Molecular Modelling of Interface Occurrence of Ti (C,N,O) – Fe Composite

A. BIEDUNKIEWICZ* AND P. NOWOROL

Institute of Material Engineering, Technical University of Szczecin
al. Piastów 19, 70-310 Szczecin, Poland

High demands that are posed to modern materials exposed to the action of thermal, mechanical or chemical loads oblige one to seek new solutions and technologies. Compliance with these expectations requires designing the composite materials without structural notches, and the application of gradient materials. Transient zone, determining the interphase compound, is an essential element of each composite. Interaction forces creating transient structural zones determine the value of the adhesion forces. Among all forces determining the adhesion the strongest are the forces of a chemical bond. Therefore, the molecular modeling should be a valuable method to investigate and design the composites. In the presented research the conditions of coat adhesion of the Ti (C,N,O)-type to steel substrate are taken into consideration. Using a standard quantum-chemistry program, the energies of the following systems (clusters) — $\text{Fe}-\alpha-\text{N}-\text{Ti}$, $\text{Fe}-\alpha-\text{C}-\text{Ti}$, and $\text{Fe}-\alpha-\text{O}-\text{Ti}$ — are calculated. The aim of the analysis was to determine the conditions for preparation of initial substrate, which are advantageous for the process of coat formation. This analysis confirmed benefits arising from nitriding as an initial treatment of the steel.

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1. Introduction

The method used most often to reduce the wear is a special formation of the surface layer upon the blades of cutting tools and coating them with thin films, formed primarily by the compounds of carbon, nitrogen, and boron with transient metals. There is a technical trend to make universal multifunctional coatings such

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*corresponding author; e-mail: anbied@safona.tuniv.szczecin.pl

that the coat and the steel substrate combine together to create a kind of composite. Such composite should exhibit an appropriate quality, which is determined by several parameters such as structure, chemical composition, hardness, thickness, surface roughness, coefficient of friction, and primarily adhesion. Film adhesion is one of the major qualities for every industrial coating.

In recent years the techniques based on a nonconventional synthesis of a material from plasma, i.e. plasma assisted chemical vapour deposition (PACVD) have achieved a significant position in terms of hard coating manufacturing [1–3]. One of the major advantages of the methods incorporated into the range of plasma techniques is a low temperature coating deposition, which allows coating of tools made of high-speed steel without a risk of their tempering. There are also low-temperature techniques of coatings deposition, which are based on the conventional synthesis of material performed by the sol-gel method [4, 5]. The problems of adhesion characteristic of low-temperature techniques have received much attention [6, 7].

The design of composites without the so-called structural notches has to comply with high fatigue resistance, along with corrosion resistance and wear in the friction process. To achieve a satisfactory adhesion without creating the diffusion zone, the chemical bonds between material layers should occur [8, 9]. A question arises how the conditions of coating synthesis with the participation of substrate could be achieved. The answer to this question can be found among the solutions already existing in practice. A trend associated with the integration of various kinds of the surface treatment methods has been observed, e.g. the nitriding of steel substrate and the formation of composite coating TiC/Ti(C,N)/TiN [10]. Can these processes be predicted and optimised? One of the ways to solve such problems is a thermodynamic analysis.

The aim of the present work is the analysis of thermodynamic functions of the reactions proceeding the process of deposition of the Ti-layer on the Fe-substrate. The calculations were performed using the method of stationary calculation described in the literature as “HyperChem” program. HyperChem is a molecular modeling and simulation program that enables us to perform complex chemical calculations [11].

2. Theory

The energy and a spatial arrangement of elements forming the structure as well as a character of the chemical bond is the decisive factor affecting the material properties. Development of the quantum chemistry in connection with the computer techniques resulted in creation of the theoretical models describing interactions occurring between atoms and molecules. The molecular modeling enables one a prediction of the real properties and the simulation of molecular behaviour under specific conditions. This provides an important advantage, because such a theoretical solution of technical problems does not require performing tedious experimental works.

In this paper the results of thermodynamic calculations for the systems (clusters) of the following types: Fe- α -N-Ti, Fe- α -C-Ti, and Fe- α -O-Ti, are presented. As the workspace for calculation of the total energy of reagents was limited, the Fe- α crystal contains 16 atoms of Fe. The space group is *Im3m*. The atomic positions of particular Fe atoms were taken from [12]. Heat of formation of particular products of the reaction under standard conditions was calculated by subtracting the total energy of the reagents participating in the formation of products.

In the first stage, the total energies of the respective bonds and the heats of the formation were determined for the systems Fe- α -Fe5/Fe, Fe- α -Fe5/Ti, Fe- α -Fe5/Ti-C, Fe- α -Fe/Ti-N, and Fe- α -Fe5/Ti-O, taking into consideration all possible locations of the non-metal atoms in the α -Fe cell and outside this cell. By studying the sensitivity of the systems against the location of the carbon, nitrogen or oxygen atoms in the Fe- α -Fe5/Fe and Fe- α -Fe5/Ti cells, the optimization of the clusters Fe- α -Fe5/Ti-C, Fe- α -Fe/Ti-N, and Fe- α -Fe5/Ti-O has also been carried out. As the optimization criterion the minimum of the system energy was chosen. The lowest value of minimum on the energy surface for reagents was calculated by geometry optimization method-ZINDO/1. This method is a variation of intermediate neglect of differential overlap (INDO) method extended to transition metals [13].

3. Results

The results of analyses performed by means of HyperChem program are presented below. Visualization of the analysed systems is presented in Fig. 1, in which the positions of titanium, carbon or nitrogen atoms are shown. Values of the system energy, used for plotting the energy diagram for the reaction of titanizing of iron, are given below

$$Q = 50751.92 \text{ kcal/mol};$$

$$Q = 2374.38 \text{ kcal/mol};$$

$$Q = 78.80 \text{ kcal/mol};$$

nitrogen in front of the crystal $Q = -7.94 \text{ kcal/mol}$,

on the surface of the crystal $Q = -64.92 \text{ kcal/mol}$,

inside the crystal $Q = -87.30 \text{ kcal/mol}$;

Fig. 1. Energy diagram for the reaction of titanizing the iron.

carbon in front of the crystal $Q = -117.78$ kcal/mol,
on the surface of the crystal $Q = -222.2$ kcal/mol,
inside the crystal $Q = -301.00$ kcal/mol;

oxygen in front of the crystal $Q = -48.14$ kcal/mol,
on the surface of the crystal $Q = 80.16$ kcal/mol,
inside the crystal $Q = 44.53$ kcal/mol;

$Q_{\text{optimum}} = -17.74$ kcal/mol;

$Q_{\text{optimum}} = -878.37$ kcal/mol.

Numbers given in brackets represent the reaction formation of the analysed systems and the lowest value of the energy.

4. Conclusions

1. The thermodynamic analysis show that the system composed of the iron, titanium, and nitrogen atoms, $15\text{Fe-}\alpha\text{-N-Fe5/Ti}(0,0.25,0.255)$, is energetically favourable.
2. From the viewpoint of adhesion the nitriding, before the process of deposition of the titanium coatings on the steel substrates, is a beneficial treatment.

3. The results obtained do agree with experimental results [14–17].
4. The technologies for producing steel, with properties improved as a result of treatment by nitriding and the formation of the titanium layers, have been already developed; e.g. Ti(N,C,O) by the PACVD–WIMP technology, developed in the Institute of Precision Mechanics, Warsaw.

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