The effect of soaking and tempering temperatures on high vanadium alloys for grinding media

AD Mabeba[1,2] and CW Siyasiya[1]

[1] University of Pretoria**,** Lynnwood Rd, Hatfield, Pretoria, 0002, South Africa

[2] Mintek**,** 200 Malibongwe Drive, Randburg 2125, South Africa

Email:absalomm@mintek.co.za

Abstract. Vanadium produces the hardest carbides and can influence wear properties positively. However, due to the minerals' price fluctuations as a result of the current economic climate, vanadium is currently expensive and seldom used in wear resistant materials despite its valuable properties. Nevertheless, it is still important to study the effects of vanadium carbides on wear properties and later compare the cost/durability ratio to the other currently used industrial alloys. Vanadium has been used as a secondary alloying element in high chromium cast iron and has produced positive results through the influence of orientation and morphology of the eutectic carbide M_7C_3. Vanadium carbides are known to be discontinuous, which is helpful with regards to impact properties. Vanadium carbides alone cannot maintain high macro-hardness values and for improved results carbon is needed to increase the strength of the matrix. In this paper, the influence of the soaking and tempering temperatures on hardness and wear properties in a high vanadium alloy, 1.91C-0.82Mn-0.96Si-0.90Ni-1.35Cr-0.25Mo-6.12V, were investigated. The soaking temperatures were 1150 and 1250°C while the tempering temperatures were varied at 100°C interval from 300 °C to 600 °C. It was found that soaking at 1250°C increased the amount of retained austenite, but at the same time also improved the wear resistance in as quenched condition as well as after tempering up to 500 °C.

1. Introduction

Abrasive wear is a combination of indentation and scratching. It is often referred to as ploughing or micro plaguing of the contact surface. Restricting indentation of abrasive particles by hardening has proved to improve wear resistance. The main factors which have considerable effect on strengthening materials are heat treatment, alloying addition, influence of carbon content, the effects of carbides and work hardening. For improved wear properties, the hardness of the surface must be between 0.5 and 1.3 times the hardness of the abrasive [1]. Most common abrasives are hard and to produce a surface hardness that matches 1.3 times their hardness values may introduce brittleness.

The use of multi-alloy phase systems where the microstructure comprises of the matrix and a carbide phase are widely used in abrasive applications. The hard secondary phases improves the macro-hardness whilst the matrix maintains the toughness of the material. From literature V produces the hardest carbides (MC). Similar to Cr, V can also ensure the stability of a carbide phase. In addition to their hardness, VC precipitates are generally discontinuous and spherical and, therefore, are less detrimental to strength and toughness. The VC precipitates are also known to have a good cohesion to the matrix

owing to a cubic lattice which matches the austenitic lattice [2]. To promote their spheroisity, many authors have reported the addition of rare earths metals to the melts. The rare earth metals scavenges sulphur (S) and phosphorus (P) which segregates on the corners of the solidifying VC particles to promote dendritic growth through heterogeneous nucleation [1-3]. The dendritic carbide structures increase with C and V content as indicated Figure 1 [4]. Furthermore, the hardness increases with an increase in the volume fraction of the carbide phase to a point beyond which it declines due to increased volume fraction of the retained austenite (RA), Figure 2 [4].
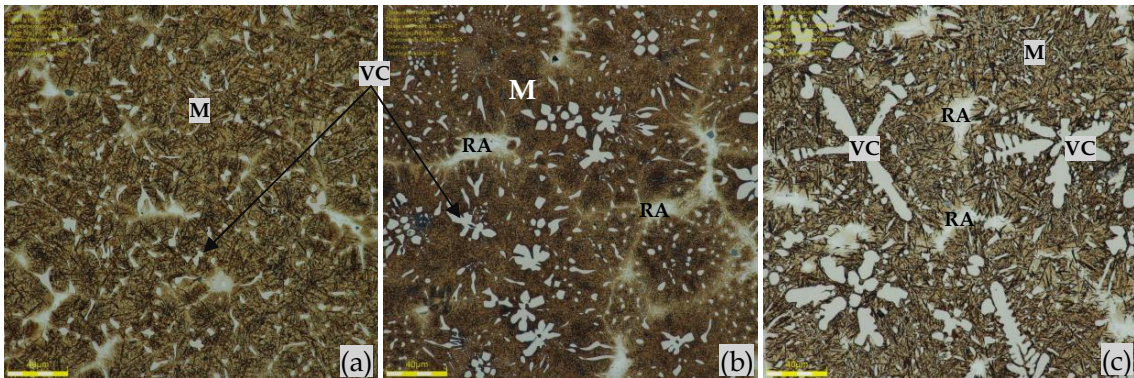

Figure 1. Micrographs of HVGM_alloys etched with Le-Pera's etchant showing martensite (M), V carbides (VC) and retained austenite (RA). (a) 1.70 mass% C, 6.74 mass% V, (b) 2.14 mass% C, 9.14 mass% V, (c) 2.91 mass% C, 11.0 mass% V [4], micrograph scale = 40um.
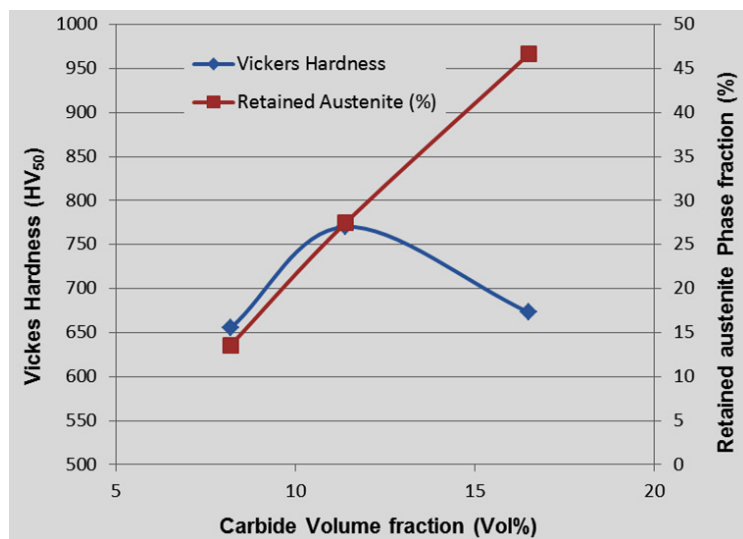

Figure 2. Photographs showing the relationship between carbide phase volume fraction, hardness and retained austenite [4].

Vanadium carbides form as VC, although a large degree of non-stoichiometry has been reported between $VC_{0.74}$ and $VC_{0.91}$ [5]. For the reaction: V + C = VC, the ratio of V to C is 4.2413:1 and for V + 0.74C = $VC_{0.74}$ and the ratio becomes 3.1412:1. For equilibrium conditions, the C needs to be in excess to strengthen the martensitic matrix. In this work the influence of soaking and tempering temperature in the high V alloy (HVGM-1) on the evolution of the microstructures and their subsequence influence on wear behaviour was investigated.

2. Experimental procedure
The experimental high HVGM-1 was produced in a 150 kg induction furnace fitted with an alumina crucible. The alloy was produced using scrap metal and ferro-alloys. The alloy was heated gradually

until 1550 °C where it was fully molten and tapped into a transfer ladle. The metal was cast into sand moulds made from silica sand and sodium silicate gel dried with CO_2.

The spark analysis chemical composition was as follow: 1.91C-0.82Mn-0.96Si-0.90Ni-1.35Cr-0.25Mo-6.12V. C and high amount of V was deliberately added to form the VC carbides for abrasion resistance. Cr, Mo and Ni were added for hardenability, toughness and strength of the matrix. Cr and V were also added to suppress graphitisation by utilising most of the C for carbide formation. Si was added to aid castability by improving fluidity.

The alloy was solution treated at 1150 and 1250 °C to allow for the dissolution of VC, after which it was quenched in oil. The solution treatment temperatures were based on the simultaneous thermal analyser (STA) results which indicated that the dissolution temperatures of VC are just below 1100°C [4]. The alloy was tempered between 300 and 600 °C at 100 °C intervals to study the effects of tempering temperature of the wear behaviour of the material.

The samples cross sections were mounted, ground with silicon carbide papers and polished to 1μm. The polished surfaces were etched with Le-Pera's etcant [6] (a mixture of 4% picric acid in ethanol and 1% potassium metabisulphide in water) to reveal the microstructures. The samples were further etched with 6% potassium metabisulphide and 2% sulphamic acid [6] in water to prepare for carbide phase quantification. The carbide phase was identified, quantified and ten measurements were made from each as quenched sample. The carbides were analysed using high resolution scanning electron microscope equipped with EDX (HRSEM-EDX).

Abrasion wear was evaluated under a three-body abrasion test rig as shown in Figure 3. Prior to testing the samples were cleaned ultrasonically. The initial mass of each sample was determined using an analytical balance. After each test was completed the samples were cleaned ultrasonically and the final sample mass determined. The wear rates of the samples were calculated using material mass loss as a function of time. The specimens were pressed under a constant load of 130N against the rim of a rotating wheel for 30 minutes. The average sand flow rate between the specimen and the rubber wheel was 350 g/min according to ASTM G65.
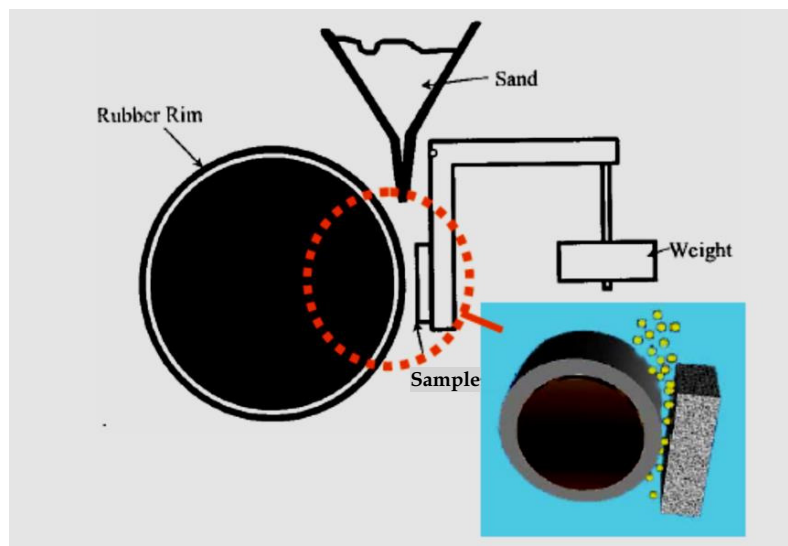

Figure-3: Schematic diagram of the dry sand/rubber wheel abrasion testing, DSRWAT, (adopted from ASTM G65)

XRD was used in order to determine the amount of the RA. The specimens were polished to 1μm and thereafter were electropolished in a 20% $HClO_4$-ethanol solution for XRD preparation to eliminate any strain induced martensite. The phase analysis was performed using a Bruker D8 equipped with a

LynxEye detector and Fe-filtered Co-Kα radiation. The phases were identified using EVA software. The relative phase amounts (wt%) was estimated using the Rietveld method (Topas program).

3.   Results and Discussion
3.1. Microstructural Analysis
The as-cast microstructure is shown in Figure 4. As may be seen, the alloy, HVGM-1, consisted of pearlite and VC precipitates.
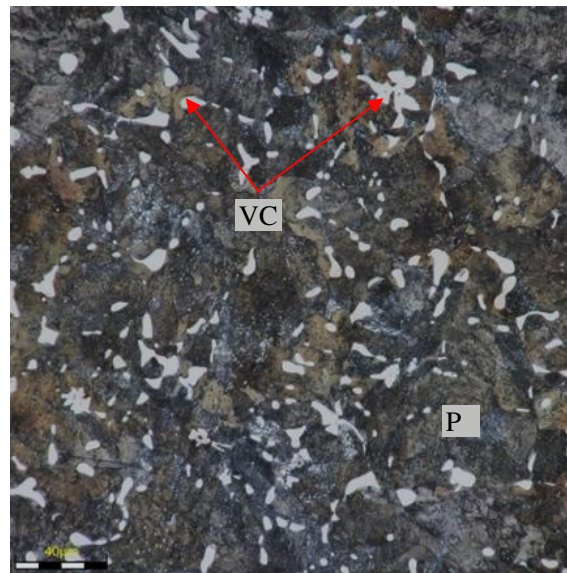

Figure-4: Micrograph of the as-cast microstructures of HVGM-1, micrograph scale = 40um.

After heat treatment, the alloy consisted of VC in a martensitic matrix. The smaller carbide structures were mostly spherical particles. The larger carbides also nucleated as spherical particles and grew heterogeneously by dendritic growth to form flower-like structures, Figure 5 (a). When the solution treatment was increased to 1250°C, the larger flower-like carbide structures dissolved partially and became spherical again as they reduced their surface energy, Figures 5 (b). The average carbide volume fractions of the as-quenched 1150°C and 1250°C was found to be 9.88 and 8.72% respectively when analysed by optical microscopy phase analysis software. Figure 6 shows the backscatter micrograph and EDX spectrum to confirm the composition of the vanadium carbides and they were found to be VC.
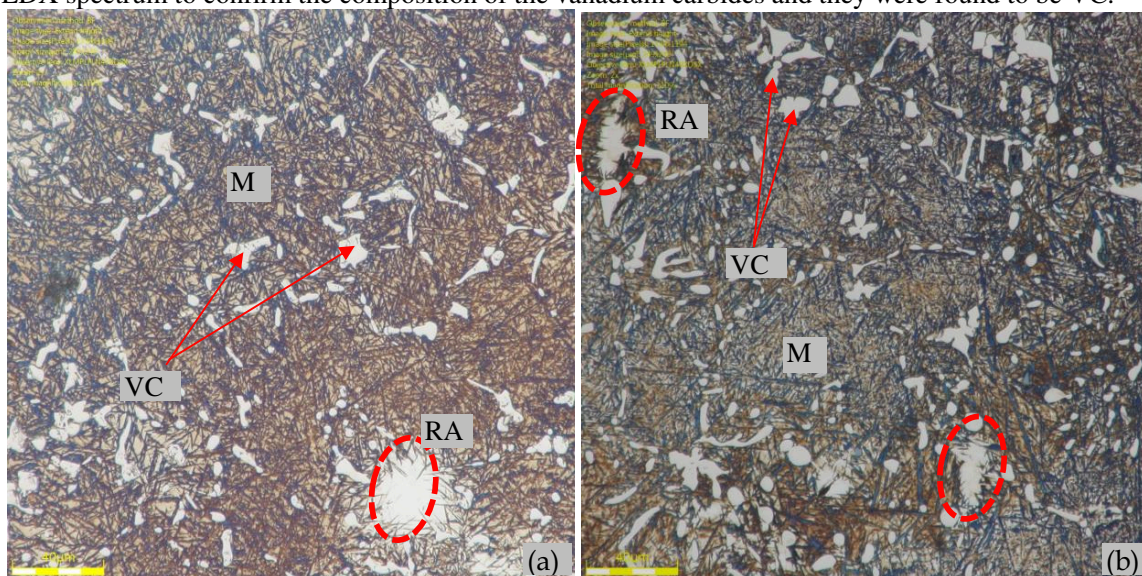

Figure-5: Micrograph of the as-quenched alloy, HVGM-1, solution treated at (a) 1150 °C and (b) 1250 °C. Micrograph scale = 40um.
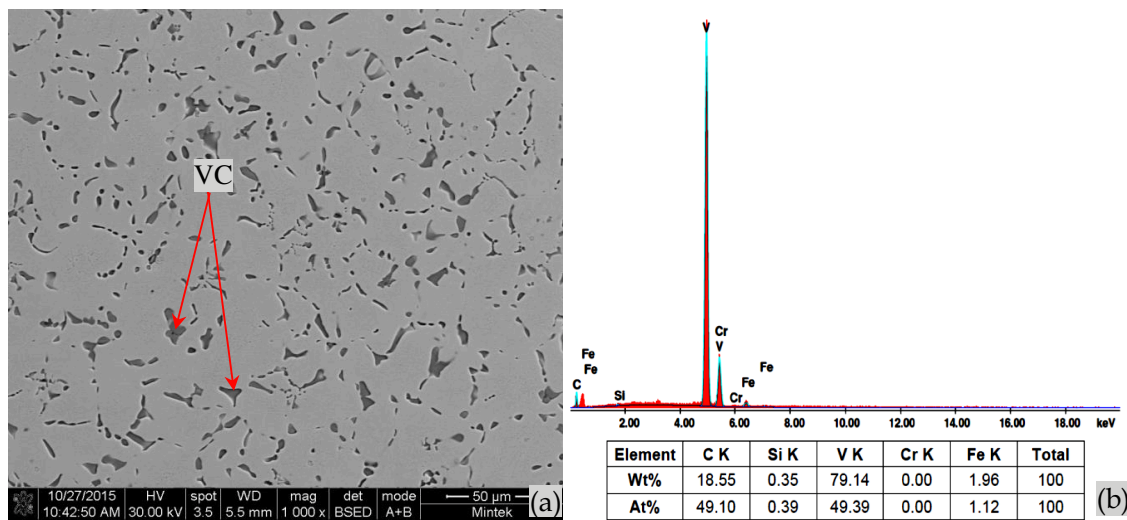
Element	C K	Si K	V K	Cr K	Fe K	Total
Wt%	18.55	0.35	79.14	0.00	1.96	100
At%	49.10	0.39	49.39	0.00	1.12	100

Figure-6: (a) Micrograph showing back scatter image of HVGM-1 1150°C and (a) EDX spectrum.

3.2. Hardness Measurements

The HRC hardness values of the alloy are graphically plotted in Figure 7. After solution treating at 1150 °C, the as-quenched hardness was higher. The relatively lower as-quenched hardness value after solution treating at 1250 °C was attributed to an increased amount of RA. After tempering at 300 °C the hardness drops significantly as a result of tempering and the hardness values were found to be similar. For both solution temperatures, the secondary peak hardness was observed at 400 °C. This was attributed to the precipitation of fine, coherent vanadium carbides. The matrix hardness dropped after tempering beyond 500 °C as the fine precipitates began to coarsen and lose their strengthening effect.
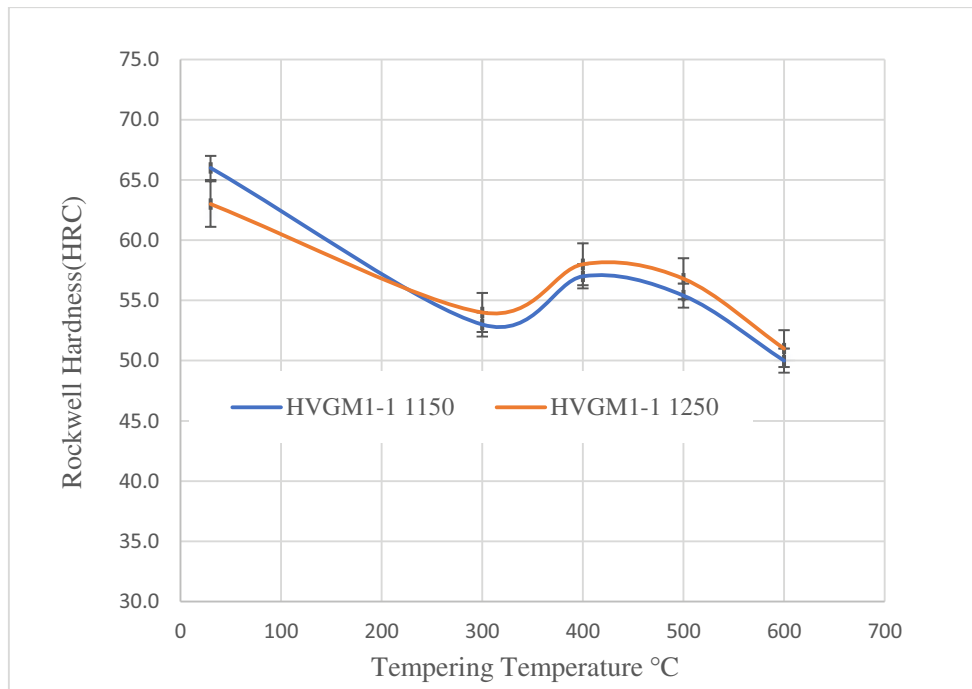

Figure-7: Rockwell hardness values as a function of the tempering temperature

3.3. Three Body Abrasion Wear Testing

The amount of RA as well as the Three Body Abrasion (TBA) wear resistance as a function of the tempering temperature are shown in Figure 8. As expected the RA increased with soaking temperature and decreased with an increase in tempering temperature. The RA only drastically reduced after tempering at 600 °C as a result of reduced stabilization of the austenite. However, as may be seen from

Fig 8, the reduction in the RA did not generally contribute to improved wear resistance because of the trade-off with coarsening of carbides. In other words, the increased wear rate at 600 °C simply meant that wear properties were best when the V precipitates were still fine. It would appear that in as-quenched condition, the combination of the hard carbide, hard martensitic and soft austenitic phases in both solution heat treatments of 1150 and 1250 °C was the optimum condition for wear resistance. Figure 9 (a) of as-quenched HVGM-1 shows less scratching from the three body abrasion test. After tempering at 600 °C, the scratches become deeper, and the softer martensitic matrix allows for the abrasion wear to plough out the carbides, Figure 9 (b).
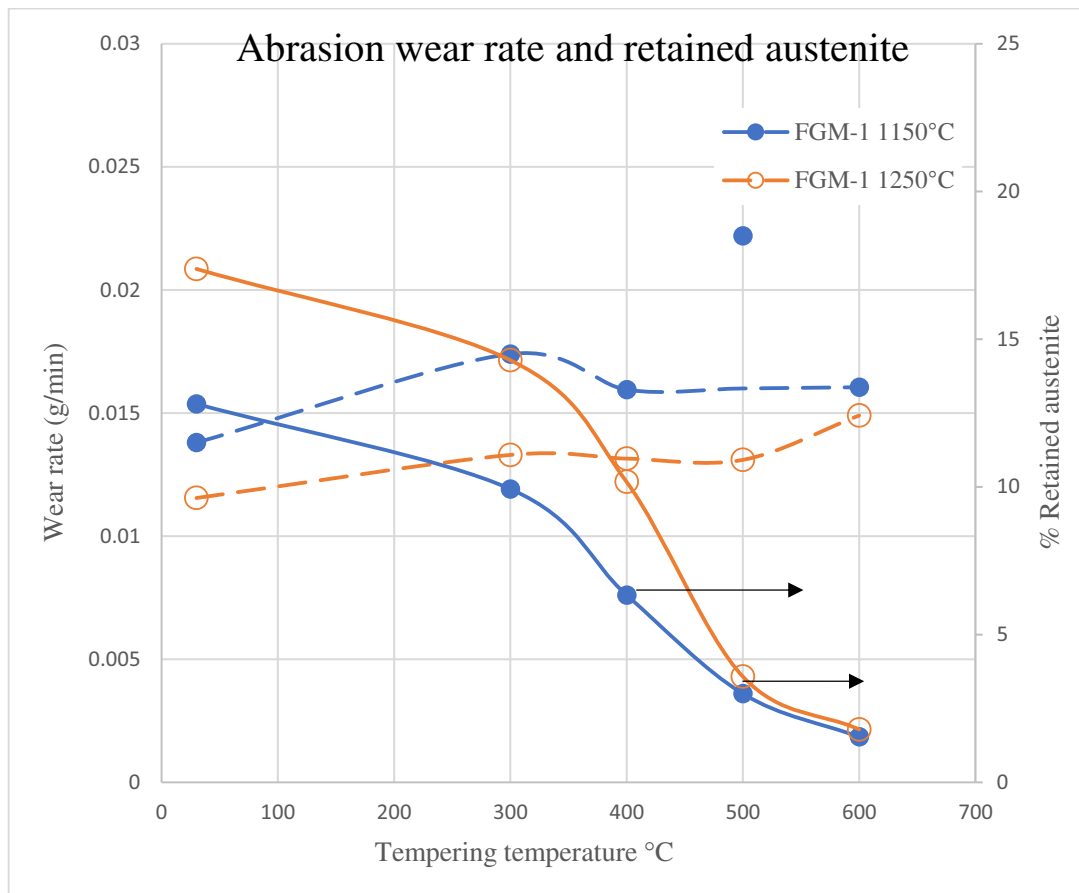

Figure-8: Three body abrasion wear rate and percentage retained austenite (RA) plotted as a function of the tempering temperature
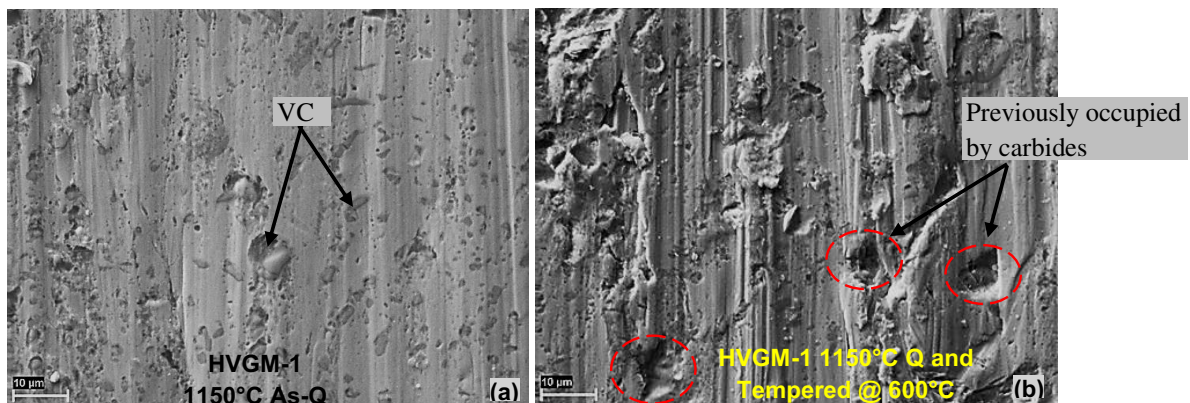

Figure-9: Dry sand/rubber wheel abrasion testing wear surfaces (a) HVGM-1 in as-quenched condition and (b) after tempering at 600 °C

4. Conclusions

- The alloy solution treated at 1250 °C with higher amount of RA exhibited better wear resistance.
- The combination of the hard carbide, hard martensitic and soft austenitic phases in both solution heat treatments of 1150 and 1250 °C was found to be optimum condition for wear resistance.

5. Acknowledgements

6. References

[1]　　Fleishchmann A H 1995 *The manufacture and investigation of abrasion of abrasion resistant FE-V-C alloys*

[2]　　Efremenko, V.G., Shimizu, K., Cheiliakh, A.P., Kozarevs'ka, T.V., Chabak, Y.G., Hara H. and Kusumoto K 2013 Abrasive wear resistance of spheroidal vanadium carbide cast irons. *Friction and Wear*, 34 (6), 466-474

[3]　　Wang Chao Chang, Hsu Heng Tsun, Ma Quin 1990 *Formation of spheroidal carbide in vanadium white cast iron by rare earth modification*

[4]　　Mabeba AD and Jonck J 2016 The use of vanadium carbides to produce a wear and impact resistant alloy for grinding balls *Ferrous and Base Metals Development Network Conference 2016*, Proceedings, AMI Symposium Series S91

[5]　　Stephen R. Shattynski Revised May 18 1978 *The Thermochemistry of Transition Metal Carbides*

[6]　　G.F. Vander Voort, Metallography principles and practice *Material Science and Engineering Series*