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# Growth of Vanadium Carbide by Halide-Activated Pack Diffusion

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**Abstract.** The present work investigates growth of vanadium carbide (VC) layers by the pack diffusion method on a Vanadis 6 tool steel. The VC layers were produced by pack diffusion at 1000°C for 1, 4 and 16 hours. The VC layers were characterized with optical and electron microscopy, Vickers hardness tests and X-ray diffraction. Homogeneous VC mono-phase layers with Vickers hardness of more than 2400 HV were obtained. Hardening and tempering of the vanadized Vanadis 6 steel did not affect the VC layers.

## Introduction

Transition metal carbides have been studied due to their excellent properties, such as high hardness, elevated melting temperature, good chemical and mechanical stability, and high thermal conductivity [see e.g. 1,2]. These characteristics ensure their application as high-temperature materials and/or components requiring high wear resistance [2].

Surface modification methods to produce hard metal carbides include physical vapor deposition (PVD), chemical vapor deposition (CVD) and thermo-reactive deposition/diffusion (TRD) techniques. The pack cementation method is a TRD technique that involves burying the substrate in a powder mixture containing a source of the element to be deposited, an inert element (usually Al<sub>2</sub>O<sub>3</sub>) and an activator. The process is an inexpensive and relatively easy way to obtain hard layers with the possibility of processing pieces with complex geometries [3].

Vanadium carbide (VC) layers produced by the TRD process have been successfully employed in e.g. the forging industry improving the service life of dies and tools [4]. In this sense it is important to study the mechanism of carbide layer formation and factors controlling the growth rate.

In the present work commercial Vanadis 6 tool steel was selected as a substrate for deposition of vanadium carbide by TRD using the pack cementation method. The growth and microstructure of vanadium carbide layers are investigated.

## Experimental

Vanadis 6 is a chromium-molybdenum-vanadium alloyed powder metallurgical tool steel, which is characterized by high compressive strength and is usually applied in forming operations, powder compacting, plastics moulds and tooling subjected to abrasive wear conditions. The nominal chemical composition of the steel is Fe- 2.1C- 1.0Si- 0.4Mn- 6.8Cr- 1.5Mo- 5.4V (wt-%). Initially cylindrical samples of Vanadis 6 with 20 mm in diameter and 3 mm in thickness were ground and polished to a mirror like surface finish. The samples were cleaned in ethanol and subjected to a pack cementation treatment for 1, 4 and 16 hours at a temperature of 1000°C.

The TRD process was carried out in a tube furnace with an argon protective atmosphere. The pack mixture consisted of 25 wt.% of Fe-V (containing 40 % V), 69 wt.% of Al<sub>2</sub>O<sub>3</sub> and 6 wt.% of NH<sub>4</sub>Cl. Precursors for the pack were weighed and mixed thoroughly. The pack was heated to 1000°C using a heating rate of approximately 8°C/min and cooled to room temperature inside the furnace in argon flow after the treatment; cooling took a least 4 hours.

The specimen vanadized for 16 hours was subjected to heat treatment at 1050°C for 20 min (under a protective atmosphere of Ar) followed by air cooling and tempering at 560°C for 1h three times.

For metallographic analysis cross sections of the samples were hot mounted, ground and polished with 3 and, finally, 1  $\mu\text{m}$  diamond suspension. For revealing the microstructure two etching procedures were applied: one using a 2% Nital solution and another applying Murakami's reagent, i.e. an aqueous solution of 10% NaOH + 10%  $\text{K}_3[\text{Fe}(\text{CN})_6]$ , to reveal the carbide grain structure of the layers.

Scanning electron microscopy was carried in a Phenom ProX table-top microscope operating in backscattered mode. Microhardness profiles over the vanadium carbide layers were measured with a Future Tech model FM-700 tester applying a load of 10 g and a dwell time of 5s.

For phase identification, X-ray diffraction (XRD) was performed on the surface of the samples using a Bruker D8 Discovery diffractometer equipped with Cr-K $\alpha$  radiation. The scans were obtained with step size of 0.03° and step time of 3s applying a symmetric Bragg-Brentano geometry.

In addition to the experimental work, thermodynamic equilibrium calculations were done using the software Thermo-Calc [5] with the Thermo-Calc Software SSUB SGTE Substances database version 3 [6].

## Results and discussion

**Pack chemistry - thermodynamic calculations.** The concept of the pack method is that the components of the pack react with each other and form gaseous species of the element to be transported to the steel surface, in this case vanadium compounds. Thus, the composition of the pack is important in order to obtain an effective process. Results of equilibrium calculations of the applied pack composition for vanadizing are shown in Figure 1.

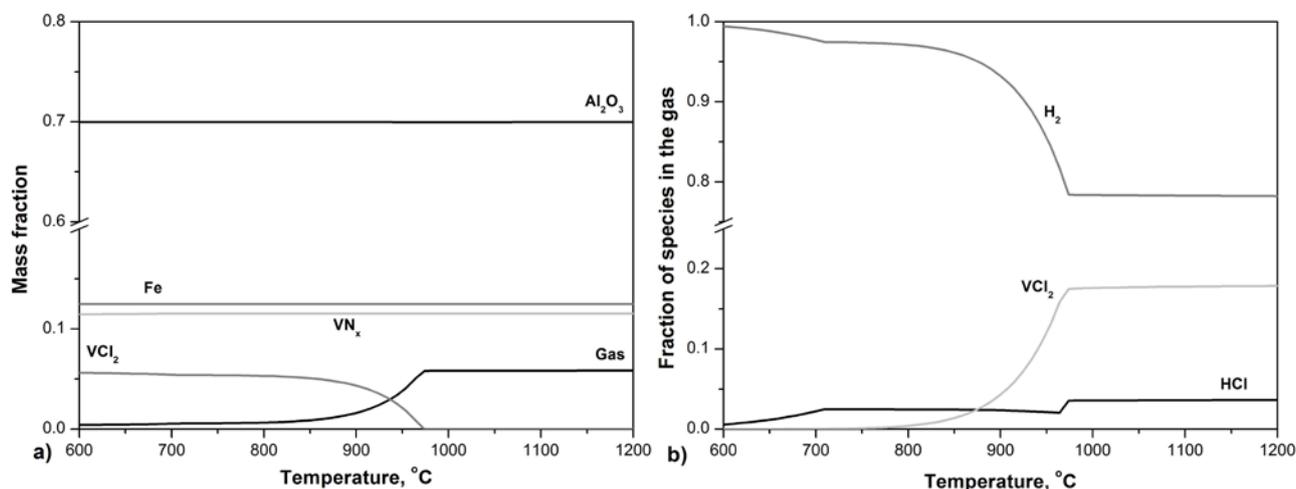


Figure 1 - Equilibrium calculations for a pack consisting of 69 wt%  $\text{Al}_2\text{O}_3$ , 6 wt%  $\text{NH}_4\text{Cl}$  and 25wt% Fe-V (60/40 mix): (a) mass fraction of the stable phases as a function of temperature; (b) fraction of species in the (produced) gas phase.

From Fig. 1a it is clear that  $\text{Al}_2\text{O}_3$  is inert and solely has the role as filler. The nitrogen released from the activator will give rise to the formation of  $\text{VN}_x$  nitrides; the chlorine from the activator forms  $\text{VCl}_2(\text{s})$ . At around 850-900°C the solid  $\text{VCl}_2$  begins to disappear and a significant amount of gaseous phase is formed mainly due to formation of  $\text{VCl}_2(\text{g})$  (Fig. 1a).

The gaseous phase consists largely of  $\text{H}_2$ ,  $\text{VCl}_2(\text{g})$  and  $\text{HCl}(\text{g})$  (Fig. 1b). Obviously,  $\text{VCl}_2(\text{g})$  is the active species for the vanadizing process. According to the calculations, vanadizing with a pack of the chosen composition should be possible from around 850°C where a significant fraction of  $\text{VCl}_2(\text{g})$  is formed.

The reaction responsible for depositing V on the surface, which then further reacts with carbon from the substrate material to form the VC layer is:



The HCl released through the above reaction is available to react with the pack and form new  $VCl_2(g)$ . At a process temperature of  $1000^\circ C$ , the fraction of  $VCl_2$  in the gas phase has reached its maximum, see Fig. 1b.

**Pack vanadizing.** Figure 2 presents a series of micrographs obtained from the cross section of Vanadis 6 samples which were pack vanadized at  $1000^\circ C$  for different times. Figs. 2a and 2b show light optical micrographs of the pack vanadized steel produced after 1 and 4 hours of treatment, respectively. After 1 hour a layer thickness of about  $7\mu m$  is obtained and both the surface and interface are relatively rough. A prolongation of the treatment time to 4 hours results in a layer of  $11\mu m$  and reduced surface roughness. Moreover, dark inclusions are observed in both layers which ascribed to the existence of originally present primary carbides.

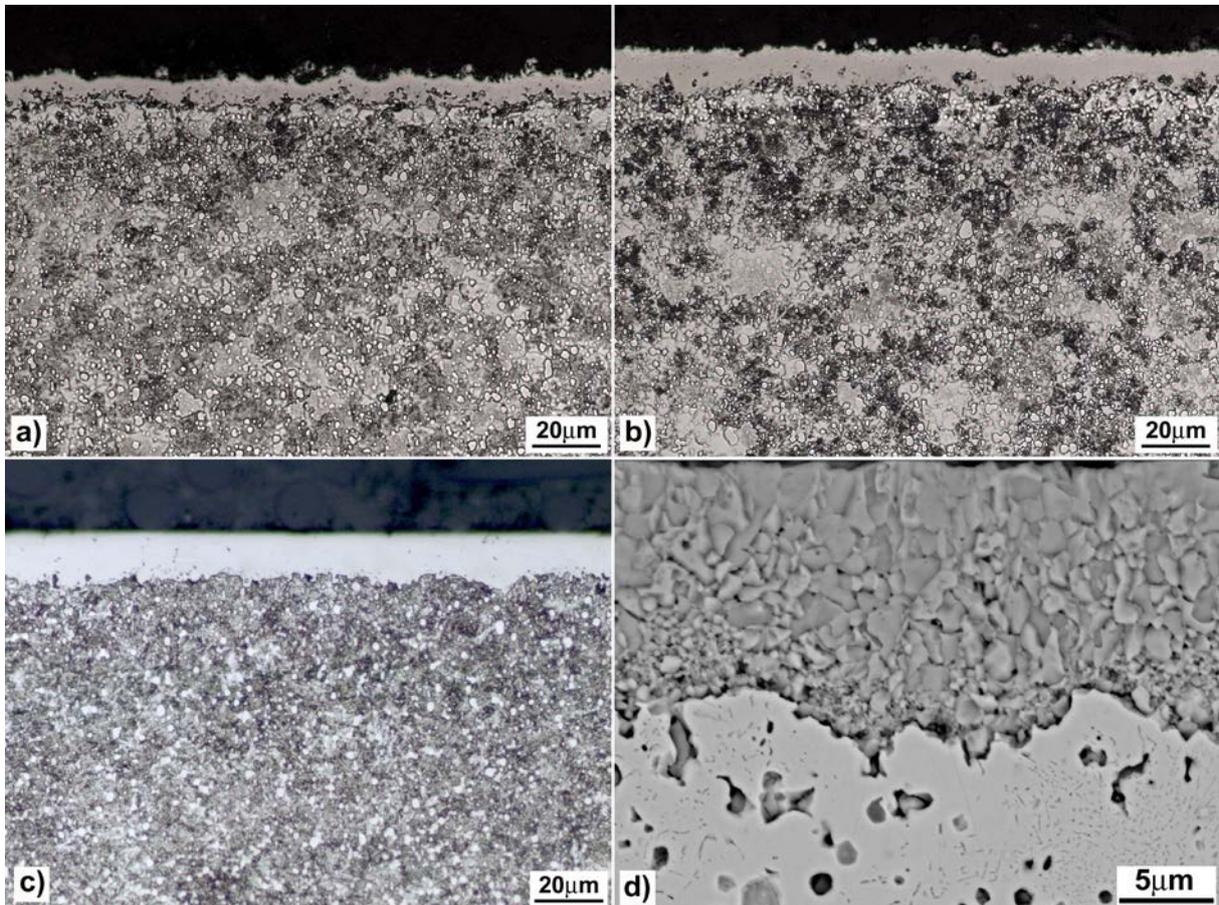


Figure 2 - Light optical micrographs of Vanadis 6 samples pack vanadized at  $1000^\circ C$  for: (a) 1h, (b) 4h, (c) 16h (after subsequent hardening) and (d) backscatter electron image after vanadizing 16h (and hardening). Etchant: (a-c) Nital 2% and (d) Murakami's reagent.

During heating the pack to the treatment temperature the activator decomposes releasing corrosive gases (most notably HCl, cf. Fig. 1b) that may cause etching on the sample surface and the appearance of a rough surface and interface. Clearly, Figs 2a and 2b support the argument that the first step may be influenced by this gas-phase etching. At a later stage in the vanadizing process, when the excess of the corrosive species decreases in the pack, the surface is covered with a certain

amount of stable vanadium carbide nuclei and the etching decreases and thus favoring the growth of the VC case.

Figs. 2c and 2d present the pack vanadized layer produced after 16 hours of treatment followed by austenitizing at 1050°C for 20min and tempering at 560°C for 1 hour three times. Before the hardening heat treatment the surface of the sample was cleaned by polishing. The light optical micrograph (Fig. 2c) reveals a featureless layer not attacked by the 2% Nital solution. The substrate has a microstructure consisting of tempered martensite and small rounded primary carbides. No significant differences in terms of layer morphology were observed in the layer after heat treatment. This indicates that there is a strong chemical bond and mechanical interlocking between the VC layer and the steel substrate.

Scanning electron microscopy (Fig. 2d) was performed on a sample etched with an alkaline Murakami solution aiming to reveal the carbide grain structure in the VC layer. The etchant attacks preferentially the carbides indicating that along the layer different carbide grain sizes are produced after pack cementation. The microstructure in Fig.2d shows very small grains close to the substrate surface. Estimations based on electron micrographs indicate that the vanadium carbide grain size is around 1-1.5 $\mu\text{m}$ . A few elongated grains may be found but it appears that the majority of the grains are equiaxed and in the micrometer range. It is noted that small grains are found more abundantly close to the substrate. It is contemplated that the region associated with larger grains corresponds to the part of the VC layer that grows outwardly and the region characterized by very small grains is growing into the substrate. This interpretation implies that repeated nucleation of VC occurs at the substrate/layer interface.

Previous studies reported that the carbide grain size gradually increases from the interface to the surface [2,7]. Fan *et al.* found very similar equiaxed vanadium carbide grains produced on a H13 tool steel sample after salt bath TRD [7,8]. The present results are in agreement with these published work, despite the use of a distinctively different process and substrate material.

The hardness profile measurements on the sample vanadized for 16 hours showed a hardness of at least 2500 HV (Fig. 3); the hardness values of the carbide layer obtained for the samples treated for 1 and 4 hours were comparable in magnitude.

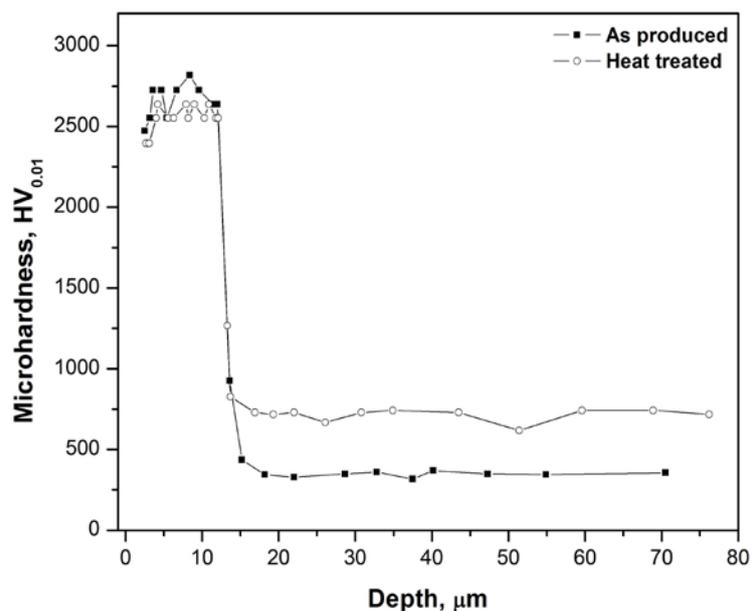


Figure 3 - Microhardness profiles of the pack vanadized Vanadis 6 for 16 hours before and after hardening heat treatment.

No indications of a decarburized sub-surface zone after the pack cementation treatment are observed in the hardness profiles in Fig.3. Such decarburization has been reported to develop as a consequence of carbon consumption to sustain growth of the carbide layer [4]. Absence of carbon

depletion implies that transport of carbon in the substrate towards the growing layer is not rate determining in layer development.

The influence of heat treatment on the hardness profile follows readily from the difference in substrate hardness for samples given in Fig.3. The hardness of the vanadium carbide layer is slightly reduced by the heat treatment, while the layer thickness is unaffected. The average hardness of the substrate after the pack cementation was found to be  $346 \pm 17 \text{HV}$  and after performing the austenitization and triple tempering the hardness is augmented to  $713 \pm 42 \text{HV}$ .

Hardness indentations close to and at the interface between the carbide layer and the substrate did not induce cracking or spalling of the layer, indicating strong adhesion of the layer produced by pack cementation.

X-ray diffractograms of Vanadis 6 pack vanadized for 16 hours - before and after heat treatment are given in Fig.4. According to the diffractograms the as-produced layer consists mainly of near-stoichiometric vanadium carbide (VC) with a very small amount of the  $\text{V}_2\text{C}$  carbide type. In addition, reflections from the iron ( $\alpha$  Fe) substrate are also clearly visible. Comparing the diffractograms of the as-produced and heat treated layer no significant differences regarding the obtained carbide type are encountered. Both present very narrow VC peaks with similar intensity ratio. This indicates a high thermal stability of the VC layer.

Scrutinizing the reflections from the Vanadis 6 substrate shows broadening of the  $\alpha$ -Fe line profiles in the as-deposited state. The sharper defined ferrite (tempered martensite) peaks observed for the heat treated sample are attributed to microstructural changes associated with the development and tempering of martensite.

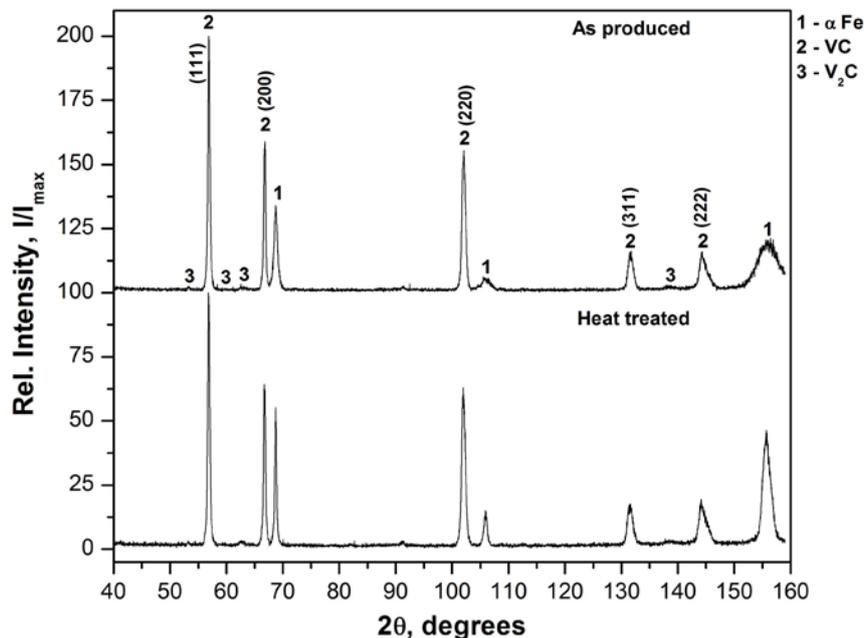


Figure 4 - X ray diffractogram of the VC layer pack vanadized for 16 hours - before (top) and after hardening heat treatment (bottom).

By using the symmetric Bragg-Brentano geometry the information depth increases with increasing  $2\theta$  angles. The diffractograms for both as-produced and heat treated samples show a pronounced peak asymmetry for high-angle reflections of VC -(311) and (222)- which may be associated with the presence of a compositional and/or stress gradient. Generally surface films grow in a preferential direction inducing a stress (and texture) gradient. Therefore further research is needed to unravel the stresses and the main factors contributing to the growth of the vanadium carbide layers on carbon containing materials.

Preliminary results of stress measurements by X-ray diffraction based techniques indicated compressive stresses of -1.9GPa before and -1.5GPa after the heat treatment of a Vanadis 6 sample vanadized for 16h.

## Summary

Pack cementation proved to be a straightforward and efficient process to obtain hard vanadium carbide layers on the Vanadis 6 tool steel. Thermodynamic equilibrium calculations indicate that  $VCl_2(g)$  is the active species responsible for transport of V, from the pack to the steel surface, that enables vanadizing. Increasing the vanadizing treatment time appears to mitigate surface roughness. Hardness values of up to 2750 HV were obtained for the grown VC layers. No significant differences were observed on hardness and vanadium carbide type after heat treatment of the vanadized steel.

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