

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

**SURFACE MODIFICATION OF STELLITE HARDFACINGS BY POST
SURFACE MELTING PROCESSES**



Ph.D. THESIS

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Metallurgical and Materials Engineering Department

Metallurgical and Materials Engineering Programme

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

**STELLİTE SERT DOLGU KAPLAMALAR SONRASI UYGULANAN YÜZEY
ERGİTME PROSESLERİ İLE YÜZEY MODİFİKASYONU**

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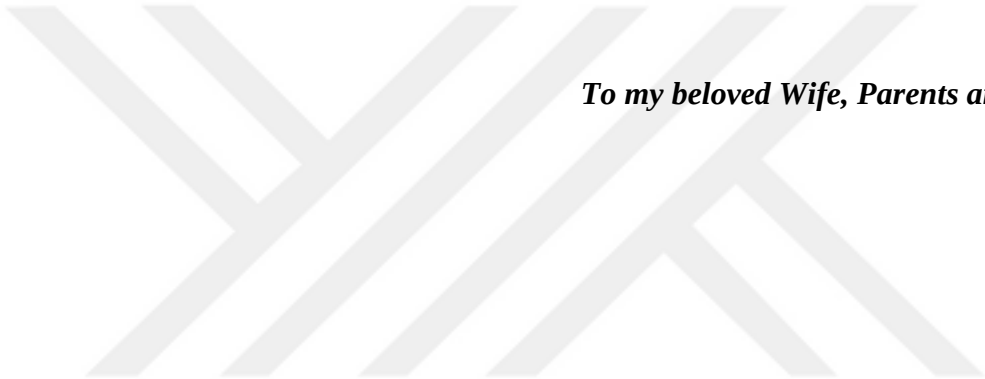
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To my beloved Wife, Parents and Teacher



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TABLE OF CONTENTS

	<u>Page</u>
FOREWORD	vii
TABLE OF CONTENTS	ix
LIST OF TABLES	xi
LIST OF FIGURES	xiii
SUMMARY	xv
ÖZET	xix
1. INTRODUCTION	1
1.1 Classification of wear	2
1.2 Surfacing technology for protection against wear	8
1.2.1 Surface treatments	8
1.2.2 Surface coating or hardfacing	9
1.3 Cobalt-based hardfacing alloys	15
1.4 Modification of Stellite hardfacings.	16
1.4.1 Modification of Stellite hardfacings by additives	17
1.4.2 Modification of Stellite hardfacings by surface melting treatments	17
2. RESEARCH OBJECTIVES	21
2.1 Effect of Electron Beam Surface Melting on the Microstructure and Wear Behavior of Stellite 12 Hardfacing	22
2.2 Effect of Electron Beam Surface Melting on the Structure and Wear Characteristics of Cobalt-Based Hardfacing and Its Mo-Alloyed Version	22
2.3 Room and High Temperature Sliding Wear Characteristics of Laser Surface Melted Stellite 6 and Mo-alloyed Stellite 6 Hardfacings	23
3. EFFECT OF ELECTRON BEAM SURFACE MELTING ON THE MICROSTRUCTURE AND WEAR BEHAVIOR OF STELLITE 12 HARDFACING	25
3.1 Introduction	25
3.2 Materials and methods	26
3.3 Results and discussion	27
3.3.1 Microstructure and hardness	27
3.3.2 Dry sliding wear performance	29
3.4 Conclusion	32
4. EFFECT OF ELECTRON BEAM SURFACE MELTING ON THE STRUCTURE AND WEAR CHARACTERISTICS OF COBALT-BASED HARDFACING AND ITS Mo-ALLOYED VERSION	33
4.1 Introduction	33
4.2 Experimental procedure	34
4.3 Results	36
4.4 Discussion	47
4.5 Conclusions	49
5. ROOM AND HIGH TEMPERATURE SLIDING	

WEAR CHARACTERISTICS OF LASER SURFACE MELTED STELLITE 6 AND Mo-ALLOYED STELLITE 6 HARDFACINGS	51
5.1 Introduction	51
5.2 Experimental Procedure	52
5.3 Results	54
5.3.1 Microstructural Examinations	54
5.3.2 RT Wear Tests.....	57
5.3.3 HT Wear Tests	59
5.4 Discussion	62
5.5 Conclusions	66
6. CONCLUSIONS	67
6.1 Conclusions	67
6.2 Recommendations	69
REFERENCES	71
CURRICULUM VITAE	89



LIST OF TABLES

	<u>Page</u>
Table 4.1: Chemical composition of the constituent phases observed in the SEM micrographs of the examined hardfacings obtained by EDX	39
Table 4.2: Quantified volume fraction and average size of constituent phases with the surface hardness of the examined hardfacings	41
Table 4.3: RWR results of the examined hardfacings.....	43
Table 5.1: Principle parameters used during PTA and the post LSM processes	53
Table 5.2: Operational parameters used for sliding wear tests.....	54
Table 5.3: Results of the EDX analysis conducted on the examined hardfacings	57
Table 5.4: Average results of the hardness tests conducted on the surfaces of the examined hardfacings.....	57



LIST OF FIGURES

	<u>Page</u>
Figure 1.1: Schematic drawing of (a) two-body and (b) three-body modes of abrasive wear	3
Figure 1.2: Schematic representation of (a) microploughing, (b) Microcutting and (c) microcracking mechanisms of abrasive wear	3
Figure 1.3: Mechanism of adhesive wear	4
Figure 1.4: Schematic illustration of the process of surface crack initiation and propagation during fatigue wear	5
Figure 1.5: Schematic drawing shows the sever and mild wear regimen could be encountered during the oxidative wear	6
Figure 1.6: Possible mechanisms of erosion wear	7
Figure 1.7: Schematic diagram of the laser/electron surface alloying process	9
Figure 1.8: Schematic drawing of (a) evaporation PVD, (b) ion-plating PVD, (c) sputtering PVD, (d) CVD and (e) ion implantation plasma based coating processes.....	11
Figure 1.9: Schematic drawing of thermal spray coating processes; (a) air flame spraying, (b) air plasma spraying, (c) detonation-gun spraying and (d) electric arc spraying	12
Figure 1.10: Schematic drawing of conventional welding processes used in hardfacing; (a) Oxyacetylene gas welding, (b) gas metal arc welding, (c) shielded metal arc welding and (d) submerged arc welding.....	13
Figure 1.11: Schematic drawing of PTA welding proces used in hardfacing	15
Figure 1.12: Schematic diagram showing interaction between the beam-based heat source and the base metal	18
Figure 3.1: XRD patterns of the examined hardfacings (a) PTA and (b) EBSM'ed Stellite 12.....	27
Figure 3.2: Surface SEM micrographs of the examined hardfacings (a) PTA and (b) EBSM'ed Stellite 12	28
Figure 3.3: High Magnification surface SEM micrograph of EBSM'ed Stellite 12 hardfacing.....	28
Figure 3.4: Cross sectional (a) optical and (b) SEM micrographs of EBSM'ed Stellite 12 hardfacing	29
Figure 3.5: 2D wear track of (a) PTA and (b) EBSM'ed Stellite 12 hardfacing under testing load of 1 N and 4 N	30
Figure 3.6: Worn surface SEM micrographs of PTA and EBSM'ed deposits worn under loads of 1 N and 4 N	31
Figure 4.1: Surface and cross-sectional optical micrographs (OM) of the examined hardfacings	37
Figure 4.2: Surface SEM micrographs with the inset of corresponding cross-sectional views of (a) PTA Stellite 6, (b) PTA Stellite 6+10 wt% Mo, (c) EBSM'ed Stellite 6 and (d) EBSM'ed Stellite 6+10 wt% Mo hardfacings	38

Figure 4.3: XRD patterns of (a) PTA Stellite 6, (b) PTA Stellite 6+10 wt% Mo, (c) EBSM'ed Stellite 6 and (d) EBSM'ed Stellite 6+10 wt% Mo hardfacings. 1: α -Co, 2: M_7C_3 , 3: $M_{23}C_6$, 4: M_6C and X: unidentified peak	40
Figure 4.4: 2D profiles formed on the surface of the examined hardfacings under testing loads of 1 N and 4 N	42
Figure 4.5: SEM micrographs of the worn surfaces of the examined hardfacings. The transverse arrows on the upper left corners show the sliding direction.....	45
Figure 4.6: The appearance of the counterface (alumina ball) worn at 1 N and 4 N testing loads against the examined hardfacings. The transverse arrows on the upper left corners show the sliding direction	46
Figure 5.1: Surface SEM micrographs of (a) PTA Stellite 6, (b) LSM'ed Stellite 6 and (c) LSM'ed Mo-alloyed Stellite 6 hardfacings.....	54
Figure 5.2: Surface SEM micrographs of (a) PTA Stellite 6, (b) LSM'ed Stellite 6 and (c) LSM'ed Mo-alloyed Stellite 6 hardfacings.....	56
Figure 5.3: Results of the RT wear tests of the examined hardfacings presenting the variation of V with respect to P. V was calculated from the average WT area (mm^2), WT length (mm) and total sliding distance (m)	58
Figure 5.4: Worn surface SEM micrographs of (a) PTA Stellite 6, (b) LSM'ed Stellite 6 and (c) LSM'ed Mo-alloyed Stellite 6 hardfacings after RT wear tests. (The transverse arrows in the upper right corners indicate the sliding direction).....	59
Figure 5.5: Surface and cross-section SEM micrographs of (a) PTA Stellite 6, (b) LSM'ed Stellite 6 and (c) LSM'ed Mo-alloyed Stellite 6 hardfacings after HT wear tests. (The bent arrows on the right corner of the surface views indicate the sliding direction).....	61
Figure 5.6: Raman and EDX spectra of the tribo-oxides formed on contact surfaces of (a) PTA Stellite 6, (b) LSM'ed Stellite 6 and (c) LSM'ed Mo-alloyed Stellite 6 hardfacings during HT wear tests	62
Figure 5.7: Effect of hardness on K values of the examined hardfacings obtained after RT and HT wear tests.....	65

SURFACE MODIFICATION OF STELLITE HARDFACINGS BY POST SURFACE MELTING PROCESSES

SUMMARY

Wear, the process of material removal from the surface by means of mechanical, thermal, or chemical action, causes a complete failure of various components in different industries. A key method of reducing the wear loss in lubrication starved applications is the use of materials with enhanced surface properties. This can be obtained by either selection of an appropriate bulk material, which is economically infeasible, or application of a suitable surfacing treatment to the surfaces subjected to wear conditions. In this respect, depositing of hardfacing material has come as a promising technical solution to obtain improved surface properties and protect different metallic substrates against wear attack with no change in the properties of the bulk material. Owing to their poor machinability, these alloys are generally employed in the form of coating by using the conventional welding processes. Stellite hardfacing is a group of cobalt-based alloys designed as protective coatings on components subjected to harsh service conditions at elevated temperatures. With specific carbon content and carbide promoters like Cr, W and Mo, Stellite hardfacings exhibit microstructures composed of high fraction of hard carbides such as Cr-rich eutectic carbides (in the form of M_7C_3 and $M_{23}C_6$) and W/Mo-containing complex carbides (in the form of M_6C) dispersed in a solid solution strengthened Co-matrix. Although they exhibited superior tribological properties at room temperature (RT), higher ambient temperatures and/or heavy loads are still serious problems affecting the lifetime of Stellite coatings. Therefore, intensive researching efforts have been devoted to overcoming these shortcomings. One well-investigated approach to improve the properties of these materials is alloying of Stellite hardfacings with carbide promoters like Mo during the depositing process which enhance the surface properties by the virtue of enriching the microstructure with excessive amounts of complex carbides. Even though modifying the chemical composition of Stellite alloys can enhance the hardness and wear resistance via mainly increasing the carbides fraction but it is not always feasible especially with higher alloying rate. Therefore, application of a post surface melting treatment by high-energy beams (i.e. electron beam and laser beam) has been envisaged as an alternative strategy for further improving the surface properties of deposited hardfacings as it can modify the microstructure of the melted zone due to associated rapid cooling characteristics.

By alloying with 10% Mo, alone or in combination with a post surface melting treatment; namely electron beam surface melting (EBSM) and laser surface melting (LSM), this dissertation work has been created, aiming to extend the understanding of the positive effects of Mo alloying and post EBSM/LSM treatments on both microstructure and dry sliding wear characteristics of Stellite hardfacings. Since the mechanical related surface properties, surface hardness and wear resistance, of the Stellite hardfacings are mainly chemical composition dependent, two commercial Stellite alloys were selected in this work, having different contents of alloying elements; Stellite 12 (30 wt.% Cr, 8.5 wt.% W and 1.45 wt.% C) and Stellite 6 (28.5

wt.% Cr, 4.6 wt.% W and 1.2 wt.% C). The plasma transferred arc (PTA) technique was selected to lay down a single layer of the coating material on AISI 4140 steel substrate. The high deposition rate along with the characteristic low heat input, excellent arc stability and the high flexibility in achieving the desired composition of the material to be deposited were the reasons for choosing the PTA depositing process. The surfaces of PTA deposited hardfacings were then exposed to a single pass of an electron/laser beam for surface melting.

The microstructural features of the unalloyed and Mo-alloyed PTA Stellite 6 hardfacings and their EBSM'ed/LSM'ed versions were examined by X-ray diffractometer (XRD) and scanning electron microscope (SEM) in secondary electron (SE) mode as well as Energy dispersive X-ray spectrometer EDX equipped SEM in back scattered electron BSE mode. For sliding wear tests, two configurations were conducted; ball-on-flat (reciprocating) and ball-on-disc. The wear loss and wear mechanism were evaluated by scanning the wear tracks (WT) with a 2D contact type profilometer and SEM, respectively.

In the first phase, a Stellite 12 hardfacing alloy deposited by PTA technique and subjected to a post treatment of EBSM. The microstructure and RT dry sliding wear resistance of EBSM'ed Stellite 12 hardfacing have been evaluated and compared with those of PTA Stellite 12 hardfacing. The microscopic examinations showed an extensive refinement in the microstructure of the EBSM'ed Stellite 12 hardfacing, resulting in about 15% increment in surface hardness as compared to PTA state. In spite of the increase in its surface hardness, EBSM'ed Stellite 12 hardfacing showed lower wear resistance (in about 50 %) as compared with PTA version. According to the SEM examinations of the worn surfaces, the deteriorated wear resistance of EBSM'ed Stellite 12 hardfacing has been associated with the extensive refinement of the carbides which made their removal from the matrix much easier during the sliding contact.

In the second phase, a post treatment of EBSM has been applied to PTA deposited Stellite 6 hardfacing and its 10 wt.% Mo-alloyed version. With reference to the PTA Stellite 6 hardfacing, the microstructural changes and RT sliding wear properties of PTA Mo-alloyed Stellite 6, EBSM'ed Stellite 6 and EBSM'ed Mo-alloyed Stellite 6 hardfacings were evaluated and compared. While Mo addition improved the hardness and wear resistance of PTA Stellite 6 hardfacing due to the formation of high fraction of carbides, its combination with the post treatment of EBSM in one approach further increased the hardness and wear resistance by encouraging hypereutectic solidification, forming a 3D network of carbides surrounding the refined Co-matrix. However, application of EBSM on Stellite 6 hardfacing resulted in a considerable decrease in wear resistance as compared to the PTA Stellite 6 hardfacing, which can be attributed to easier removal of the finer carbides from the Co-matrix.

In the final phase, a post treatment of LSM was employed on Stellite 6 and 10 wt.% Mo-alloyed Stellite 6 hardfacings deposited by PTA process. Microstructures and sliding wear performance at RT and high temperature (HT) of LSM'ed unalloyed and Mo-alloyed Stellite 6 hardfacings were evaluated and compared with those of commercial PTA Stellite 6 hardfacing. The LSM process refined the microstructures of both hardfacings, while favoring a network-like complex carbide dominated microstructure in the Mo-alloyed version. With reference to the PTA Stellite 6 hardfacing, LSM process led to an increment in surface hardness albeit a subsequent reduction of wear loss at RT, where abrasive wear mechanism was dominant. At 500 °C, oxidative wear contributed to the progress of wear by favoring CoO and Co₃O₄

type tribo-oxides on the contact surfaces of the PTA and LSM'ed hardfacings, respectively. However, Co_3O_4 type tribo-oxides exhibited poor mechanical stability, than CoO , which led to easier removal from the contact surface and aggravated the wear loss by abrasive wear mechanism. In this respect, LSM'ed hardfacings exhibited higher wear loss than PTA Stellite 6 hardfacing at 500 °C, while the opposite was witnessed in wear tests conducted at RT.

In brief, the results of microstructural examinations showed that PTA deposited Stellite 6 and Stellite 12 hardfacings consisted of three phases; Co-matrix, Cr-rich and W-rich carbides. Upon 10 wt.% Mo addition into PTA deposited Stellite 6 hardfacing, a considerable increment in the volume fraction and size of complex carbides is resulted, leading to enhanced surface hardness and wear resistance. The application of post surface treatment led to a severe microstructural refinement favouring a three-phase microstructures for unalloyed Stellite versions, like PTA deposits, while two-phase microstructure (cellular Co-matrix and complex carbides in network morphology) for the Mo-alloyed version.

Regarding the post EBSM treatment, its application solely on PTA deposited unalloyed Stellite 12 and Stellite 6 hardfacings enhanced the surface hardness while aggravated the wear loss due to the easier removal of the refined carbides from the matrix. Contrarily, minimum wear loss was obtained from Mo-alloyed EBSM'ed Stellite 6 hardfacings where the network-like complex carbides assisted in hindering the plastic deformation of the Co-matrix. This indicates that the size, volume fraction and morphology of the carbides become particularly important when wear resistance is governed by the surface hardness. The LSM process showed contradictory results for Stellite 6 hardfacings in terms of RT and HT wear resistance. With reference to the PTA Stellite 6 hardfacing, LSM process led to an increment in surface hardness albeit a subsequent reduction of wear loss at RT, where abrasive wear mechanism was dominant. At HT (500 °C), oxidative wear contributed to the progress of wear by favoring tribo-oxides on the contact surfaces of the PTA and LSM'ed hardfacings. While the tribo-oxides formed on the contact surface of LSM'ed specimens were nonprotective and their subsequent removal accelerated the wear loss of the thermally softened matrix by abrasive wear mechanism, those formed on the contact surfaces of PTA deposited hardfacing were found to be thicker and adherent; thus provided better protection against wear.



STELLİTE SERT DOLGU KAPLAMALAR SONRASI UYGULANAN YÜZEY ERGİTME PROSESLERİ İLE YÜZEY MODİFİKASYONU

ÖZET

Mekanik, termal veya kimyasal etkenler nedeniyle yüzeylerde meydana gelen malzeme kaybı olarak tanımlanabilen aşınma, birçok endüstriyel uygulamada parçaların tamamen arızalanmasına neden olur. Yağlamayla ilgili problemlerin olduğu uygulamalarda, aşınma kaybını azaltmanın en etkin yöntemi gelişmiş yüzey özelliklerine sahip malzemelerin kullanılmasıdır. Buna göre istenen aşınma direnci, ya ekonomik olmayan bir çözüm olarak parçanın tüm malzemesinin aşınmaya dirençli olan bir malzemeden seçilmesiyle ya da malzemenin sadece aşınma koşullarına maruz kalan yüzeylerine uygun bir yüzey işleminin uygulanmasıyla elde edilebilir. Bu anlamda, farklı metalik bileşenlerin yığınsal özelliklerini değiştirmeden malzemelerin yüzey özelliklerini iyileştirmek ve aşındırıcı koşullara maruz kalan yüzeyleri korumak amacıyla yüzeylerin sert dolgu kaplama malzemesi ile kaplanması umut verici bir çözüm olarak ortaya çıkmıştır. Zayıf işlenebilirlikleri nedeniyle, bu alaşımlar genellikle oksiasetilen gaz kaynağı (OAW), gaz metal ark kaynağı (GMAW), korumalı metal ark kaynağı (SMAW) ve plazma transferli ark (PTA) gibi geleneksel kaynak işlemleri ile kaplama şeklinde kullanılır. Stellite sert kaplamalar yüksek sıcaklıklardaki ağır kullanım koşullarına maruz kalan bileşenler üzerine uygulanan koruyucu kaplama olarak tasarlanmış kobalt bazlı bir alaşım grubudur. Belirli bir karbon ve Cr, W ve Mo gibi karbür yapıcı element içeren Stellite sert kaplamalar, yapılarında yüksek oranlarda bulunan M_7C_3 ve $M_{23}C_6$ formundaki Cr içeriği zengin karbürler ve katı çözelti ile sertleştirilmiş Co matris içinde disperse olmuş W / Mo içeren M_6C formundaki kompleks karbürler gibi son derece sert karbürlerden oluşan mikro yapılar sergilerler. Oda sıcaklığında (RT) üstün tribolojik özellikler sergilemelerine rağmen, daha yüksek ortam sıcaklıkları ve / veya ağır yükler Stellite kaplamaların ömrünü etkileyen ciddi problemlerdir. Bu nedenle, bu eksikliklerin üstesinden gelmek için yoğun araştırma çalışmaları yapılmıştır. Mikroyapıyı yüksek miktarda kompleks karbürlerle zenginleştirerek sertliği ve aşınma direncini artırmak amacıyla Stellite sert yüzey kaplamaların Mo gibi karbür yapıcılarla alaşımlanması bu malzemelerin özelliklerini iyileştirmek amacıyla oldukça yoğun olarak araştırılmış bir yöntemdir. Stellite alaşımlarının kimyasal bileşimi değiştirerek mikroyapıda oluşan karbür miktarını arttırmak sertliği ve aşınma direncini artırılabilir, ancak özellikle daha yüksek alaşım oranlarında bu her zaman mümkün olmamaktadır. Malzeme bileşimindeki yapılan çok fazla değişiklik Stellite sert kaplamaların katılaşma davranışını değiştirerek katılaşma sırasında kaplamada çatlamalara neden olmaktadır. Bu nedenle uygulanan kaplama işlemi sonrasında, yüksek enerjili ışınlarla (elektron ışını ve lazer ışını gibi) bir yüzey ergitme işleminin uygulanması, ergimiş bölgenin hızlı soğuma davranışı ile ilişkili olarak mikroyapısının değiştirebilmesi nedeniyle, kaplanmış sert yüzeylerin yüzey özelliklerinin daha ileri seviyede iyileştirilmesi alternatif bir strateji olarak düşünülmüştür.

Bu tez, Plazma Transferli ark (PTA) ile kaplanmış Stellite 12 ve Stellite 6 sert yüzey kaplamaların %10 Mo ile alaşımlandırılması ve PTA işlemi sonrasında Elektron Işını ile Yüzey Ergitmesi (EBSM) ve Lazer Yüzey Ergitmesi (LSM) olarak adlandırılan

ilave yüzey ergitme işlemlerinin, malzemenin aşınma davranışı üzerindeki olumlu etkilerinin araştırılmasını ve bu konudaki bilgilerin geliştirilmesini amaçlamaktadır. Stellite sert kaplama yüzeylerin sertlik ve aşınma direnci gibi mekanik özellikleri esas olarak kimyasal bileşime oldukça bağlı olduğundan bu çalışmada iki farklı alaşım içeriğine sahip ticari Stellite alaşımları seçilmiştir, bunlar; ağırlıkça 1.45% C, 30% Cr ve 8.5% W içeren Stellite 12 ve ağırlıkça 1.2% C, 28.5% Cr ve 4.6% W içeren Stellite 6 alaşımlarıdır. Çalışmada AISI 4140 çelik altlık üzerine yapılan sert dolgu kaplamanın tek bir tabaka olarak uygulanabilmesi için uygun teknik olarak plazma transfer ark (PTA) tekniği seçilmiştir. PTA kaplama yöntemi ayrıca, karakteristik yüksek kaplama oranı, düşük ısı girdisi, mükemmel ark kararlılığı ve en önemlisi sert dolgu kaplama malzemenin istenen bileşimini elde etmede yüksek esneklik sağlaması gibi birçok avantaja sahiptir. PTA tekniği ile kaplanan sert dolgu kaplamaların yüzeyleri kaplama işleminin ardından tek geçişli elektron ve lazer ışınına maruz bırakılarak işlem sonrası yüzey ergitme işlemi uygulanmıştır.

PTA ile kaplanmış alaşımsız ve Mo alaşımlı Stellite 6 sert dolgu yüzeylerin ve bunların EBSM ve LSM yüzey işlemi uygulanmış versiyonlarının mikroyapısal özellikleri, X-ışını difraktometresi (XRD), X-ışını enerji dağılım spektrometresi (EDX) donanımlı taramalı elektron mikroskopu (SEM) ile geri saçılmış elektron BSE modu ve ikincil elektron (SE) modlarında incelenmiştir. Kaymalı aşınma testlerinde iki farklı test yöntemi olan (reciprocating-ileri geri) “ball-on-flat” ve “ball-on-disc” testleri uygulanmıştır. Testler sonucunda elde edilen aşınma kaybı ve aşınma mekanizması, aşınma izlerinin (WT) iki boyutlu (2D) temaslı tip yüzey profilometresi ile taranması ve yapılan SEM çalışmaları ile değerlendirilmiştir.

İlk aşamada, PTA ile kaplanmış Stellite 12 sert kaplama yapılmış ve ardından işlem sonrası EBSM işlemine tabi tutulmuştur. EBSM uygulanan Stellite 12 sert kaplamanın mikroyapısı belirlenerek oda sıcaklığında kuru kayma aşınma direnci belirlenmiş ve başlangıç PTA Stellite 12 sert kaplamada elde edilen değerlerle karşılaştırılmıştır. Mikroskobik incelemelerle EBSM uygulanan Stellite 12 sert kaplamanın mikro yapısında büyük oranda tane küçülmesinin meydana geldiği ve PTA kaplamaya kıyasla sertlik değerinde yaklaşık %15 artışa yol açtığı belirlenmiştir. Yüzey sertliğindeki artışa rağmen EBSM uygulanan sert kaplama, kayma aşınma testinde alümina bilye aşındırıcıya karşı kuru PTA sert kaplamaya göre yaklaşık %50 daha düşük aşınma direnci göstermiştir. Testler sonra aşınmış yüzeyler üzerinde yapılan yüzey incelemesi çalışmalarında, EBSM işleminden sonra Stellite 12'nin aşınma direncinde meydana gelen azalmanın, EBSM uygulamasıyla karbürlerde meydana gelen yüksek oranda tane küçülmesine bağlı olarak kayma teması sırasında matrsten ayrılmaları daha kolay hale getirmesi ile ilişkili olduğu anlaşılmıştır.

İkinci aşamada, PTA işlemi sonrasında EBSM uygulaması PTA yöntemi ile kaplanmış Stellite 6 sert kaplamaya ve bunun ağırlıkça%10 Mo ile alaşımlı versiyonuna uygulanmıştır. PTA işlemi ile kaplanmış ve Mo-alaşımlı Stellite 6, işlem sonrası EBSM uygulanmış Stellite 6 ve işlem sonrası EBSM uygulanmış Mo-alaşımlı Stellite 6 sert yüzey kaplamalarında meydana gelen mikroyapısal değişiklikler ve oda sıcaklığında uygulanan kaymalı aşınma testi sonuçları, PTA işlemi ile kaplanmış Stellite 6 sert kaplamaya ait sonuçlarla karşılaştırılarak değerlendirilmiştir. Mo ilavesi, mikroyapıyı kompleks karbürler (M_6C) ile zenginleştirerek PTA Stellite 6 sert kaplamanın sertlik ve aşınma direnci gibi yüzeyle ilgili özelliklerini iyileştirirken, Mo ile alaşımlamanın işlem sonrası uygulanan EBSM işlemiyle birleştirilmesi, ötektik üstü katılaşmayı teşvik etmekte ve inceltmiş Co matrisi saran bir karbür ağı oluşturarak sertlikte ve aşınma direncinde daha fazla artışa neden olmaktadır. Bununla

birlikte, Stellite 6 sert kaplama üzerine uygulanan işlem sonrası EBSM ile elde edilen sert kaplama PTA uygulaması ile kaplanmış Stellite 6 sert kaplama ile karşılaştırıldığında, tane boyutu incelmış karbürlerin Co-matristen daha kolay ayrılmasına dayandırılabilir aşınma direncinde önemli bir düşüşe neden olduğu belirlenmiştir.

Yapılan çalışmaların son aşamasında, PTA işlemiyle kaplanan Stellite 6 ve ağırlıkça %10 Mo alaşımlı Stellite 6 sert dolgu yüzeyler üzerinde işlem sonrası LSM işlemi uygulanmıştır. LSM uygulanmış alaşımsız ve Mo-alaşımlı Stellite 6 sert dolgu yüzeylerin oluşan mikro yapıları ve oda sıcaklığı (RT) ve yüksek sıcaklıkta (HT) kaymalı aşınma performansı değerlendirilmiş ve PTA ile uygulanmış ticari Stellite 6 sert dolgu kaplama ile karşılaştırılmıştır. Mo alaşımlı versiyonda LSM işlemi, ağ yapısında kompleks karbür ağırlıklı bir mikro yapı oluştururken, her iki sert yüzeyin mikro yapısında da tane incelmeye yol açmıştır. PTA Stellite 6 sert kaplama ile karşılaştırıldığında sonradan uygulanan LSM işleminin yüzey sertliğinde bir artışa neden olmakla birlikte abrasif aşınmanın hakim olduğu oda sıcaklığı testlerinde aşınma kaybının azalmasına neden olmuştur. 500 °C'de yapılan testlerde, PTA ve kaplama işlemi sonrası LSM uygulanan sert kaplamaların temas yüzeylerinde oluşan sırasıyla CoO ve Co₃O₄ tipi tribo-oksidler meydana gelen oksitleyici aşınmayı destekleyerek ilerlemesine katkıda bulunmuştur. Bununla birlikte, Co₃O₄ tipi tribo-oksidler CoO 'dan daha zayıf mekanik dayanım göstererek temas yüzeyinden daha kolay ayrılmalara yol açarak abrasif aşınma mekanizması ile aşınma kaybını arttırmıştır. Buna göre PTA işlem sonrası LSM uygulanan sert dolgu kaplamalar 500 °C'de PTA Stellite 6 sert kaplamadan daha yüksek aşınma kaybı gösterirken oda sıcaklığında gerçekleştirilen aşınma testlerinde tam tersi bir durum sergilemiştir.

Özetle yapılan mikroyapısal incelemeler PTA ile uygulanan Stellite 6 ve Stellite 12 sert sert dolgu kaplama yüzeylerin Co-matris, Cr bakımından zengin ve W bakımından zengin karbürler olmak üzere üç fazdan oluştuğunu göstermiştir. PTA tekniği ile yüzeye uygulanan Stellite 6 sert kaplama malzemesinin ağırlıkça % 10 Mo ile alaşımlandırılması, kompleks karbürlerin hacim oranlarında ve boyutunda önemli bir artışa neden olarak yüzey sertliği ve aşınma direncinin artmasına yol açmaktadır. PTA işlemi sonrası uygulanan yüzey işlemi uygulaması, alaşımsız Stellite sert dolgu malzemesinde üç fazlı mikro yapılarının oluşumunu teşvik ederek mikroyapıda oldukça yüksek tane küçülmesine yol açarken, Stellite in Mo alaşımlı versiyonu için ağ morfolojisinde hücreli Co-matris ve karmaşık karbürlerden oluşan iki fazlı mikro yapıyı oluşturmaktadır. PTA işlemi sonrasında alaşımsız Stellite 12 ve Stellite 6 sert dolgu yüzeyler üzerine EBSM uygulaması, tane yapısı incelen karbürlerin matristen daha kolay ayrılması nedeniyle aşınma kaybını artırırken yüzey sertliğini artırmıştır. Bunun aksine işlem sonrası EBSM işleminin Mo-alaşımlı Stellite 6 sert yüzeylere uygulanması, oluşan ağ yapısındaki kompleks karbürlerin Co-matrisin plastik deformasyonunu engellemeye yardımcı olmasıyla minimum aşınma kaybına ulaşılmasını sağlamıştır. Bu, aşınma direncinin yüzey sertliği tarafından belirlendiği durumlar için, aslında karbürlerin boyutunun, hacim oranının ve morfolojisinin de oldukça önemli olduğunu göstermektedir. PTA sert dolgu yüzeylere uygulanan LSM işlemi, oda sıcaklığı ve yüksek sıcaklıkta aşınma dirençleri açısından Stellite 6 sert dolgu yüzeyler için değişken sonuçlar göstermiştir. PTA işlemi ile uygulanan Stellite 6 sert dolgu kaplama için LSM işlemi yüzey sertliğinde bir artışa yol açmasına rağmen, abrasif aşınma mekanizmasının etkin olduğu oda sıcaklığında aşınma kaybının azalmasına yol açmıştır. Yüksek sıcaklıkta (500 °C), oksitleyici aşınma mekanizması PTA ile uygulanmış sert dolgu ve PTA işlemi sonrasında LSM uygulanan sert

dolguların temas yüzeylerinde tribo-oksitleri destekleyerek aşınmanın ilerlemesine katkıda bulunmuştur. İşlem sonrası LSM uygulanan numunelerin temas yüzeyinde oluşan tribo-oksitlerin oluşturduğu tabakası koruyucu özelliğe sahip değildir ve bunların abrasif aşınma mekanizması ile yüzeyden ayrılmaları yüksek sıcaklık nedeniyle sertliği azalan matrisin aşınma kaybını hızlandırırken, PTA ile kaplanmış sert dolgu yüzeylerin temas yüzeylerinde oluşan oksitlerin daha kalın olduğu ve buna bağlı olarak aşınmaya karşı daha iyi koruma sağladığı bulunmuştur.



1. INTRODUCTION

The mechanical systems in which surfaces do not slide against or roll over each other are rare; therefore, the progressive loss of material from the interacting surfaces occurs consequence of the relative motion, causing increased clearances between the moving parts and loss of accuracy in the mechanical components. This is, in general, the main concept of wear which basically can be defined as the most predominant surface damage that affects the service life of the machine parts in applications like aerospace, oil production and refineries, chemical, nuclear and mining industries, etc. [1-3].

From the economical point of view, wear is an important topic because loss of small amounts of material can cause a complete failure of large and complex components. Likewise, a worn out tools or molds in any production line can directly affect the quality of the products and profitability of the manufacturing operations [4,5]. These involve not only the costs of replacement of the worn parts but also the expenses due to machine downtime and loss of production. The automotive industry is another relevant example where engines have complex moving parts subjected to wear and high temperatures (HT) working conditions from the combustion of fuels. The failure of these parts can cause a reduction in the service life and efficiency of the engines. When these costs reviewed on the basis of a single machine, the losses are small and can be negligible but if the repeating of the same loss on perhaps a million machines is taken in consideration, then the costs become very large.

However, this may not always be the case and wear is, sometimes, highly beneficial and desirable in every-day life. Grinding and polishing, for example, are manufacturing processes that employ wear to remove material in a controlled manner, giving flat and smooth surfaces [6]. Moreover, initial small amount of wear is often anticipated and even welcomed during the running-in phase of many machines for smoothening of the tribosurfaces, leading to improved conformity, reduced stress concentrations, and enhanced lubrication conditions [7-9].

1.1 Classification of wear

Wear of materials is a combination of many mechanical, chemical and thermal phenomena, hence, classification of wear is, in itself, a rather confusing issue and it must be thought of as a multi parameter and sensitive phenomenon. However, under the different types of materials in contact and operating conditions, a variety of wear types have been recognized such as abrasive, adhesive, fatigue, delamination, fretting, oxidative, corrosive, erosive along with other types [1,10,11]. In broader terms, these types can be generalized into three main categories [12-14]:

- Abrasive wear.
- Sliding wear.
- Erosive wear.

Conceptually, abrasive wear and sliding wear are not too different from each other, thus the boundary between them is not a distinct one and the term of abrasive wear is sometimes used to describe sliding wear [3]. However, abrasive wear is the loss of material whenever a solid body is loaded against and slides across hard particles, or even against protuberances attached on the counterface [3,10,15,16]. While sliding wear occurs when two metallic or nonmetallic solid surfaces slide over each other with or without the existence of lubricants [17]. As a result, abrasive grooves are imposed on the contact surfaces parallel to the sliding direction, which is the main characteristic feature of this type of wear [18,19]. Subsequent to the progress of sliding action, individual grains from the structure of one or both mating surfaces could be removed, contributing in additional abrasive agents. Accordingly, two-body or three-body abrasive wear encountered which are qualifying terms used in describing abrasion modes; the former is caused when the protuberances on the counterface or even the hard particles are being attached, while in later the abrasive particles freely roll/slide between the two sliding surfaces [20-22]. These two modes of abrasive wear are schematically shown in Figure 1.1.

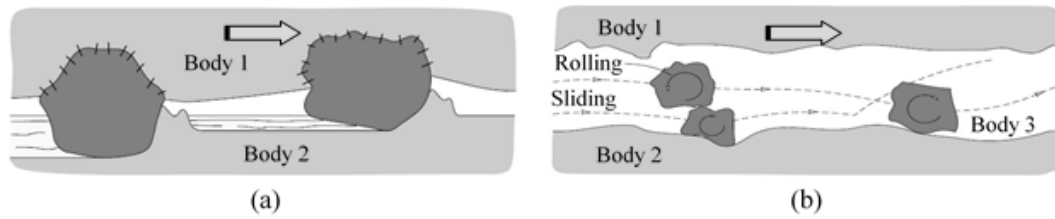


Figure 1.1 : Schematic drawings of (a) two-body and (b) three-body modes of abrasive wear (adapted from [1]).

In abrasive wear, three mechanisms have been mainly distinguished, they are: microploughing, microcutting and microcracking [1,23]. Microploughing takes place when the harder of the two rubbing surfaces ploughs into the material and displaces a fraction of it to the edges but without losing [15]. Differently, in microcutting, the material removal from the worn surface is in the form of chips [24]. Microploughing and microcutting mechanisms which are the dominant interactions in more ductile materials, are schematically represented in Figure 1.2a and b, respectively. However, microcracking occurs in the brittle materials leaving behind cracks beneath and at the surface of the worn material (Figure 1.2c).

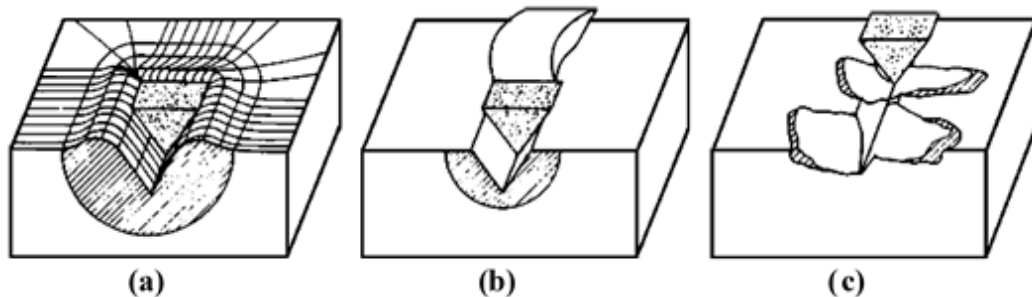


Figure 1.2 : Schematic representation of (a) microploughing, (b) Microcutting and (c) microcracking mechanisms of abrasive wear [24].

In adhesive wear, the high contact pressure between unlubricated sliding surfaces results in localized welding between the asperities. If the surfaces are now forced to move tangentially relative to each other, the joints are torn apart and separated from the mother body [26-28]. Depending on many factors like normal load, sliding velocity and relative hardness of the two surfaces in contact [11], some of the junctions may be deformed in such a way that fragments of the softer surface are plucked out, removed and transferred from the weaker metal to the stronger, providing adhesive wear debris [21,29-31]. Stable tribochemical layers (like oxides) as well as lubricants may aid the prevention of adhesive wear by separating the metal surfaces and preventing their direct contact, promoting mild adhesive wear; otherwise, severe adhesion wear would

have occurred, resulting in high wear rate [26,32,33]. This sequence of events taken place during the process of adhesive wear is schematically illustrated in Figure 1.3.

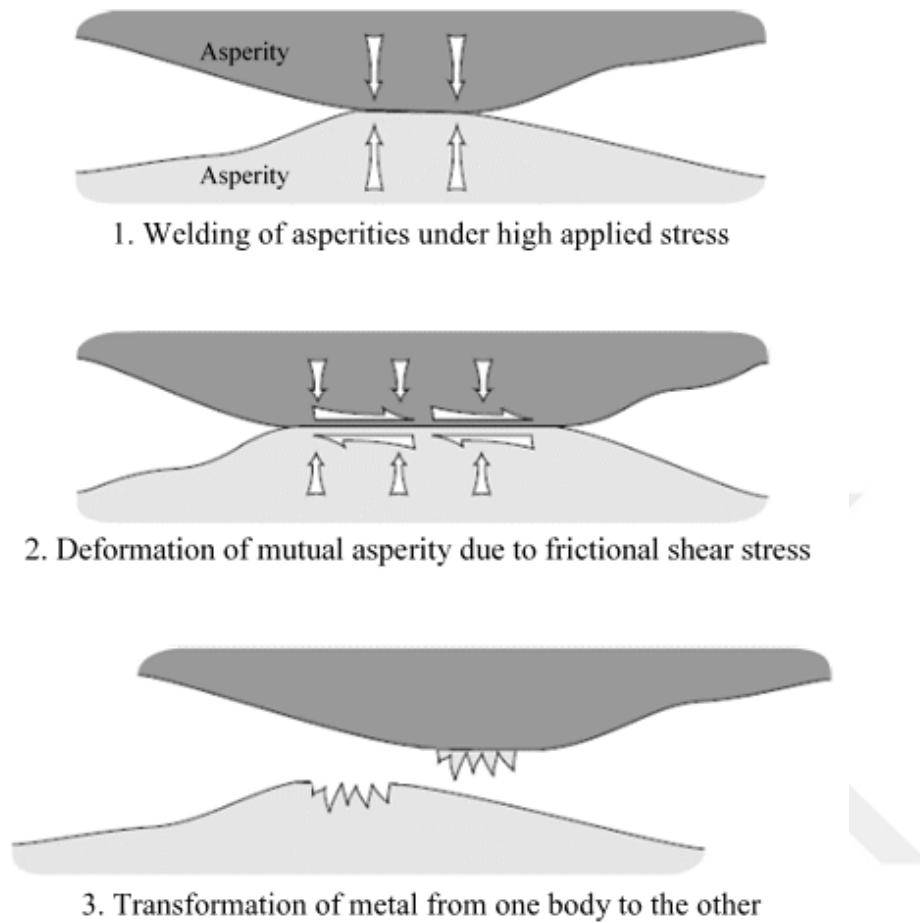


Figure 1.3 : Mechanism of adhesive wear (adapted from [1]).

When a solid surface is subjected to repetitive stresses by a harder counterbody under reciprocating sliding, rolling or fretting action, fatigue cracks are initiated and propagated parallel to the surface, metal loss is induced by delamination process [21,34-36]. This is, in general, the descriptive form of material removal in fatigue wear [37]. The primary cracks initiate at the surface and propagate downward which then can connect with an existing ones. When the crack reaches the surface again, a wear particle is detached from the surface in form of flake [38]. The mechanism of fatigue wear is schematically illustrated in Figure 1.4.

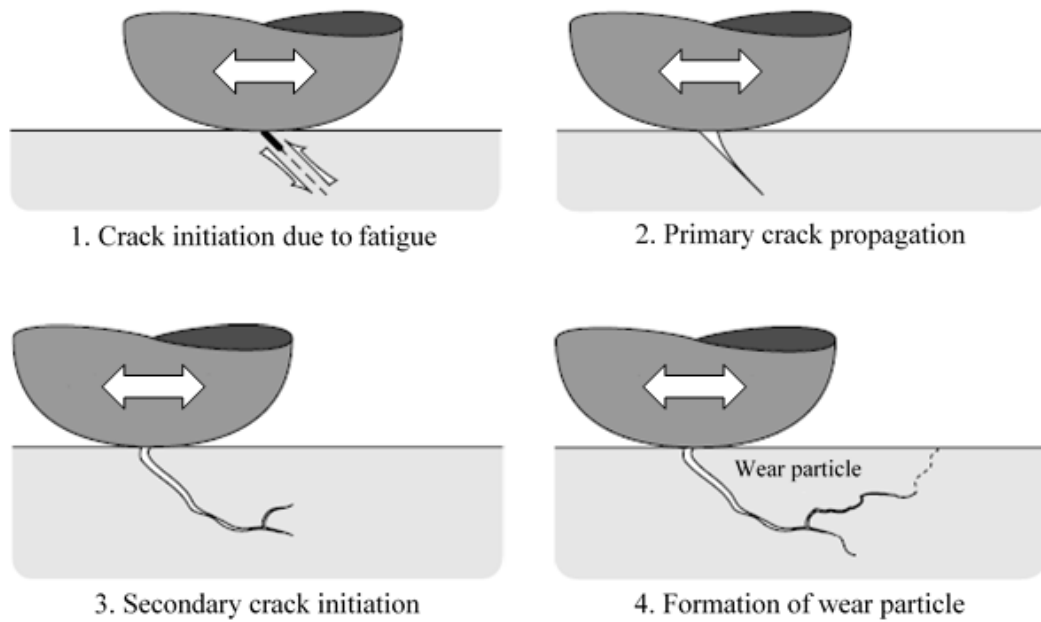


Figure 1.4 : Schematic illustration of the process of surface crack initiation and propagation during fatigue wear [1].

In fretting wear, two bodies rub against each other in oscillatory movement, particularly of small amplitudes of less than 100 μm . This first leads to the formation and growth of oxide films on the contact surfaces and hence reduces metal-to-metal contact. After reaching a steady state of fretting wear, material loss is caused by a delamination process in which thin plates of oxide-covered metal become detached from the surface by the propagation of subsurface cracks [39-42].

Oxidative and corrosive wear might be defined as covering those situations in which chemical reaction with the environment predominates over mechanical interactions. In oxidative wear, a reaction between the metallic surfaces and atmospheric oxygen takes place, leading to formation of tribo-oxides on the real areas of contact. This type of wear becomes more intense when the ambient temperature is progressively increased, or when the sliding speed and/or applied load are sufficiently high to increase the frictional temperature (flash temperature) to several hundred degrees [43-46].

The type and properties of oxides formed on the surfaces of a tribosystem, like chemical composition, structure and adherence to substrate can significantly influence the wear process and cause changes in the overall wear rates. It, in other words, means that formation of stronger and more adherent oxides reduces or completely eliminates metal-to-metal contact and thereby a protection against wear damage is provided, while if the oxide films were nonprotective in nature and broken down during the

rubbing action of the counterbody then ‘severe wear’ is inevitable [47-49]. These events are schematically shown in Figure 1.5.

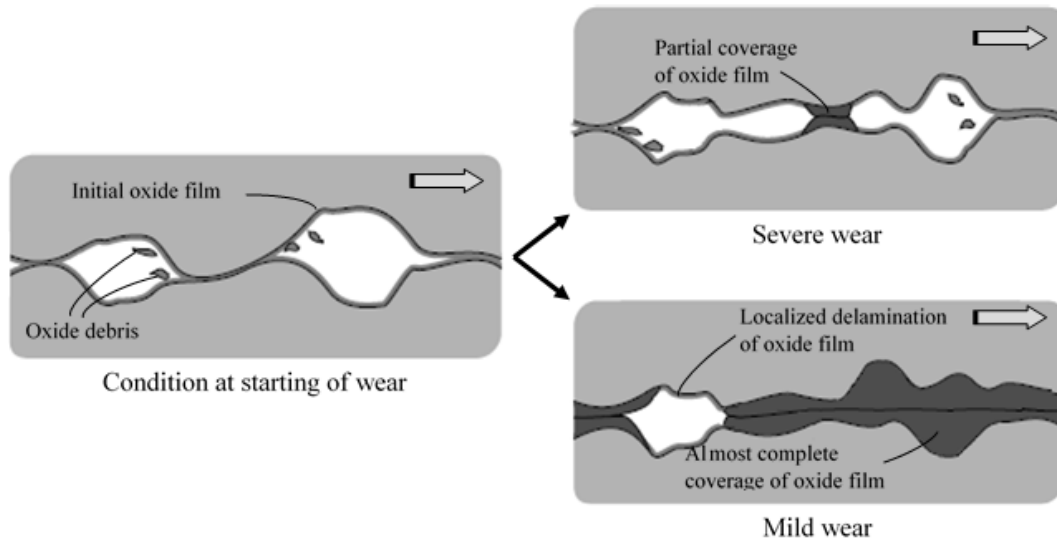


Figure 1.5 : Schematic drawings show the severe and mild wear regimen could be encountered during the oxidative wear [1].

However, corrosive wear involves an interaction between the worn surface and the corroding medium, which can be either a chemical reagent or reactive lubricant [11,50,51].

When hard particles, either carried by a gas stream or a flowing liquid, strike the surface, the material is removed by erosive wear. The hardness, velocity, size and shape of the particles influences the rate of wear [3], while the wear mechanism strongly depends on the angle of incidence of the striking particles [1,12,15,37] as illustrated in Figure 1.6.

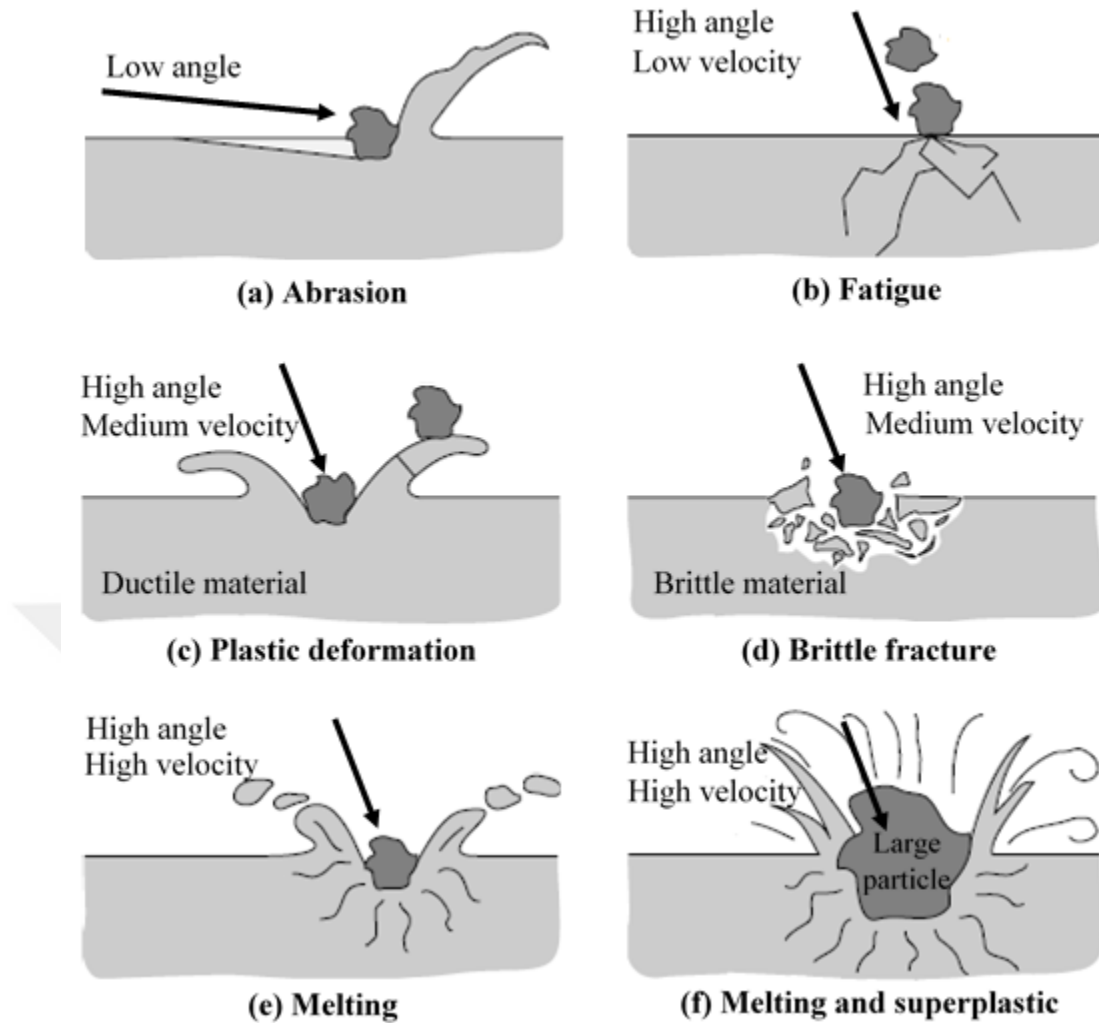


Figure 1.6 : Possible mechanisms of erosion wear [1].

1.2 Surfacing technology for protection against wear

As stated above, wear resistance in tribological components can be obtained by using appropriate bulk materials but this is expensive and economically inconvenient. Performance and economics of a product can however be developed by the application of a suitable surfacing process, whereas the substrate is chosen for its structural properties, low cost and ease of manufacture. In this respect, an increasing number of studies have been devoted to provide outstanding resistance against most types of wear attacks and thereby extend the service life of wide range of components. The term “surfacing” covers both surface treatments and surface coating [52]. While 'Surface treatment' is used for processes wherein the build up of a protective layer on the surface is not applied, 'surface coating' is termed for those in which a coating layer is deposited.

1.2.1 Surface treatments

Until few decades, conventional surface treatments have been predominantly employed to modify the tribological properties of different components and increase their resistance against wear. These treatments can be classified as thermal treatments, including induction and flame hardening, and chemical (diffusional) when the surface layer of the material is alloyed with nitrogen, carbon, or boron. Despite their low cost and profitability for processing, a number of disadvantages arising from the need for heating the substrate to a HT, the problem of oxidation, distortions, the loss of strength at elevated temperature applications [53] as well as the probability of formation of unwanted phases when the chemistry of a surface is altered [54]. To avoid these drawbacks, conventional heat sources for surface treatments have been replaced by more advanced ones like laser and electron beams. The intense albeit localized heat of these sources appears to have several advantages such as exact control of the zone to be treated as well as its depth by optimizing the process parameters, low distortion in the processed parts and avoidance of oxidation problem and other interactions as the process is carried out in evacuated or gas-shielded environments [55,56]. As far as the process parameters like voltage, current, scan speed, etc. are concerned, it is reported that a strong relationship is there between them and the type of the surface treatment. More clearly, heat treating or surface melting tend to occur under different settings of parameters [57-61]. In heat treating regimen, so called solid state quenching, the surface is rapidly heated to a temperature lower than the melting point of that material whereas the melting of a very shallow surface layer is ensured in surface melting process. In both cases, the self-quenching of the heated/melt surface layer by the cold underneath substrate results in unique microstructural developments, which in turn modify the surface properties [62-65].

Surface alloying is also possible when the surface of a workpiece is melted to a desired depth using the laser or electron beam with a simultaneous feeding of powdered alloying elements. The subsequent solidification of the molten substrate and alloying elements provides a rapid method of localized alloy synthesis [66-71]. A schematic diagram of laser/electron surface alloying is shown in Figure 1.7.

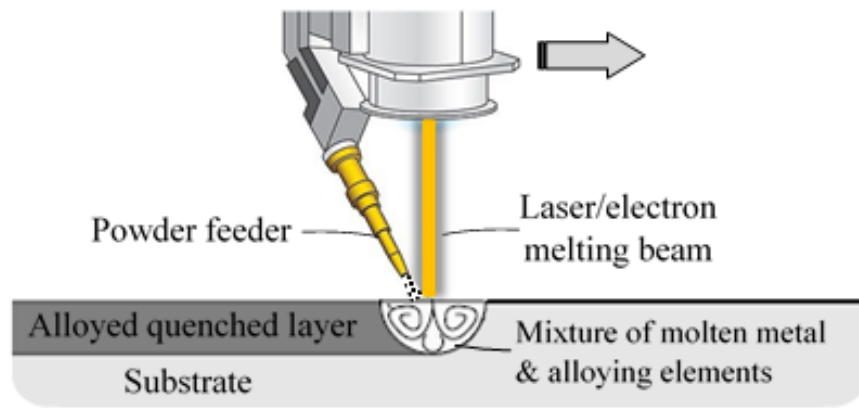


Figure 1.7 : Schematic diagram of the laser/electron surface alloying process (adapted from [1]).

1.2.2 Surface coating or hardfacing

Laying down of a protective material on a relatively softer metallic substrate is a rapidly growing surfacing technology to overcome the inherent tribological problems of components submitted to severe service conditions like wear and HTs. This technique is known as “Hardfacing”, which can be performed by a variety of materials and processes [2,50,72,73]. The materials used for hardfacing are normally chosen for their properties, i.e. hardness and wear/corrosion resistance, but this is not only the decisive factor for achieving the optimum performance. Indeed, aspects, other than the ability to withstand wear, should also be considered in choosing the hardfacing materials. The reasonable compatibility between the coating and substrate materials can be taken as examples especially in terms of thermal properties, i.e. the coefficient of thermal expansion (CTE), and chemical composition [52]. The large differences in the CTE between the deposited material and base substrate gives rise to initiate thermal crack at the coating-substrate interface during processing [74], which could finally lead to separation of the coating layer, especially at intense wear conditions [75]. The factor of chemical compatibility is, likewise, of high necessity and should be taken into account during the selection of hardfacing materials. With large difference between the composition of the surfacing material and that of substrate, a significant change is expected in the chemistry of deposited hardfacing by inter-diffusion with the substrate material particularly when the surface melting of substrate is ensured during the depositing process. This condition is referred to as dilution which contributes in lower hardness and other properties of the coatings [76,77].

Not least the selection of hardfacing process is also surface properties determinant like the material selection, both are determined by service requirements. Thus, the type of hardfacing process significantly affects the resultant surface properties of the deposited hardfacing material by affecting the microstructure [50,78]. Typically, the selection of the most suitable, economic and efficient hardfacing process for a given job depends on the type of the material to be deposited (metal or ceramic), the form of consumables (powder, wire or rod), size, shape and number of the component to be hardfaced as well as the required thickness of the deposited layer [79,80]. Among these factors, the thickness of the deposited layer is found to be the most critical selection criterion between the different deposition processes. This is due mainly to the characteristic variations between the deposition processes in producing coatings with different thicknesses. The plasma based coating methods, for example, are the most convenient and versatile technique for producing thin coating layers with thicknesses range between 0.1 and 10 μm on the surface of small and complicated components. In this technique, a vapor of the material to be deposited is condensed on the workpiece through different methods like [81,82]:

- Physical vapor deposition (PVD), including evaporation, ion-plating and sputtering.
- Chemical vapor deposition (CVD).
- Ion implantation.

As shown in schematic diagrams of Figure 1.8, these coating processes are generally carried out at low pressures gas condition by which the atmospheric oxygen is removed, giving better bonding with the substrate [11,74].

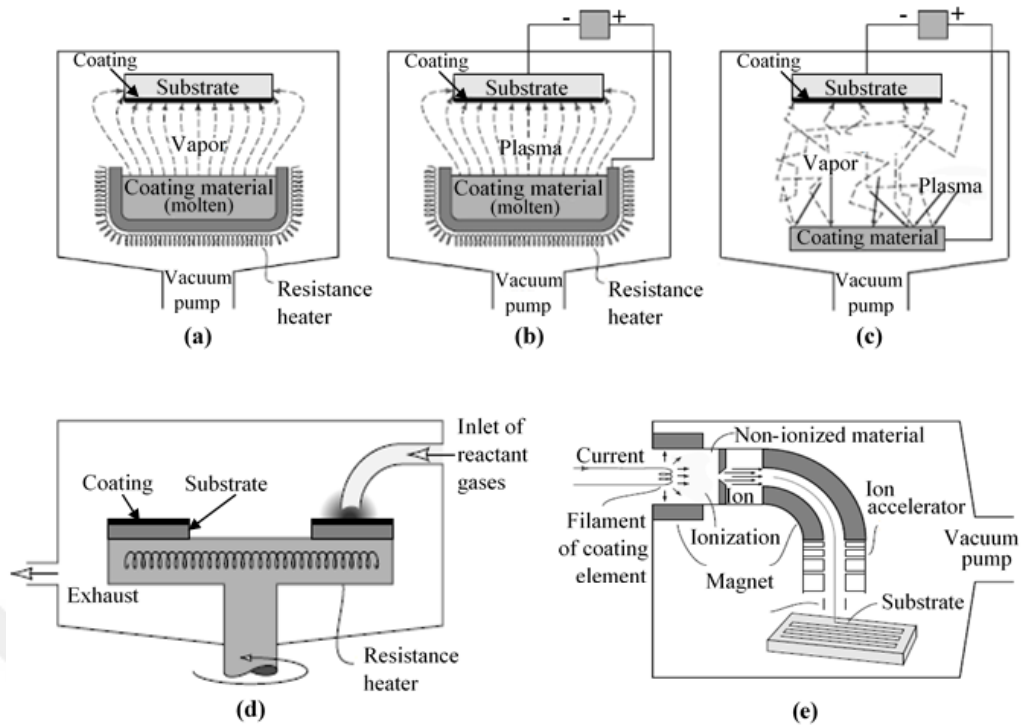


Figure 1.8 : Schematic drawings of (a) evaporation PVD, (b) ion-plating PVD, (c) sputtering PVD, (d) CVD and (e) ion implantation plasma based coating processes [1].

In the light of the fact that the thickness of deposited layer¹ should be in conformity with the encountered deterioration mechanisms [83,84], those thin coating layers, overlaid by plasma based coating methods, could only be adequate to decrease friction or to resist corrosion and some forms of wear but not intense mechanical interactions [85]. Therefore, techniques with localized intense sources of heat such as thermal spraying, surface welding and laser cladding are utilized to overlay deposits with higher thicknesses where the resisting to severe operational conditions or intense wear is required [75,81,86].

In thermal spraying processes, material to be deposited is fed to a heating zone in form of powder, wire or rod before it becomes molten, and then is accelerated to the preheated substrate by the action of compressed air to overlay coating layers with thickness of up to few hundreds of microns [87,88]. The molten particles, which are cooled to a semi molten condition, splatter on the substrate surface and instantly get bonded by mechanical interlocking [89]. A number of thermal spray techniques are utilized to melt and propel the coating material, the most commonly applied are [90]:

¹ The thickness of deposited layer should be designed as greater than the depth of maximum Hertzian stresses [84].

air flame spraying (AFS), air plasma spraying (APS), detonation-gun spraying, electric arc spraying (EAS) and others. The schematic diagrams of the thermal spraying processes are shown in Figure 1.9.

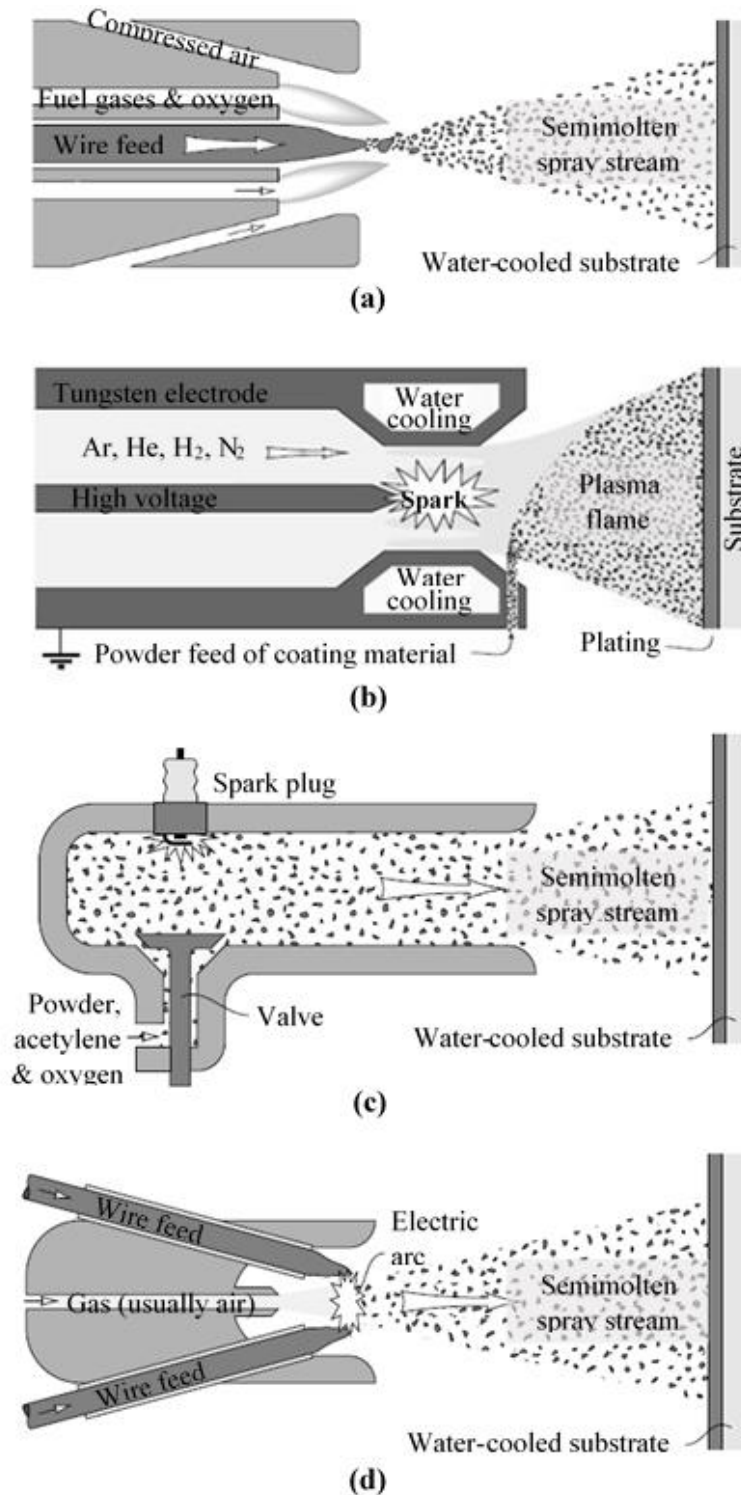


Figure 1.9 : Schematic drawings of thermal spray coating processes; (a) air flame spraying, (b) air plasma spraying, (c) detonation-gun spraying implantation and (d) electric arc spraying [1].

The cohesion between splattered particles themselves alongside the adhesion between the deposited layer and the substrate are critical to the wear resistance and must be strong especially for heavily loaded components. These conditions are often unachievable in thermal spray processes due to the low coating strength and low interface strength between the substrate and coating when the coating material is deposited as partially molten particles [86,91]. Therefore, dense and well bonded deposits with the base substrate have been successfully attained in surface welding techniques where the heating source melts the whole amount of material to be deposited and only a thin film of substrate surface [92]. By using this technique, a large variety of hardfacing materials is not only applied to a new parts during their production but also used to restore a worn-down and damaged surfaces to reduce the cost of replacement [78,80,93]. For this purpose, the conventional welding processes like gas metal arc welding (GMAW), oxyacetylene gas welding (OAW), submerged arc welding (SAW) and shielded metal arc welding (SMAW) are utilized. These welding techniques are commonly used for their low cost, easier application and providing coatings with relatively large thicknesses in comparison with the other coating processes like thermal spraying [88,94]. In Figure 1.10, different conventional welding processes used for deposition of hardfacing layer are schematically illustrated.

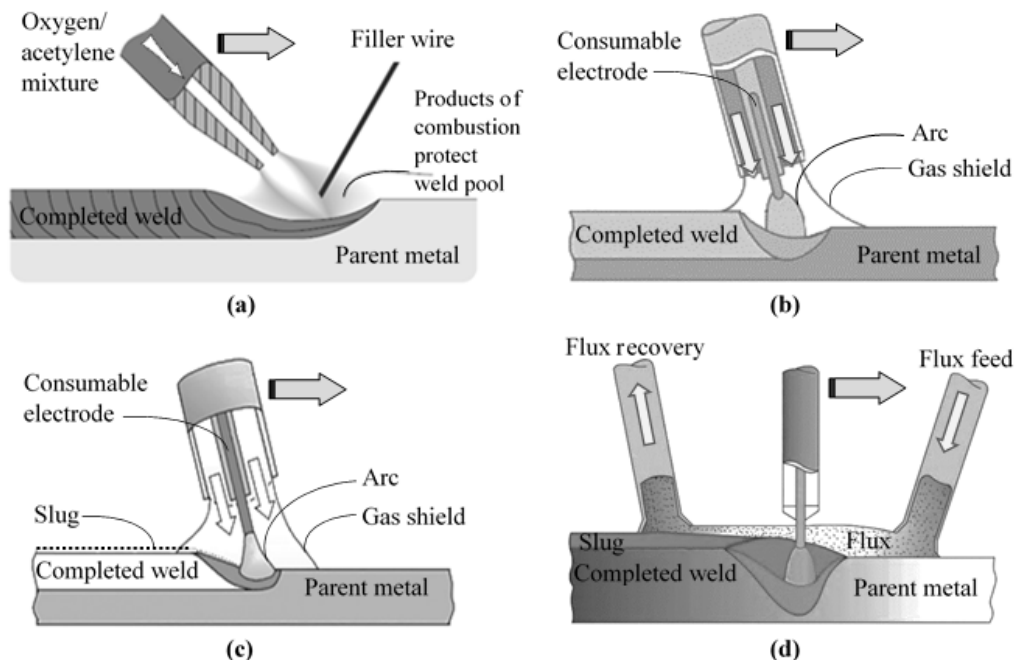


Figure 1.10 : Schematic drawings of conventional welding processes used in hardfacing; (a) Oxyacetylene gas welding, (b) gas metal arc welding, (c) shielded metal arc welding and (d) submerged arc welding [1].

Another promising surface welding technique which has quite successfully been employed for the deposition of wear resistant coatings is the plasma transferred arc (PTA) depositing process. This technique was developed during the sixth decade of the last century from the plasma arc welding (PAW) method with distinct differences between them in term of plasma arc and the nature of the input material [95]. In PTA hardfacing technique, two independent arcs are employed; non-transferred arc generated within the body torch and a transferred arc initiated between tungsten cathode and the work piece where the plasma gas (generally argon) is provided and ionized. Regarding the form of the material to be deposited, unlike the wire-based welding processes like GMAW, PTA typically utilizes consumables in form of powder which blown into the area of the arc by using a carrier gas feeding system. This allows for two significant advantages; first, it shows more flexibility in achieving the desired composition by selecting the appropriate combination, second, it does not need to as high heat input as other arc-based overlaying processes for same amounts of deposition [96,97].

A brief survey of relevant literatures [77,98-103] reveals that homogeneous microstructure can be obtained from PTA depositing process with minimum dilution values (5 ~ 10%) between the deposit and substrate in comparison with those detected in other arc welding processes in the order of 20–25%, thanks to the low heat input, excellent arc stability and the very high energy concentration over the area to be surfaced [104]. Refined microstructure is also an advantage of this technique due to the relatively high cooling rates (10^2 to 8×10^3 K/s), high adhesion between coating and base substrate [95,105]. Schematic drawings of PTA depositing process is shown in Figure 1.11.

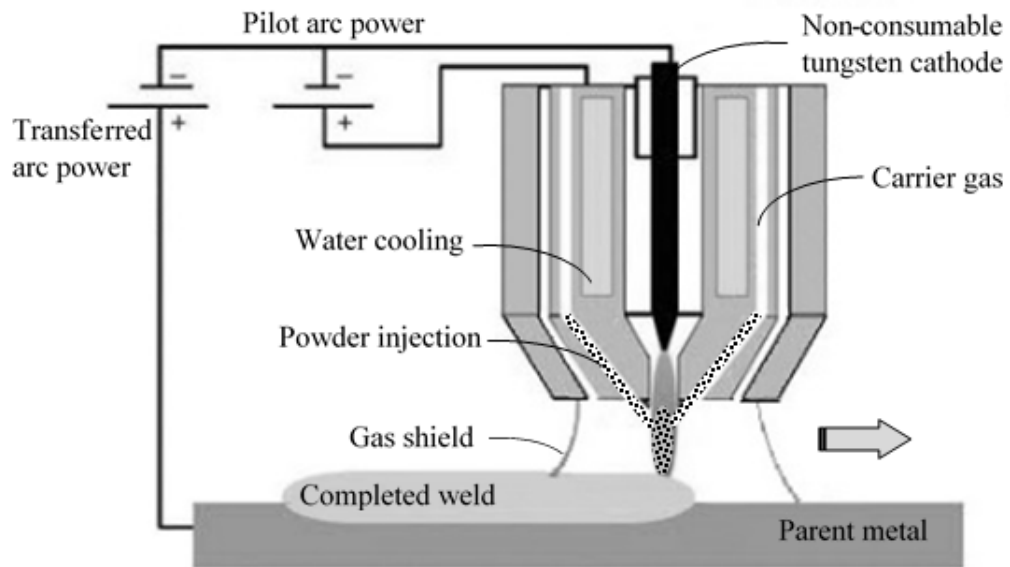


Figure 1.11 : Schematic drawing of PTA welding machine used in hardfacing process [1].

Laser cladding is also pointed out as a unique depositing process of wide variety of hardfacing materials uses an intense laser beam to melt the coating material (either preplaced powder, blown powder or wire feeding) and a thin surface layer of the substrate, forming coating of thickness ranges from 50 μm to 2 mm with low dilution and perfect bonding properties with the substrate [81,106,107].

As for the materials used for hardfacing, they are basically Fe-, Co- or Ni- based alloy with microstructures composed of mixture of hard carbides embedded in a relatively ductile matrix. However, in this work, emphasis has been placed on Co-based Stellite hardfacings which is explained in bellow.

1.3 Cobalt-based hardfacing alloys

Cobalt-base alloys have extensively used in various applications due to their inherent high-strength, wear/corrosion resistance, as well as its ability to retain hardness at high temperatures. Microstructurally, these alloys consist of high fraction of hard carbides dispersed in Co-Cr solid solution matrix [108-111], providing an outstanding resistance against wear and high temperature oxidation that encountered in turbine blades, vanes, hot dies, components in combustion or exhaust systems, and petrochemical and power generation components [112].

Stellite hardfacing alloys, the most popular Co-based group, were simple binary Co-Cr alloys when first developed by Elwood Haynes in 1900s, but subsequently they

were modified and improved by addition of different contents of W, Mo, Y, Si and others. This has resulted in introducing of several modifications and grades which are broadly categorized into two major types: Co-Cr-W-C and Co-Cr-W/Mo-Ni/Fe-C. In Stellite alloys, Cr (between 20-30 wt%) plays a significant role, whilst it is the predominant carbide former, it also has a major role as a solid solution hardening element in the Co matrix. It, furthermore, boosts the resistance to corrosion and oxidation especially at HTs [113,114]. The carbides formed by Cr are mostly in the form of M_7C_3 and $M_{23}C_6$, the formation of which is governed by Cr to C ratio [115]. Refractory elements like W (between 4 ~ 17 wt%) and Mo (up to 28 wt%) both have similar effects on Stellite alloys. They contribute to the solid-solution hardening of the matrix phase along with formation of complex carbides (M_6C) and intermetallic compounds [116]. C content in Stellite alloys, which varies from 0.1 to 3.2%, is considered the key element that influences both the mechanical and chemical properties. Depending on the C content, Stellite alloys are either hypoeutectic or hypereutectic [117,118]. At C content of < 2.5 wt%, Stellite alloys are hypoeutectic with microstructures consist of primary Co-rich solid solution matrix surrounded by eutectic compounds; otherwise they are hypereutectic in which the first phase is the primary carbides or intermetallic compounds and then the interdendritic eutectic matrix solidified. Typically, the microstructure of hypereutectic Stellite alloys have higher fraction of carbides making them possess greater hardness and wear resistance than hypoeutectic alloys [96]. However, Stellite alloys with very low C content (about 0.1 wt%) are well-known as solid-solution-strengthened alloys [13,117,119,120].

1.4 Modification of Stellite hardfacings

Depositing of Co-based Stellite hardfacings has been found to be beneficial in overcoming the problem of the wear loss in different components but the ever-growing industries and the demands for new high-performance materials have motivated toward the development of Stellite hardfacings. Since the performance of Stellite hardfacing alloys are functions of the microstructure which mainly depends on the chemical composition and the processing conditions (solidification kinetics) [58], a great deal of researching efforts has been put into the modification of commercial Stellite hardfacings, aiming to achieve further improvements in surface related properties.

1.4.1 Modification of Stellite hardfacings by additives

One ever promising approach to achieve better mechanical properties in Stellite hardfacings is altering the chemical composition. This modification process, which is done during the depositing process, is based on mixing of commercial Stellite alloys with either alloying elements [121-129] or carbide particles [30,130-133]. Depending on the weight fraction of these additives, considerable microstructural changes have been resulted, particularly, in term of the volume fraction, morphology and type of carbides which consequently improved the wear properties.

In Stellite hardfacing alloys, Mo, which is the alloying element that we were concerned with in our study, can serve in providing better performance via enriching the microstructure with excessive amounts of Mo-rich complex carbides with some portion dissolved in the Co-matrix as a solid solution strengthening element. It should be mentioned here that the increment in the volume fraction of complex carbides upon Mo addition is often at the expense of Cr-rich eutectic carbides. This competition between Mo- and Cr-carbides formation upon Mo addition into Stellite hardfacings can be explained thermodynamically on the basis of mixing enthalpy (ΔH_{mix}) values of Mo and Cr, separately, with C. The large negative ΔH_{mix} value of Mo-C (-21.35 kJ/mole) relative to that of Cr-C (-14.98 kJ/mole) [134] makes it evidential that too much of C is captured by Mo at the earliest stage of solidification to form Mo-rich complex carbide in the form of M_6C whereas the only remaining C will be available for combination with Cr, forming Cr carbides [135].

1.4.2 Modification of Stellite hardfacings by surface melting treatments

Even though modifying the chemical composition of Stellite alloys can enhance the hardness and wear resistance but it is not always an applicable approach especially when the alloying rate goes higher. For examples, with the increase of the Mo content in Stellite hardfacings, large-size and brittle carbides are formed in the microstructure, which are vulnerable under wear attack, thus providing more carbide fragments to the wear loss when they are broken. W also causes significant microstructural changes in Stellite alloys and hence their wear behaviour when its content is greatly increased. It can result in hypereutectic alloys, even if the C content was lower than the eutectic concentration, i.e. 2.5% [117]. Therefore, scanning the surface of deposited Stellite hardfacings by concentrated heat sources such as electron and laser beam has widely

been applied as an alternative solution to modify the microstructure of the outermost layer and enhancing the surface properties without changing the composition [86,136-141]. Under the action of electron beam surface melting (EBSM) and laser surface melting (LSM) processes, a very thin surface layer is melted in fractions of a second. The large differences between the melt pool and unaffected underneath solid in term of their volume along with their intimate contact have a great impact on the solidification characteristics via accelerating the heat removal toward the cooler bulk. This provides an extremely rapid cooling rate in the range of 10^{-5} K/s [142,143], which produces non-equilibrium microstructures and often enhances the surface properties of the processed material [144-146]. These processes are also characterized by relatively low heat input, which result in narrow heat-affected zone (HAZ) and low rate of distortion [147-149]. Moreover, the thickness of the processed layer can be highly controlled by adjusting the process parameters like voltage, current, travelling speed of the workpiece, etc. [150]. Figure 1.12 schematicly shows the surface melting process using beam assisted techniques.

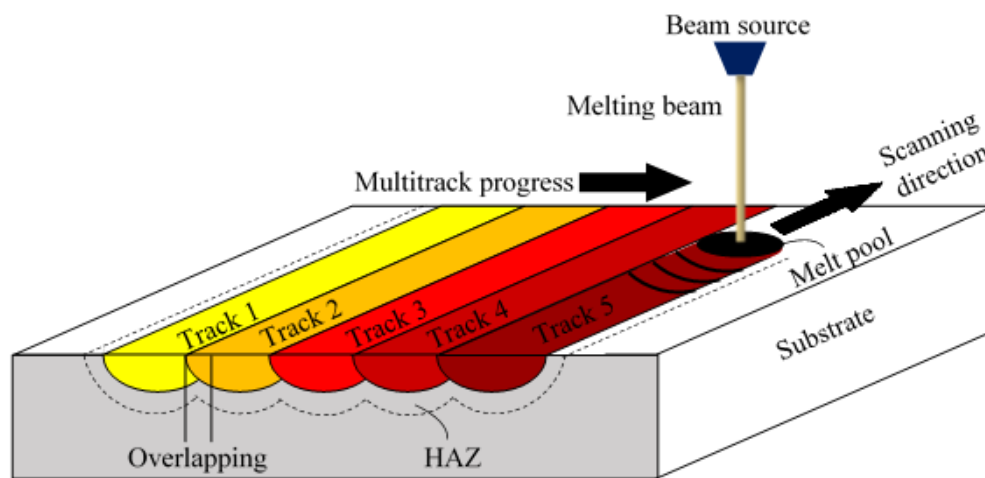


Figure 1.12 : Schematic diagram showing interaction between the melting beam and the base metal.

Regarding the processing environments, unlike the LSM process in which the vacuum conditions are not needed, the propagating of electron beam in the air makes the electron beam loses 90% of its energy due to ionization of the gap between the electron source and the workpiece; therefore, EBSM process is most typically performed under high vacuum conditions of 10^{-4} to 10^{-6} torr. This provides a significant advantage of processing of reactive metal alloys such as magnesium and titanium as well as providing a contamination-free surface. On the other hand, it drastically reduces the

benefits of EBSM technique since these equipment are relatively expensive and limit the possibility of processing of large products [151,152]. Another notable difference between laser and electron beams is the variation in absorption characteristic which is typically less for laser than electron under most circumstances. This is closely linked with the back-reflection of the laser beam from the metallic surfaces which undoubtedly makes the LSM process of lower amount of heat input, providing a thinner melted layer [153,154].





2. RESEARCH OBJECTIVES

Taking into consideration the fact that the properties of Stellite hardfacings can be modified by altering their chemical composition and/or applying of a post deposition surface melting treatment, our research group, under the leadership of Prof. Dr. Hüseyin ÇİMENOĞLU, started with modifying of Stellite hardfacing when Motallebzadeh et al. [124] alloyed the commercially available Stellite 12 with 10 wt.% Mo, depositing the mixture by PTA process. In this publication, the microstructural developments upon Mo addition were discussed in details and the dry sliding wear behavior of the depositions was evaluated both at RT and HT (300-700 °C). This work has been followed by a series of studies wherein Dilawary et al. [150] evaluated the effect of LSM post depositing treatment on the RT sliding wear resistance of PTA Stellite 12 hardfacings. Employing of LSM treatment to Mo-alloyed Stellite 12 hardfacing, in a next study, showed an additional improvement in the hardness and RT wear resistance due to the formation of a unique carbide structure [155]. Finally, the beneficial effect of combination of Mo alloying and post LSM treatment on HT (500 °C) sliding wear resistance of Stellite 12 hardfacing has been reported in a recent study [156].

As a continuation of previous strategies in modifying the surface related mechanical properties of Stellite hardfacings (the hardness and sliding wear resistance), this Doctoral thesis is devoted to the experimental study of the effects of post treatments of EBSM and LSM on the microstructure and associated surface properties of two different PTA deposited Stellite hardfacings (Stellite 12 and Stellite 6). AISI 4140 steel substrate has been selected as it is one of most popular low alloy steel frequently used in different industries like shafts, molds, guides, fixtures and many engineering components. Even though surface properties of 4140 steel can be enhanced through conventional hardening heat treatments, heating and fast cooling cause big problems of distortion. Therefore, hard and wear/corrosion resistant coatings are commonly applied with the purpose of increasing the surface life of these substrates without significant loss in ductility and toughness.

This Doctoral thesis consists of a series of three papers, all dealing with different aspects of this topic as following:

2.1 Effect of Electron Beam Surface Melting on the Microstructure and Wear Behavior of Stellite 12 Hardfacing

As mentioned above, the positive effects of LSM treatment on the surface mechanical properties of PTA Stellite 12 hardfacing has been well reported by Dr. Shaikh Asad Ali Dilawary; therefore, an alternative post deposition treatment of EBSM process was chosen for this module, aiming to investigate if a different surface modification mean could also enhance the surface properties of Stellite 12 hardfacing as compared to those of PTA deposited version. It should be mentioned here that identical parameters were used for PTA deposition process in all these studies, so the issue of heat input variation during the deposition process which could have affected the resultant microstructure is not expected. The results of this study are presented in Chapter 3.

2.2 Effect of Electron Beam Surface Melting on the Structure and Wear Characteristics of Cobalt-Based Hardfacing and Its Mo-Alloyed Version

In literatures, the effects of Mo alloying and application of post EBSM process on both the structure and wear resistance of Stellite 6 hardfacing were separately studied [121,122,137,138]. However, no efforts were given toward the combination of these approaches in one strategy which could provide better surface properties than they were separately applied. For this reason, a commercial Stellite 6 hardfacing and its 10 wt. % Mo-alloyed version were deposited by PTA process. The deposits of unalloyed and Mo-alloyed Stellite 6 hardfacings were subjected to a post EBSM treatment and the microstructure and sliding wear properties of PTA Stellite 6, PTA Mo-alloyed Stellite 6, EBSM'ed Stellite 6 and EBSM'ed Mo-alloyed Stellite 6 hardfacings were examined and compared. The results of this study are presented in Chapter 4.

2.3 Room and High Temperature Sliding Wear Characteristics of Laser Surface Melted Stellite 6 and Mo-alloyed Stellite 6 Hardfacings

A post treatment of LSM was employed on Stellite 6 and its 10 wt.% Mo-alloyed version to investigate how the LSM process, with its characteristic low heat input as compared to EBSM, would affect the microstructure and wear resistance. By considering the fact of performance and properties of the metallic materials

characterized at RT are not valid with increasing the temperature and the application environment of these material coatings, the wear characteristics of the examined hardfacings were evaluated at both RT and HT (500 °C).





3 EFFECT OF ELECTRON BEAM SURFACE MELTING ON THE MICROSTRUCTURE AND WEAR BEHAVIOR OF STELLITE 12 HARDFACING ²

3.1 Introduction

One of the most commonly applied processes used to enhance the performance of metallic surfaces is hardfacing mainly by Fe-, Ni- and Co-based alloys [80]. Compared to Ni- and Fe-based hardfacing, Co-based ones have been extensively used in the applications that require a good combination of wear, corrosion and heat-resistant properties such as aerospace, gas turbines and power plants [157,158]. Among the Co-based hardfacings, Stellites developed as CoCrWC type are the most popular group [124,159] that can be found in several modifications and commercial grades such as Stellite 1, 6 and 12 [160,161]. The main difference in these grades is C which is considered as a key element that influences the hardness by virtue of varying the fraction of carbides in the microstructure [124,162]. In that respect, Stellite 12 appeared to have an optimum combination of hardness and toughness thanks to its moderate C contents [155,163]. There are still research studies on Stellite 12 hardfacings for further improvement in the surface-related properties by laser surface melting (LSM) applied as post deposition treatment [155,156]. Thereby, it was reported that heat input realized by LSM plays a crucial role in developing a favorable surface microstructure.

In this respect, this study has been initiated by adopting electron beam surface melting (EBSM) as an alternative option for post treatment, as electron beam is known for better control, reliability, cleaner environment (vacuum) and deeper penetration [164-167].

The authors of current study have applied EBSM to plasma transferred arc (PTA) deposited Stellite 12 hardfacing alloy to investigate if the surface structure and

² This chapter is based on the paper “Effect of electron beam surface melting on the microstructure and wear behavior of Stellite 12 hardfacing”, published in “Industrial Lubrication and Tribology 71-5 (2019) 636-641, <https://doi.org/10.1108/ILT-05-2018-0182>.”

properties could be improved. More specifically the dry sliding wear performance of PTA and EBSM'ed hardfacings have been focused in the scope of this study.

3.2 Materials and methods

In this study, Commercial Stellite 12 powder produced by Kennametal Stellite™ Company with a particle size of 53-150 μm was deposited in a single pass on AISI 4140 steel by PTA technique using the process parameters of current 92 A, voltage 32 V, travel speed 85 mm/min. The thickness of deposited hardfacing layer was 5 mm. The surface of the deposition was flattened by grinding to a thickness of 2.5 mm before EBSM process. For EBSM, an electron beam of a current of 4 mA, voltage of 40 kV and spot size of 1 mm in diameter scanned the work piece in a single pass at a rate of 171 mm/min in vacuum environment (0.01 bar).

The structural features of the hardfacings have been examined by optical light microscope (Olympus GX71, Japan), scanning electron microscopes (SEM) (energy dispersive X-ray spectrometer equipped Zeiss-Ultra Plus, Germany and Hitachi TM-1000 Tabletop Microscope, Japan) and X-ray diffractometer with Cu K α radiation (XRD, GBC, Australia). The hardness of the examined hardfacings were measured in HV scale using a conventional microhardness tester (Shimadzu, HMV2, Japan) with an indentation load of 1 kg. Ten measurements were made on the surfaces of each hardfacing and the average was the final result of the hardness.

Dry sliding wear performance of the hardfacings was examined on a reciprocating tester (Tribotech Oscillating Tribotester) using an alumina ball with a diameter of 6 mm and a sliding speed of 10 mm/sec. The stroke of the reciprocating motion and the overall sliding distance was 5 mm and 100 m, respectively. The wear testing loads were chosen to be 1 and 4N corresponding to the lowest and highest limits of the tribotester. The temperature and the relative humidity during the test were maintained at 25 ± 5 °C and 35 ± 3 per cent, respectively. The wear tracks (WTs) were scanned by a 2D contact type profilometer (Veeco Dektak 6M, USA) and a SEM.

3.3 Results and discussion

3.3.1 Microstructure and hardness

Figure 3.1 presents the XRD patterns of the examined hardfacings. Analysis of these patterns reveals the main constituent phases of the examined hardfacings are α -Co (ICCD 01-088-2325), Cr-rich carbides in the form of M_7C_3 and $M_{23}C_6$ (ICCD 00-036-1482 and ICCD 00-003-1172, respectively) and complex carbides in the form of W and Co rich M_6C (ICCD 00-023-09390). These results are consistent with previous studies on Stellite 12 [117,122,124,156]. After EBSM process, M_7C_3 peak at 2θ of 41° disappeared whilst the intensity of α -Co peak at 2θ of 51° was noted to be significantly higher.

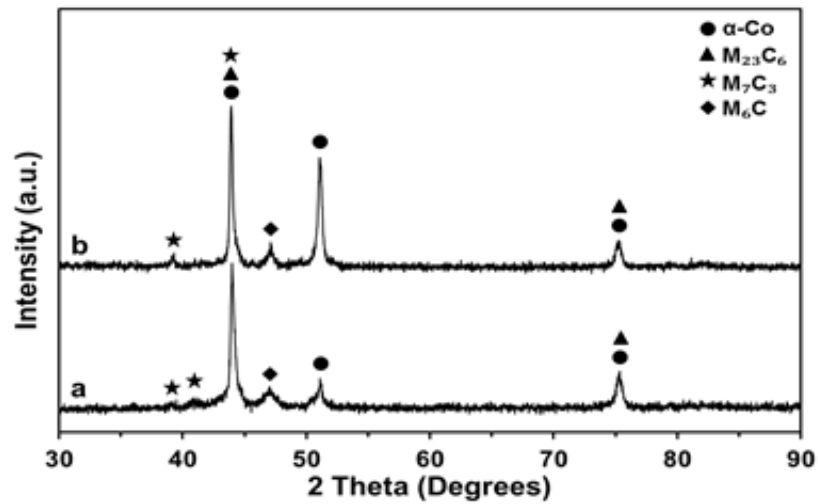


Figure 3.1 : XRD patterns of the examined hardfacings (a) PTA and (b) EBSM'ed Stellite 12.

This is a preliminary indication of the existence of fractional changes in the constituent phases formed in Stellite 12 hardfacing alloy after EBSM process as compared to PTA state.

The surface SEM micrographs of the examined hardfacings are presented in Figure 3.2. It can be seen that the microstructure of the PTA Stellite 12 (Figure 3.2a) consisted of three distinct phases: dendritic α -Co matrix (with a size range of 10-20 μm) surrounded by dark gray and white colored compounds, which were identified as Cr-rich (in the form of M_7C_3 and $M_{23}C_6$) and W and Co-rich complex carbides (in the form of M_6C), respectively, according to EDX analysis conducted during SEM surveys, XRD patterns presented in Figure 3.1 and relevant literature [124,155,163,168]. At a magnification of 5,000x, the microstructure of the EBSM'ed

hardfacing (Figure 3.2b) appeared to consist of two distinct phases, i.e. α -Co matrix and fine M_6C type complex carbides, unlike PTA. However, high magnification SEM examinations revealed the presence of three distinct phases in the microstructure. It can be seen from the SEM micrographs given in Figure 3.3 (30,000x) that the α -Co matrix of the EBSM'ed hardfacing has a cellular-dendritic morphology with a cell size of 1-3 μm . It is also apparent that, α -Co matrix is surrounded by eutectic carbides ($M_7C_3/M_{23}C_6$) with very narrow inter-lamellar spacing and fine M_6C type complex carbides having a rod shape morphology with the longer dimension of less than 2 μm .

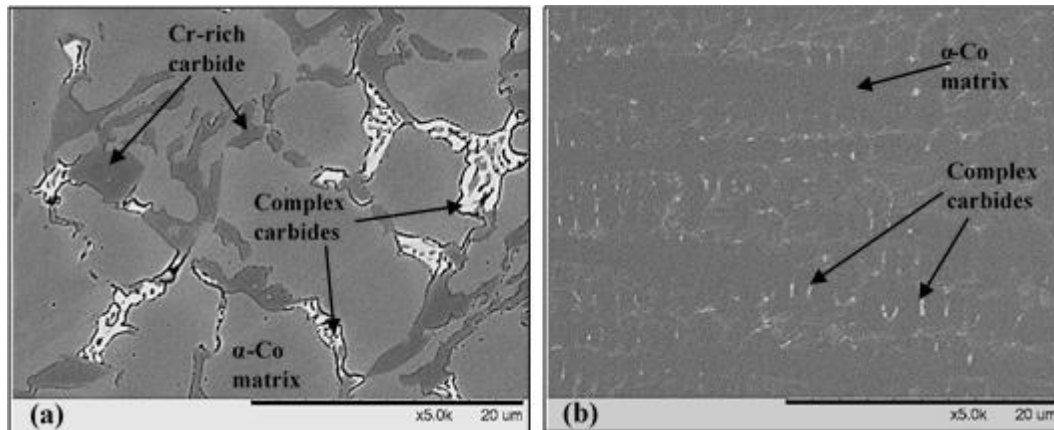


Figure 3.2 : Surface SEM micrographs of the examined hardfacings (a) PTA and (b) EBSM'ed Stellite 12.

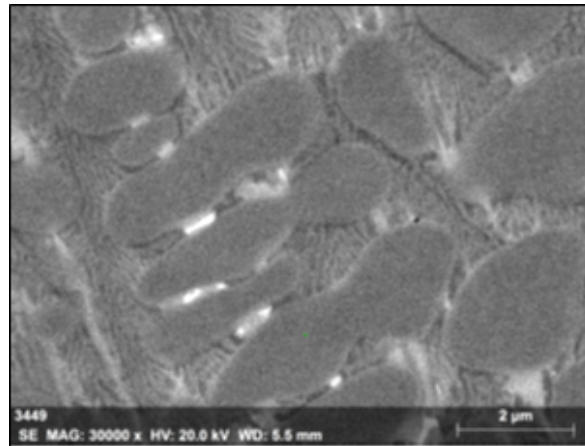


Figure 3.3 : High Magnification surface SEM micrograph of EBSM'ed Stellite 12 hardfacing.

In Figure 3.4, the cross section optical and SEM micrographs of the EBSM'ed hardfacing are presented. The optical micrograph (Figure 3.4a) shows that the width and the maximum depth of the EBSM'ed zone have been measured as approximately 1,000 and 300 μm , respectively. High magnification inset of Figure 3.4a revealed that

the solidification of the melt pool (EBSM'ed zone), which started at the solid-liquid interface, progressed toward the surface opposite to the heat removal direction [169]. According to SEM, micrograph taken from the near surface region (Figure 3.4b) confirmed cellular-dendritic solidification morphology.

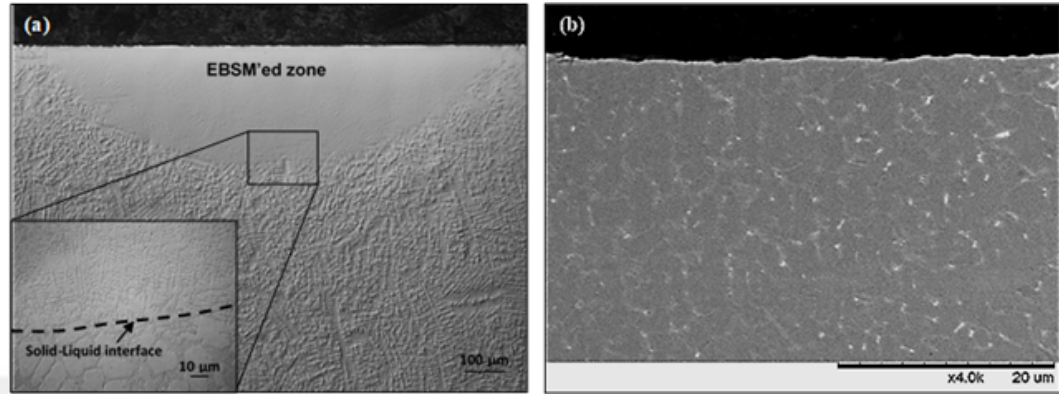


Figure 3.4 : Cross sectional (a) optical and (b) SEM micrographs of EBSM'ed Stellite 12 hardfacing.

On the basis of these microstructural examinations, fine natures of α -Co matrix and M_6C type complex carbides along with narrow inter lamellar spacing of Cr-rich eutectic carbides (M_7C_3 and $M_{23}C_6$) is the result of the rapid cooling of the melt following the EBSM process originating from very limited volume of the melt pool as compared to that of solid bulk underneath it [131,170,171]. It is suggested that this rapid cooling rate limits the diffusion of the alloying elements (W and Cr) so that the solidification of the liquid causes formation of a number of rod shaped fine complex carbides while the remaining melt solidifies as eutectic carbides with very fine inter lamellar spacing. As a result of the microstructural refinement, the surface hardness values were measured as 599 ± 30 which is 14 per cent higher than the PTA value of 528 ± 25 HV.

3.3.2 Dry sliding wear performance

Representative 2D profiles of the WTs formed on the examined hardfacings under wear testing loads of 1 and 4N are given in Figure 3.5. It can be noticed that the PTA and EBSM'ed Stellite 12 hardfacings followed similar trend during wear tests, i.e. the higher the wear testing load, the wider and deeper were the WTs (bigger WT area). In spite of having higher hardness, EBSM'ed hardfacings showed bigger wear loss (by the quantified WT area shown in Figure 3.5) as compared to PTA state. Approximately 50 per cent higher wear loss was witnessed for EBSM'ed hardfacings.

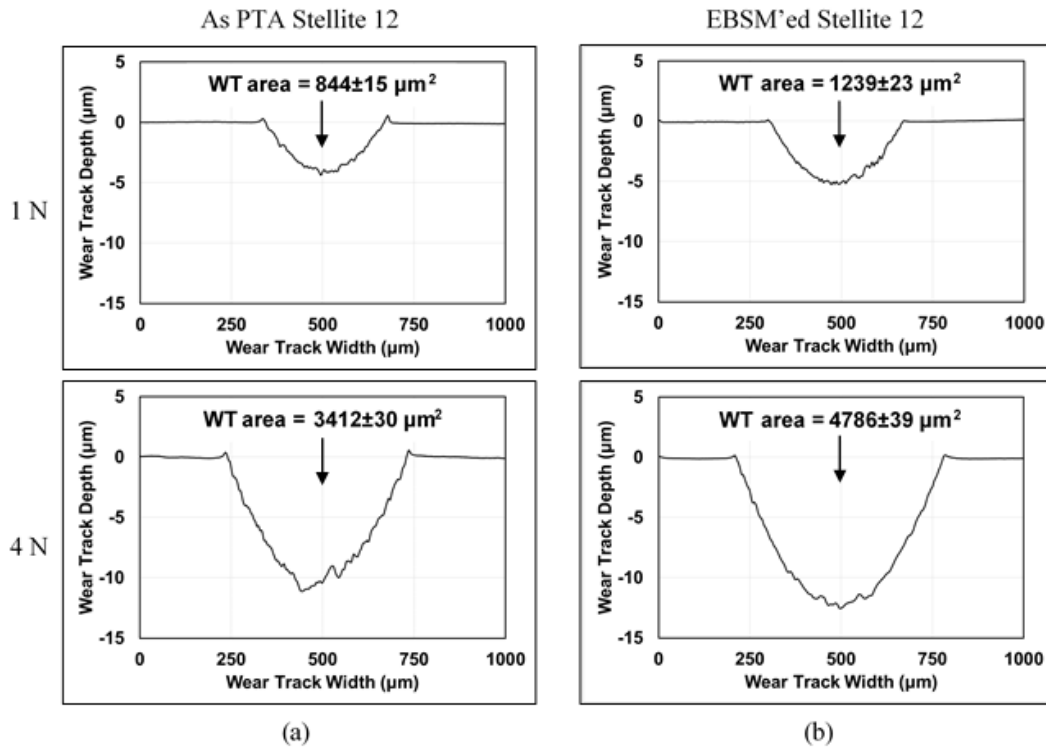


Figure 3.5 : 2D wear track of (a) PTA and (b) EBSM'ed Stellite 12 hardfacing under testing load of 1 N and 4 N.

Worn surface SEM micrographs of the examined hardfacings are presented in Figure 3.6. In general, worn surface appearance of the PTA and EBSM'ed hardfacings was quite distinct. In case of the PTA hardfacing, worn surface can be described by grooving of the matrix and cracking of the carbides. Increase of wear testing load from 1 N to 4 N led to localized covering of the worn surface by tribo-oxide patches. For the EBSM'ed Stellite 12 hardfacings, worn surfaces are featured by continuously ploughed matrix and absence of tribo-oxide patches. Interestingly while carbides can be identified on the WTs formed at 1 N testing load, the worn surfaces at 4N testing load appeared in carbide free nature. High magnification inset revealed accumulation of the carbides within the grooves and some evidence of fatigue wear at 4 N testing load.

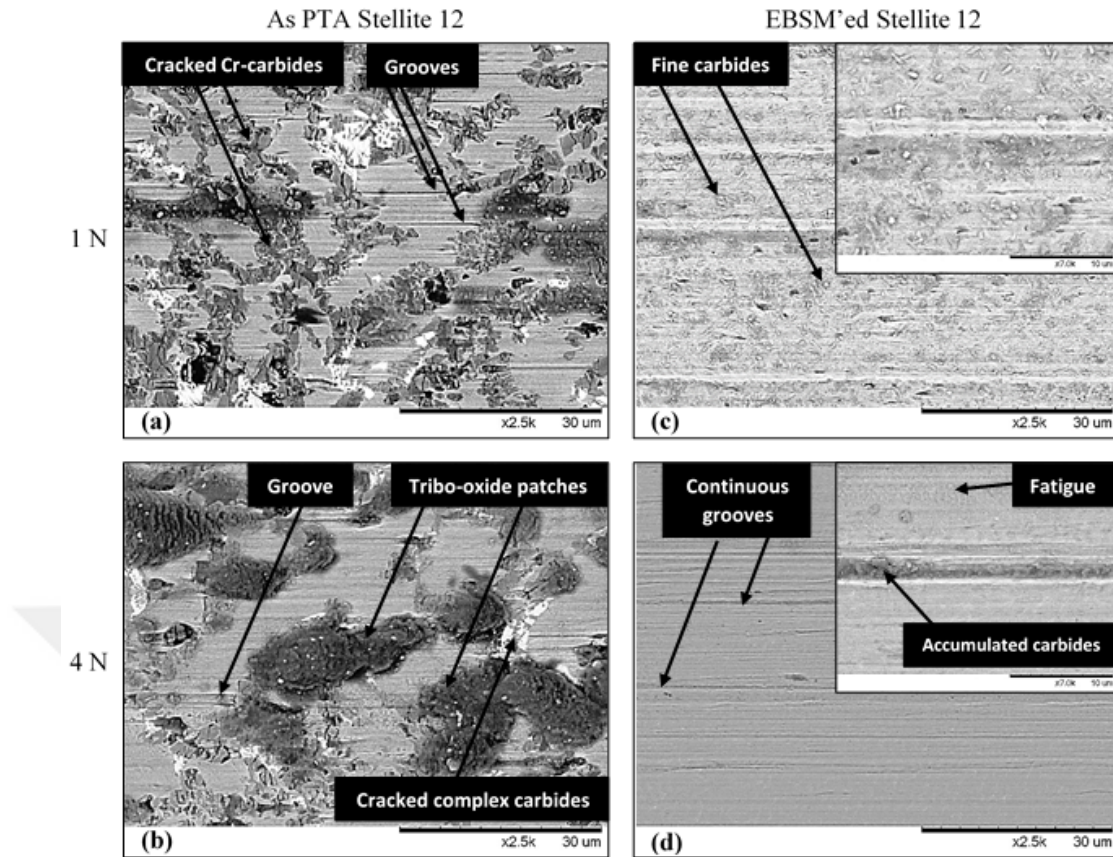


Figure 3.6 : Worn surface SEM micrographs of PTA and EBSM'ed deposits worn under loads of 1 N and 4 N.

As wear resistance of the hardfacings is a function of volume fraction and size of the carbides, their removal during sliding action of the counterface has potential to deteriorate the wear resistance as they are unable to resist its destructive action [2,23,30,88,94,168,172]. Their easier removal also devoid matrix of their support accelerating groove formation and is responsible for the absence of tribo oxide patches on the worn surfaces as is the case for the EBSM'ed hardfacing. It is well established that the formation of tribo-oxide patches at the energetically favorable carbide-matrix interfaces assists in resisting the direct contact between the tribo pairs, leading to better wear resistance as is the case of PTA hardfacing [76,156,173,174].

It is concluded that the reduction in the wear resistance of Stellite 12 hardfacing after EBSM process arises from high cooling rates not allowing protective coarse carbides in the microstructure during solidification.

It is suggested that either slowing down the cooling rate by the optimization of the EBSM parameters (i.e. beam power and/or scanning speed etc.) or modification of Stellite hardfacing with carbide forming elements, providing formation of relatively

coarser carbides with a higher fraction even at rapid cooling conditions, could be promising for enhancement in wear resistance after EBSM.

As a future work, authors seek to investigate the effect of same EBSM parameters upon modification of Stellite hardfacings with Mo which has reportedly shown better results after LSM process [155,156].

3.4 Conclusion

In this study, the microstructure and dry sliding wear properties of EBSM'ed Stellite 12 hardfacing were examined and compared with those of PTA. The conclusions can be summarized as follows:

1. Microstructurally, carbides and matrix phases were significantly refined after EBSM process as a result of high solidification rate.
2. Hardness of EBSM'ed Stellite 12 slightly increased because of structure refinement.
3. Despite 14 per cent increase in hardness, a considerable decrease in wear resistance (approximately 50 per cent) after EBSM was observed mainly due to the extensive refinement of carbides making them easier to remove during sliding contact while eliminating favorable sites for tribo-oxide patch formation.

4 EFFECT OF ELECTRON BEAM SURFACE MELTING ON THE STRUCTURE AND WEAR CHARACTERISTICS OF COBALT-BASED HARDFACING AND ITS Mo-ALLOYED VERSION³

4.1 Introduction

Among cobalt-based hardfacings, the Stellite group is commercially well known, especially for wear-related engineering applications mostly in aerospace, power plant, chemical, and petrochemical industries [162,175]. The exceptional wear resistance of Stellite hardfacings is mainly obtained from the high fraction of hard carbides such as Cr-rich carbides in the form of M_7C_3 and $M_{23}C_6$ and W/Mo-containing complex carbides in the form of M_6C dispersed in a solid solution–strengthened Co matrix [176,177]. Depending on the C content, which dictates the fraction and type of carbides formed in the microstructure, Stellite hardfacings are found in many modifications and commercial grades [23,161,162,168].

Despite their good surface mechanical properties such as hardness and wear resistance, efforts are still being made to boost their performance. Such attempts involve altering the chemical composition during the deposition of Stellite alloys by introducing alloying elements such as Y [125,126], W [127], and Mo [122-124,155]. It was reported that the addition of ≤ 2 wt% Y into Stellite hardfacings refines the microstructure and forms a Co_2Y intermetallic phase. This modified microstructure not only provides an increment in hardness but also enhances the sliding wear resistance [125,126]. W- and Mo-modified Stellite hardfacings have shown overall superior mechanical and tribological properties as a result of the formation of complex carbides/intermetallic compounds, along with solid solution hardening of the Co matrix [122-124,127,155].

In addition to chemical modification, there are studies on the application of surface melting as a post treatment to further extend the service life of Stellite hardfacings.

³ This chapter is based on the paper “Effect of Electron Beam Surface Melting on the Structure and Wear Characteristics of Cobalt-Based Hardfacing and Its Mo-Alloyed Version”, published in “Tribology Transactions 62-5 (2019) 907-918, <https://doi.org/10.1080/10402004.2019.1640328>.”

Surface melting of Stellite hardfacings has been employed by laser [150,155,156] and electron beam [137,178] techniques, and subsequent rapid solidification of the melt caused an enhancement in hardness. However, surface melting by laser and electron beam showed contradictory results for Stellite 12 hardfacing in terms of wear performance. Laser surface melting (LSM) resulted in better wear resistance [150,155,156], whereas electron beam surface melting (EBSM) deteriorated the wear performance [178]. These conflicting results can be explained in terms of the microstructure that developed near the surface following these processes. Unlike EBSM, LSM favored the formation of a carbide enrichment zone at the outermost surface, providing more resistance against sliding action of the counterface, whereas EBSM caused carbide depletion and/or severe carbide refinement [178].

Because EBSM is performed in an evacuated environment and offers good thermal isolation and efficiency compared to LSM [164,165,179], it merits further investigation for its application on Stellite alloys. Hence, it was previously proposed that modifying Stellite hardfacings with carbide-forming elements like Mo may provide better wear performance after a post-surface melting process [150,178]. In the light of this proposal, authors have alloyed Stellite 6 with 10 wt% Mo during plasma-transferred arc (PTA) deposition and have employed EBSM as post deposition treatment. Mo is selected for its reported better carbide-forming ability [180], and Stellite 6 is known for its high toughness due to its moderate C content ~1.2 wt% [181].

4.2 Experimental procedure

In this study, commercially available Stellite 6 powder and its mixture with 10 wt% commercially available Mo powder were deposited separately on quenched and tempered AISI 4140 steel substrate (0.42% C, 0.84% Mn, 0.017% P, 0.001% S, 0.25% Si, 1.01% Cr, 0.16% Mo, and balance Fe) with a hardness of 322 ± 5 HV1 using a PTA technique. The particle sizes of the Stellite 6 and Mo powder were in the range of 53-150 and 38-75 μm , respectively. All PTA depositions were performed with identical parameters (current 92 A, voltage 32 V, travel speed 85 mm/min) in a single layer with a thickness of 5 mm. The PTA-deposited surfaces were flattened by grinding, leaving behind a hardfacing layer with a thickness of 2.5 mm. The surfaces of unalloyed and Mo-alloyed PTA Stellite 6 hardfacings were then scanned by an electron beam for surface melting in a single pass. The EBSM process was applied in

a vacuum (0.01 bar) with the following parameters: voltage 40 kV, current 4mA, and scanning velocity 171 mm/min.

The microstructural features of the unalloyed and Mo-alloyed PTA Stellite 6 hardfacings and their EBSM versions were examined by light optical microscopy (LOM), scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectrometry (EDX), and X-ray diffraction (XRD) with Cu K α radiation. For microscopic examinations, the surfaces and cross sections of the samples were prepared according to standard metallographic procedures; that is, grinding, polishing, and etching with a mixture of 80 ml HCl and 20 ml H₂O₂ [124]. Image analysis software was utilized to quantify the volume fraction and average size of the constituent phases in the surface SEM micrographs of the examined hardfacings using the method prescribed in the user guide [182]. The quantified volume fractions and sizes are the average of at least three different measurements for each hardfacing.

The hardness measurements were done on the surfaces of the examined hardfacings in HV scale using a conventional microhardness tester with an indentation load of 500 g. The hardness values reported in this study are an average of at least 10 indentations with a mutual distance of more than or equal to five times the indent diagonal. A reciprocating wear tester operated in ball-on-disc configuration was utilized to examine the dry sliding wear performance of the examined hardfacings at wear testing loads of 1 N and 4 N. Three tests were performed at each load. A wear testing at a load of 1 N was chosen because it is the lowest limit of our tribotester. As for the upper limit, a testing load of 4 N was chosen to avoid sudden shutdown of the wear tester due to a severe increase in tangential force. Additionally, the applied testing loads provide unique conditions wherein the Hertzian contact pressure ranges from 800 to 1,200 MPa, which is the typical range for the peak pressures (1,000 MPa) experienced by the tools in metal-forming operations such as die punching [150,183-185].

An alumina ball with a 6 mm diameter was slid on the hardfacings at a sliding speed of 10 mm/s. The stroke length and overall sliding distance were 5 mm and 100 m, respectively. The high hardness, chemical, and structural stability were behind the selection the alumina ball as a counterface to determine the sole wear characteristics of Stellite 6 hardfacings and avoid any contribution from the counterface [65,186]. During the wear tests, the temperature and relative humidity were maintained at 25 ± 5 °C and $30 \pm 3\%$, respectively. The wear tracks (WTs) formed on the surfaces of the

hardfacings were examined by a 2D contact-type profilometer and SEM. Five locations on each wear track were selected to profile its cross section. The contact surfaces of the alumina ball were also examined by LOM.

4.3 Results

Figure 4.1 presents the surface and cross-sectional LOM images of the examined hardfacings. As the reference microstructure, PTA Stellite 6 hardfacing has a dendritic matrix morphology surrounded by lamellar interdendritic regions. The microstructure of Mo-alloyed PTA Stellite 6 hardfacing shows almost similar structural features with a slight reduction in the dendritic size along with widening of the interdendritic regions. In general, application of EBSM on unalloyed and Mo-alloyed Stellite 6 hardfacings caused extensive refinement of the microstructures. The cross-sectional microstructures revealed the orientation of dendrites toward the surface in the melt pool of EBSM hardfacings, unlike the cross-sectional appearances of PTA hardfacings. Even with identical EBSM parameters, the width and depth of the EBSM zones of unalloyed and Mo-alloyed hardfacings were different. Thus, the EBSM zone had a depth and width of 400 and 1,200 μm , respectively, for unalloyed hardfacings, whereas they were 500 and 1,000 μm , respectively, for the Mo-alloyed version. The characteristic low-magnification appearances of the EBSM zones are shown as inset in the corresponding cross sectional micrographs in Figure 4.1.

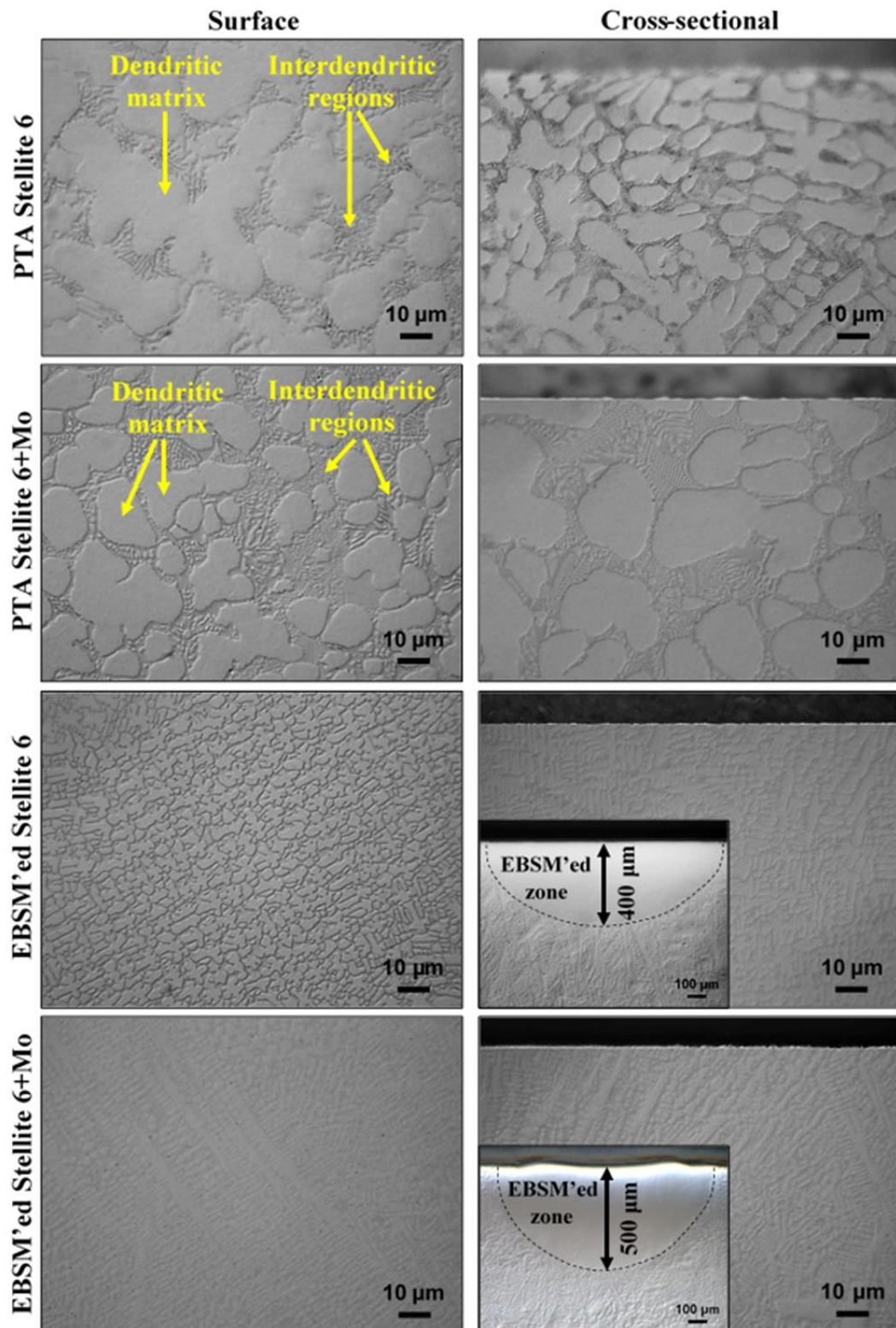


Figure 4.1 : Surface and cross-sectional optical micrographs (OM) of the examined hardfacings.

Surface SEM micrographs of the examined hardfacing with the insets of their cross-sectional view are presented in Figure 4.2. In general, three distinctly colored phases (i.e., a light grey dendritic matrix and interdendritic regions with dark grey- and white-colored compounds) appeared on the SEM micrographs. According to the results of the EDX analysis (Table 4.1), the light grey dendritic matrix is Co-rich and has a high Cr content with smaller amounts of Fe, Ni, and W. The dark grey compounds have a high Cr content, in which the addition of Mo caused substitution of Cr by Mo, whereas the white-colored compounds are found to have high Co, Cr, and W/Mo contents. It can be seen that the Mo content in the white-colored compound increased abruptly after Mo addition, which was offset by a reduction in W content.

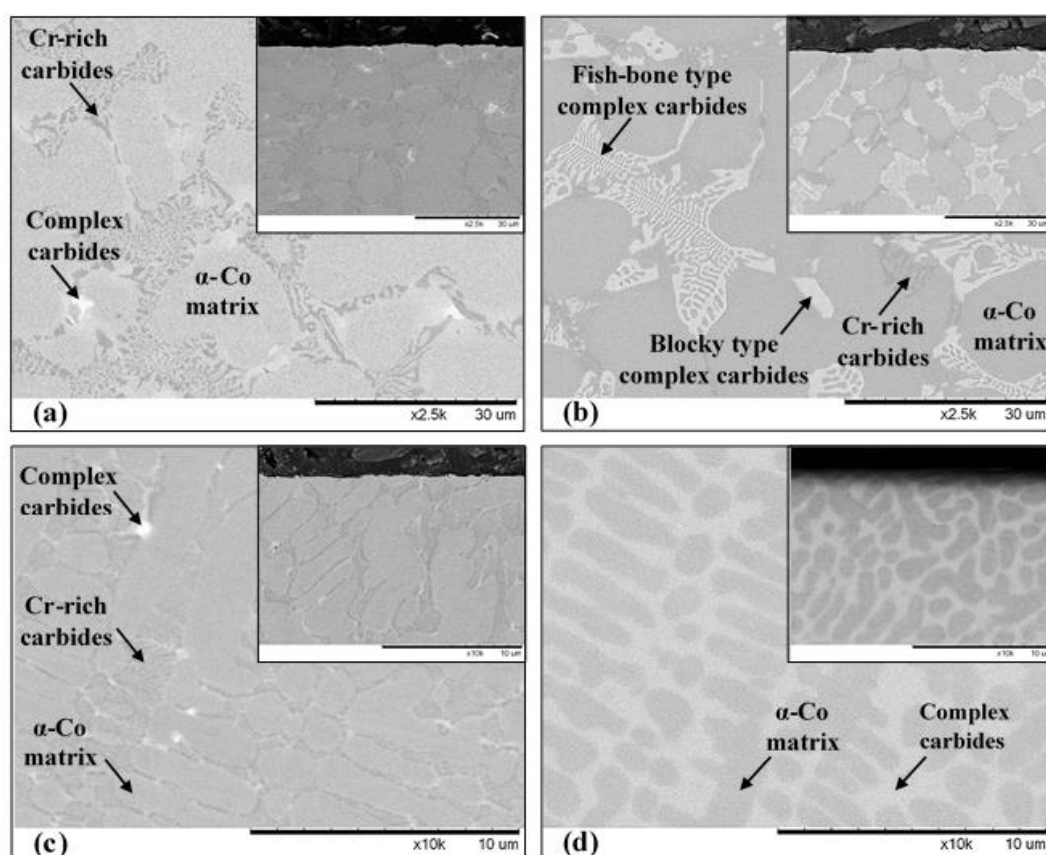


Figure 4.2 : Surface SEM micrographs with the inset of corresponding cross-sectional views of (a) PTA Stellite 6, (b) PTA Stellite 6+10 wt% Mo, (c) EBSM'ed Stellite 6 and (d) EBSM'ed Stellite 6+10 wt% Mo hardfacing.

Table 4.1 : Chemical composition of the constituent phases observed in the SEM micrographs of the examined hardfacings obtained by EDX.

Hardfacing	Microstructure constituents	Co (at%)	Cr (at%)	W (at%)	Fe (at%)	Ni (at%)	Mo (at%)
PTA Stellite 6	Light grey coloured matrix	66.51	25.55	1.06	4.04	2.84	-
	Dark grey coloured compound	20.54	76.98	0.89	1.58	-	-
	White coloured compound	46.88	36.67	13.92	2.53	-	-
PTA Stellite 6+10% Mo	Light grey coloured matrix	63.25	25.78	0.66	3.93	2.77	3.61
	Dark grey coloured compound	29.60	59.24	1.32	2.18	-	7.66
	White coloured compound	39.99	31.59	4.72	0.93	-	22.77
EBSM'ed Stellite 6	Light grey coloured matrix	65.17	24.24	3.70	3.68	3.21	-
	Dark grey coloured compound	19.53	77.57	1.01	1.89	-	-
	White coloured compound	47.32	37.25	12.66	2.77	-	-
EBSM'ed Stellite 6+10% Mo	Light grey coloured matrix	62.54	24.67	0.88	3.40	2.47	6.04
	Dark grey coloured compound	-	-	-	-	-	-
	White coloured compound	48.75	32.90	3.91	1.17	-	12.97

The results of XRD analysis presented in Figure 4.3 revealed that the light grey-colored matrix is α -Co with a face-centered cubic crystal structure (ICCD 01-088-2325). Dark-colored compounds are identified as Cr-rich carbides in the form of M_7C_3 and $M_{23}C_6$ (ICCD 00-036-1482 and ICCD 00-003-1172, respectively), and the white-colored compounds represent the complex carbides in the form of M_6C (ICCD 00-023-09390). It should be mentioned that M_7C_3 and $M_{23}C_6$ Cr-rich carbides were not distinguishable from each other in microstructural appearance. On the relevant XRD patterns, alloying of Stellite 6 with 10 wt% Mo (Figure 4.3b) resulted in the detection of additional peaks, which were indexed as complex carbides in the form of M_6C , whereas the peaks related to M_7C_3 Cr-rich carbides disappeared. XRD analysis of EBSM Stellite 6 hardfacing (Figure 4.3c) showed that the constituent phases are similar to those of PTA Stellite 6, whereas in the EBSM'ed Mo-alloyed Stellite 6 (Figure 4.3d), peaks related to Cr-rich carbides were no longer observed. This indicated that its microstructure only consisted of an α -Co matrix and complex carbides (M_6C).

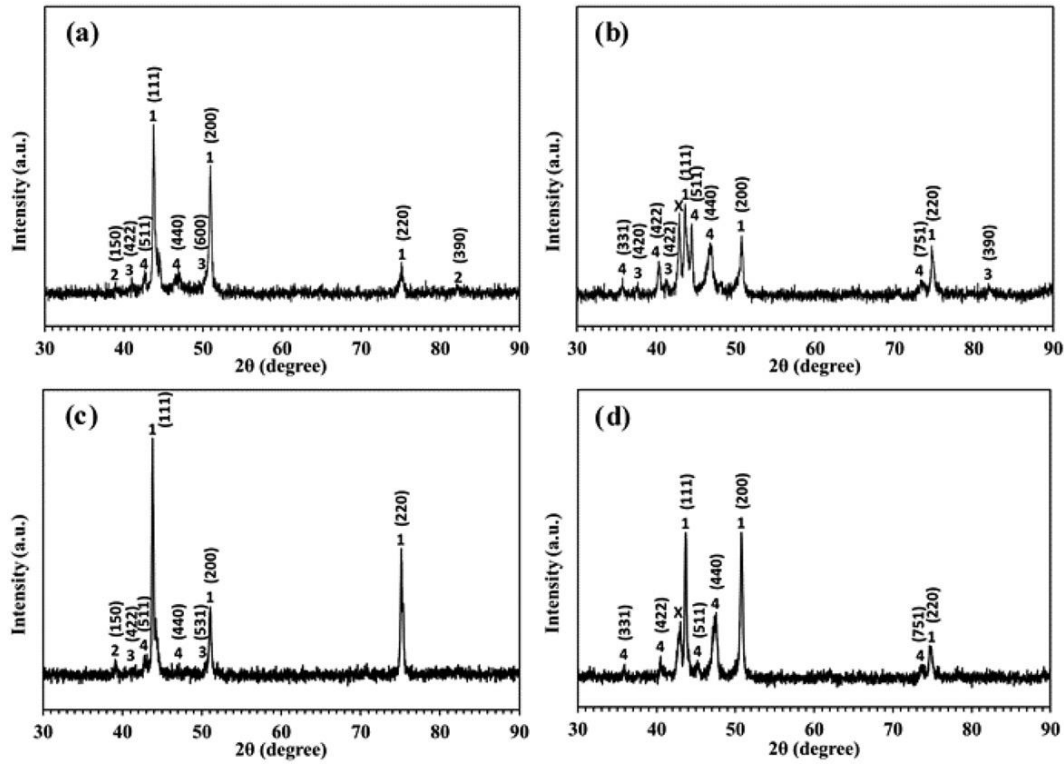


Figure 4.3 : XRD patterns of (a) PTA Stellite 6, (b) PTA Stellite 6+10 wt% Mo, (c) EBSM'ed Stellite 6 and (d) EBSM'ed Stellite 6+10 wt% Mo hardfacings.
1: α -Co, 2: M_7C_3 , 3: $M_{23}C_6$, 4: M_6C and X: unidentified peak.

The quantified volume fraction and average size of constituent phases along with the surface hardness of the examined hardfacings are provided in Table 4.2. It is evident that the microstructure of PTA Stellite 6 hardfacings (Figures 4.2a and b, respectively) consisted of a dendritic α -Co matrix (with an average size of about 15 μm) surrounded by eutectics of Cr-rich carbides with some blocky complex carbides. However, alloying of PTA Stellite 6 with 10 wt% Mo encouraged the formation of complex carbides (in fishbone and blocky morphologies) but reduced the fraction of Cr-rich carbides. EBSM'ed unalloyed Stellite 6 hardfacing (Figure 4.2c) exhibited a microstructure similar to its PTA version in terms of constituent phases. However, they were extensively refined so that the matrix had an average grain size in the range of 1–5 μm surrounded by submicrometer-sized Cr-rich and complex carbides with average sizes of 1.7 and 0.3 μm , respectively. For the EBSM'ed Mo-alloyed version (Figure 4.2d), only two distinct phases were observed even at higher magnifications, whereby the complex carbides appeared in a network nature (about 1.5 μm in width) and the matrix phase appeared in a fine cellular dendritic morphology (about 2 μm in size) with no evidence of Cr-rich carbides.

Table 4.2 : Quantified volume fraction and average size of constituent phases with the surface hardness of the examined hardfacings.

Hardfacings	Microstructural constituents	Vol. (%)	Average size (μm)	Hardness, HV _{0.5}
PTA Stellite 6	α -Co matrix	65.9 $\pm$ 3	13.5 $\pm$ 2	450 $\pm$ 11
	Cr-rich eutectic carbides	29.8 $\pm$ 2	13.4 $\pm$ 3	
	M ₆ C complex carbides	4.3 $\pm$ 1	1.4 $\pm$ 0.1	
PTA Stellite 6+10% Mo	α -Co matrix	56.4 $\pm$ 3	15.1 $\pm$ 3	545 $\pm$ 11
	Cr-rich eutectic carbides	12.9 $\pm$ 2	6.0 $\pm$ 1	
	M ₆ C complex carbides	30.7 $\pm$ 2	15.9 $\pm$ 4	
EBSM'ed Stellite 6	α -Co matrix	64 $\pm$ 4	3.1 $\pm$ 2	527 $\pm$ 7
	Cr-rich eutectic carbides	31.6 $\pm$ 3	1.7 $\pm$ 0.4	
	M ₆ C complex carbides	4.4 $\pm$ 1	0.3 $\pm$ 0.1	
EBSM'ed Stellite 6+10% Mo	α -Co matrix	43 $\pm$ 1	1.9 $\pm$ 0.6	748 $\pm$ 8
	Cr-rich eutectic carbides	-	-	
	M ₆ C complex carbides	57 $\pm$ 1	1.5 $\pm$ 0.4*	

*Average width of carbides' network.

Taking into consideration the volume fractions of constituent phases, it can be seen in Table 4.2 that the volume fraction of Cr-rich carbides was more than half lower in Mo-alloyed PTA Stellite compared to PTA Stellite 6 hardfacing. Application of the EBSM process caused the disappearance of Cr-rich carbides in Mo-alloyed Stellite 6 and favored the highest volume fraction of the complex carbides in the microstructure (about 14 times more than that of PTA Stellite 6). Alloying with 10 wt% Mo caused a severe increment in the volume fraction of complex carbides in the PTA state (about seven times), whereas the EBSM process did not alter the volume fractions of microstructural constituents in Stellite 6 hardfacing. In general, the total carbide volume fractions increased from 34% (in PTA Stellite 6) to 43 and 57% upon alloying with Mo and application of EBSM to Mo-alloyed hardfacing, respectively. As a result of these microstructural changes, the addition of 10 wt% Mo caused an almost 21% increment in hardness of PTA Stellite 6. The subsequent EBSM process of the unalloyed and alloyed Stellite 6 hardfacings led to increases of 17 and 66%, respectively, in surface hardness compared to the PTA Stellite 6.

2D profiles of the WTs formed on the surfaces of the examined hardfacings tested under loads of 1 N and 4 N are shown in Figure 4.4. A comparison across wear testing loads shows that increasing the load resulted in wider and deeper WTs. Yet, if compared across hardfacings, it can be noticed that Mo addition resulted in a smaller WT area compared to those on PTA Stellite 6 at the same testing load, and this trend

continued for the EBSM version of Mo-alloyed Stellite 6 hardfacing. However, unalloyed EBSM Stellite 6 showed different trends during wear tests, where larger WTs were formed compared to PTA Stellite 6 hardfacing.

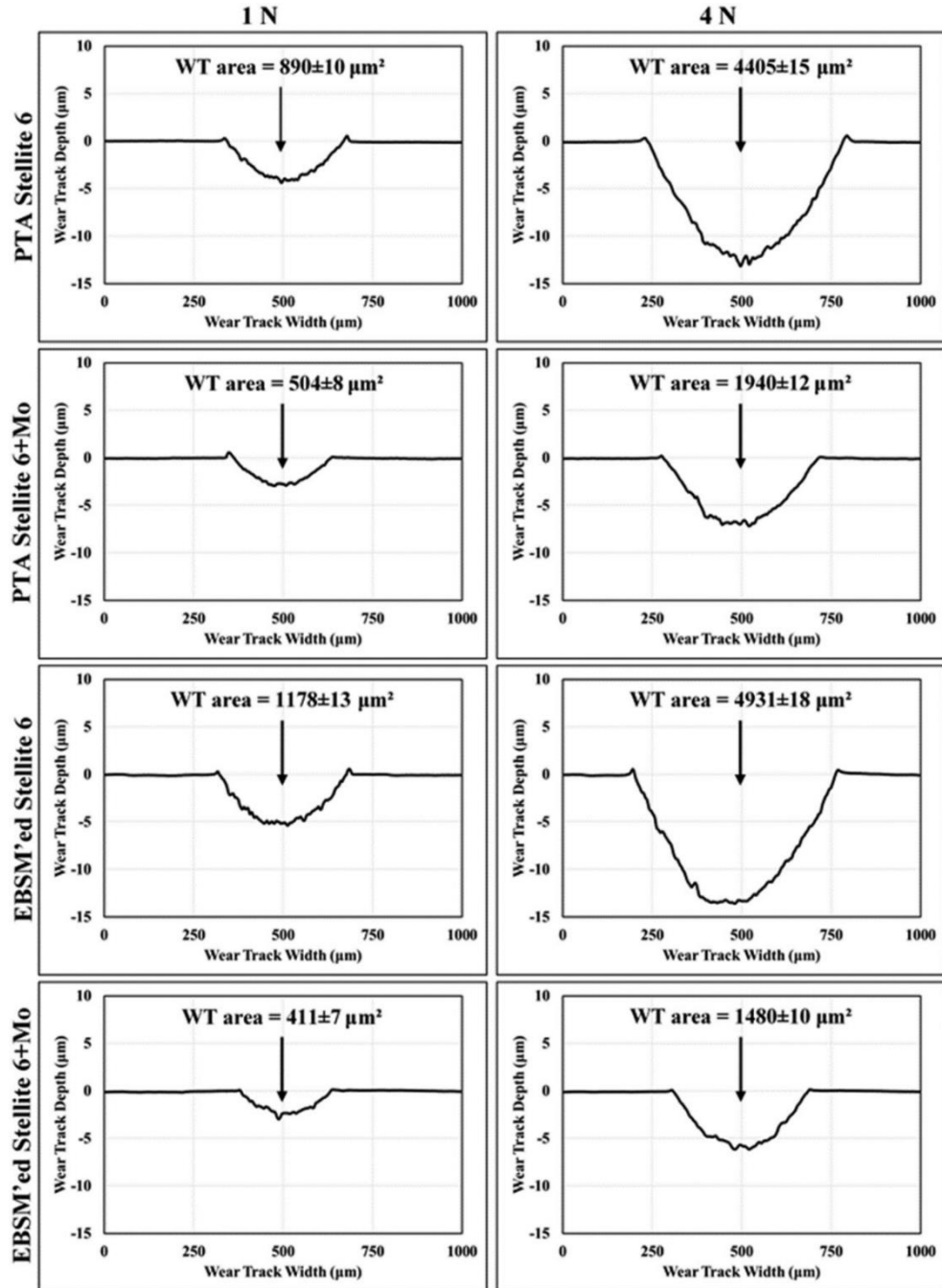


Figure 4.4 : 2D profiles formed on the surface of the examined hardfacings under testing loads of 1 N and 4 N.

Table 4.3 presents the relative wear rate (RWR) of the examined hardfacings. The values are taken by considering the WT area of PTA Stellite 6 hardfacing worn at the testing load of 1 N as 1.0. The WT areas of Mo-alloyed PTA Stellite 6 and the EBSM versions of unalloyed and alloyed Stellite 6 hardfacings tested at 1 N and 4 N were

divided by that of PTA Stellite 6 hardfacing. At the testing load of 1 N, the RWR value of Mo-alloyed PTA Stellite 6 was almost 0.55, but for unalloyed and alloyed EBSM versions of Stellite 6 they were 1.32 and 0.45, respectively. However, when the testing load was increased to 4 N, the RWR value of PTA Stellite 6 was approximately 5.0, whereas after Mo addition it was almost twice that of PTA Stellite 6 at 1 N. For unalloyed and alloyed EBSM Stellite 6 samples, the RWR values were 5.55 and 1.66, respectively. Among the data listed in Table 4.3, minimum RWR values were obtained from Mo-alloyed EBSM Stellite 6 hardfacings at both testing loads of 1 N and 4 N.

Table 4.3 : RWR results of the examined hardfacings.

Hardfacing	RWR	
	1 N	4 N
PTA Stellite 6	1.00	4.95
PTA Stellite 6+10 wt% Mo	0.55	2.18
EBSM'ed Stellite 6	1.32	5.55
EBSM'ed Stellite 6+10 wt% Mo	0.45	1.66

SEM micrographs of the worn surfaces of the examined hardfacings are shown in Figure 4.5. At the testing load of 1 N, the worn surfaces of unalloyed and alloyed PTA Stellite 6 exhibited discontinuous grooves on their matrices, which were deeper for the unalloyed sample. Cracking of carbides into fine fragments followed by removal can be observed on both hardfacings, with less severity on the alloyed version. For the EBSM hardfacings, the worn surface appearances of the unalloyed and alloyed versions did not show any carbide cracking and removal. In terms of matrix grooving, continuous ploughing was observed on the worn surface of the unalloyed sample as opposed to its alloyed version. In addition, oxide patches were detected on the worn surface of Mo-alloyed EBSM hardfacing.

For the wear testing load of 4 N, the worn surface of unalloyed PTA hardfacing exhibited severe damage in terms of carbide cracking and removal, but this phenomenon was less severe for its alloyed version. In addition, fatigue damage and oxides patches were evident on the surfaces of both versions in equal severity in terms of coverage. For EBSM hardfacings worn under the load of 4 N, the unalloyed version showed the presence of small particles of different shapes and sizes locally accumulated within the wear grooves (enclosed by dashed ellipses in Figure 4.5), but evidence of oxidation and fatigue damage was absent. On the other hand, the alloyed

version did not show the presence of fragmented particles, although more severe oxidation/fatigue damage can be seen on the worn surfaces.

The appearance of the counterface alumina ball after wear tests is shown in Figure 4.6. The contact surface of the alumina ball has dark-colored patches as evidence of material transfer from the mating surface (marked by the circles) and scratches (marked by arrows). Compared to the unalloyed PTA hardfacing, the EBSM version of Stellite 6 hardfacing imposed severe scratches on the contact surface of the alumina ball at the expense of material transfer. For the Mo-alloyed PTA version, both features (material transfer and scratches) appearing on the contact surface of the alumina ball were of mild severity. Finally, the EBSM version of the alloyed hardfacing showed very minor material transfer to the alumina ball. However, these features were not very clearly identified after the wear test at the load of 1 N.

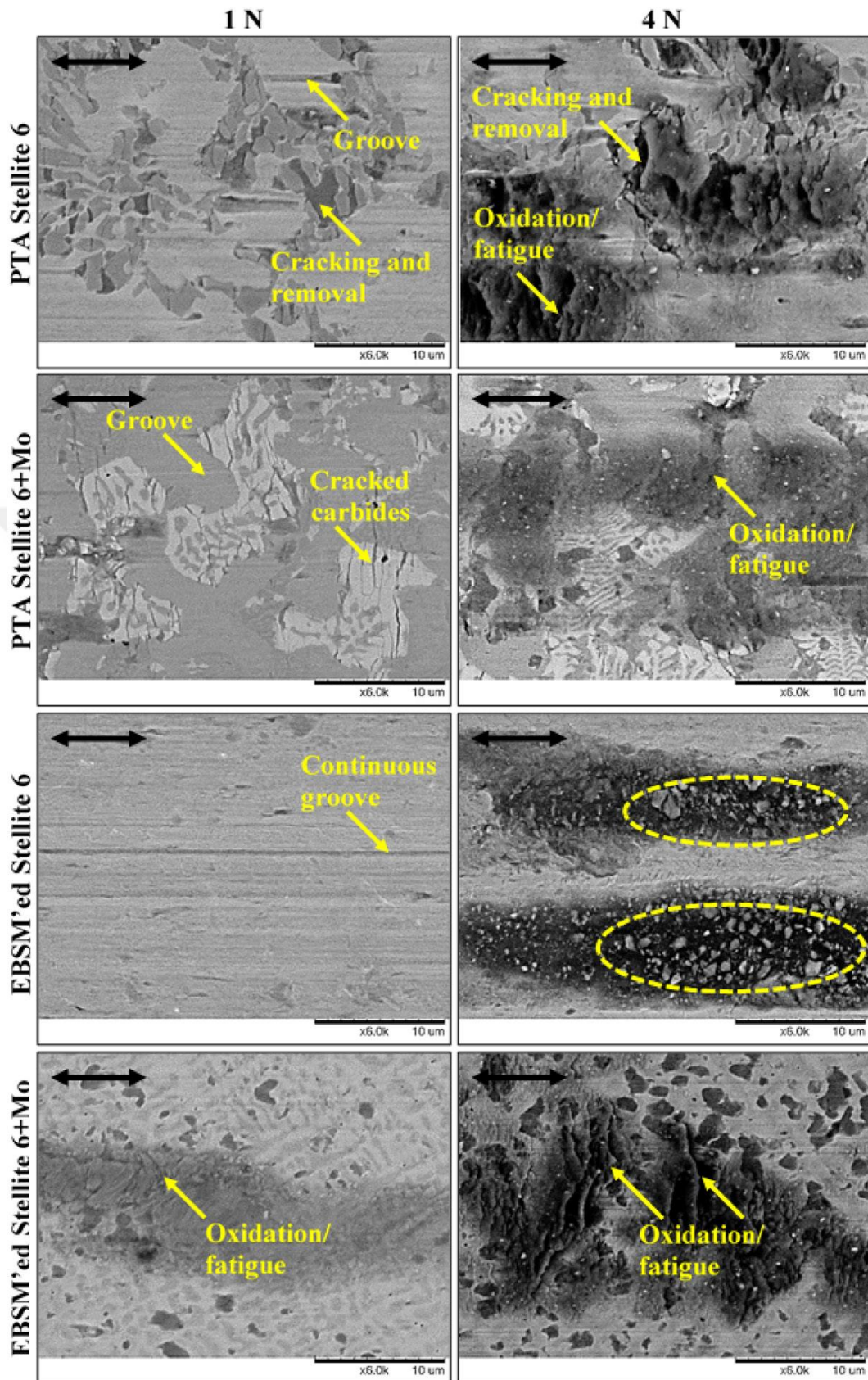


Figure 4.5 : SEM micrographs of the worn surfaces of the examined hardfacings.
The transverse arrows on the upper left corners show the sliding direction.

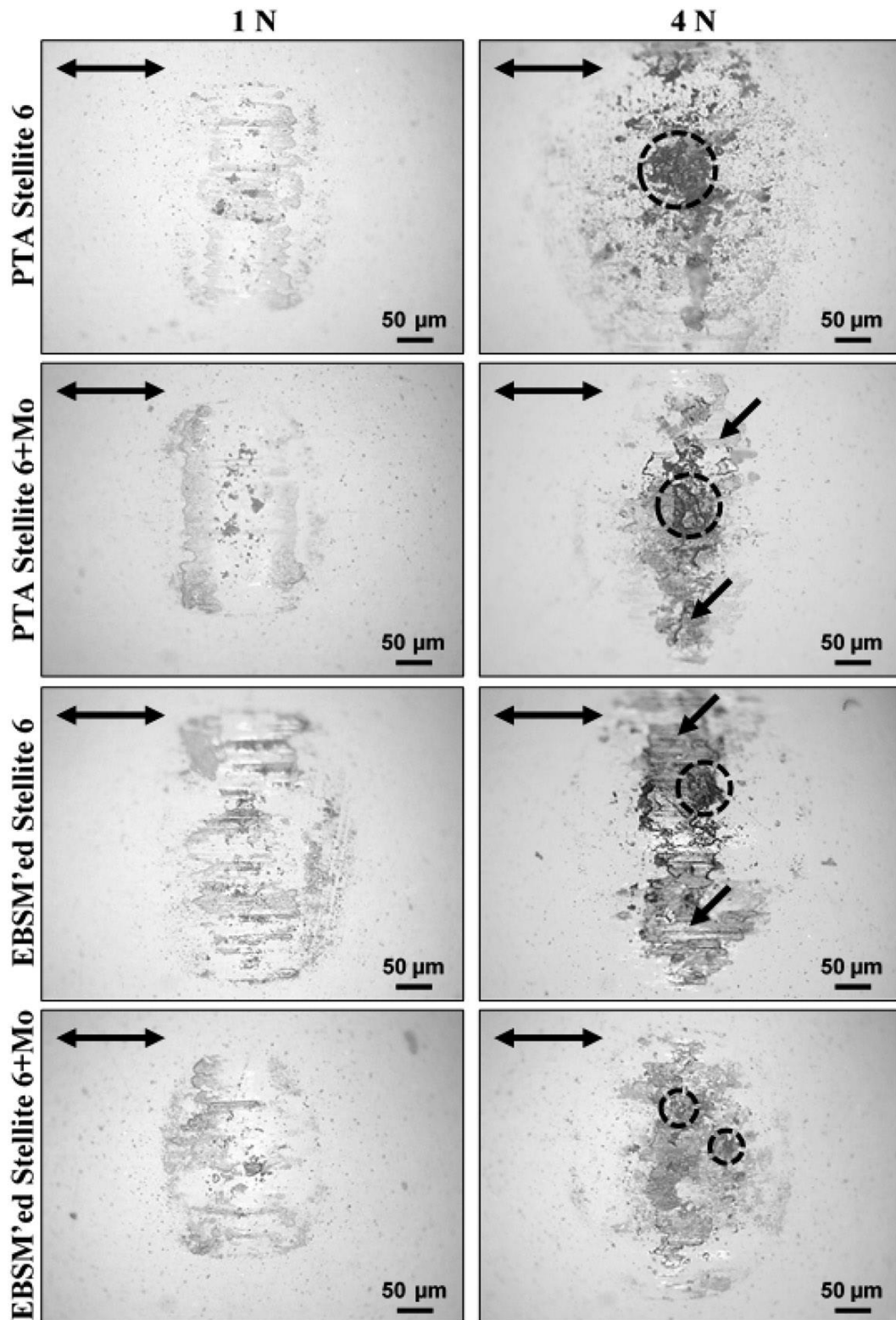


Figure 4.6 : The appearance of the counterface (alumina ball) worn at 1 N and 4 N testing loads against the examined hardfacings. The transverse arrows on the upper left corners show the sliding direction.

4.4 Discussion

The microstructure of PTA Stellite 6 hardfacing is similar to that reported for as-cast Stellite 6; that is, a hypoeutectic structure featuring primary α -Co dendrites surrounded by Cr-rich eutectic carbides (M_7C_3 and $M_{23}C_6$) with some minor fractions of M_6C complex carbides [103,160,187,188]. However, the addition of 10 wt% Mo resulted in a considerable increase in the volume fraction of M_6C complex carbides at the expense of some of M_7C_3 Cr-rich carbides yielding an overall increase in carbide volume fraction. The high tendency toward the formation of Mo-rich complex carbides can be attributed to the lighter atomic weight and smaller atomic size of Mo compared to those of W, which allow higher mobility during solidification in addition to the great affinity for C [124,168,189]. As the M_6C complex carbides formed, C in the remaining liquid was depleted and therefore the low carbon concentration favored the formation of $Cr_{23}C_6$ rather than Cr_7C_3 in the microstructure [122,190]. These findings are in accordance with studies regarding Mo addition in Stellite 6 [121,122] and in Stellite 12 [124,155].

In the EBSM versions, rapid solidification of the melt due to the large inequality between the volume of the melt pool and that of solid bulk underneath it led to heat removal toward the cooler bulk, which resulted in directional solidification. This ensured the formation of very fine microstructures due to several nucleation events coupled with limited growth rates [156,190,191]. In this respect, the high cooling rates after EBSM resulted in a microstructure identical to that of its PTA state, only at a much finer scale. Alloying of Stellite 6 with 10 wt% Mo caused solidification of the melt pool in hypereutectic mode after the EBSM process [119]. In this regard, the primary phase to solidify for the EBSM Mo-alloyed hardfacing is thought to be M_6C complex carbides followed by solidification of the Co matrix in a cellular dendritic nature [116]. Further, rapid cooling conditions are known to suppress the formation of Cr-rich carbides; hence, the Co matrix is richer in Cr for the EBSM version of Mo-alloyed hardfacing [192]. As far as the melt pool geometry is concerned, the difference in penetration depths of the electron beam between the unalloyed and alloyed Stellite 6 samples can be attributed to the reduction of the melting point of Stellite 6 hardfacing upon Mo addition [156].

The increment in hardness upon Mo addition can be associated with factors such as the increased overall fraction of carbides, solid solution hardening of the Co matrix

due to Mo dissolution, and the replacement of softer Cr-rich carbides with harder complex carbides [30,168]. For EBSM unalloyed hardfacing, the increment in hardness can be related to extensive refinement of the microstructure [176]. The highest hardness for the alloyed EBSM hardfacing is attributed to its hypereutectic solidification mode coupled with its very fine microstructure [114].

The changes in the microstructure not only affected the hardness but also influenced the sliding wear response of these hardfacings. For unalloyed PTA hardfacing at a 1 N wear testing load, the wear progressed by matrix grooving and carbide cracking, but for the alloyed version, these mechanisms were suppressed due to the decreased volume fraction of the matrix and larger fraction of harder complex carbides, leading to 45% better wear resistance [122,124,155]. A similar mechanism is operative in the EBSM version of alloyed hardfacing, which showed the highest wear resistance, in accordance with its highest hardness, due to a carbide-rich hypereutectic microstructure and the appearance of oxide patches on worn surfaces [30,96]. Despite improved hardness, the EBSM version of unalloyed hardfacing showed the lowest wear resistance, which is attributed to the formation of fine carbides that did not provide the desired protection against wear compared to the PTA state [23,94].

For the highest testing load of 4 N, the wear resistance followed the same pattern whereby the wear progressed by severe cracking and removal of carbides along with oxidation and fatigue damage in unalloyed PTA hardfacing, resulting in more than five times higher wear loss compared to the wear loss at 1 N. This confirms the inability of Cr-rich carbides to adequately resist the destructive action of the counterface when the contact pressure is beyond their compressive strength [155]. For the alloyed PTA version of Stellite 6, the wear mechanism is predominantly oxidation and fatigue, and the higher fraction of carbides is still resistant to cracking at testing load of 4 N. Thus, the absence of carbide cracking imparts a 100% improvement in wear resistance compared to the unalloyed version at a testing load of 4 N. Interestingly, the best wear resistance was obtained from the alloyed EBSM hardfacing in which wear progressed by severe oxidation and fatigue with no discernable signs of carbide cracking. The higher fraction of carbides and finer size of matrix grains contributed to severe oxidation, which is thought to reduce wear by providing a barrier against direct contact between the counterface and the hardfacing [156,189]. It is also suggested that the interconnected complex carbides appear to be more effective in protecting against

wear in contrast to isolated carbide particles [194]. Increasing the wear testing load to 4 N increased the wear damage almost six fold for the unalloyed EBSM hardfacing. The mechanism in this case is pull-out of weakly supported finer carbides. Their removal during sliding action has the potential to deteriorate the wear resistance, because they are unable to resist its destructive action. Further, it is suggested that the accumulation of large volumes of detached carbides within the grooves of the worn surfaces results in third-body abrasion, which accelerates material removal from the softer matrix [20,194].

On the basis of the above explanations, it was determined that the wear properties of Stellite 6 hardfacing are strongly affected by the size, volume fraction, and morphology of carbide phases. It was clearly observed that coarse carbides (mainly Cr-rich ones) of PTA unalloyed and Mo-alloyed hardfacings tended to crack easily and their subsequent removal accelerated the wear rate, as reported in previous studies [122,134]. Application of the EBSM process provided better wear resistance in Mo-alloyed Stellite 6 hardfacing by refining the microstructure and favoring complex carbide formation in a network-like morphology. In this context, the closed spacing of carbides at the surroundings of the Co matrix was reported to have a beneficial effect on the wear resistance by supporting the matrix and reducing its ability to undergo plastic flow [157]. However, the individual dispersion of fine carbides (as in the case of EBSM Stellite 6 hardfacing) caused a reduction in wear resistance because they could be easily pulled out from the Co matrix.

4.5 Conclusion

The results of the current study that examined the influence of Mo addition and application of EBSM as a post treatment on the microstructure and surface-related mechanical properties of PTA Stellite 6 hardfacing are summarized as follows:

1. The hardness and sliding wear resistance of PTA Stellite 6 hardfacing were improved by the addition of 10 wt% Mo due to the increase in the volume fraction of carbides. Furthermore, Mo favored the formation of complex carbides (M_6C) at the expense of Cr-rich carbides (M_7C_3 and $M_{23}C_6$).
2. Application of the EBSM process caused a refinement in the sizes of the Co matrix and carbides and a consequent increase in hardness. With regard to the volume fraction of the carbides, there was no remarkable difference between

PTA Stellite 6 and its EBSM version. In the case of Mo-alloyed Stellite 6, application of EBSM increased the volume fraction of carbides by the formation of complex carbides in a network morphology rather than eutectic Cr-rich carbides.

3. The improved wear resistance of Mo-alloyed Stellite 6 hardfacings followed the increment in hardness pattern whereby the increased volume fraction of coarser complex carbides resisted the counterface action in the PTA state. The higher fraction of network-like complex carbides in the EBSM version resulted in the formation of protective oxide patches, providing a shield against the wear action of the counterface.
4. Counterintuitively, the increment in hardness of the Stellite 6 hardfacing following EBSM treatment did not result in better wear resistance, which can be attributed to easier removal of the finer carbides from the matrix, which accelerated material loss in the absence of an effective oxide layer barrier.
5. Under the employed contact pressures (800 and 1,200 MPa), the best sliding wear resistance was obtained from Mo-alloyed Stellite 6 hardfacing after application of the EBSM process as a post treatment.

5 ROOM AND HIGH TEMPERATURE SLIDING WEAR CHARACTERISTICS OF LASER SURFACE MELTED STELLITE 6 AND Mo-ALLOYED STELLITE 6 HARDFACINGS ⁴

5.1 Introduction

Stellite alloys are the most popular group of Co-based alloys especially for oil and gas, automotive, aerospace and nuclear industries, etc., where enhanced wear and/or high temperature (HT) and/or corrosion resistances are the main requirements. In their composition, they contain about 30 wt.% Cr with C varying in range of 0.25 to 2.5 wt.% along with W (up to 14.5 wt.%) or Mo (up to 9 wt.%). Carbide forming elements such as W and Mo contribute towards hardness and wear resistance not only by forming carbides at high fractions but also strengthening of the Co-matrix by solid solution hardening mechanism [2,12,195,196]. Due to the high cost and poor machinability of bulk products, Stellite alloys are most widely used as coatings (hardfacings) to protect relatively soft alloys against wear under harsh service conditions [78,161]. Even with their superior wear performance, some attempts have been made to extend the service life of Stellite hardfacings via alloying during deposition [122,123,125-127,129] and/or by post laser and electron beam surface melting treatments [137-140,178,197], which provide rapid cooling and solidification of the re-melted surfaces by the cooler underlying metal. Although electron beam surface melting treatment offers some advantages like minimal part distortion, high repeatability and controlled depth of processed layers; laser surface melting (LSM) is favored due to simpler operation and not needing for vacuum conditions, enabling the processing of larger components [179].

In this context, our interest on PTA deposited Stellite hardfacing started with alloying of W containing Stellite 12 (having nominal composition of 30 wt.% Cr, 8.5 wt.% W and 1.45 wt.% C) with 10 wt.% Mo, which led to increment in hardness and sliding wear resistance both at room temperature (RT) and HT (300-700 °C) [124]. Another

⁴ This chapter is based on the paper “Room and High Temperature Sliding Wear Characteristics of Laser Surface Melted Stellite 6 and Mo-alloyed Stellite 6 Hardfacings”, published in “Journal of Materials Engineering and Performance 30-1 (2021) 302-311, <https://doi.org/10.1007/s11665-020-05375-8>.”

study made with the aim of evaluating the effect of post LSM treatment on the RT sliding wear performance of PTA Stellite 12 hardfacings revealed that, LSM has a potential to enhance the wear resistance by refining the microstructure [150]. Employing post LSM treatment to 10 wt.% Mo-alloyed PTA Stellite 12 hardfacing, in a following study, showed an additional improvement in hardness and RT wear resistance owing to the formation of a unique carbide structure [155]. Beneficial effect of combination of Mo alloying and post LSM treatment on HT (500 °C) sliding wear resistance of Stellite 12 hardfacing has been reported in our latest study [156]. In brief, these studies clearly showed that alloying with carbide forming elements like Mo and employing LSM as a post treatment, separately or in combination, played a crucial role on microstructure and, hence, wear resistance of Stellite 12 hardfacing.

Motivated by how the similar modification strategies (i.e. Mo alloying and LSM post treatment) affect the microstructure and, hence, the associated surface properties of a Stellite alloy with lower contents of C and carbides forming elements; authors have chosen Stellite 6 hardfacing having nominal composition of 28.5 wt.% Cr, 4.6 wt.% W and 1.2 wt.% C [156] for this study. In this regard, microstructures and sliding wear performances (at RT and HT) of LSM'ed Stellite 6 hardfacing and LSM'ed Mo-alloyed Stellite 6 hardfacings were evaluated and compared with those of commercial PTA Stellite 6 hardfacing.

5.2 Experimental procedure

Commercially available Co-based Stellite 6 powder and its 10 wt.% Mo added version were deposited separately on 4140 steel substrates by PTA technique in a single layer with a thickness of 5 mm. The surfaces of deposits were then flattened by grinding to a thickness of 2.5 mm using a surface grinding machine. A single pass of continuous mode carbon dioxide laser was applied to melt the surface, of unalloyed and Mo-alloyed deposited hardfacings, using a CNC table to ensure the controlled movement of the processed specimen under the laser beam ensuring a uniform distribution of the heat input. Laser melting tracks were partially overlapped in order to fully cover the surface and nitrogen shielding gas was fed through a nozzle to avoid any probability of oxidation during the process. Principle parameters of PTA and LSM processes are listed in Table 5.1.

Table 5.1 : Principle parameters used during PTA and the post LSM processes.

Process	Process Parameters	
PTA	Current	95 A
	Voltage	35 V
	Travel speed	90 mm/min
	Plasma gas flow rate	3 liter/min
	Feeding gas flow rate	3 liter /min
	Shielding gas flow rate	20 liter /min
LSM	Focal length	120 mm
	Laser beam diameter	2.5 mm
	Scanning speed	375 mm/min
	Overlap width	0.3 mm
	Shielding gas flow rate	10 liter/min
	Shielding gas pressure	50 kPa

The microstructural features of the hardfacings were surveyed by scanning electron microscopes (SEM, Hitachi TM-1000 Tabletop Microscope, Japan, in secondary electron (SE) mode and Energy dispersive X-ray spectrometer EDX equipped SEM, Zeiss-Ultra Plus, Germany, in back scattered electron BSE mode). For this purpose, surface and cross-sectional specimens were manually ground using a series of silicon carbide papers from 600 to 2500 grit and then polished with 9, 6, 3, 1 and 0.05 μm diamond paste before cleaning with alcohol. During metallographic preparation, surface cracks were detected on the LSM'ed Mo-alloyed Stellite 6. According to the statements in previous works related with laser surface treatments [156,198-200], they were assumed as tolerable surface cracks.

Mechanical properties of the hardfacings were determined by hardness and sliding wear tests. For hardness measurements, a conventional Vickers microhardness tester (Shimadzu, HMV2, Japan) was used with indentation load of 500 g. The number of indentations for each sample were 10 with mutual distance between indentations of more than 10 times the indent diagonal.

Sliding wear tests were conducted at RT and 500 °C under ball-on-flat configuration using reciprocating wear tester (Tribotech™ Oscillating Tribotester, France) and ball-on-disc configuration (CSM High temperature tribotester, Switzerland), respectively, with the parameters given in Table 5.2. At each testing load three wear tests were done. Examples of wear tracks formed on the surfaces of hardfacings after sliding wear tests conducted under ball-on-flat (reciprocating) and ball-on-disc configurations at RT and 500 °C, respectively, are shown in Figure 5.1. It should be notified that in order to examine the sole wear characteristics of the hardfacings, alumina balls (Al_2O_3) supplied by CSM with purity of 99.8%, hardness of 1900 HV and surface roughness

of 0.02 μm were used as the counterface. After the wear tests, wear tracks (WT) were analyzed by using a 2D contact type profilometer (Dektak-6M, Veeco, USA) at 5 different locations. Worn surfaces were also examined by SEM in SE mode and Raman spectroscopy under excitation wavelength of 532 nm (Renishaw, inVia Reflex spectrometer, UK). Additionally, cross-section of the WTs were surveyed by a SEM.

Table 5.2 : Operational parameters used for sliding wear tests.

Testing Temp.	Testing Parameters	
RT	Configuration	Ball-on-flat
	Testing loads	1, 2, 3, 4 N
	WT length	5 mm
	Sliding speed	10 mm.s ⁻¹
	Total sliding distance	100 m
	Relative humidity	25 $\pm$ 3%
	Counter body	Al ₂ O ₃ ball (6 mm in diameter)
500 °C	Configuration	Ball-on-disc
	Testing load	3 N
	WT Radius	4 mm
	Sliding speed	10 mm.s ⁻¹
	Total sliding distance	500 m
	Relative humidity	25 $\pm$ 3%
	Counter body	Al ₂ O ₃ ball (6 mm in diameter)



Figure 5.1 : Macroscopic photographs of the WTs after (a) RT and (b) HT sliding wear tests employed under ball-on-flat (reciprocating) and ball-on-disc configurations, respectively.

5.3 Results

5.3.1 Microstructural Examinations

Surface SEM microphotographs of the examined hardfacings are presented in Figure 5.2. Considering the results of the EDX analysis given in Table 5.3 and relevant studies conducted on Stellite 6 alloy [121,122,190,201,202], microstructural constituents are

displayed on the low magnification SE-SEM microphotographs of Figure 5.2 (the left column). In general, the microstructures of PTA Stellite 6 and LSM'ed Stellite 6 hardfacings (Figure 5.2a and b, respectively) consisted of Co-matrix, eutectic carbides (Cr-rich) and blocky complex carbides (W-rich). Application of LSM to PTA Stellite 6 hardfacing refined the microstructure so that the average grain size of the Co-matrix was decreased from ~ 15 to ~ 5 μm , while the size and fraction of W-rich complex carbide were also reduced. The higher magnification BSE-SEM microphotographs (the right column of Figure 5.2) therefore revealed that average inter-lamellar spacing of eutectic carbides was reduced from about 1 μm to 150 nm after the LSM process.

On the other hand, application of LSM to PTA Mo-alloyed Stellite 6 hardfacing as a post treatment yielded a microstructure composed of two phases (Figure 5.2c); Co-matrix in a fine cellular morphology (~ 2 μm grain size) and complex carbides in a network like structure without any evidence of eutectic carbide precipitation. The results of EDX analysis conducted on the LSM'ed Mo-alloyed Stellite 6 hardfacing (Table 5.3) show that Mo had a significant participation in the chemical composition of constituent phases alongside Co and Cr. It is noteworthy that the Mo content in complex carbides were about three times than that found in Co-matrix. The LSM'ed layer was also found to be thicker in the Mo-alloyed Stellite 6 hardfacing as compared to the unalloyed Stellite 6 hardfacing, i.e. it was ~ 85 μm for the former and ~ 60 μm for the later as estimated from the cross section SEM microphotographs.

The results of the hardness measurements conducted on the surfaces of the examined hardfacings are given in Table 5.4. Application of post LSM treatment on PTA Stellite 6 hardfacing caused about 13% increment in the hardness, while combination of Mo alloying and LSM process in one strategy provided 44% higher hardness as compared to PTA Stellite 6 hardfacing.

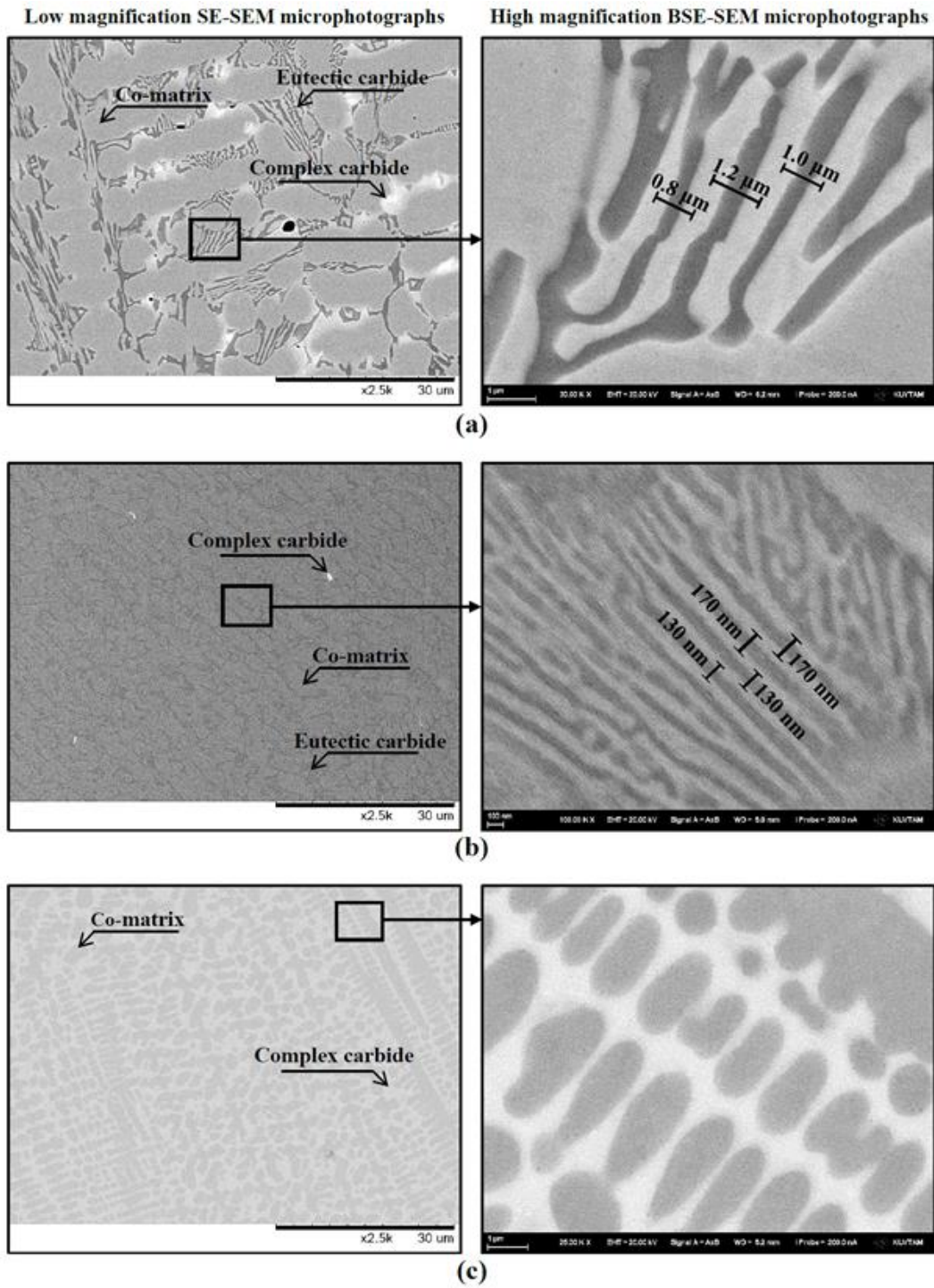


Figure 5.2 : Surface SE- and BSE-SEM microphotographs of (a) PTA Stellite 6, (b) LSM'ed Stellite 6 and (c) LSM'ed Mo-alloyed Stellite 6 hardfacings.

Table 5.3 : Results of the EDX analysis conducted on the examined hardfacings.

Versions of Stellite 6	Phases observed during SEM scanning	Co %at	Cr %at	W %at	Fe %at	Ni %at	Mo %at
PTA	Co-Matrix	66.51	25.55	1.06	4.04	2.84	-
	Eutectic Carbide	20.54	76.98	0.89	1.58	-	-
	Complex Carbide	46.88	36.67	13.92	2.53	-	-
LSM'ed	Co-Matrix	65.17	24.24	3.70	3.68	3.21	-
	Eutectic Carbide	19.53	77.57	1.01	1.89	-	-
	Complex Carbide	47.32	37.25	12.66	2.77	-	-
LSM'ed Mo-alloyed	Co-Matrix	64.33	24.18	1.01	3.79	2.39	4.30
	Complex Carbide	44.15	36.76	2.52	2.53	1.60	12.45

Table 5.4 : Average results of the hardness tests conducted on the surfaces of the examined hardfacings.

Hardfacing	Average Hardness
PTA Stellite 6	470 ± 8 HV
LSM'ed Stellite 6	529 ± 10 HV
LSM'ed Mo-alloyed Stellite 6	677 ± 17 HV

5.3.2 RT Wear Tests

Results of the reciprocating wear tests conducted at RT are presented in Figure 5.3 as plots of variation of volumetric wear loss per unit sliding distance (V , mm^3/m) with respect to wear testing loads (P , N). For all the examined hardfacings, the increase of P imposed higher V values linearly, where the slopes represent normalized wear coefficient (K , mm^3/Nm) of the respective hardfacings. The highest K value was obtained from PTA Stellite 6 hardfacing, and application of LSM process as a post treatment caused about 26 % reduction in the K value. In the case of the LSM'ed Mo-alloyed version, the reduction in K was about 74 % with reference to the PTA Stellite 6 hardfacing.

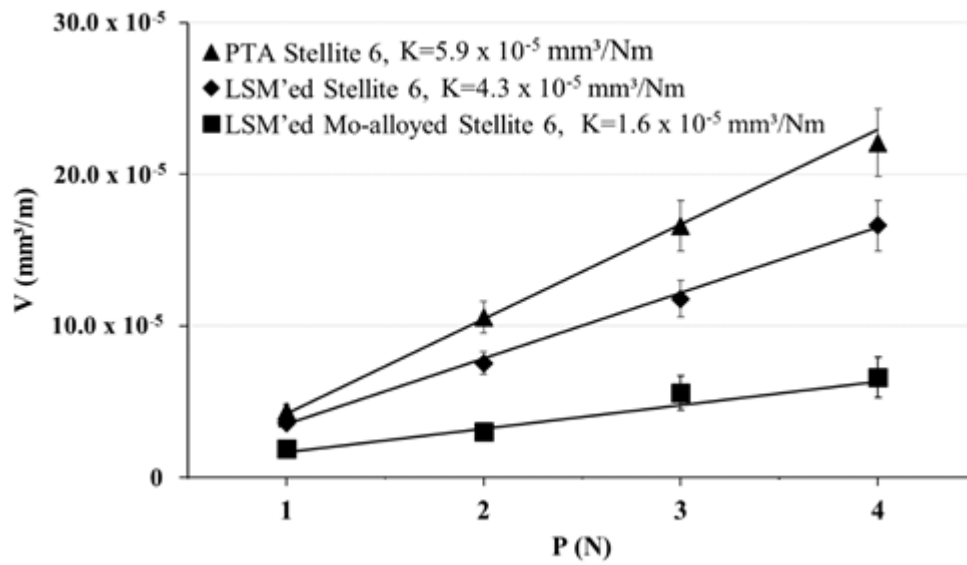


Figure 5.3 : Results of the RT wear tests of the examined hardfacings presenting the variation of V with respect to P. V was calculated from the average WT area (mm^2), WT length (mm) and total sliding distance (m).

Since the linear relationship between V and P indicates no remarkable difference in the operative wear mechanism with respect to P, worn surface appearances of the hardfacings tested under the highest load (4 N) employed in this study are given in Figure 5.4. According to the SEM microphotographs, dominant RT wear mechanism was determined as abrasive wear, owing to detection of abrasion grooves aligned in the sliding direction of the counterface [3]. It can be noted that, abrasion grooves on the worn surfaces of the LSM'ed hardfacings (Figure 5.4b and c) were of scratch type as compared to those on the worn surface of PTA Stellite 6 hardfacing, wherein the fragmentation of eutectic carbides (to sizes of about $2 \mu\text{m}$ as depicted in Figure 5.4a) was observed. In this respect, the highest K value of the PTA Stellite 6 hardfacing and formation of deeper abrasion grooves on its worn surface can be associated with the removal of relatively coarse ($\sim 2 \mu\text{m}$ in size) carbide fragments, imposing three body abrasive effect between the matting surfaces [72,203]. From this point of view, the formation of shallow abrasion grooves could be the result of fine (sub-micron sized) third bodies having relatively limited abrasion capability as compared to coarse micron sized ones (as in PTA Stellite 6 hardfacing).

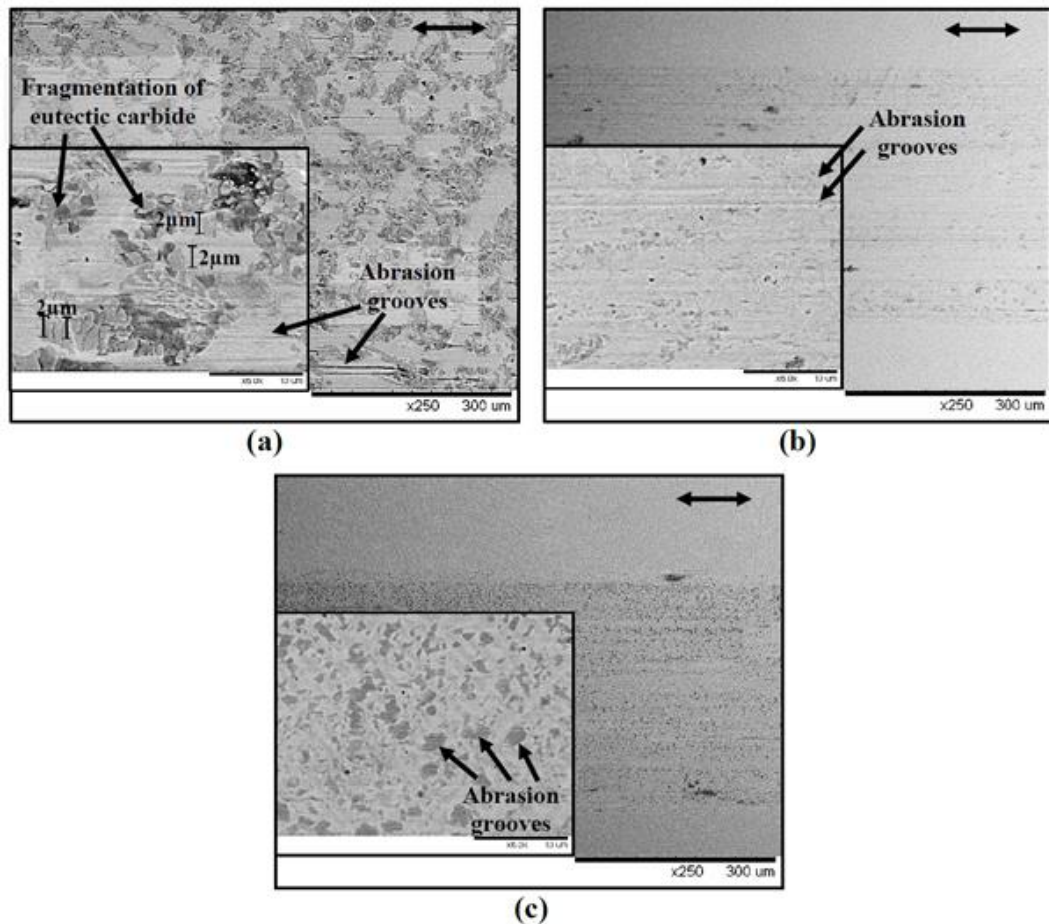


Figure 5.4 : Worn surface SE-SEM microphotographs of (a) PTA Stellite 6, (b) LSM'ed Stellite 6 and (c) LSM'ed Mo-alloyed Stellite 6 hardfacings after RT wear tests. (The transverse arrows in the upper right corners indicate the sliding direction).

5.3.3 HT Wear Tests

Normalized wear loss (K) values were calculated as; $3.0 \times 10^{-5} \text{ mm}^3/\text{Nm}$ for PTA Stellite 6, $5.8 \times 10^{-5} \text{ mm}^3/\text{Nm}$ for LSM'ed Stellite 6 and $6.0 \times 10^{-5} \text{ mm}^3/\text{Nm}$ for LSM'ed Mo-alloyed Stellite 6 hardfacings after HT wear tests. These values clearly revealed that at 500 °C wear loss of LSM'ed hardfacings were almost twice that of PTA deposited Stellite 6 hardfacing, as opposed to RT, and there was no remarkable difference between the LSM'ed hardfacings.

Surface and cross-section SE-SEM microphotographs of the WTs formed on the examined hardfacings tested at 500 °C are depicted in Figure 5.5. For the PTA Stellite 6 hardfacing (Figure 5.5a), the worn surface was completely covered by a tribo-oxide layer. On the cross-section SEM microphotographs of this WT, it is obvious that tribo-oxide had a thickness of about 3 µm but underwent a localized thinning by delamination. However, worn surfaces of the LSM'ed hardfacings (Figure 5.5b and c)

were partially covered with tribo-oxides. Cross-section examination of the WTs of the LSM'ed hardfacings revealed that the tribo-oxides were not as thick as that on the PTA Stellite 6 hardfacing. The thickness of the tribo-oxide layers were ~ 2 and ~ 1 μm for LSM'ed Stellite 6 and LSM'ed Mo-alloyed Stellite 6 hardfacings, respectively. High magnification SEM images, given as insets, clearly showed that tribo-oxide free regions were exposed to abrasive wear similar to RT. Thus, it is concluded that at 500 $^{\circ}\text{C}$, wear progressed on the LSM'ed hardfacings by a combination of oxidative and abrasive wear mechanisms.

Raman spectra in the range of 400–800 cm^{-1} and results of EDX analysis taken from the tribo-oxides formed on the contact surfaces of the examined hardfacings are presented in Figure 5.6 (right and left column, respectively). According to the literature [124,156,204–206], Raman peaks of PTA Stellite 6 (Figure 5.6a) were assigned as CoO, having a rocksalt structure [207], while the prominent Raman peaks of the LSM'ed hardfacings (Figure 5.6b and c) corresponded to Co_3O_4 and Cr_2O_3 , having normal spinel and corundum structures, respectively [208,209]. EDX spectra also confirmed the enrichment of the tribo-oxides of LSM'ed hardfacings by Cr, unlike PTA Stellite 6 hardfacing. In addition, no significant contribution of Mo was found in the chemical composition of the tribo-oxide formed on the contact surface of LSM'ed Mo-alloyed Stellite 6 hardfacing.

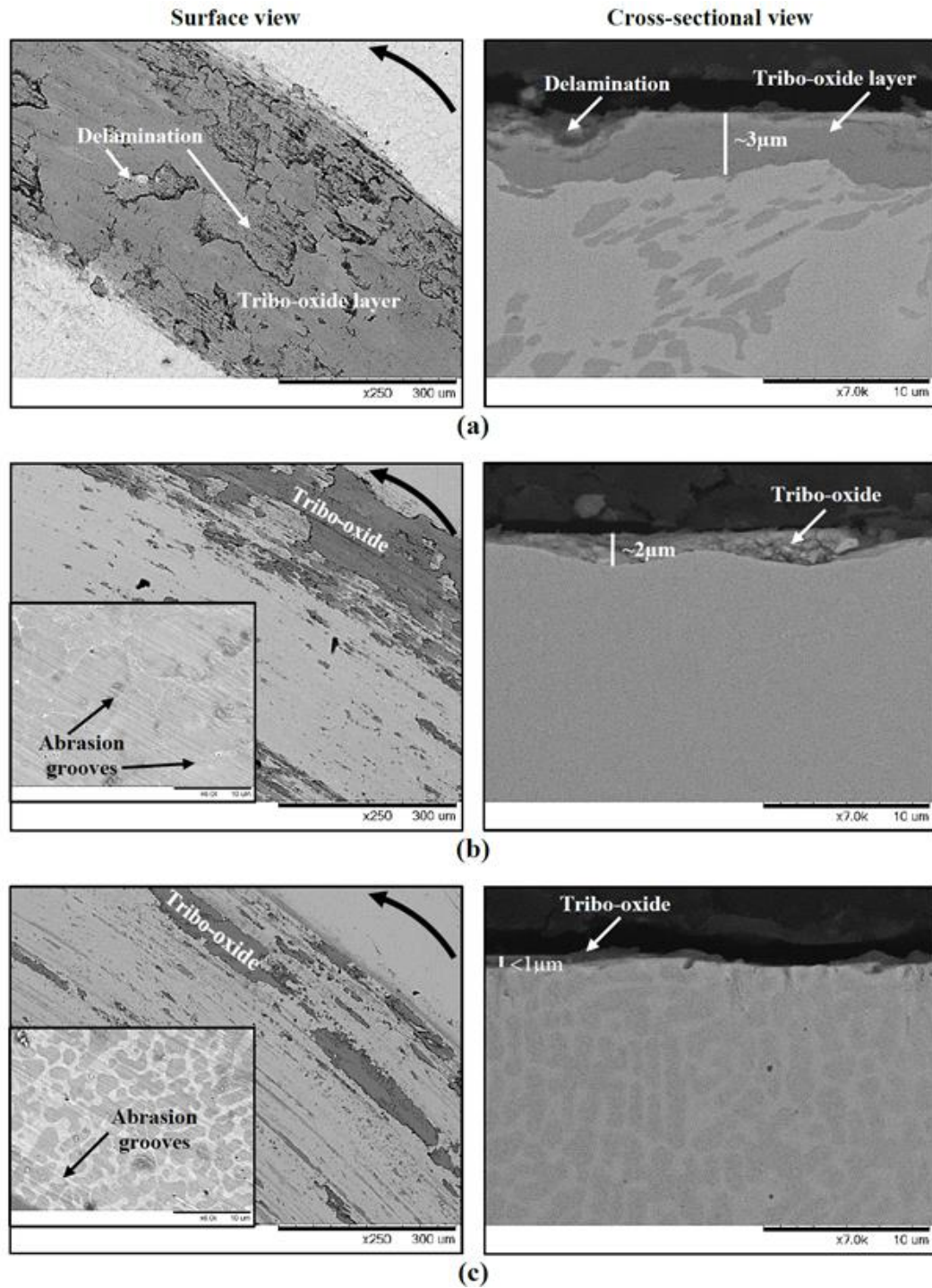


Figure 5.5 : Surface and cross-section SE-SEM microphotographs of (a) PTA Stellite 6, (b) LSM'ed Stellite 6 and (c) LSM'ed Mo-alloyed Stellite 6 hardfacings after HT wear tests. (The bent arrows on the right corner of the surface views indicate the sliding direction).

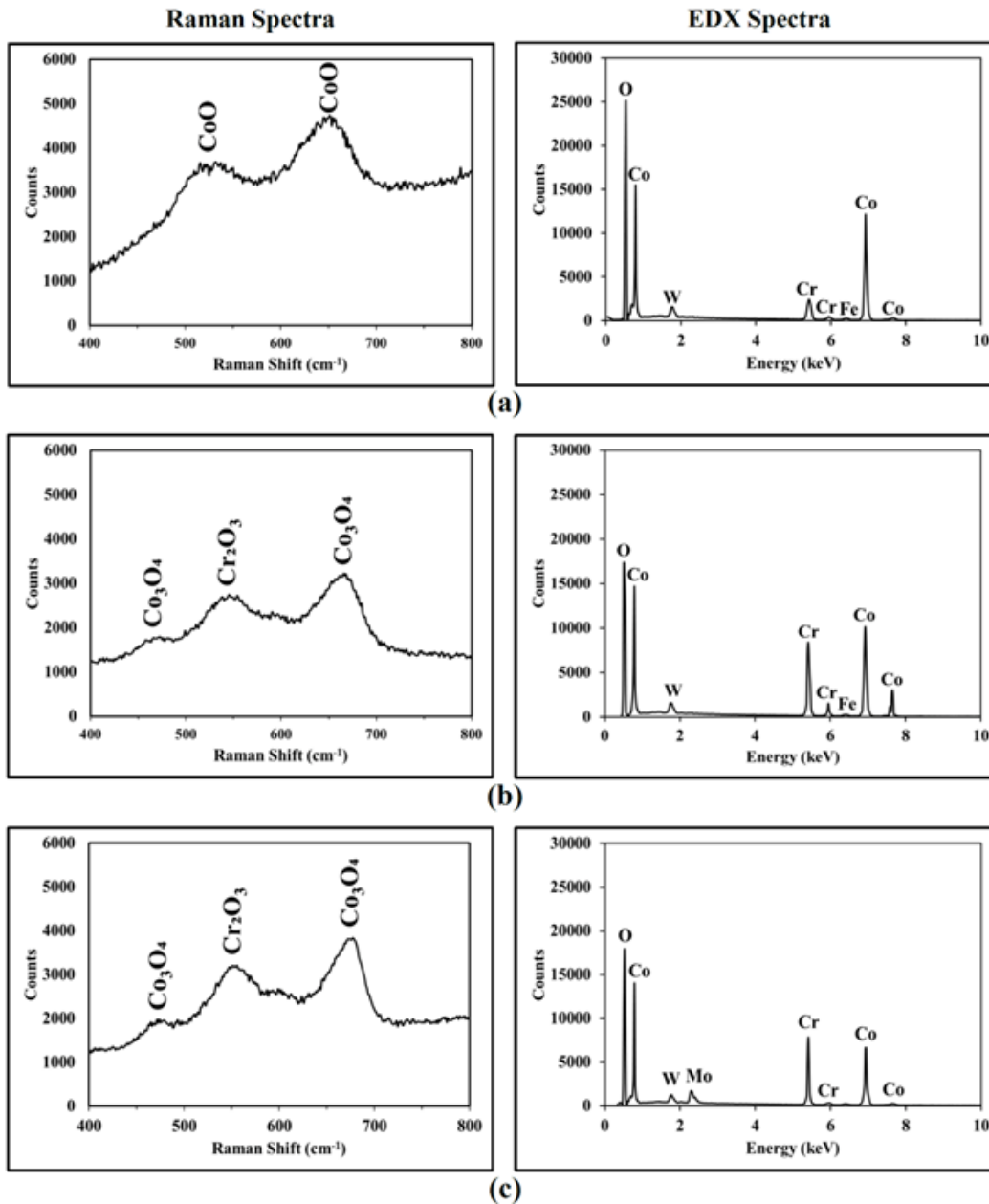


Figure 5.6 : Raman and EDX spectra of the tribo-oxides formed on contact surfaces of (a) PTA Stellite 6, (b) LSM'ed Stellite 6 and (c) LSM'ed Mo-alloyed Stellite 6 hardfacings during HT wear tests.

5.4 Discussion

Microstructural features of the PTA Stellite 6 hardfacing fabricated in this study was almost identical to as-cast Stellite 6 alloy [210,211], exhibiting hypoeutectic solidification features. Accordingly, the first phase formed during solidification of Stellite 6 after PTA process was the Co-matrix, while the remaining melt was enriched by the carbide forming elements (i.e. Cr and W), resulting in the precipitation of eutectic Cr-rich carbides and blocky W-rich complex carbides. Since W contents of the Stellite 6 is low (< 5 wt.%), the formation of eutectic Cr-rich carbide at higher

fraction was favored [116,158]. LSM exposed surface of PTA Stellite 6 hardfacing exhibited about 13 % higher hardness, which can be attributed to the refinement of the microstructure as a result of rapid solidification/cooling of the re-melted surfaces [212,213]. Unlike the LSM'ed Stellite 6 hardfacing, microstructure of the LSM'ed Mo-alloyed version was eutectic Cr-rich carbide free (i.e. mainly consisted of Co-matrix and complex carbides).

As far as the effects of Mo addition into Stellite 6 hardfacing during the PTA deposition process is concerned, the authors have already discussed it in detail in their previous publication [197]. Therein, it is reported that addition of 10 wt.% Mo into Stellite 6 hardfacing contributed in increasing not only the size but also volume fraction of complex carbide and these increments were offset by reductions in the size and fraction of eutectic carbides. Furthermore, complex carbides were enriched by Mo at the expense of W, and some portion of Mo was also dissolved in the Co-matrix. The higher affinity of Mo towards C, in contrast to Cr, let C to react with Mo in the early stages of solidification forming Mo-rich complex carbide, while leaving a very little amount of C to combine with Cr for formation of eutectic carbides [139,197]. Therefore, the Mo-addition during the PTA deposition process along with the higher cooling rate encountered in the LSM'ed layer are argued to suppress the formation of eutectic carbide in the microstructure of the LSM'ed Mo-alloyed Stellite 6 hardfacing [192]. Furthermore, the Mo alloying affects the solidification manner of Stellite 6 hardfacing, as it leads to lowering of melting point of Stellite 6 alloy; thereby, the formation of 30-35 % thicker LSM'ed layer in Mo-alloyed Stellite 6 is favored in relation to that of unalloyed Stellite 6 [156,197]. However, this lowering of melting point led to an increment in the solidification range, which in turn triggered formation of surface cracks [156], owing to rapid solidification/cooling induced thermal stresses after the LSM treatment [111,198]. It should be noted that both PTA deposits and LSM'ed layers enabled strong metallurgical bonding with respective underlying solids owing to starting of the solidification from the melt/solid interface. It is well established that the Stellite alloys principally derive their hardness and wear resistance from the type, size and volume fraction of hard carbides distributed in the softer albeit much tougher Co-matrix [195]. This can be likened to a composite microstructure wherein hard and brittle phases are distributed in a soft matrix phase, acting as a binder and holding the hard phases together. Now the hardness of the composite is directly

linked with the hardness of the matrix and hard second phase, which can simply be expressed mathematically by rule of mixtures [53]. As far as the LSM of the Stellite alloy is concerned, it definitely influences the volume fraction of hard carbides formed in the Co-matrix and, in turn, is expected to alter the hardness of the resultant alloy. Hence, the LSM'ed Mo-alloyed Stellite 6 hardfacing exhibited about 44% higher hardness than that of PTA Stellite 6 hardfacing, thanks to the remarkable increment in volume fraction of carbides, appearing as a network in the microstructure [197]. Furthermore, the higher hardness is expected from the LSM'ed Mo-alloyed Stellite 6 hardfacing due to replacement of eutectic carbide with relatively harder complex carbide, having reported hardness values of 900-1050 HV and 1450-1750 HV, respectively, [168]. In short, the higher hardness increment for the LSM'ed Mo-alloyed version hardfacing is due to increased volume fraction of harder complex carbides in the microstructure at the expense of relatively soft eutectic carbides.

Normalized wear loss values calculated after RT and HT wear tests are compared in Figure 5.7 with respect to the hardness of the relevant hardfacings. At RT, reduction in K value with increasing hardness obeys the well-known fact of hard surfaces have high potential to restrict material removal by the attack of hard bodies [3,214]. However, this was not valid for the wear tests conducted at 500 °C due to the formation of tribo-oxides at the worn surfaces. Complete coverage of the worn surface of the PTA Stellite 6 hardfacing by a thick rocksalt structured CoO type tribo-oxide layer, inhibited the direct contact between mating surfaces and prevented the destructive action of the counterface to some extent. Even though this tribo-oxide layer could have undergone local delamination, it remained largely intact on the worn surface throughout the testing period and therefore resulted in a lower wear loss even than that of RT. However, tribo-oxides of the LSM'ed hardfacings, which were mainly spinel Co_3O_4 (with some Cr_2O_3), were as not protective as that of PTA hardfacing so that, their easy removal from the contact surface during wear tests caused progress of wear by an abrasive wear mechanism. Almost similar wear loss values of the LSM'ed Stellite 6 and LSM'ed Mo-alloyed Stellite 6 hardfacings at 500 °C indicated that microstructure and room temperature hardness of the LSM'ed layer did not play as a crucial role on their HT wear performance as their Co_3O_4 containing tribo-oxides did.

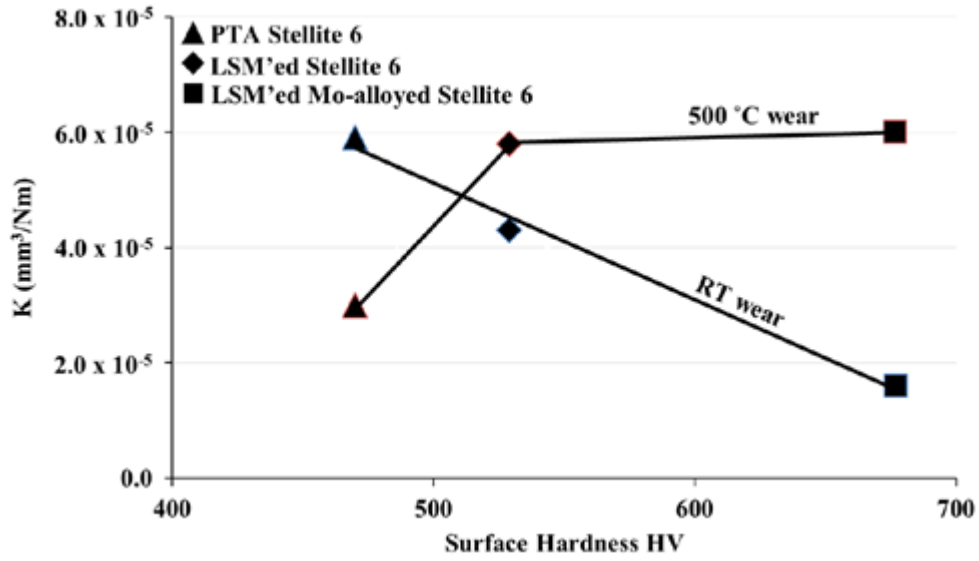
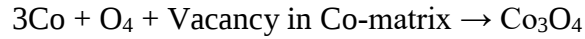


Figure 5.7 : Effect of hardness on K values of the examined hardfacings obtained after RT and HT wear tests.

The formation of Co_3O_4 (with some Cr_2O_3) type tribo-oxide on the contact surfaces of LSM'ed hardfacings rather than CoO type tribo-oxide can be associated with the exposure of the LSM'ed surfaces to rapid solidification/cooling, favoring quench-in vacancies in the Co-matrix in substantial numbers, while refining the microstructure. Thus, it has been suggested that increased number of vacancies in the Co-matrix contributed to formation of Co_3O_4 according to [215]:



Whereas the formation of Cr_2O_3 is attributed to easy outward diffusion of Cr atoms along the grain boundaries of the refined Co-matrix [216]. Easy removal of the Co_3O_4 type tribo-oxides from the contact surfaces of the LSM'ed hardfacings by rubbing action of the counterface can be associated with its spinel structure induced brittleness [217]. As a consequence of removal of tribo-oxides, contact surfaces were exposed to abrasive wear which would be more severe than RT due to thermal softening of the Co-matrix at elevated temperatures [116,162].

Regarding the very limited contribution of Mo in tribo-oxides formed on contact surface of LSM'ed Mo-alloyed Stellite 6 hardfacing, it is suggested that capturing of considerable amount of Mo in the composition of complex carbide inhibited its contribution in the oxides formed, thanks to the high stability of complex carbides at elevated temperatures [122]. In addition, the large atomic size of Mo atom as well as its low concentration in relation to the other predominant alloying elements in the Co-

matrix phase, i.e. Co and Cr, lowered its mobility which in turn contributed in detecting of a negligible Mo content in these oxides.

5.5 Conclusion

In this study, the effect of LSM process on the microstructures and wear behaviors of PTA Stellite 6 and 10 % Mo-alloyed Stellite 6 hardfacings were examined. Results of the experimental works are briefly given below:

1. Application of LSM process as a post treatment caused severe microstructural refinement at the surfaces of both Stellite 6 hardfacing and its Mo-alloyed version as compared to the PTA Stellite 6 hardfacing. While the microstructure of the LSM'ed Stellite 6 hardfacing consisted of three phases namely: Co-matrix, Cr-rich and complex carbides; similar to the PTA Stellite 6 hardfacing, that of the LSM'ed Mo-alloyed Stellite 6 hardfacing consisted of only two phases namely: Co-matrix and network of complex carbides.
2. In accordance with the changes in the microstructure, application of LSM to PTA Stellite 6 hardfacing increased the surface hardness from 470 ± 8 to 529 ± 10 HV. In the case of LSM'ed Mo-alloyed Stellite 6 hardfacing, hardness was measured as 677 ± 17 HV, which corresponds to about 44% increment as compared to PTA Stellite 6 hardfacing. This increment is associated with the increased fraction of carbides in a network-like appearance, following the LSM process.
3. According to the results of sliding wear tests conducted at RT, increment of hardness upon LSM process reduced the wear loss by 26% and 74% in unalloyed and Mo-alloyed versions of Stellite 6, respectively, as wear progressed by abrasive wear mechanism.
4. At 500 °C, the lowest wear loss was obtained from the PTA Stellite 6 whose worn surface was covered by CoO type tribo-oxide layer, having a rocksalt structure. LSM applied hardfacings yielded almost two times higher wear loss than that of PTA Stellite 6 as a result of easy removal of Co₃O₄ type tribo-oxides of normal spinel structure from the worn surfaces under sliding contact.

6. CONCLUSIONS

In this dissertation, effects of Mo alloying and application of post EBSM/LSM treatment, alone or in a combination with each other, on PTA deposited Stellite hardfacings were investigated in term of the microstructural changes and sliding wear resistance. Mo has been selected as a strong carbide promoter in Stellite hardfacings while post deposition surface melting treatments were imposed as they are very effective means in modifying the microstructure and the associated wear characteristics of hardfacing alloys. Major conclusions that can be drawn from this study as well as the recommendations suggested to be a novel and promising direction for future work regarding the improvements of hardfacing deposits are as follows:

6.1 Conclusions

The microstructure of PTA deposited Stellite 6 and Stellite 12 hardfacings are found to be consisted of three distinct phases, namely, dendritic Co-matrix, eutectic Cr-rich carbides in the form of M_7C_3 and $M_{23}C_6$ and blocky W-rich complex carbides in the form of M_6C . The volume fraction of the constituent phases varied from Stellite 6 to Stellite 12 thanks to the differences in their chemical composition, especially in C and W contents. Alloying of Stellite 6 hardfacing alloy with 10 wt.% Mo during the PTA deposition process generally contributed in increasing not only the size but also volue fraction of complex carbide. EBSM'ed/LSM'ed Stellite coatings, in general, presented refined structures. In term of constituent phases, while application of a post surface melting treatment solely on unalloyed Stellite 6 and Stellite 12 hardfacings exhibited three-phase microstructures similar to that of PTA version, its combination with Mo alloying in one strategy introduced microstructures consisted of two-phase; cellular Co-matrix and a network of complex carbides. Both PTA deposits and EBSM'ed/LSM'ed layers enabled strong metallurgical bonding with respective underlying solids owing to starting of the solidification from the melt/solid interface. As for the geometrical aspects of the surface melted layers, a comparison across the hardfacings shows that Mo-alloyed Stellite 6 hardfacings had always thicker melted zones with respect to the unalloyed versions under the same melting process. However, if they compared across the applied surface melting processes, the EBSM'ed layers

were thicker than LSM'ed ones in both unalloyed and Mo-alloyed Stellite 6 hardfacings.

Regarding the surface related mechanical properties, the resultant microstructural changes upon Mo addition led to enhance the hardness of PTA Stellite 6, in accordance, the PTA Mo-alloyed Stellite 6 hardfacing exhibited enhanced wear resistance relation to its unalloyed Stellite 6 version. Further enhancement in surface hardness and wear resistance was obtained in Stellite 6 hardfacing when Mo alloying combined with a post deposition treatment of EBSM process. The high fraction of complex carbides in PTA Mo-alloyed Stellite 6 hardfacing provided a higher resistance against the destructive action of the counterface, whereas the development of network structure of complex carbides in EBSM'ed Mo-alloyed Stellite 6 hardfacing assisted in hindering the plastic deformation of the matrix phase and reduced the wear loss. However, the wear resistance of unalloyed Stellite 6 and Stellite 12 hardfacings deteriorated after application of post EBSM treatment. The pulling out of weakly supported finer carbides and their removal during sliding action has a potential to aggravate the wear loss of EBSM'ed unalloyed Stellite hardfacings where the abrasive wear was the predominant wear mechanism.

Under the effect of post LSM treatment, unalloyed and Mo-alloyed versions of Stellite 6 hardfacings showed contradictory results as compared to PTA Stellite 6 in terms of RT and HT wear resistance. With reference to the PTA Stellite 6 hardfacing, LSM process led to an increment in surface hardness and a subsequent reduction of wear loss at RT, where abrasive wear mechanism was dominant. At HT (500 °C), the tribo-oxides formed on the contact surfaces of the LSM'ed hardfacings exhibited poor mechanical stability, than those found on the PTA Stellite 6 hardfacing, whereby their easier removal from the contact surface during the sliding action aggravated the wear loss of the thermally softened matrix by abrasive wear mechanism along with oxidative wear.

6.2 Recommendations

In this dissertation, only two hardfacings alloys were studied, i.e. Stellite 12 and Stellite 6. Although they cover the widely used Stellite alloys in wear applications, a wider range of Stellite alloys with different chemical composition could be selected for a subsequent study, particularly alloys with varying amounts of C like Stellite 1 and Stellite 21, having relatively very high and very low concentrations of C in their

compositions, respectively. Multi surface remelting strategy of the deposited hardfacings is also recommended as a future work and a direct and quite straightforward idea to continue this research would be to investigate the alloying effect of Mo into Stellite hardfacings on the impact-sliding or fretting wear characteristics. The effect of lubrication on sliding wear behavior of Stellite hardfacings is still not completely clear, so our recommendation is, therefore, to study the wear characteristics of Stellite hardfacings under lubricated sliding conditions.





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