10th International Symposium on the Science and Processing of Cast Iron – SPCI10

Cast iron and the self-lubricating behaviour of graphite under abrasive wear conditions

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Cast iron is assessed as a self-lubricating material under sliding conditions. This is due to the graphite particles distributed in the matrix, which come out from their pocket, and form a tribofilm between the mating surfaces, and by which improve the tribological characteristics. In this study, the directionality and the interaction between the graphite and matrix material was investigated by micro-indentation and micro-scratch techniques. The results showed that the graphite is fractured and pushed out from the middle of graphite lamellas as a result of indentation. It was also observed that the graphite orientation below the surface intensely influenced the pushing out behaviour. For the graphite oriented toward the indenter position, the effect was more pronounced. Moreover, it was found that a scratch test can be used to investigate and explain the graphite pushing out tendency. The result was used to explain the directionality and the closing tendency of the graphite lamellas during sliding.

Keywords: lamellar graphite iron, graphite self-lubricating behaviour, tribological performance, micro-indentation test, micro-scratch test.

Introduction

Cast iron as a metal matrix composite contains graphite particles which are distributed as embedded constitutes throughout the matrix. Due to its relatively low production cost, excellent thermal conductivity, and good tribological performance, it is widely used in applications where the component is exposed to wear and heat. One particular case is piston ring-cylinder liner system, where usage of the lamellar graphite iron is quite common. The foremost reason for good tribological properties is attributed to the presence of graphite as a solid phase self-lubricating agent in the matrix.[1] It is generally accepted that lamellar (also called flake) graphite has a layered crystal structure where carbon atom has a strong covalent bond to its three adjacent carbon atoms. The layers are linked by weak long ranged van der Waals forces.[2] This weak bonding between the interlayers allows the graphite layers to easily slide over each other when are subjected to the shear forces. It is well accepted that under sliding conditions, the graphite embedded in matrix; which are extremely softer than the matrix, is extracted as carbon atoms from the graphite pocket. This happens as a result of surface and subsurface deformation of matrix induced by shear stress. As a result, graphite particles are come out and distributed between the sliding surfaces.[2, 3] Previous investigations carried out by Eyre et al.,[4] and Hironaka et al.,[5] showed that formation of the graphite film improved the tribological properties significantly, and reduced the coefficient of friction. When the graphite is removed from the graphite flakes, empty pockets are left behind.[6] These pockets potentially act as oil reservoirs sites and that supplies oil at dry starts or similar conditions of oil starvation. It has also been observed that some of these pockets are covered earlier under sliding conditions as a result of matrix deformation.[6] This in turn deteriorates the expected behaviour, and might in worst case leads to scuffing issue. In addition, it has also been found that the graphite lamellas which closed earlier were oriented predominantly parallel to the sliding direction. Moreover, it is believed that the easier conditions for shearing and continuously supplying of graphite will result in substantial improvement in tribological performance.[7]

Presence of hard particles has explicitly pronounced impact on resulting abrasive wear. Besides the wear debris particles, some of these hard particles are external contaminants such as catalyst (CAT) fines (rich in aluminum, silicon and oxygen) in oil lubricant.[8, 9] Wear phenomenon in piston ring-cylinder liner application is considerably abrasive wear controlled. The worst scenario of abrasion wear could result in seizure of the piston ring-cylinder liner. From this standpoint, a single hard asperity can indent a mating elastic surface.[10] In addition to the importance of its abrasion effect, it was found that there exists a relationship between the lamellar graphite orientation and their covering resistance under sliding and abrasive wear condition, so that those graphite flakes were parallel or close to the sliding direction were covered earlier rather than the deviated ones.[6] Deformation of the metal matrix near the graphite was found as the main controlling factor on closing the graphite lamellas.

In the present work, this directionality and the interaction between the graphite and matrix material is investigated by means of a micro-hardness indenter. The results obtained from indentation and scratch tests presented are the attempts to better understanding of the graphite's smearing mechanism under abrasive and sliding wear conditions.

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Experimental Procedure

Test specimens used in the present study were selected from a pearlitic lamellar cast iron. Polishing was performed following the standard procedure down to 1 µm diamond polishing, to get a mirror like polished surface, and then the achieved surface was cleaned with ethanol prior to examination. To explain the interaction between hard abrasive particles and lamellar graphite under abrasion conditions micro-indentation and micro-scratch techniques were carried out on plenty of graphite lamellas. The conventional Vickers indenter was used for both experiments. Indentations were made under applying a load of 500 g sufficiently far relative to each other to prohibit the overlapping issues. Nano-indentation was also employed to make a grid of indentations on lamellar graphite to determine the hardness variation within the graphite structure. After micro-indentations, metallographic studies were conducted on residual indentation marks using optical microscopy and scanning electron microscopy (SEM) with the aim of determining the matrix deformation pattern and matrix-graphite interaction. In addition, the deep etched technique using Aqua regia (Nitro-hydrochloric acid) solution was selected to reveal the orientation of the lamellar graphite beneath the surface.

Results and discussion

Interaction between the micro-indentation and graphite lamellae

It has been accepted that the improvements in tribological performance is achieved when the graphite is continuously supplied into the sliding surfaces.[11] The graphite lubricating effects were investigated by Rohatgi et al.[7] on aluminium alloy-graphite particle composite, and Sarmadi et al.[12] on copper–graphite composites. They indicated that the surface and subsurface deformation, which occurred as a result of sliding; had a major influence on graphite film formation between the sliding parts. One of the main difficulties in describing the influence of matrix deformation and how it contributes to from the lubricating film is connected to the 3D complex configuration of the graphite which makes the present interpretation a little bit difficult. One of the most important factors in controlling the wear surface appearance during sliding is the hard particles. The significance of these particles was discussed elsewhere.[13] These particles are hard enough to indent and scratch the mating surfaces during the sliding condition. Therefore, micro-indentation tests were carried out close to the several graphite lamellas in order to better understanding of graphite film formation and its contribution to sliding wear.

As found earlier,[6] graphite lamellas with different orientations with respect to the abrasive wear particle showed dissimilar characteristics. Hence, it is believed that the orientation of the graphite play an important role on pushing out the behaviour of graphite under abrasive condition. To simplify the present explanation, it is necessary to specify the individual orientation of the lamellar graphite beneath the sliding surface. Fig. 1 (a) and (b) show two typical virgin graphite lamellas before indenting. Two indentations were made on both sides of the lamellar graphite.

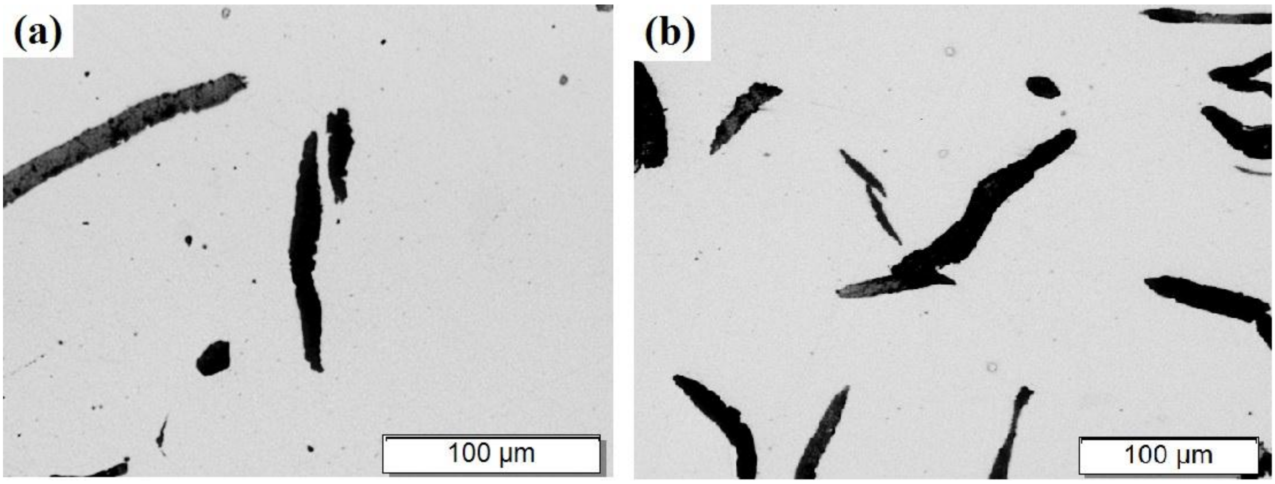

Fig. 1: Virgin graphite lamellas present in cast iron matrix**.**

Fig. 2 (a) and (b) illustrates the same graphite flakes after indentations. As being identified by comparing the images before and after indentations, graphite lamellae presented in Fig. 2 (a) compared with the virgin graphite showed no response to the indentation and was remained almost unaffected, although the indentations were made very close. However, SEM examinations revealed that the other graphite was squeezed and pushed out from its pocket as a result of indentation, clearly observed in Fig. 2 (b). Matrix deformation occurred around the indentation mark stimulated the graphite to be fractured and pushed out from its pocket. This particular tendency is simply recognizable from the shiny appearance of the pushed out graphite. A most likely reason for such difference may relate to the orientation of the lamellar graphite beneath the surface with respect to the indenter tip which strongly controls the pushing out tendencies of the graphite. A fast and simple way to reveal the flake graphite orientation is to remove the metal matrix by aggressive solutions such as Aqua regia or Nital solution. This etching technique (also called deep etching) was performed to determine the 3D morphology of the interconnected cell structure and orientation of the graphite flake under the affected regions, illustrated in Fig. 2 (c) and (d). As shown in deep etched image microstructure mainly consisted of a pearlite constituent. Hard phases are least affected constituents during etching process and stand out throughout the matrix after etching, as shown in Fig. 2 (c).

The SEM studies conducted on deep etched samples provided valuable information on graphite responses under abrasive (here indentations) conditions. Fig. 2 (c) shows a particular case, where the graphite remained almost unaffected. It confirms that the graphite perpendicular to the projected area obtained maximum resistance without indicating any pushing out tendency, whereas for the graphite towards the tip of indenter pushing out behaviour is observed as a result of deformation of the matrix. Interestingly, such phenomenon occurs only for those graphite lamellas which had particular orientation with respect to the indenter tip.

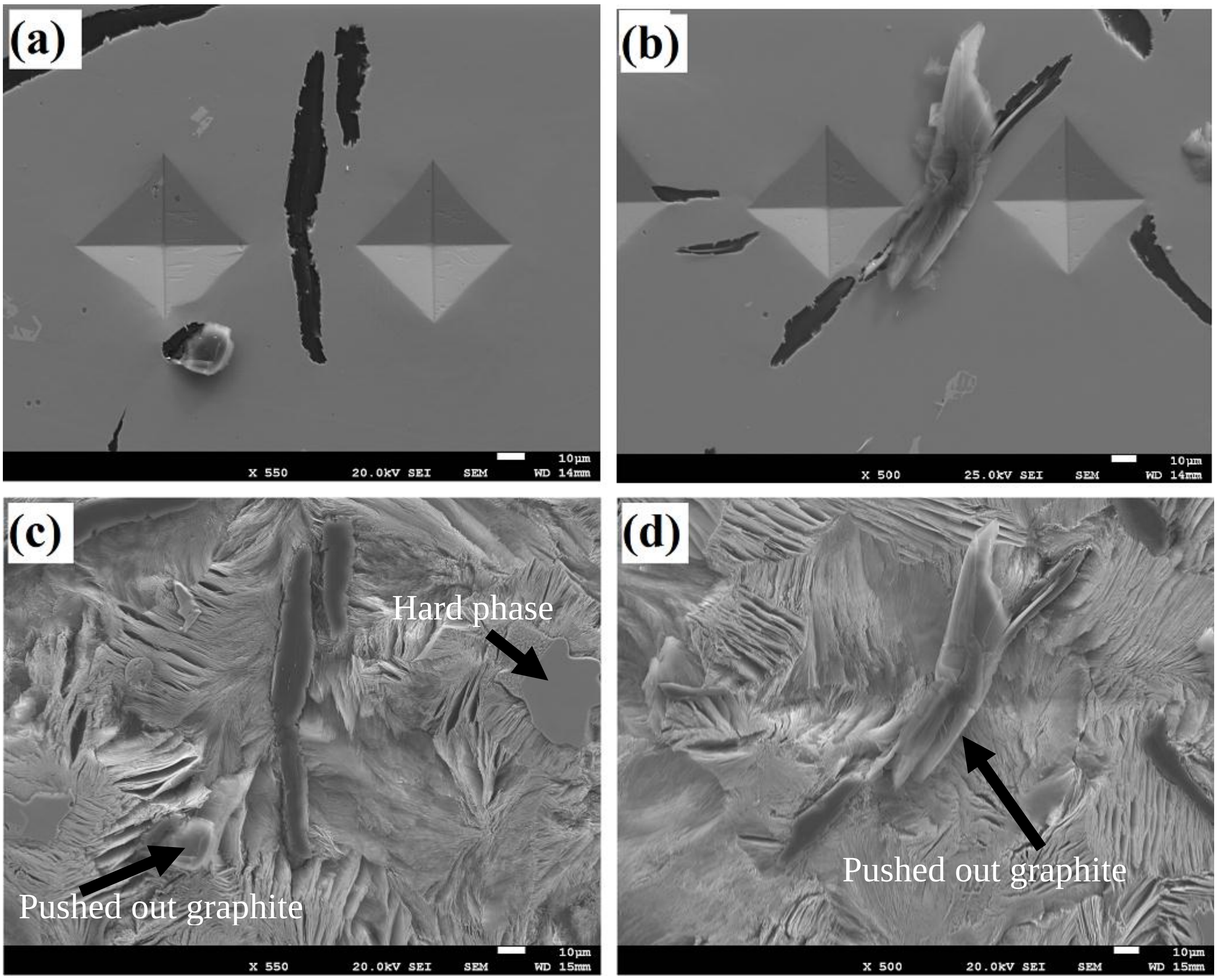

Fig. 2: SEM micrographs showing the graphite lamellas response when subjected to the indentation; (a) before etching, (b) after etching (deep etched by Aqua regia solution).

Fig. 3 illustrates two more cases where the graphite lamellas have been pushed out as a result of indentation made close to the graphite. Dissimilar behaviours are observed. These characteristics could represent that not only the applied load, but also the orientation of the graphite is an important factor to determine whether the graphite will be pushed out under a certain applying load or not. So that, two graphite flakes presented in Fig. 3 showed different responses when subjected to an individual indentation. These indicate that apart from the discussed variables (orientation and applied load), the size of the graphite seems to have a significant influence on observed phenomena. These parameters will be presented in details in upcoming studies.

Fig. 4 summarizes and illustrates schematically various positions of the graphite lamellas with respect to the indenter tip. In all cases, the indentation was made almost in the same distance from the graphite. Based on the observations on graphite lamellas responses when are subjected to similar indentation conditions such as load, dwell time and distance condition, case (a) shows the highest tendency due to less material under the indenter. Consequently, the deformation of the matrix is significantly higher compared to the other cases which stimulates the graphite to be compressed and pushed out for the pocket. In this circumstance the displacement of the graphite is accompanied by severe matrix deformation followed by covering the graphite pocket. The present occurrence is confirmed by SEM image presented in Fig. 3 (a).

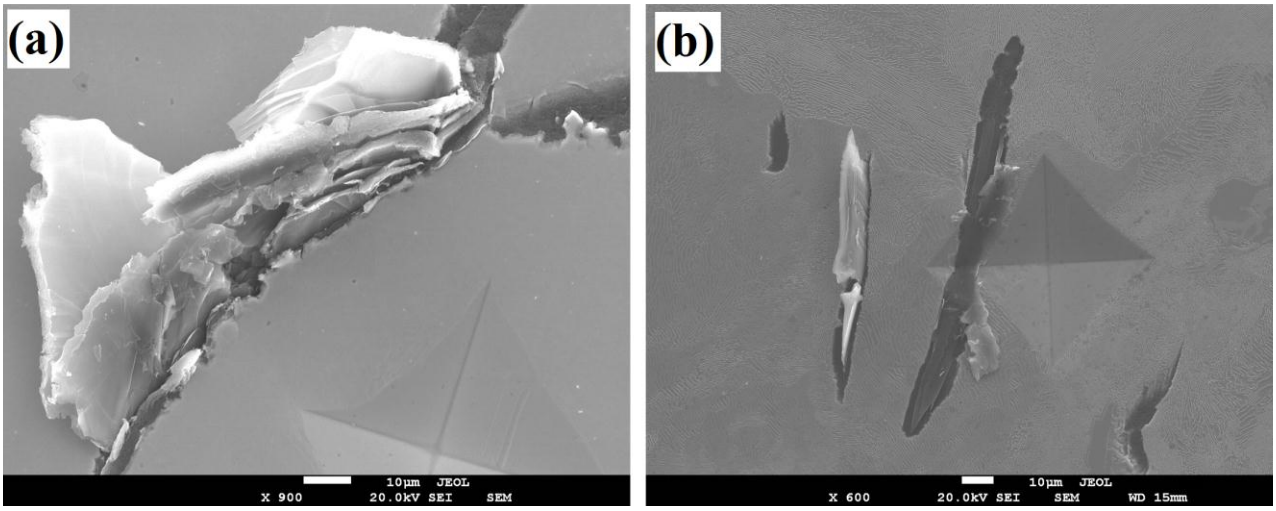

Fig. 3: Relationship between the graphite lamellas' orientation and their corresponding pushing out tendency.

As known strains are related to the stiffness of the material. Plastic flow appears when the stresses on the surface exceed the yield strength of the metal.[8] Consequently, in Fig. 4 (b) the highest resistance is resulted, as the stresses generated by indentation are carried by a larger volume of the matrix, and subsequently this reduces the net transferred strain to the graphite instead. As shown in Fig. 3 (b), under a sufficient load, the graphite is pushed out perpendicular to the indentation's projected area. However, the bigger graphite beside that did show an insignificant response to the same indentation which might be related to either its size or the orientation with respect to the indenter tip. Moreover, case (c) behaves between the cases (a) and (b). With regard to this matter that, however, there is much amount of matrix beneath the indenter carrying the applied load, when the load exceeds a certain limit (can be called threshold), the graphite will be subjected to the stress and fractured. In such instance, not the compressive stresses, but the tensile stress results in fracturing and extract the graphite form its natural state. However, but surprisingly, even in this situation the fractured area are located in centre of the flake graphite.

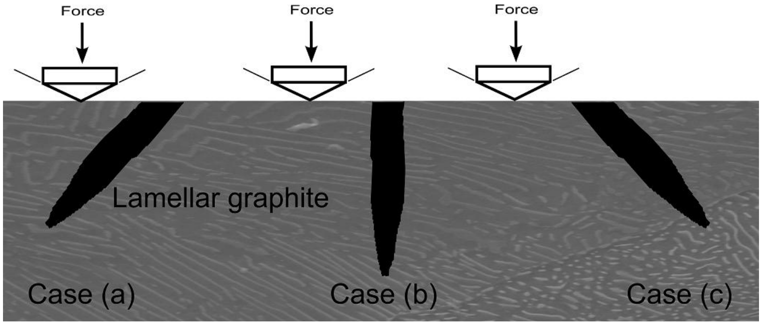

Fig. 4: Three possible cases of graphite lamellas' position in relation to the indenter tip.

From the above observations, and previous study,[13] it can be concluded that why the graphite lamellas are fractured and pushed out from the middle is mainly connected to either the presence of a soft area, together with a weak bonding in the centre of the graphite or the effect of the matrix which supports the graphite. The first assumption could be interpreted by the graphite flake nucleation theory. Based on that, the weak bonding between the graphite interlayers/or graphite and oxide particles in the middle of graphite may cause to this phenomenon. The nucleation mechanism of the lamellar graphite has been investigated for many decades. So, many theories have been proposed regarding the graphite nucleation mechanism. Warrick[14] proposed that the nucleation of lamellar graphite occurs on the complex oxides and sulfides particles. Campbell[15] proposed the concept of double films in order to highlight the role of silica-rich oxide (bifilms) in providing the substrates for the formation of oxysulfide particles as favored substrate for the graphite nucleating mechanism. There are also investigations, such as that performed by Riposan,[16] which have examined the influence of the MnS on the lamellar graphite nucleation theory. Considering the second claim, it is possible to show that the hardness gradually decreses reaching the minium in the center of the graphite. It might be directly connected to the fact that as closer the graphite to the matrix it is more supported by the surrounding matrix. This results in pushing the graphite out always from the center.

In order to verify this hypothesis, a gird includes (10×10) of nanoindents was performed on a typical lamellar graphite. A very low applied load of 10 mN with a 7μm distance was selected to hit the graphite. The results obtained in shown in Fig. 5, which was a bit contradictory with our expectation. The middle part of the graphite was found the softest area. The presence of the oxide particles or any other constituents (according to the graphite flake nucleation theory) should have shown a higher value which was not observed. The nano-hardness value is presented in GPa. The first indent (upper left corner of the pattern) showed a very high hardness which could be due to the hard phase such as carbides which distributed in the cast iron examined sample.

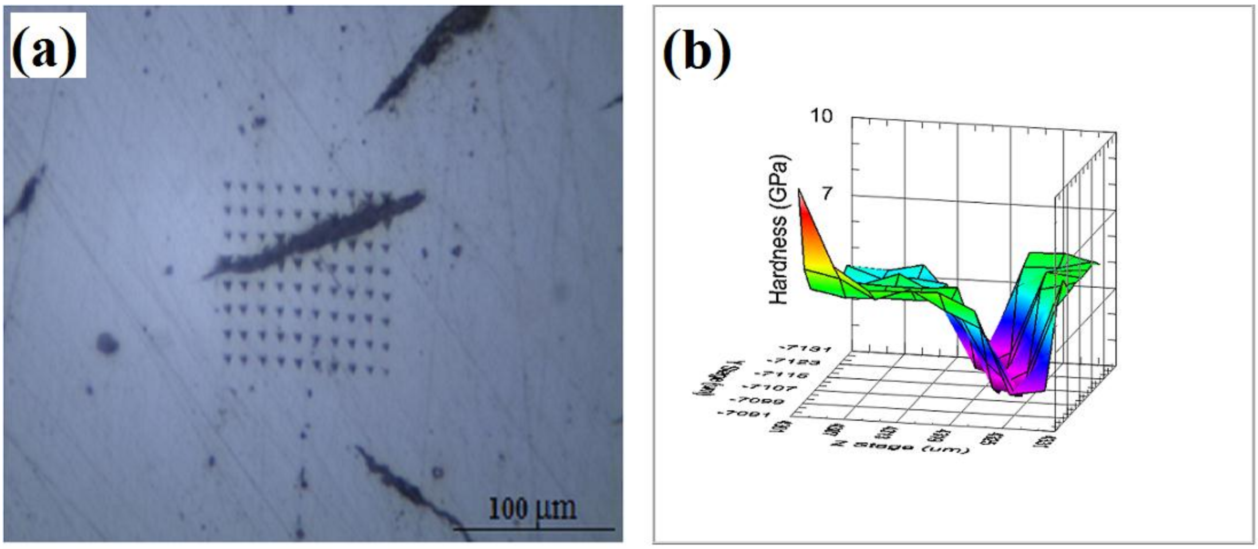

Fig. 5: (a) lamellar graphite with 10×10 nanoindents; (b) hardness value obtained from nano-indentation around and over the lamellar graphite

Interaction between the micro-scratch and lamellar graphite

The above demonstration could only give a crude clue about how the graphite lamellas with different orientation relative to the sliding direction contribute to forming the graphite solid lubricating film when are subjected to the abrasive sliding conditions. Meanwhile, it should be noted that the presented situation should only be considered as an extreme condition like sliding under dry conditions. To verify the ability of graphite to come out of their embedded state, the micro-scratch testing method was selected. Similar to the micro-indentation, different scenarios exist in scratching the matrix consisting of lamellar graphite with individual orientation in relation to the indenter tip.

As explained above, the lubricating behaviour of the graphite lamellas highly depends upon their orientation with respect to the sliding direction of the abrasive particles. On the interaction between a single hard particle, metal matrix and graphite lamellas, Fig. 6 demonstrates variant possible scenarios which may control the graphite film formation, simulated by scratching technique. In Fig. 6 (a), the indenter embedded into the graphite and scratched the graphite pocket. It resulted in chipping the graphites and in turn generating graphite particles. The current interaction is typically followed by smearing of graphite and lubricate both sliding surfaces by developing a very thin graphite later.

For those lamellas which were positioned parallel to the sliding direction, the deforming of the matrix caused by passing the particles along the lamellas lead to push out the graphite with similar mechanism which discussed above, as marked by white arrow in Fig. 6 (a). This was not the case for the graphites perpendicular to the sliding direction which behaved differently. The matrix near the graphite collapsed, and gave rise to cover the graphite pocket Fig. 6 (b). A slight pushed graphite was observed, indicated by arrows. The consequence is limiting further graphite supplying during the sliding. As observed in Fig. 6 (c) there was an appreciable difference in response of the graphite lamellas in which positioned with a particular angle relative to the sliding direction. No pushing out phenomenon was detected. With regard to the above discussion, this can be linked to the orientation of the lamellar graphite beneath the surface.

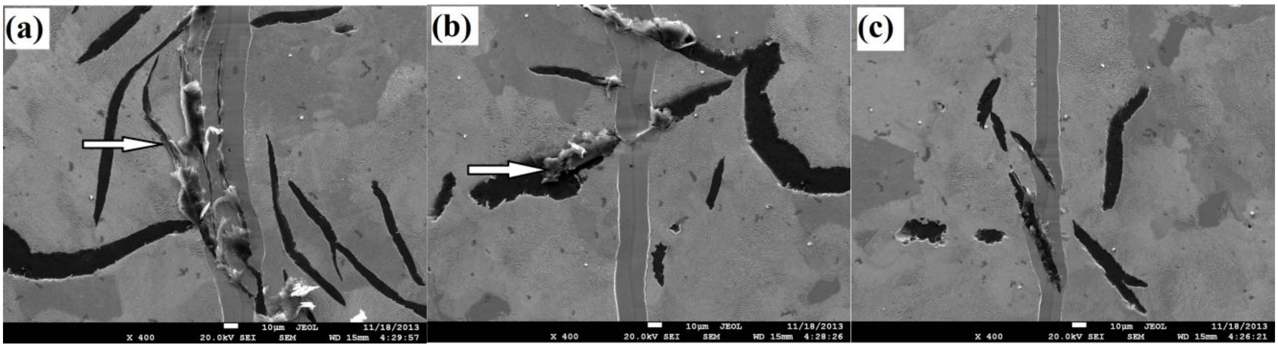

Fig. 6: Interaction between a single scratch pass made by Vickers micro-indenter, and graphite lamellas with different orientations with respect to the indenter tip.

A summarized possibilities of graphite lamellas' orientation when subjected to the scratching is schematically depicted in Fig. 7. In all cases only a 2D cross-sectional view of the graphite appears on the polished surface, therefore, it is fairly essential once more to emphasize on 3D feature of the graphite which makes the present interpretation more complicated. Fig. 7 (a) shows a case where the graphite in 2D is parallel to the scratch direction. In this situation the interaction includes the pushing out tendencies of the graphite controlled by both elastic and plastic deformation of the matrix during passing the particle along the graphite. Out of different graphite orientation potentials, only three possible occasions are illustrated with this consideration that in real case the graphite lamellas can position within range of -90° and +90°. Considering these three possibilities, the incorporation of each graphite would be individually different. With regard to the experimental evidence, during scratching the surface; case (a) has a higher tendency to the matrix deformation and pushing out tendency rather than cases (b) and (c).

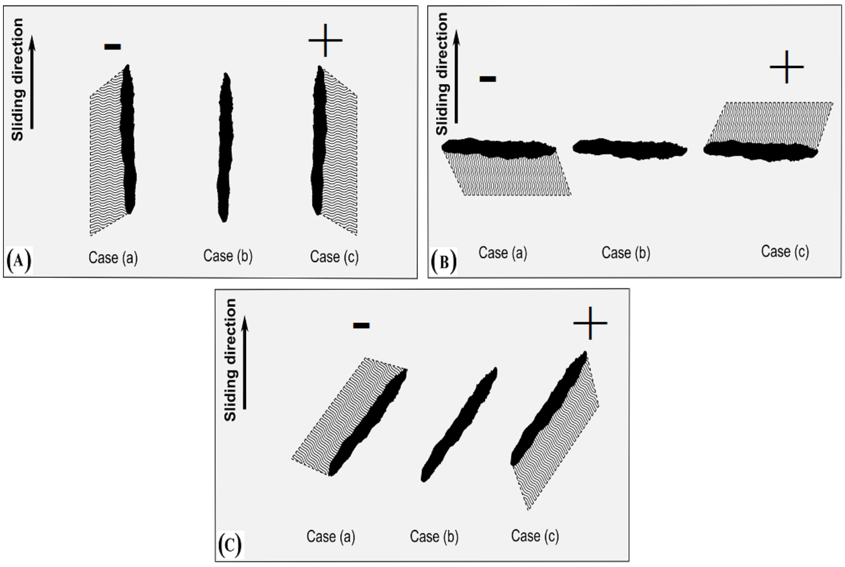

Fig. 7: Graphite lamellas with different orientations in relation to the sliding direction.

Furthermore, Fig. 7(b) shows a different case where the graphite is perpendicular to the scratching direction nevertheless different responses were detected for each. As studied in earlier work,[6] in general these graphite lamellas have higher resistance to be covered by deformed matrix than does the paralleled graphite, conformed by Fig. 6 (b). In the same study it was found that among graphite lamellas with different orientations those which had a certain range of orientation, i.e. around 60°, showed the highest covering resistance compared to the other ones.

Conclusions

The following conclusions are possible to make:

1. During a single scratch pass, it was observed that graphite lamellas were fractured and pushed out from the middle region similar to the micro-indentation test.
2. The orientation of the graphite lamellas controls the pushing out tendencies, so that if the graphite is oriented toward the position of the indenter the effect is more pronounced.

3. The graphite which is perpendicular to the micro-indentation projected area shows the highest pushing out resistance.
4. The nano-indentation test revealed that the centre part of the graphite is the softest part in lamellar graphite which could might the reason why the graphite starts to be pushed out from the centre.

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Acknowledgment

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2011) under grant agreement no. 265861 (Helios).