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Duplex ceramic coating produced by low temperature thermo-reactive deposition and diffusion on the cold work tool steel substrate: Thermodynamics, kinetics and modeling

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Abstract

Specimens of DIN 100MnCrW4 steel (type O1 tool steel) have been cut and prepared for performing a duplex surface treatment involving nitriding and low temperature vanadium thermo-reactive deposition and diffusion (TRD) technique. The TRD process was performed in a molten salt bath at different temperatures of 575, 650 and 725 °C for 1–30 h. The treatment formed a vanadium carbonitride coating with the thickness up to 10.5 μm on a hardened diffusion zone. Characterizations by means of an optical microscope (OM), scanning electron microscope equipped with energy dispersive X-ray spectrometer (SEM–EDS) and X-ray diffraction analysis (XRD) indicated that the compact and dense coating mainly consisted of V(C,N) and V_2(C,N) phases. All the growth processes of the formed vanadium carbonitride layer obtained by TRD followed a parabolic kinetics while the calculated activation energy (Q) for the treatment was 181.1 kJ/mol. An artificial neural network (ANN) based model for predicting the layer thickness of ceramic coatings was presented. Constructing the model, training, validating and testing of experimental results from 72 different specimens were conducted. The data used as inputs in the proposed model were arranged in a format of five parameters that comprised of "*pre-nitriding time*", "*ferro-vanadium particle size*", "*ferro-vanadium weight percent*", "*salt bath temperature*" and "*coating time*". Accordingly, the thickness of duplex coating in each specimen was estimated accurately. Finally, the proposed ANN-based model showed a strong potential for predicting the layer thickness of duplex ceramic coating performed by the TRD technique on the substrate of cold work tool steel.

Keywords: Duplex surface treatment; Thermo-reactive deposition and diffusion (TRD); Thermodynamics; Kinetics; Modeling

1. Introduction

Transition metal nitrides and carbides have been commonly used in tribological applications to improve the mechanical life of components due to their higher hardness and melting point, excellent wear resistance, low coefficient of friction and good corrosion resistance [1–3]. Different techniques are being used to produce transition metal carbides and nitrides coatings such as chemical vapor deposition (CVD), physical vapor deposition (PVD) and thermo-reactive deposition and diffusion (TRD) [3–6]. Both CVD and PVD require vacuum and controlled atmospheres along with complex equipments which make them very expensive. In comparison, the TRD involves relatively simple equipment, low in cost and environmentally friendly.

TRD is a hard coating with excellent adhesion to substrate whereby transition metallic elements such as chromium (Cr), vanadium (V), titanium (Ti), or aluminum (Al) are thermo-chemically deposited on the surface of a substrate while that the

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metallic element reacts with an interstitial element such as carbon (C), nitrogen (N), or boron (B) that diffuses to the surface from the substrate [6–9]. The driving force for diffusion of the interstitial element is the thermodynamic stability of the formed surface compound(s). Previous studies have shown that the formed coating has a distinct, flat interface with the steel substrate; however, the mechanism of the formation of the distinct interface was not explained in detail [1,5,9].

The Toyota Diffusion (TD) process, developed by the Toyota Central Research Institute, is one example of TRD [10]. In the TD process, a vanadium carbide layer is formed at 800–1050 °C by outward diffusion of carbon from a steel substrate. The thickness of the layer formed under identical processing conditions is limited and differs by the carbon content of the substrate being treated [3,11].

It has been reported that vanadium carbide/carbonitride/nitride coatings grow at a faster rate by pre-treating with carburizing, nitrocarburizing and/or nitriding [12]. This is due to the fact that pre-treatment raises the concentration of interstitials in the surface of the substrate prior to TD treatment. Chicco et al. [12] carburized H13 tool steel by following TD vanadizing to yield a vanadium carbide coating with the thickness of 4.6 µm. Even thicker coatings are achievable with pre-nitrocarburizing and pre-nitriding because vanadium has a higher affinity for nitrogen rather than carbon. However, superior hardness values were reported when carbon was presented in the coating. Similar results could be expectable with other transition metals because they generally form harder carbides rather than nitrides [13].

There is some limited experimental evidences conclude that TRD coatings may be performed at lower temperatures due to the effect of superficial enrichment in interstitials. Vanadium carbonitride and chromium carbonitride coatings have been deposited on a variety of substrate materials by nitriding followed by TD salt-bath treatment at 530–700 °C [14–17]. Arai et al. [18–20], at the *Toyota Central Research and Development Laboratory*, claimed to have formed 8 µm thick CrN layers on pre-nitrided substrates after 50 h of treatment at 570 °C in a fluidized-bed reactor. Ohta et al. [14], formed chromium carbonitride coatings by nitriding followed by TRD at 530–700 °C in a salt bath. They revealed that a dark zone occupied a region approximately extended 2–4 µm directly beneath the coating layer in which iron was found to be the major remaining element. Diffusion of nitrogen from this area towards the surface was assumed to be the cause.

No matter what coating method was utilized, the nature of the surface formed during pre-treatment have an important influence on the final coating's properties [21–25]. It is also vital to understand the processes whereby interstitial atoms diffuse to the surface during TRD.

Neural networks can be applied to variety of engineering problems that do not have algorithmic solutions or algorithmic solutions that are too complex to be found. To overcome this problem, ANN uses the samples to obtain the models of such systems. Their ability to learn by example makes ANNs very flexible and powerful. Therefore, neural networks have been extremely used for solving regression and classification problems in many fields [26–28]. Recently, neural networks have been used in the areas that require computational techniques, such as pattern recognition, optical character recognition, predicting outcomes, and problem classification [29,30]. However, in materials science and engineering fields, the researchers have used ANN-based techniques to develop prediction models for different properties of materials [31–38].

To the authors' knowledge, little has been reported in the literature regarding the duplex vanadizing of steels at temperatures below 700 °C. Therefore, the purpose of this study is to produce vanadium carbonitride layer on pre-treated and nitrocarburized steel substrate through TRD and also to investigate the cross-section morphology, phase structure and microhardness, as well as, thermodynamics and growth kinetics of the formed layer. Based on the performed literature survey, there is no work investigating the effects of chemical compositions and coating parameters on the layer thickness of vanadium carbonitride on DIN 100MnCrW4 steel substrate. Meanwhile, ANN was used to model the deposited duplex layer; hence, 72 coating thickness data were examined, trained, validated and tested by an ANN algorithm. The obtained results were also compared by experimental ones to evaluate the approach power for predicting the effects of inputs on the layer thickness of duplex ceramic coating of the cold work tool steel substrate.

2. Materials and methods

DIN 100MnCrW4 steel (type O1 cold work tool steel) specimens, employed as the substrate in this study, with dimensions of 10 mm × 10 mm × 10 mm were polished, cleaned and then nitrided for 1.5–3 h through salt bath process at 570 °C. The chemical composition of utilized steel is listed in Table 1. Meanwhile, continuous cooling transformation (CCT) diagram for the applied material is also illustrated in Fig. 1. The used nitriding bath mixture was comprised of 30 $NaCN+25\ Na_2CO_3+45\ KCl$ (wt%) which was aged for 12 h before nitriding. For vanadizing, the specimens were immersed in baths of 33 $NaCl+67\ CaCl_2$ (wt%). Both nitriding and vanadizing have been done in the molten salt baths at temperature below 725 °C. Vanadizing with three different bath composition ratios ($NaCl/CaCl_2=$ 0.25, 0.5, 0.75), different pre-nitriding times (0, 1.5, 3 h), different vanadizing

Table 1
Chamical composition of DIN 100MnCrW4 steel introduced as substrate in this study.

Element	Mass percentage (wt%)
C	0.950
Mn	1.000
W	0.500
Cr	0.500
Si	0.250
V	0.100
S	0.035
P	0.035
Fe	Bal.