THE INTERACTION OF CW CO_2 LASER WITH Zr-COATED Cu-SUBSTRATES

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الملخص

تم تعريض عينات من النحاس (10×10×5 مم) بعد تغطيتها بطبقة من الزركونيوم (بطريقة التبخير الحراري والترسيب في مجال مفرغ من الهواء) لأشعة الليزر في جهاز يعمل بثاني أكسيد الكربون دائم التشغيل ذي قدرة 720 واط والقطر المؤثر للشعاع هو 0.5 مم و سرعته 200 سم/ث. وقد تم صهر أربعة خطوط على سطح جميع العينات كل اثنان منها متوازيان وعموديان على الخطين الآخرين.

وقد بينت قياسات الصلادة المجهريه أن جميع الملامح والتشكيلات المختلفة على السطح المعالج بالليزر لا تختلف عن بعضها من ناحية الصلادة بينما قد حدث انصهار وانتقال للمادة وتبريد فائق السرعة في هذه المناطق. ونتج عن هذه الظواهر تكون رقائق ملساء دقيقة للغاية ملتصقة بالسطح المحبب للمجرى المعالج وكذلك ظهور تموجات على شكل أقواس دائرية متوازية ومتعاقبة تغطي كل السطح المعالج.

كما تم دراسة الطبقات تحت السطحية للمجرى المعالج وذلك على مقاطع مائلة (بزاوية مقدارها ~6.5°) تمر عبر المجرى. وبينت هذه الدراسة أن قاع المجرى يحتوي على عدد كبير من فقاعات دائرية كبيرة نتج عنها انخفاض كبير في الصلادة في هذه المنطقة. ولوحظ أيضا أن بنية المنطقة الوسطى من المجرى ذات حبيبات مستطيلة متوازية (دليل على النمو الموجي للحبيبات) وقد صاحب هذه البنية ارتفاع ملحوظ في الصلادة والذي يعتقد انه ناتج عن الإجهادات الناتجة عن تجمد هذه الطبقة تحت ضغط البخر الذي يحدث في الطبقات السفلى. وقد أظهرت القياسات ارتفاع قيمة الصلادة في أعلى المجرى والذي قد يكون سببه انضغاط الطبقات السطحية للمعدن المصهور أو بسبب ألتسابك أو كليهما. التبريد فائق السرعة قد يكون سبب أخر في ارتفاع قيمة الصلادة.

وقد اتفقت نتائج قياسات مقاومة البلى للعينات المعالجة مع نتائج قياسات الصلادة المجهريه.أظهرت تجارب المعالجة الحرارية للمجرى المعالج أن بنية المجرى مستقرة ولم يحدث لها أي تغير نتيجة معالجتها حراريا عند درجة حرارة 350 م° لساعة واحدة.

ABSTRACT

An attempt has been performed to alloy locally a copper specimen with Zirconium to improve the hardness and wear resistance. Copper specimens were coated with Zirconium by vacuum thermal evaporation. The coated specimens were then laser treated by means of CW CO_2 laser of nominal power of 720 watt. The laser beam diameter was 0.5 mm with traveling speed of 200 cm/sec. Four tracks were melted on the surface of each specimen; each two tracks were mutually parallel and perpendicular to the other two. Visual and microscopic investigations of the laser fused tracks revealed intensive re-evaporation of Zirconium from the track positions and subsequent re-deposition on the surrounding material.

The morphology and microhardness of the surface features formed on the laser-fused tracks showed no changes in microhardness. Indications of melting, mass transfer and perturbations followed by rapid solidifications were observed. The effects, of the laser treatment, were thin films attached to the grinding surface of the laser fused tracks and arc ripples covering the whole surface of the fused tracks. The sub-surface effects, of the laser treatment, were studied on oblique sections (at an angle of ~ 6.5^{o}) cut through the laser fused tracks. The bottom of the tracks was characterized by a number of large spherical voids causing an appreciable decrease in hardness. The middle layers of the tracks were characterized by columnar structure (indicating directional growth) accompanied by increased hardness values. The hardening effect was attributed to a deformation action caused by evaporation at the bottom of the track while the middle layers are solidifying. The upper portion of the tracks showed a slight increase in hardness due to melt surface deformation and/or alloying. The fast rate of cooling might be another reason for such increase in hardness.

Wear characteristics of the laser treated specimens confirmed the morphological and hardness observations of the laser-fused track. Heat treatment experiments showed that the as-cast structure of the laser fused tracks is stable for heating to temperatures up to 350^{o}C (for 1 hour).

KEYWORDS: Copper; Zirconium coating; Laser beam; Columnar structure; Heat treatment; Micro-hardness; Wear resistance

INTRODUCTION

Concentrated energy fluxes (CEF) such as Light Amplification by Stimulated Emission of Radiation (LASER) is finding ever increasing applications in materials science and engineering [1]. Laser beam applications increases in research and industry uses because of the versatile control and easy optimization of their parameters [2]. The problem of metal welding [3], melting, alloying [4,5], splat cooling, amorphization, surface hardening [1,6] and micro-drilling by means of laser beam are only examples. The laser beam techniques brought a revolution in optical technology and had a great influence in many fields. Such as sciences, medical sciences, telecommunications and even in nuclear fusion [7]. The main advantage of laser is its ability to deliver a very high power per unit area to localized regions on a target surface. That opened many potential applications and led to emergence of a number of industrial techniques of laser as welding, heat treatment, cutting, annealing, alloying, hole piercing and thermal evaporation fields.

Surface alloying is one of the laser applications to get desirable surface properties for the material. These properties include increase in hardness, wear resistance and strength. The laser alloying can also be used to increase the corrosion resistance by introducing a protective film on the surface called glazing [2,4]. There are many ways to introduce surface alloying on the material surface [1,4,6]. These include spreading a powder containing the required alloying elements on the surface of the material, and then the surface is laser treated. As a result the powder and the surface of the material will be melted and mixed to form a thin surface layer of the substance material. The other method is done by coating the surface of the material by a thin layer of the required alloying elements by one of the coating methods (electroplating, thermal evaporation….etc.) followed by laser treatment.

Laser beam offers the opportunity to change the surface properties of materials in any planed way [8,9,10]. One of the ways by which copper articles can be hardened is to alloy them with other elements such as Zn, Sn, Al and Be. However, the strength achieved will be on the expense of the ductility. One way of increasing the surface hardness of copper keeping a ductile bulk is by laser alloying of the surface by alloying elements which are liable to be highly supercooled and have a tendency for glass formation. One of such elements is zirconium.

The aim of this research work is to investigate the change in the surface and near surface properties (hardness and wear resistance) of the copper substrates coated by thin film of zirconium and then laser treated in a trial to end up with surface alloying between the copper and the zirconium in a surface network form.

EXPERIMENTAL PROCEDURE

General

The processes taking place during the melting of the surface layers, the inward propagation of the solid liquid interface and the subsequent solidification phenomena have been traced out by morphological and microhardness measurements and observations along the depth of the laser-fused tracks. The wear test was also used to confirm the morphological and microhardness investigation.

Raw materials

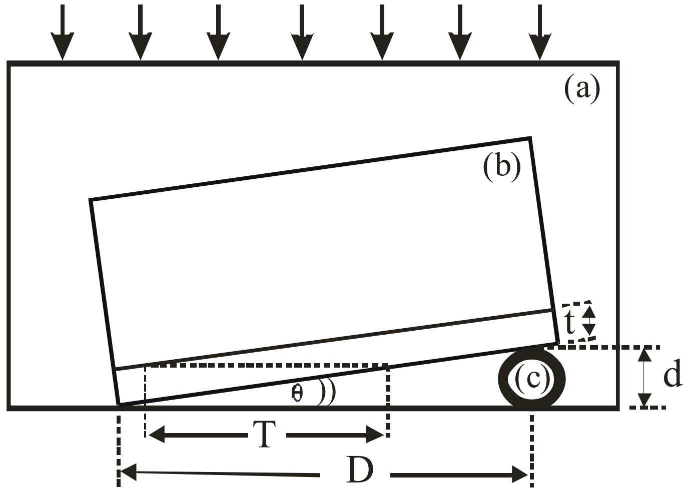
A rod of pure electrolytic copper with a diameter of 70 mm was used as a base substrate material. The rod was cut into slices of 5 mm in thickness and these slices were further cut to small specimens of 10x10x5 mm. the copper-substrate specimens were metallographicaly prepared by grinding using grits 80 to 1000. Some specimens were ground to grit 500 only, while other specimens were further polished by fine alumina paste.

Zirconium coating

A small plate of zirconium was used as a coating material. This plate was sheared into small pieces to be ready for the coating process. The coating process was carried out using EDWARDES E306A high vacuum coating unit. This unit was used to thermally evaporate zirconium and deposit it on the copper-substrates. The coating material was allowed to deposit on the substrate surface without contamination. The pressure inside the evaporation unite was $1x10^{-4}$ mbar or below. In order to limit the alloying process to a thin surface layer of Cu-substrates, the surface was coated by a thin zirconium layer of controlled thickness.

Laser beam treatment

After coating of the copper substrate specimens by thin film of zirconium the specimens were treated by laser beam to achieve surface alloying between the copper and zirconium. The laser beam was made to strike the specimen surface in a network pattern. The molten tracks done by the laser beam were of 0.5 mm in width. The distance between parallel tracks was ~3 mm with each track was ~3 mm from the edge. Laser beam treatment was performed at Braunschweig University in Germany using 720 watt continuous action CO_2 laser beam. The traveling speed of the laser beam was selected to be 200 cm/sec to allow rapid cooling.



(a) Mounting material (b) Specimen (c) Supporting wire

Figure 1: Oblique mounting of the specimens.

Micro-hardness of laser melted layers

In these series of experiments the surface and near surface layers of the laser treated specimens were studied on oblique sections through the specimens surface layers particularly at the tracks. This has been done by an oblique cold mounting of the specimens by means of a 1 mm in diameter aluminum wire inserted below one edge of the specimen surface before pouring the cold resin mixture, Figure (1). The laser treated surface of the specimens was inclined at an angle of ~ 6.5^o. The mounted specimens were then grounded by SiC abrasive paper of subsequent grits 220, 320, 500 and 1000 and finally polished by alumina past.

These mounted specimens were subjected to microhardness measurements using the Knoop indentations where a ZWICK (3112) was utilized with a load of 30 g. The indentations were put inside the traces of molten tracks to investigate the hardness difference across the track depth.

Heat treatment

The effect of heat treatment on the laser re-melted tracks of the Cu-substrates has been investigated. The laser treated specimens was further annealed at 350^oC for one hour and then furnace cooled. The annealing process was performed in a protective N_2 gas atmosphere in tubular furnace of type STROHLEIN.

Wear testing

The system used to perform the wear test consist of: (i) Motor to rotate a steel disc at rotating speed of 30 r.p.m (ii) medium carbon steel disc (30 cm in diameter and HB = 190) in contact to the specimen surface to accomplish the wear process (iii) Specimen holder (iv) Fan for cooling the system and removing the wear debris (vi) Load to press the specimen to the steel disc (219 g). The laser treated specimens were subjected to wear testing under a constant load for a total sliding distance of 2500 m divided into 10 steps (each 250 m sliding which was passed in 15 min.). The sliding rate was kept constant throughout the whole test (16.67 m/min). The loss in weight during each step was divided by the sliding distance constituting the step to calculate an average wear rate for the step. This average wear rate was considered as an actual one for the middle point of the step. A total of 2500 m of sliding distance was enough to remove the laser molten tracks from the specimens' surfaces.

RESULTS AND DISCUSION

Morphological observations

The preliminary visual inspection of the laser treated specimens revealed four lines each two parallel to each other and intersecting the other two. The lines were different in color; one was reddish, the others were yellow, green and blue. The microscopic examinations of the treated surfaces showed that the parallel reddish and yellow tracks pass above the green and blue tracks at their intersection zones. Figure (2) shows the intersection zone of the yellow and green tracks The difference in color of the laser treated tracks is a consequence of differences in the refraction index of the surface layers in these zones, which in turn reflexes the differences in thickness of thin metallic layers deposited on the surface of the laser fused tracks after their complete solidification. Similar observation was confirmed by other researchers [11]. Since the original color of copper is reddish means that this track is the last one to receive laser treatment. The yellow track is the one before the last in the sequence of laser treatment. It is parallel to the reddish one and passes above the other two tracks. The green track is the second in laser treatment, while the blue is the first track to form. The dark blue layer is a consequence of the thickest layer deposited on the first track during the laser fusion of the subsequent three tracks. The green track received deposited layers only during the fusion of the last two tracks. The yellow was covered with deposited matter only during the fusion of the last reddish one, which did not receive any deposited layer. These color changes indicated that the laser fusion of the material surface layer was accompanied by an intensive evaporation of the outermost layers which deposit later on the specimen surface. Based on these observations it seems that the probability of alloying under the used conditions is small.

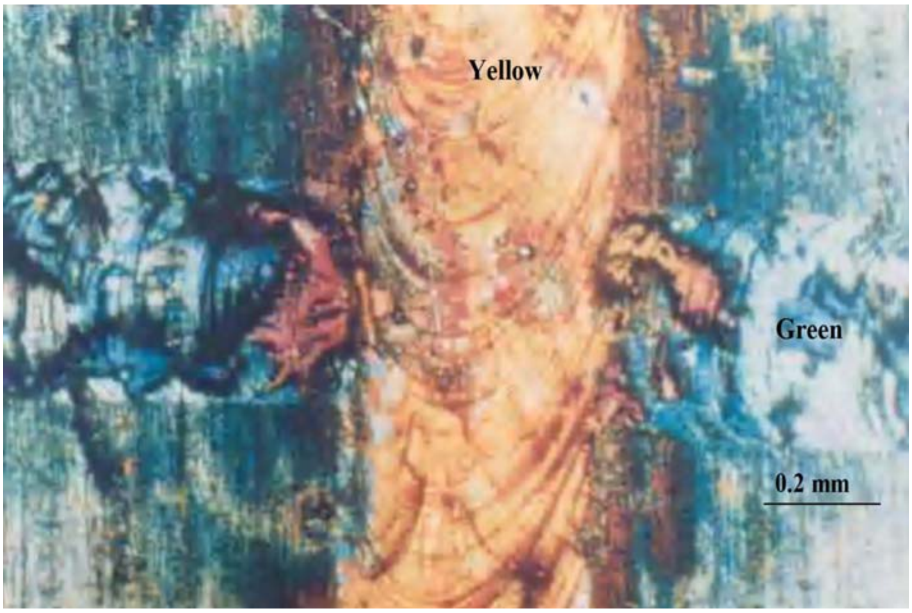


Figure 2: Zone of intersection of the second track (green) and the third track (yellow).

From Figure (2) it is evident that the surface of the fused tracks is composed of a large number of circular ripples. These ripples are the result of dynamic effects such as the reactive pressure due to the evaporation of some fraction of the liquid phase or thermal convective flows in the melt or other which lead to melt surface deformation forming ripple weaves moving from the center to the periphery of the fusion region. These ripples have no time to decay during fast freezing which constitutes about few seconds [2]. The marked rippling is also an indicative of high level of the applied laser power density [2]. The ripple waves were of capillary nature induced by perturbation factors acting on the central area of the molten pool [2].

On the laser fused tracks some islands of bright thin layers were observed attached to diffuse grainy background, Figure (3), Figure (4) and Figure (5). These islands may be rare and thin, Figure (4), or large and frequent, Figure (3), or almost continuous, Figure (5). These thin islands are of cellular structure with boundaries, Figure (3) or sub-boundaries, Figure (5) oriented perpendicular to the solidification front (indicated by the ripple circular arches). These bright islands may be of complex compounds of Cu and Zr formed by laser melting of the residual Zr layer and some of the Cu substrate and their subsequent mixing by convective currents and capillary effects before their rapid solidification on the outermost surface. However the final decision concerning the nature of these islands requires the use of more advanced techniques such as electron microscopy and micro-analysis.

Figure 3: Bright layer formation at the top of the laser fused tracks.

The cellular form of growth of the thin bright layers seems to be connected with high heating, melting and cooling rates at the surface; only nuclei favorably oriented with their high growth rate directions parallel to the laser beam direction of movement are capable of growth. At some places of the laser-fused tracks some voids are observed, Figure (5). They maybe either the result of gas evolution by laser beam into the surrounding vacuum arrested by rapidly solidifying melt, or the result of shrinkage of solidifying melt itself.

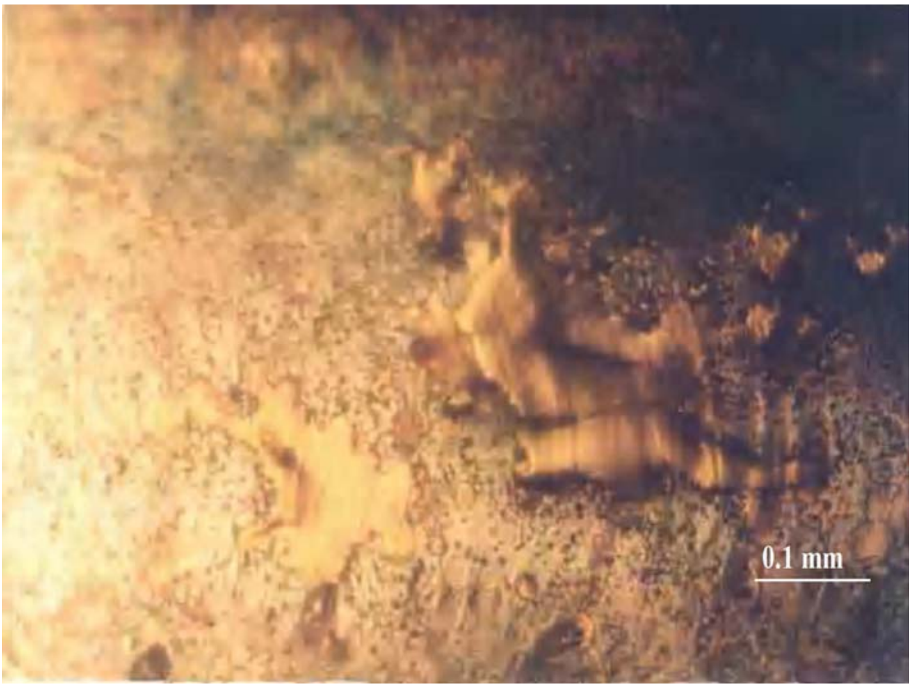


Figure 4: Grain boundaries separating two grains of the bright layer. These boundaries are oriented perpendicular to the ripple wave fronts.

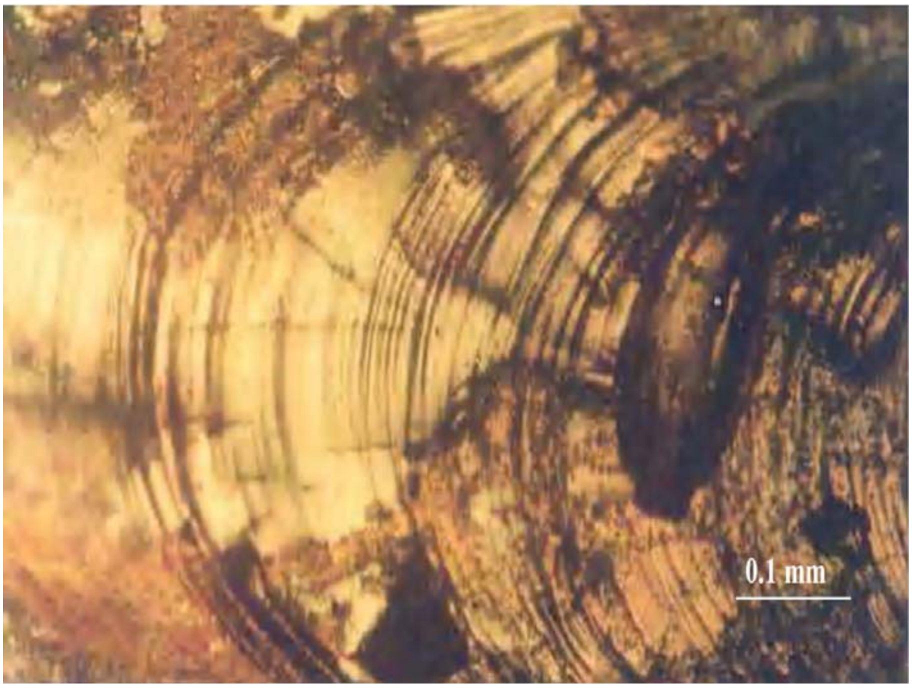


Figure 5: Sub-grain boundaries outline the cellular growth of the thin surface layers. They are perpendicular to the ripple wave fronts.

Occasionally, at some places of the fused tracks parts of the bright surface layers were cracked. The cracks were situated either parallel or perpendicular to the ripple waves, Figure (6). These cracks may be formed due to differences in the linear expansion coefficients of the uppermost surface layers and the underlying substrate metal. They also may be the result of the stresses formed by surface tension of the melt just before solidification. These stresses had no time for relaxation during the high cooling rate.

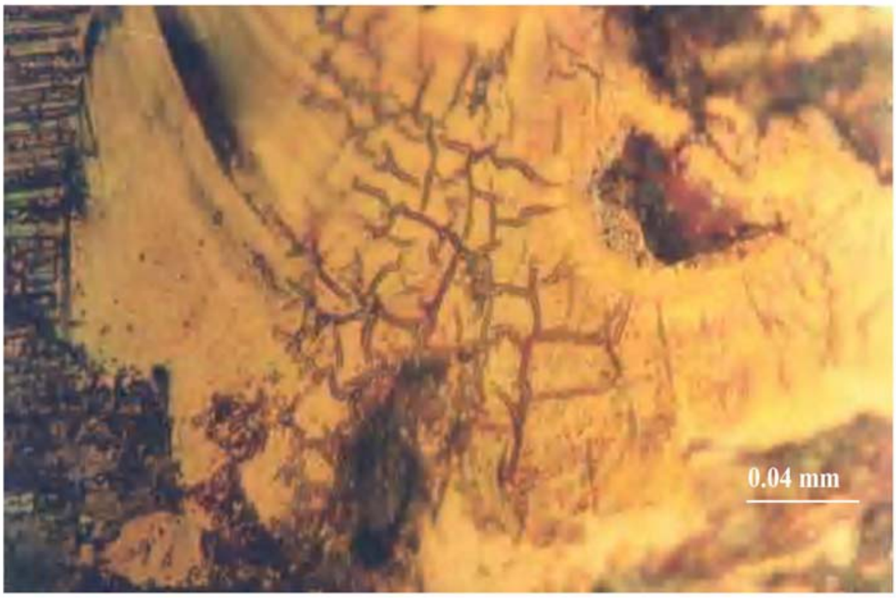


Figure 6: The thin bright layer at the side of heat affected zone. Note the crack direction.

Change in microhardness with the depth of laser fused tracks

The microhardness values measured along the depth of laser fused tracks on oblique sections (two samples were used for each reading point) are graphically plotted in Figure (7) as a function of the real distance from the bottom of the tracks calculated by the formula; $t=T\sin(\tan^{-1}(d/D))$ (see Figure 1) where;

t- The real distance from the bottom of the track
T- The apparent distance from the track bottom measured on the oblique section
d- The diameter of the wire used for mounting
D- The distance of the wire axis from the specimen edge

Figure (7) shows that the hardness at the track bottom is substantially below that of the hardness level of the untreated base metal. It is thought that the marked decrease in microhardness at the bottom of the laser fused track is a consequence of the high voids (bubble) content in this region. However, with departing from the track bottom the microhardness increases reaching values well in excess of that of the base metal (the peak value is ~97.5 Hv as compared with ~76.6±7 Hv for the base metal). This hardness increase is probably effected by the pressure exerted by evaporation taking place at the bottom of the laser track, while the metal in this middle zone was about to solidify, during its solidification. The stresses caused by this pressure have no time for relaxation after solidification. Further increase in the distance from the crack bottom the hardness comes to the level characteristics of the base metal. On approaching the free metal surface a second increase in hardness is observed. This increase may be caused either by deformation exerted on the molten metal surface by back pressure due to evaporation or by some alloying taking place in the top layer of melt track [2,12].

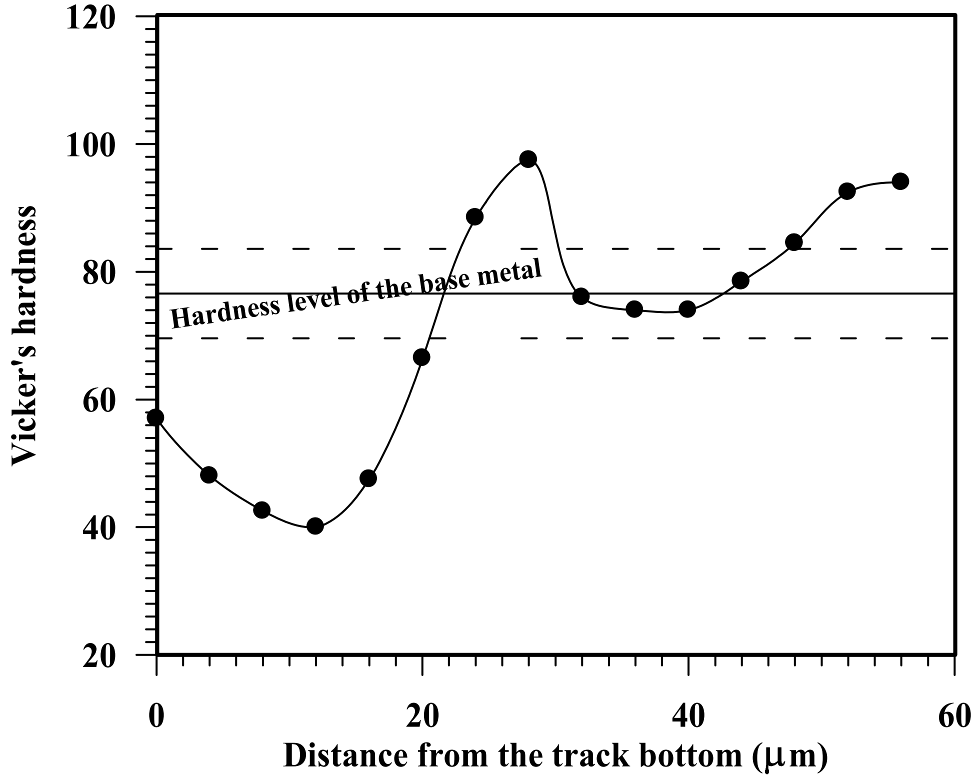


Figure 7: Microhardness through the depth of the tracks.

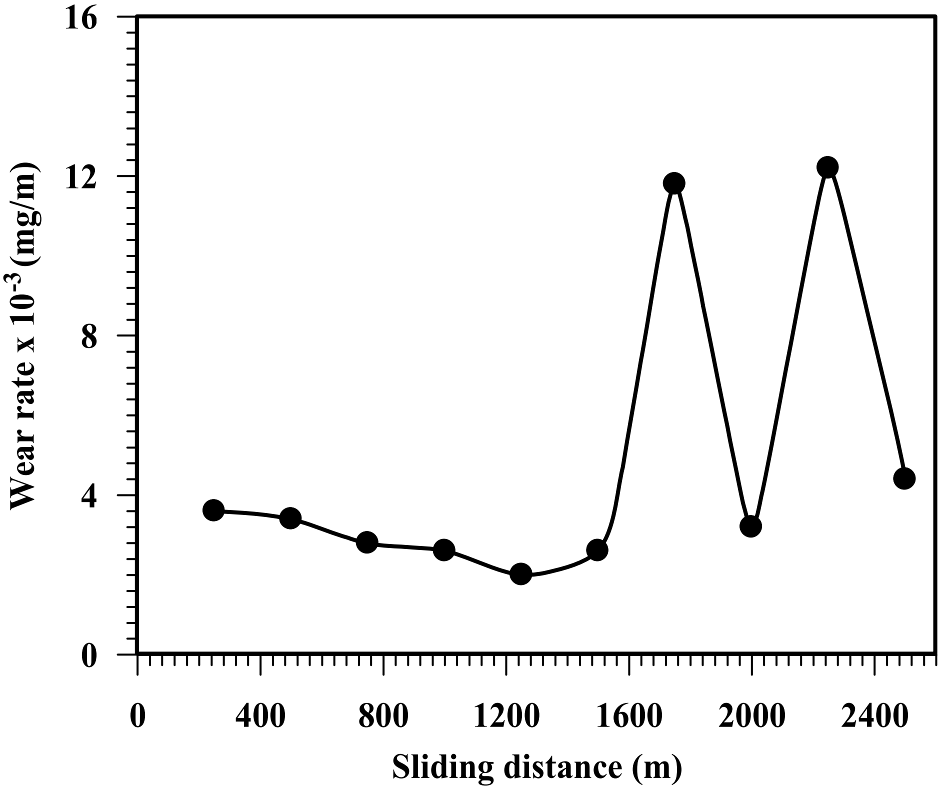


Figure 8: Average wear rates versus sliding distance.

Wear characteristics of laser treated Zr-coated specimens

The average wear rate during each step is plotted in Figure (8) versus the points representing the middle of steps (two samples were used for each reading point). The average wear for the first step starts at an average value of ~$3.5x10^{-3}$ mg/m slightly diminishes reaching a minimum value of ~$2.0x10^{-3}$ mg/m after 1100 m of sliding distance (~50% of the total sliding distance). The average wear rate then abruptly increases reaching an average value of ~$11.5x10^{-3}$ mg/m, and then drops to $3x10^{-3}$ mg/m, passes through a second maximum before decreasing approaching a steady state value characteristic of the wear system and conditions. The wear characteristics of the laser treated tracks are in general understandable. Although the hardness of the top layers of laser fused tracks was higher than the average for base metal (Figure 7) the mass transfer, taking place under the action of the reactive vapor pressure and thermocapillary processes, makes the surface irregular and the point of contact between the metal surface and disc relatively few. Under such conditions the shear stresses acting on the specimens aspirates (ripples at the top of fused tracks) are high and the wear rate is likely to be above the average. With increasing the sliding distance and progressing of wear the effect of the surface top layers disappears and the effect of the deformed strain hardened middle layers of the tracks become dominant. The wear rate reaches its minimum value. The further increase in sliding distance takes the wear front into the high void concentration zone; the wear rate abruptly increases reaching its maximum values. The reasons behind the relative minimum between the maxima are unclear. In order to reveal them, further investigations using larger number of specimens (to obtain reliable statistical data) and applying more rigorous surface metallographic investigation after each step should be carried out. In general the wear characteristics are consistent with the results of fused track morphological and microhardness investigation. In other words the wear characteristics of the laser treated specimens have confirmed the conclusions drawn from the microhardness measurements.

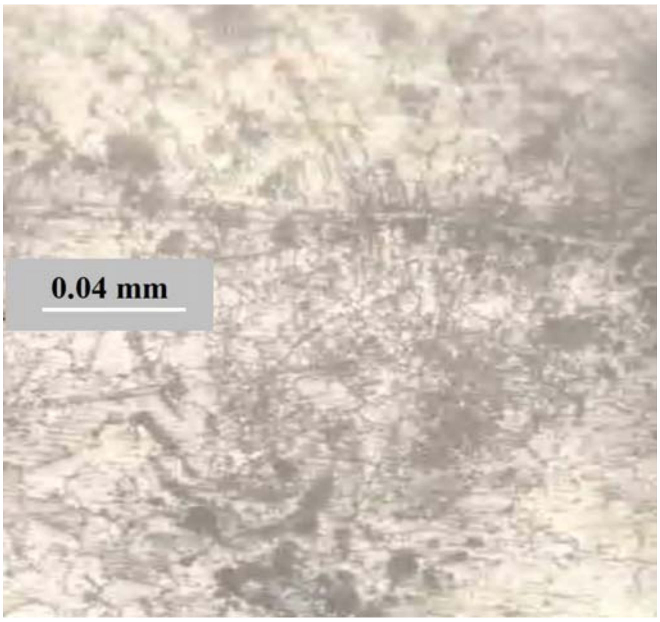


Figure 9: The effect of the heat treatment on the laser melted tracks. No changes in the microstructure up to 350°C.

The effect of heat treatment

The heat treatment regime selected for this purpose (350 ^{o}C for one hour) constitutes the threshold regime for technically pure copper [13]. Figure 9 shows a micrograph of oblique section through the track positions of a laser treated specimen further subjected to the above described heat treatment. The micrograph indicates that no recrystallization has taken place in the track; the structure of the grains remained irregular as-cast, the thin layer separating the track body from the surrounding base metal remained and voids still exist in their high concentration. These observations led to the conclusion that the laser fused structure of the track is stable enough.

CONCLUSIONS

- The homogeneity and stability of coating by thermal evaporation (checked by visual inspection) was found to be dependent on the prior mechanical preparation of the surface. Grinding to 1000 grit gives coating quality superior to those obtained on grinding to 500 grit surfaces.
- The laser treatment given to the coated specimens did not produce appreciable alloying. Intensive evaporation of the coating layer has taken place during the laser treatment of the coated specimens due to high power densities applied. Strong rippling in the form of circular arcs frozen in by rapid solidification. These ripples are indication of the high power densities applied.
- The bottom of the laser fused tracks is characterized by a considerable amount of relatively large ideally rounded voids. They seem to be the result of intensive evaporation in the material behind the advancing solid liquid interface caused by the high applied power density.
- The middle parts of the laser fused tracks have higher hardness, because of the vapor pressure due to evaporation in the underlying layers while these layers were solidifying. The uppermost of the laser fused tracks showed slightly higher hardness than of the base metal. The hardening effect is attributed either to the possible alloying or to the deformation of the melt surface by reactive vapor pressure due to surface evaporation.
- The average wear rate characteristics of laser treated specimens revealed a range of increase wear resistance, which corresponding to the middle hardened portions of the laser fused tracks, followed by a region of sharply decreased wear resistance caused by intensive void formation at the bottom of the tracks.
- The as-cast structure of laser fused tracks is stable during annealing at 350^{o}C for one hour (the threshold for recrystallization of pure copper).

ACKNOWLEDGEMENTS

The authors wish to thank Dr. Kamal Zaher for his valuable assistant in preparing this research work. The authors are particularly indebted to the Braunschweig University in Germany for allowing using laser equipments.

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