand, in band-like carbides, cracks jump from one band to another. However, crack jumps through the random carbide structure from one carbide to another, leading to intensive crack branching [10, 11].

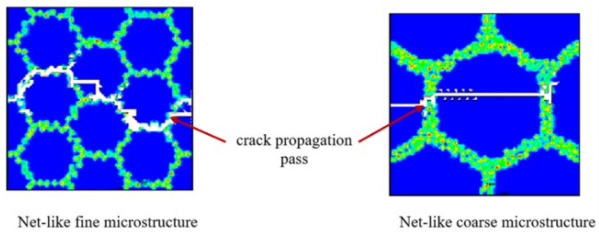


Fig. 2. Crack propagation modes at net like carbide structures [10, 11].

Fig. 3 presents values of calculated energy needed to fracture each of the different carbide precipitation mode.

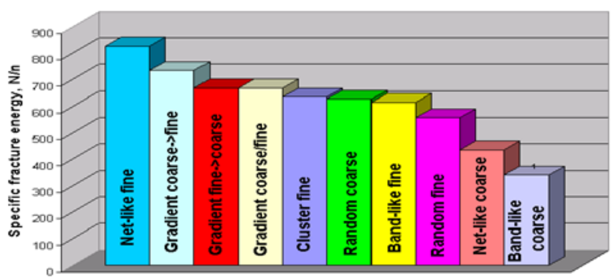


Fig. 3. Calculated energy needed to fracture different carbide structures [10, 11].

The steel alloys under investigation, undergoes microstructure phase transformations by heating. At room temperature, the steel composes of ferrite matrix scattered with different size carbides (mainly Cr and Mo carbides). On heating to higher than Ac_1, considerable portion of the ferrite matrix is transformed to austenite phase and dissolution dimensioning the volume fraction of the scattered carbides. The fraction of transformed austenite increases with the increase of heating temperature. Continuous increase of transformed austenite with few scattered carbides prevail on temperature higher than Ac_3 [6]. However, the flow stress (σf) suffers and decreases appreciably on heating from the room temperature to the Ac_1, after which σf recovers and increase as a consequence austenite phase creation and carbides dissolution.

Experimental Procedure

A steel series was cast containing 0.35-0.50 % carbon in combination with 8.5-10 % Chrome, 2-2.5% Silicon 0.99-1.28 % Molybdenum. Melting was carried out in an induction furnace. Melt steel was bottom poured and cast as round cylinder with a 105 mm mean diameter, and 360 mm height. The castings were weighting 26.5 Kg. Detailed chemical composition of processed steel is presented in Table 1.

Materials Research Proceedings 44 (2024) 374-380 https://doi.org/10.21741/9781644903254-40

Table 1. Chemical composition of procced steel alloys for Exhaust Valve.

Element, wt%	C	Si	Mn	P	S	Cr	Mo	Ni
EXH 2	0.51	2.57	0.441	0.0283	0.0115	8.45	1.28	0.226
EXH 3	0.36	2.44	0.341	0.0222	0.0104	9.15	0.986	0.202

Fig. 4 presents a schematic dimensional drawing and photo of the cast ingot in combination with the liquid steel feeding system (runner). The feeding system and raiser blocks are trimmed for further processing.

Fig. 4. presents schematic dimensional drawing and photo of the cast ingots.

Representative samples were taken and suitable prepared for microstructure investigations of the as cast structure and Brinell hardness measurements.

The cast ingots are then forged by 5-successive steps open die-controlled forging for grain size and carbide refining and homogenizing. During the 1st forging step, 105 mm diameter round cross section ingots are hot deformed to a rectangle with a cross section 118 mm x 59 mm. The 2nd step forging results in 73 mm edge square, while the 3rd step is forging to Octagon with 29 mm side length. The 4th and 5th forging steps are round bars with ϕ 61 mm and ϕ 51 mm respectively. Fig. 5 presents the mean deformation temperatures which are ranging between 1100ºC and 810ºC. Fig. 5 additionally shows the cross-sectional area reduction per each forging step.

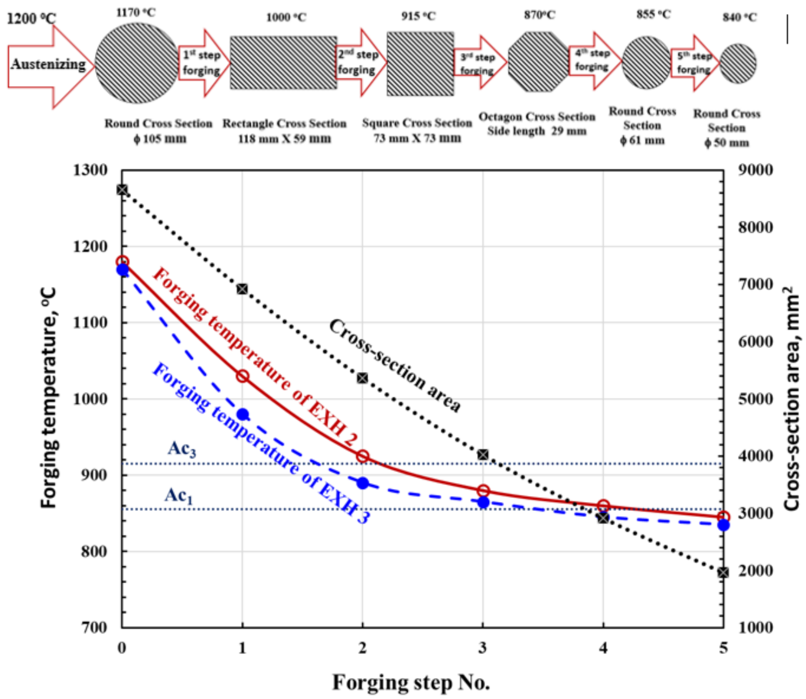


Fig. 5. Cross section reduction and forging temperature during successive 5 – steps hot deformation.

Forging stock schedule are schematically presented for successive 5-steps forging whole necessary processing data are clearly stated within the Fig. 6.

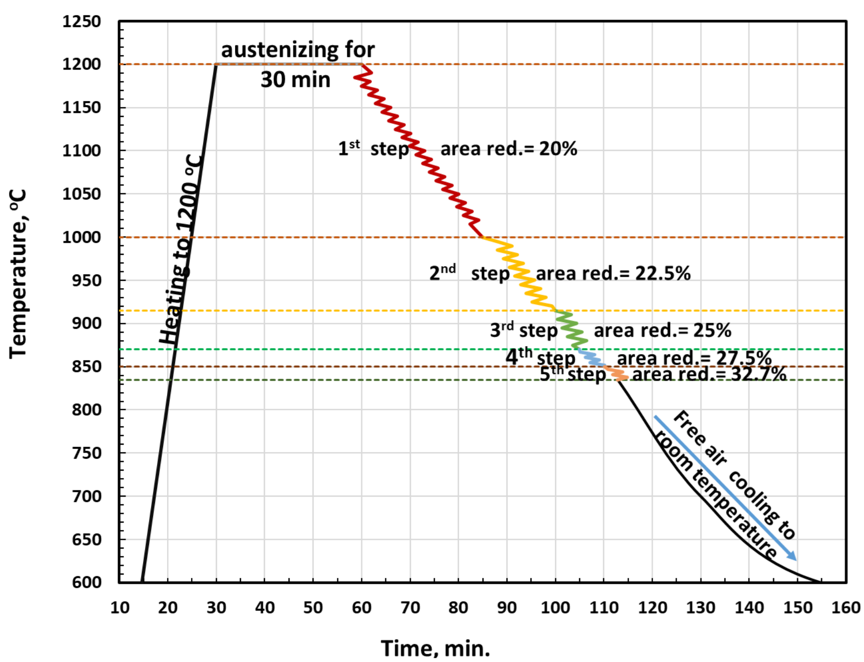


Fig. 6. Forging stock Schedule for successive 5 – steps hot deformation.

Calculated and measured results

Thermodynamic calculations of coexisting triple system Chromium (Cr) and Molybdenum (Mo) with Carbon (C) at different working temperatures ensure formation of strong (stable) carbides at temperatures up to 1100ºC [12]. Fig. 10 presents calculated Gibbs free energy (ΔGo) for Cr and

Mo carbides formations at different environment temperatures. Both $Cr_{23}C_6$ and Mo_2C are stable at the specified working temperature range. However, $Cr_{23}C_6$ possesses the most -ve ΔGo, indicating highest stability. However, importance of carbides depends mainly (in high temperature environment) on fighting against coagulations of carbides by time [6]. The phenomena are usually ruled by the Mo content in the alloy, where Mo delays and suppresses coagulations.

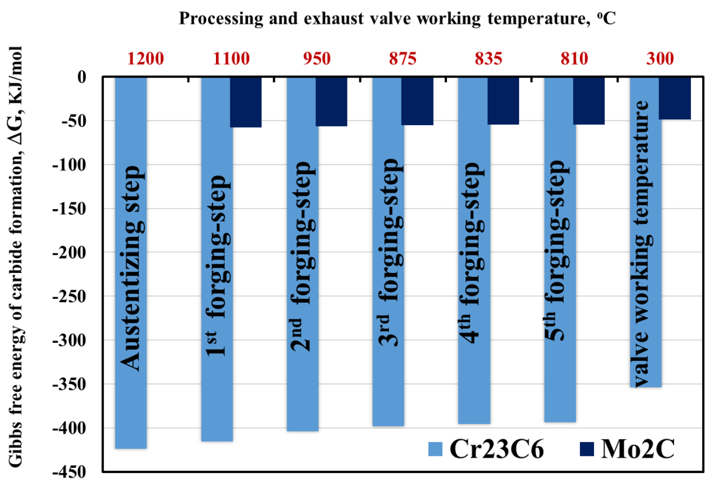
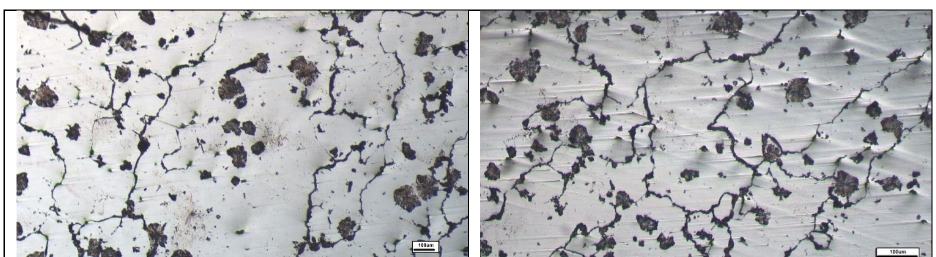


Fig. 7. Gibbs free energy of formation of the carbides $Cr_{23}C_6$, Mo_2C.

Fig. 8 contains representative microstructure of alloys EXH 2 and EXH 3 at magnifications 50X and 100X respectively. Both microstructures exhibit coarse ferrite grains due to slow rate of cooling during solidification in the sand mold. Furthermore, Chromium and Molybdenum carbides are precipitated as thin layers enveloping the solidified ferrite grains, while the majority of carbides are precipitated as clusters scattered over the grains, which are the worst case for crack initiation and propagations as presented previously in Fig. 2 [10, 11]. Further processing by multi step forging are essentially needed as previously described in Fig. 5.



EXH 2, 50 X	EXH 3, 100X

Fig. 8. Representative microstructure of alloys EXH 2 and EXH 3.

Summary

1. Cr- carbides ($Cr_{23}C_6$) possess the most -ve ΔGo, indicating highest stability
2. Mo is ruled on delays and suppresses coagulations of carbides during heating.
3. The as cast microstructures exhibit coarse ferrite grains due to slow rate of cooling during solidification in the sand mold.
4. Cr and Mo- carbides are precipitated as thin layers enveloping the solidified ferrite grains, while the majority of carbides are precipitated as clusters scattered over the grains.
5. On heating the steel to a temperature higher than Ac1, considerable portion of the ferrite matrix is transformed to austenite phase and the scattered carbides are dissolute.

Announcement
Casting and forging processes in the current work were executed at the pilot plant of CMRDI-Egypt in the fram work of finiancial support provided by the Egyptian goverment-Ministry of Higher Education and Scientific Research.

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