ENERGETIC STUDIES ON DIFFERENT TiAlN CRYSTALLINE STRUCTURES USING DFT ANALYSIS

ESTUDIO ENERGÉTICO DE LAS DIFERENTES ESTRUCTURAS CRISTALINAS UTILIZANDO ANÁLISIS DFT

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Abstract

TiN, AlN and TiAlN were simulated using density functional theory (DFT), obtaining the Mulliken population analysis, electron total density and total energy. These simulations were carried out in order to observe the influence of Al and Ti atoms inclusion in the TiN-FCC and AlN-HCP crystalline structures respectively. Single point energy calculations were performed by unrestricted Hartree-Fock method using Gaussian 98 software. Reactivity decreased in the TiAlN-FCC structure as Al percentage increased. System stabilization explains the chemical inherence of this compound, used in high temperatures applications. Inherent instability was found in TiAlN-HCP simulated systems. Energy increment, high reactivity and density polarization indicate that the formation of lateral compounds such as oxides is highly probable. Total energy shows an equilibrium point near 50/50 Ti/Al ratio, indicating the possibility of phase coexistence, with stabilization energy of -7963, 1349 Hartrees (E_h).

Keywords: DFT, Total energy, reactivity, oxide formation.

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Resumen

Se simularon las estructuras de TiN, AlN y TiAlN empleando teoría funcional de la densidad (DFT- por sus siglas en inglés density functional theory), obteniendo el análisis de población de Mulliken, la densidad total de electrones y la energía total. Estas simulaciones fueron llevadas a cabo con el fin de observar la influencia de la inclusión de átomos de Al y Ti en las estructuras cristalinas de TiN-FCC y AlN-HCP respectivamente. Se desarrollaron cálculos de energía de punto único restrictivo, y el software Gaussian 98. La reactividad disminuyó en la estructura TiAlN-FCC a medida que el porcentaje de Al incrementó. La estabilización del sistema explica la inherencia química de este compuesto usado en aplicaciones de altas temperaturas. Se encontró inestabilidad inherente en los sistemas TiAlN-HCP simulados. El incremento de la energía, la alta reactividad y la densidad de polarización indican que la formación de compuestos laterales tales como óxidos es altamente probable. La energía total mostró un punto equilibrio cerca de la relación 50/50 de Ti/Al, indicando la posibilidad de coexistencia de fase, con energía estabilización de -7963,1349 Hartrees (E_h).

Palabras clave: DFT, Energía total, reactividad, formación de óxido.

Introduction

Simulations of thin films varying the stoichiometry for producing structural have been reported in the literature, because is expected that by controlling the stoichiometry of the thin film one can reach very advantageous synergisms between several coatings properties. For example, TiAlN changes not only its structure but also other properties as hardness, chemical reactivity among others [1]. In recent years, (TiAl)N compound has been used for technological applications due to the thermal stability, chemical stability and high hardness, in the order of 30 GPa [2]. For these reason, there is a great interest in studying the fundamental physical characteristics

of this material, for understanding its behavior respect to the charge distribution, molecular orbitals and electronic density [3]. A great variety of materials have been simulated, allowing to corroborate the information obtained by advanced material characterization; some of this materials are: c-BN, TiN, TiC, TiN/TiC, TiAlN, (TiAlV)N [4–6].
In this work, simulations of Ti_xAl_1-xN structure varying the Ti/Al ratio were carried out. Moreover, the parent compounds as TiN and AlN are also analyzed, observing their evolution as a different atom is included in their crystalline structure. Simulations were carried out using the Gaussian 98 software, the density functional theory (DFT) and the unrestricted Hartree-Fock approximation.

Model Description

Using density functional theory (DFT) and the unrestricted Hartree-Fock (UHF) approximation, TiAlN-FCC (NaCl) and TiAlN-HCP crystalline structures were simulated, increasing the amount of aluminum in the first case and titanium in the second case, using the local density approximation (LDA) functional [7] defined by:

$$V(\rho)_{\mathrm{LDA}} = \iint \rho(\vec{r}_1)(\Delta\vec{r}_{12})^{-1}\rho(\vec{r}_2)dr_1r_2 \tag{1}$$

Where $\rho(\vec{r}_i)$ represents the electron total density of the system in the i-th electron and $\Delta\vec{r}_{ij}$ stands for the separation between the i-th and j-th electrons in the atom. For long range interaction, a general gradient approximation functional (GGA) [8] was used according to the form:

$$V(\rho)_{\mathrm{LDA}} = \iiint f(\rho_\alpha(\bar{r}_1), \rho_\beta(\bar{r}_1), \nabla\rho_\alpha(\bar{r}_1)\nabla\rho_\beta(\bar{r}_1))d_3\bar{r}\ldots \tag{2}$$

Where $\rho_\alpha(\vec{r})$ and $\rho_\beta(\vec{r})$ are the densities of nuclei and electrons respectively. These quantities are related to their gradients given by $\nabla\rho_\alpha(\vec{r})$ and $\nabla\rho_\beta(\vec{r})$, in order to mimic the interaction potential in the Schrödinger equation. Iterations were carried out until a

convergence factor of $1x10_{-4}$mol/cell was reached. The STO-3G database was used [9] by single point energy calculation type. By means of these calculations, total energy, Mulliken charge distribution (MPA) and electron total density were obtained. The atomic percentages used were 71.92%, 59.98%, 52.56% and 42.85% in both cases Ti and Al (as is shown in figs. 1 and 2). For observing the influence of these inclusions on the characteristics mentioned before, FCC-TiN and HCP-AlN were used as references. The atomic percentages were chosen similar to those obtained in previous experimental studies carries out by us [10]. In this work, we studied the influence of the bias voltage on the elemental concentration for TiAlN coatings produced by triode magnetron sputtering. The atomic concentration was determined by EDS. In this report, an increase of the Al percentage depending on the bias voltage was observed. The Al percentage increased from 24% to 49% as the bias voltage increased from -40 to -150 V, while Ti% decreased from 71,9% to 52.5%. These percentages are in agreement with those reported by Wuhrer y Ypeung [11], presenting a competition between Ti and Al.

On the other hand, although fig.1 and fig.2, shows unit cells, the simulations were carried out considering clusters, that are generated from periodic arrays of identical cells as those shows in fig.1 and fig.2. Moreover, because of the high computational cost required by this study, the simulations were carried out considering only the next nearest neighbors; it means, each atom presents a complete valence with energy vales and type of bonds reached using dummy atoms.

As is known, changes in the structure type are influenced by adding a critical amount of aluminum in the TiN-NaCl lattice but no reference were found when Ti atoms are added into the AlN-HCP structure [12–14]. The software used was Gaussian 98 [15, 16]. Lattice parameters used, were obtained from X-Ray diffraction analysis, using the CuK_α (1.5406Å). The diffractometer employed was D8 Bruker AXS equipment in the 2θ configuration, employing the Rietveld method [17, 18].

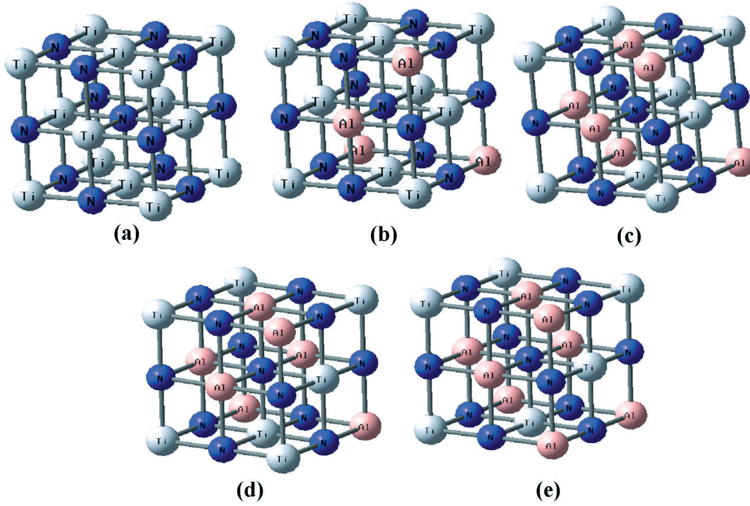

FIGURE 1. *a) TiN-FCC taken as a reference. TiAlN-FCC (NaCl) simulated cells with Ti atoms percentage: b) 71.92%, c) 59.98%, d) 52.56% and e) 42.85%.*

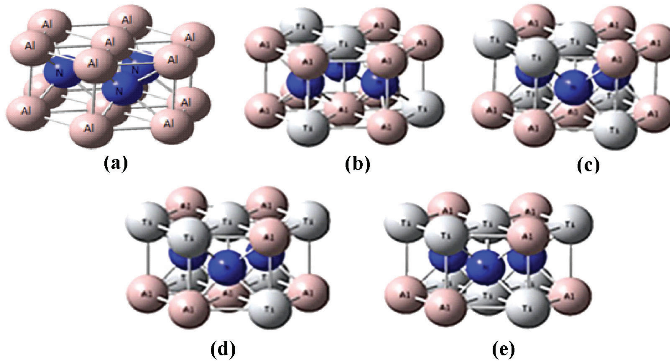

FIGURE 2. *a) AlN-HCP taken as a reference. TiAlN-HCP simulated cells with Al atoms percentage: b) 71.92%, c) 59.98%, d) 52.56% and e) 42.85%.*

Results and Discussion

Figure 3 shows Mulliken charge distribution (MPA) for TiN-FCC and TiAlN-FCC simulated systems. The charge number range increase in MPA indicates stabilization and low probability of oxide formation. Oxidation temperature of TiAlN (800$\sim$1000^{o}C) is higher compared to it for TiN ($\sim$500°C), allowing the use of this compound in high temperature applications such as cutting tools and forming dies [19].

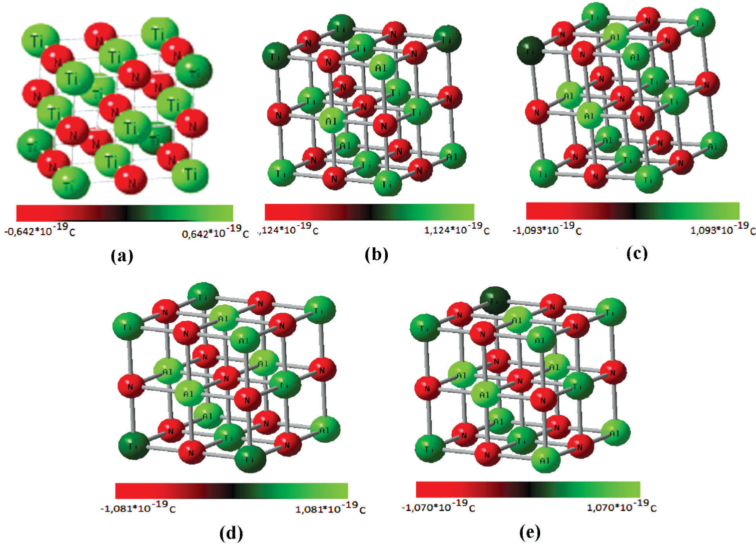

FIGURE 3. *Mulliken population analysis (MPA) for a) Reference TiN-FCC, TiAlN-FCC simulated cells with Ti atom percentage: b) 71.92%, c) 59.98%, d) 52.56% and e) 42.85%.*

AlN-HCP and TiAlN-HCP MPA are shown in figure 4(a-e), for different Ti atoms percentage, from zero to 42.85%. In this case, charge number decreases as Ti atoms are included, indicating high reactivity when high Ti contents replace Al atoms in the HCP crystalline structure. Oxide formation has higher probability in HCP crystalline structures; Al_2O_3 formation can benefit lubrication processes but brittleness and low adhesion causes film delamination and wear [17].
Figure 5 shows the electron total density for TiAlN-FCC. An increase in the Al atoms percentage causes high electron anomalies. Energy and reactivity increase as Al atoms are inserted, causing polarizations (figure 5e).
Electron total density of TiAlN-HCP is presented in fig.6. As is shown from the MPA results, HCP structures present high reactivity tending to form oxides at lower temperatures than FCC TiAlN [16]. It is reflected in the total density surfaces, total energy decreases and high polarization is observed. Cubic structures show high stability compared to HCP arrays, presenting lower reactivity, total energy and density polarization.

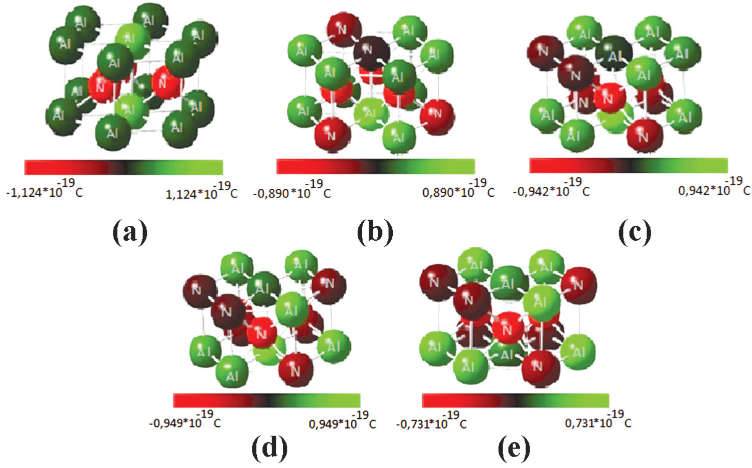

FIGURE 4. *Mulliken population analysis (MPA) for a) Reference AlN-HCP. TiAlN-HCP simulated cells with Ti atom percentage: b) 71.92%, c) 59.98%, d) 52.56% and e) 42.85%.*

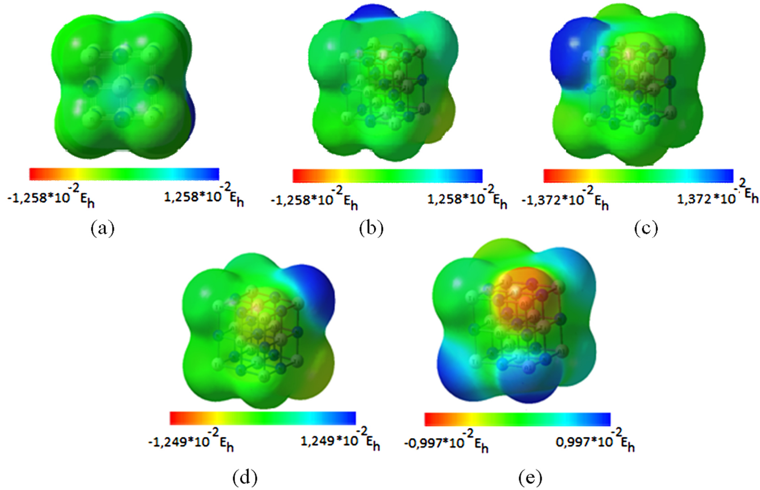

FIGURE 5. *Electron total density for a) Reference TiN-FCC, TiAlN-FCC simulated cells with Ti atom percentage: b) 71.92%, C) 59.98%, d) 52.56% and e) 42.85%.*

Figure 7 shows the energy behavior as Al atoms are included in the TiN-FCC structure and Ti atoms in the AlN-HCP cell. To include Al atoms in the TiN structure causes an increase in the total energy of the system due to the higher formation energy, related directly to the formation energy of the TiN structure, where the bond energy is

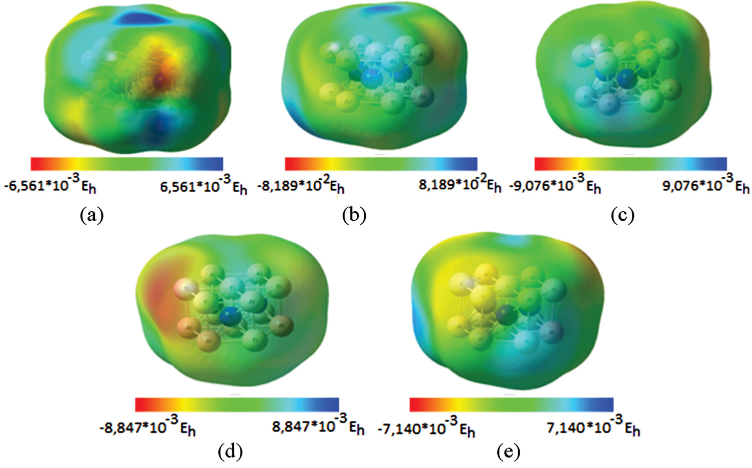

FIGURE 6. *Electron total density for a) Reference TiN-FCC, TiAlN-FCC simulated cells with Ti atom percentage: b) 71.92%, c) 59.98%, d) 52.56% and e) 42.85%.*

lower. On the contrary, adding Ti atoms to the AlN-HCP structure causes a decrease in the total energy due to higher cohesion energy needed to obtain the compound.

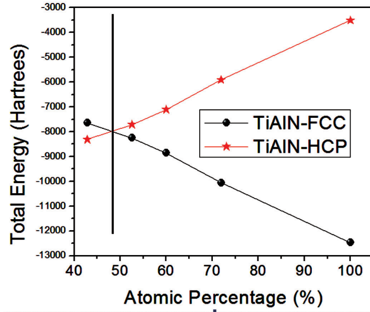

FIGURE 7. *Energy Vs atomic percentage for the TiAlN-FCC and TiAlN-HCP.*

An equilibrium point is observed at percentages close to 50% Ti 50% Al, indicating stabilization energy of -7963.1349 Hartrees. This indicates that at these percentages, the two types of structures can be obtained simultaneously and there is a coalesce in terms of energy. Although it would be important to obtain the formation enthalpy and the cohesion energy, they are difficult to obtain by means of these methods; moreover, these kind of ternary

compounds present not only a complex phase diagram but also interaction potentials difficult to obtain that require theories and physical fundaments out of the scope of this work.

Conclusion

Single Point Energy methods were used to obtain the Mulliken population analysis, electron total density surfaces and total energy of different configurations of TiAlN crystalline structures (FCC and HCP), finding an equilibrium point for both phases coexistence. Ti atoms inclusion in AlN-HCP causes an energy decrease, meanwhile Al atom inclusion in TiN-FCC produce a decrease in the total energy, indicating high reactivity of HCP structures, as is observed from the electron total density. It presents polarizations that explain low temperature formation energy of aluminum oxides. Charge distribution shows that increasing Al in the FCC structure causes an energy increase and stability reduction opposite to Ti inclusion in the AlN structure.

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