CHAPTER VII
COLOR METALLOGRAPHY AND CORROSION STUDIES

7.1 Introduction

The microstructure and corrosion behavior of specimen obtained from the stellite hard faced at optimum process parameters were studied and presented.

7.2 Color Metallography

Color etching by immersion has now become an indispensable process to supplement traditional black and white etching. The various elements present in stellite appear in different colors. However, this process needs experience in handling of color etchants. The process has the following advantages.

1. Normally almost invisible zones can be seen.

2. Etching process requires no additional equipment apart from the usual etching dishes and tongs and embedded specimens of any size can be etched without any difficulty because the etching process is carried out at the room temperature.

The photographs were taken under Mitutoyo microscope using an Olympus make digital camera. Wet etching was carried out for this process. The ground face was wetted before immersion in the etchant. The wetting being carried out with the dilutant used for the etchant concerned. Distilled water was used as the dilutant.
7.2.1 Specimen Preparation

The specimen was prepared with the cross sectional area of 1 cm$^2$ by coarse polishing in one direction only then in the opposite direction 10 times each. Similarly fine and still fine polishing were carried out in the same manner using 240, 320, 1/0, 600, 2/0, 3/0 and 4/0 grit polishing papers. The intermediate particles were removed by cleaning from one to another to avoid cracks. Then polishing was done using wet polishing cloth with cloth alumina powder A grade and distilled water by rotating the piece in opposite direction of disc rotation.

7.2.2 Preparation of Etchant

Suitable color etchant was prepared from stock solution, Beraha - III [77, 78]. The stock solution, Beraha III was prepared by mixing 50 gm of ammonium bifluoride, 600 ml of distilled water and 400 ml of concentrated hydrochloric acid. The etchant was prepared by mixing 100 ml of stock solution, B III and 1 gm of Potassium metabisulfide. 10 gm of Ammonium bifluoride is also mixed as optional addition. The stock solution was stored in a plastic bottle. The stock solution is only usable for about 1 to 2 hours after the addition of potassium metabisulfide. Potassium metabisulfide (Pottasium Pyrosulfpide, K$_2$S$_2$O$_5$) should be reduced if the usual amount no longer causes etching. Tongs with plastic tubing was used to hold the work piece. The etching time was 0.5 to 5 minutes.
7.2.3 Experimental Procedure

The specimen prepared was exposed to the etchant till the surface of the specimen coloured blue to brown. Immediately after that the coated surface of the test specimen was immersed in distilled water and dried. The prepared specimen was kept in the Mitutoyo make digital Microscope and the photographs were taken on the surface and near interface. A digital Olympus make camera was used for this purpose and the photographs were transferred to the computer for further analysis.

The element, which has the greatest influence on the microstructure of stellite, is Carbon. It combines with chromium to form very hard carbides which are mostly responsible for the alloys high room temperature hardness [79, 80]. Tungsten is indispensable to ensure that the alloys retain a high hardness at elevated temperatures. The element which is primarily responsible for the type of microstructure occurring in stellite 6 alloy is carbon.

The structure shown in Fig. 7.1 recalls that of hypoeutectic white cast iron $\beta$. The hypoeutectic type contains large idiomorphic primary carbide crystal of $M_7C_3$ type. The alloy which contains idiomorphic crystals of primary carbide yielded most promising wear resistance.

Figure.7.2.shows the metallographic structure of stellite 6, consisting of tungsten carbides of dendritic structure in the cobalt rich solid solution matrix. The surrounding eutectic carbides of tungsten and chromium responsible for high corrosion resistance of this alloy.
The corrosion resistance corresponding to sodium chloride (3%) corrosive environment is studied.

Figure.7.3. shows the micrograph of stellite 6, revealing primary Co dendrites and eutectic, frequently degenerated and consisting mainly of carbide particles. The best wear properties were shown by eutectic microstructures near interface.

Figure.7.4. shows the directly solidified microstructure from interface to near surface which is composed of FCC Co dendrites and the eutectic that solidifies last. Its morphology shows less eutectic near the surface. The tungsten remaining in solid solution is responsible for the high temperature properties.

A general view of the microstructure of Stellite 6 deposit is shown in Fig. 7.5., where the microstructure of the interface and near interface are presented for the etchant B III. Fine structure of the stellite deposit confirmed the dendritic structure. The microstructure of the base metal in grain growth region is visible and the grain sizes are not uniform.

The ground face wetted with the dilutant, distilled water before immersion in the etchant sodium thiosulphate. It could be seen from Fig.7.6. that the ferrite content were coloured blue-brown and present around 78% for the carbon content of 0.235%(wt) in the ASTM A105 low carbon steel. The tertiary grain boundary pearlite had remained around 22%. The photomicrograph was taken using Mitutoyo Microscope with the magnification of 100X in the base metal away from the heat affected zone. It is also clearly seen from Fig.7.7. with 400X magnification.
The grain growth region is next to the interface. The colour microstructure at grain growth region in HAZ with magnification of 100X is shown in Fig. 7.8. The grain sizes are nonuniform and unevenly distributed in this region. It is also clearly visible from the microstructure at 400X shown in Fig.7.9.

The grain sizes are uniform and evenly distributed in the grain refinement region next to the grain growth region. The uniform grain growth could be seen from Fig.7.10. with magnification of 100X. It is also visible from the microstructure shown in Fig.7.11 with 400X magnification.

FIG. 7.1. PHOTO MICROGRAPH SHOWING IDIOMORPHIC PRIMARY CARBIDE CRYSTALS IN WELD METAL ZONE OF OPTIMIZED WELDSPECIMEN AT 100X MAGNIFICATION USING ETCHANT B III
FIG. 7.2. PHOTO MICROGRAPH SHOWING IDIOMORPHIC PRIMARY CARBIDE CRYSTALS IN WELD METAL ZONE OF OPTIMIZED WELD SPECIMEN AT 100X MAGNIFICATION USING ETCHANT B III

FIG. 7.3. PHOTO MICROGRAPH SHOWING TUNGSTEN CARBIDES OF DENDRITIC STRUCTURE IN THE COBALT RICH SOLID SOLUTION MATRIX IN WELD METAL ZONE OF OPTIMIZED WELD SPECIMEN AT 400X MAGNIFICATION USING ETCHANT B III
FIG. 7.4. PHOTO MICROGRAPH SHOWING PRIMARY CO DENDRITES AND EUTECTIC IN WELD METAL ZONE OF OPTIMIZED WELD SPECIMEN AT 400X MAGNIFICATION USING ETCHANT B III

FIG. 7.5. PHOTO MICROGRAPH SHOWING THE STELLITE 6 DEPOSIT AND THE BASE METAL ASTM A105 LOW CARBON STEEL AT 100X MAGNIFICATION
FIG. 7.6. PHOTO MICROGRAPH SHOWING THE ASTM A105 LOW CARBON STEEL BASE METAL AT 100X MAGNIFICATION USING ETCHANT SODIUM THIOSULPHATE

FIG. 7.7. PHOTO MICROGRAPH SHOWING THE ASTM A105 LOW CARBON STEEL BASE METAL AT 400X MAGNIFICATION USING ETCHANT SODIUM THIOSULPHATE
FIG. 7.8. PHOTO MICROGRAPH SHOWING THE GRAIN GROWTH REGION IN HAZ AT 100X MAGNIFICATION USING ETCHANT SODIUM THIOSULPHATE

FIG. 7.9. PHOTO MICROGRAPH SHOWING THE GRAIN GROWTH REGION IN HAZ AT 400X MAGNIFICATION USING ETCHANT SODIUM THIOSULPHATE
FIG. 7.10. PHOTO MICROGRAPH SHOWING THE GRAIN 
REFINEMENT REGION IN HAZ AT 100X MAGNIFICATION 
USING ETCHANT SODIUM THIOSULPHATE

FIG. 7.11. PHOTO MICROGRAPH SHOWING THE GRAIN 
REFINEMENT REGION IN HAZ AT 400X MAGNIFICATION 
USING ETCHANT SODIUM THIOSULPHATE
7.3 Corrosion

Specifying an alloy combination with good wear and galling resistance will not be sufficient in applications, commonly found in the chemical and petroleum industries, where the process fluid is chemically aggressive. In such applications the hardfacing alloys should also exhibit adequate corrosion resistance. Cobalt based hardfacing alloys have, in general, very good corrosion resistance in a variety of environments [11, 81]. During welding, several other factors such as porosity, cracking, residual stresses, secondary phases etc., are introduced which have a strong influence on the corrosion behavior of the deposits. It is expected that the deposited layer will have the required corrosion resistance. To confirm with the same it was felt essential to carry out corrosion testing.

Pitting corrosion studies on the hardfaced layer were conducted using electro chemical corrosion test. Pitting corrosion test under sodium chloride (3%) environment using the standard ACM Gill 5500 computer interfaced instrument was used for data acquisition and plotting the Tofel graph to depict corrosion behavior.

7.3.1 Pitting Corrosion Procedure

ACM Gill 5500 Potentiostat and Galvanostat instrument with flat cell in three electrode configuration were used. A flat cell of 250 ml was used to carryout the pitting corrosion test. The flat cell consists of glass cylinder clamped horizontally between two end plates. One end plate houses the working electrode (WE) and the other the counter electrode. The reference
electrode (RE) is housed in lugging well, with a fixed Teflon luggin capillary protruding from the bottom of the well. A vito gasket on each end plate seals the plate to the cylinder preventing electrolyte from leaking.

The stellite coated at optimum condition was kept against wall by adjustable shoe assembly. The shoe makes electrical contact. The working electrode (WE) was connected with specimen. The auxiliary electrode (AE) is platinum and small in size. The reference electrode (RE) is saturated calomel electrode (CE). The initial conditions are:

1. Metal factor (Stellite 6) = 1085
2. Electrode Area = 0.5 cm²
3. Start potential = -200 mV
4. Reverse potential = 200 mV
5. Sweep rate = 60
6. Current limit = 120 mA
7. Custom sweep

In the corrosion test, Sodium chloride (3%) with saturated calomel reference electrode were used. It was found that $I_{corr}$ is less from the Tofel graph which indicates the stellite deposit has good pitting corrosion resistance. The results of the corrosion studies are presented in the graphical form. From Fig. 7.12 the rest potential is found to be -445 mV.
7.4 Conclusions

1. The chromium hypoeutectic in solid solution contains large idiomorphic primary carbide crystal of M\(_7\)C\(_3\) type has better wear resistance.

2. A dendritic structure of cobalt rich solid solution matrix with surrounding eutectic carbides of tungsten and chromium has the high corrosion resistance.

3. Tofel slope from pitting corrosion test under sodium chloride corrosive environment indicates less \(I_{\text{corr}}\), which implies that Stellite 6 deposit has high corrosion resistance.