

Araştırma Makalesi / Research Article

Modeling of Surface Modification of Stainless Steel by Halide Activated Pack Cementation Method

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Geliş Tarihi: 14.09.2022

Kabul Tarihi: 19.07.2023

Abstract

In high-temperature applications, ferrous-based materials are important due to their excellent combination of desirable mechanical properties, ease of production, corrosion resistance at room temperature and cost-effectiveness. However, mechanical properties must be optimized against environmental effects. Depending on the industrial applications, various corrosion types may also occur. An approach to preserve the mechanical properties of the structural alloy being protected against corrosion is the application of protective coatings to the surfaces. Diffusion coatings are an effective method to obtain corrosion, oxidation and abrasion resistance against detrimental conditions of high temperature. According to the literature, the halide activated pack cementation method has been widely used for ferrous-based materials for a long time. However, most studies concerned with developing coating applications are based on experimental investigations that include microscopic, chemical, and mechanical analyses. Limited studies have been conducted based on computational alloy approaches. In this study, Cr coating of the AISI 316L steel by halide activated pack cementation method was considered as a diffusional problem and the kinetics of the coating deposition process were examined. The effect of process variables such as temperature, time and the compositions of coating layers formed on the surfaces were investigated thermodynamically with Thermo-Calc software and kinetically with DICTRA module. This approach provides insight into the dependence of solid-state diffusions on the processing parameters, and a better understanding of the phases that form along the coating and substrate material.

Keywords

Surface modification;
Pack cementation;
Thermo-Calc; DICTRA

Halid Aktive Edilmiş Kutu Sementasyon Yöntemi İle Paslanmaz Çeliğin Yüzey Modifikasyonunun Modellenmesi

Öz

Yüksek sıcaklık uygulamalarında demir esaslı malzemeler, beklenen mekanik özellikler, üretim kolaylığı, oda sıcaklığı korozyon direnci ve maliyet etkinliğinin kombinasyonlarından dolayı önemlidir. Fakat mekanik özellikler, çevresel etkilere karşı optimize edilmelidir. Endüstriyel uygulamaya bağlı olarak çeşitli korozyon türleri oluşabilir. Korozyona karşı korunurken yapısal alaşımın mekanik özelliklerinin de korunmasına yönelik bir yaklaşım, koruyucu kaplamaların uygulanmasıdır. Difüzyon kaplamaları, zararlı yüksek sıcaklık koşullarına karşı korozyon, oksidasyon, aşınma direncinin elde edilmesinde etkili bir yöntemdir. Literatürlere göre, halid aktive edilmiş kutu sementasyon yöntemi, demir esaslı malzemeler için uzun süreli yaygın olarak kullanılmaktadır. Bununla birlikte, kaplama uygulamalarının geliştirilmesi ile ilgili çalışmaların çoğu, mikroskobik, kimyasal ve mekanik analizleri içeren deneysel araştırmalara dayanmaktadır. Hesaplamalı alaşım yaklaşımlarına dayalı sınırlı çalışmalar yapılmıştır. Bu çalışmada, AISI 316L çeliğinin halid aktive edilmiş kutu sementasyonu ile Cr kaplanması bir difüzyonel problem olarak ele alınmış olup, kaplama kinetiği simülasyon çalışmaları ile incelenmiştir. Proses değişkenlerinin etkileri

Anahtar kelimeler

Yüzey modifikasyonu;
Kutu sementasyonu;
Thermo-Calc; DICTRA

ve yüzeyde oluşturacakları kaplama tabaka bileşimleri termodinamik olarak Thermo-Calc ve kinetik olarak DICTRA ile modellenmiştir. Bu yaklaşım katı hal difüzyonlarının proses parametrelerine bağımlılığını ve kaplama ve altlık malzemesi boyunca oluşan fazların daha iyi anlaşılmasını sağlar.

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1. Introduction

The surfaces of steel parts such as heat exchangers, welded parts, gears and molds must present good wear resistance, corrosion resistance and high temperature oxidation resistance to meet the increasing demand in harsh environments characterized by high speed, heavy load, high temperature, corrosive and oxidative environment (Krauss 1992, Hu *et al.* 2019, Kong *et al.* 2012, Smith *et al.* 2013, ASM Handbook 2003). When aggressive forces reach the limits of the resistance of a material, fracture, fatigue, wear and corrosion failure at the surface occur. For these reasons, surface modification and enhancement should be applied to these materials (Krauss 1992).

Diffusion coatings formed by thermochemical procedures are relatively simple and low cost processes that produce high performance wear and/or corrosion resistant layers. The coatings are formed by the diffusion of protective elements into a substrate at elevated temperatures (Casteletti *et al.* 2009). The formation of the surface layers by thermochemical process changes the chemical composition, structure and properties of the substrate allowing the modified surface to operate under conditions which are impossible for the bulk material (Krastev 2012, Bianco *et al.* 1991).

Halide activated pack cementation process is essentially an in situ chemical vapor deposition (CVD) coating process. A typical pack consists of four components (Chen *et al.* 2012):

- substrate or parts to be coated;
- master alloy (i.e. a powder of the element or elements to accumulate on the surface of parts such as Cr, Al, Si);
- a halide salt activator (NaCl, NaF, NH₄Cl, etc.);
- inert filler powder (Al₂O₃, SiO₂ or SiC, etc.).

Master alloy powder, halide salt activator and inert filler are mixed thoroughly and the parts to be coated are embedded in this mixture in a heat-resistant retort. The sealed retort is heated to a temperature of 750-1200 °C under an inert argon atmosphere and held for a certain period of time. At the elevated temperature, the master alloy reacts with the halide salt activator to produce volatile metal halides that diffuse through the gas phase of the porous pack, such that they deposit and diffuse into the substrate to be coated. The processing temperature is so chosen that both adequate halide vapor pressures are generated and solid-state diffusion occurs (Bianco and Papp 1996, Ravi 2003, Wierzba *et al.* 2014, Sahoo *et al.* 2017, Tian and Guo 2009). The diffusion elements modify the surface chemical composition resulting in phase transformations along the depth of the material (Casteletti *et al.* 2009). Therefore, the coating composition is dependent on processing temperature, time, substrate composition, and atmosphere (Chen *et al.* 2012).

The best-known types of pack cementation coating processes are aluminizing, chromizing and siliconizing. These processes are based on coating the substrate with a single element, that is, aluminum, chromium, or silicon respectively (Ravi 2003). Due to their different metallurgical properties, each alloy requires special pack chemistry to achieve the optimum coating composition.

The aim of the present study is to investigate the effect of processing parameters on the compositional profiles and phase fraction variation during the diffusion of Cr element on the surface of iron-based material by using the Thermo-Calc software and DICTRA module. These thermodynamic and kinetic calculations to be made prior to the experimental studies will provide

information about the intermetallic compounds that may occur between the coating and the substrate material, as well as determine the suitable processing parameters. The data obtained by modeling coating processes caused by kinetic conditions will direct the inter-diffusion layers that will occur during the testing and development of coating processes. In addition, the data obtained by modeling will significantly reduce the experimental effort required for alloy development, both in terms of time and material cost.

2. Material and Method

The AISI 316L stainless steel is selected as the substrate material for the coating process of iron-based materials with the halide activated pack cementation method. The chemical composition of AISI 316L stainless steel employed for the thermodynamic and kinetic calculations is given in Table 1. Common uses for type AISI 316L stainless steel include in the construction of exhaust manifolds, furnace parts, heat exchangers, jet engine parts, valve and pump parts, chemical processing equipment, tanks, evaporators and proton exchange membrane fuel cell bipolar plates (İnt. Kyn. 1, Dong *et al.* 2019, Cho *et al.* 2008).

Table 1. The chemical composition of the substrate material (wt. %).

C	Mn	Si	Cr	Ni	Mo	Ti	Fe
0.03	2	1	16-18	10-14	2-3	-	Bal.

The study is carried out by using the thermodynamic computational software Thermo-Calc and the diffusion-controlled transformation module DICTRA. More specifically, the phase diagrams and the phases that are present in AISI 316L stainless steel with respect to carbon and chromium content at different processing temperatures under equilibrium conditions are calculated first using the Thermo-Calc software and the TCFE6 thermodynamic database for ferrous-based alloys. Then the diffusion between the elements to be coated and the substrate material is simulated with the DICTRA software and the MOB2 mobility database.

According to the coating process temperatures and times in the literature, the temperatures at which the thermodynamic and kinetic calculations will be performed for the coating processes are determined as 600, 800, and 1000 °C and the times are 4, 8, 10, and 12 hours.

While the formation of equilibrium phases gives information about the microstructure formed under equilibrium conditions at a certain temperature, the microstructure is usually controlled by kinetic at high temperature processes. The simulation of transformations with diffusion control has been known for a long time. Very good results have been obtained by making some simplifications in boundary conditions and assuming that the system consists of only two components. However, in reality there are multi-component systems in materials. As the number of components increases, it becomes difficult to obtain the values of mobility and activation energy, which are parameters related to diffusion. Therefore, modeling is not possible without computer assistance. Calculations are based on the modeling of diffusion transformations in a system determined geometrically (e.g. plane, cylinder or spherical planar, cylindrical and spherical) (Souza *et al.* 2017, Li *et al.* 2019, Kučera and Mazancová 2014, Borgenstam *et al.* 2012, T.C. Software 2015, T.C. Software 2016). In the halide activated pack cementation process, substrate material and coating element (Cr) are embedded in the powder mixture in a closed vessel and then heated under a constant temperature. Series of chemical reactions occur between the coating element and system components during heating, resulting in activations of the coating element atoms. These atoms diffuse into the substrate. The coating is formed at high temperatures by reactions of metal halide vapors on the substrate surface, followed by solid state diffusion between the diffusion elements and the substrate. Process atmosphere, composition, temperature and time are the most important factors in such processes. Considering the processing temperature, time and solid-state diffusions of the elements during the chromizing, it is planned to model how the elements to be coated behave at the interfaces with a

computer-calculated program. As with all diffusion coatings, the microstructure is largely dependent on the substrate material being coated.

1D multi-component diffusion simulations are performed using the DICTRA module in Thermo-Calc with the TCFE6 and MOB2 databases. During the simulations it is assumed that the chromizing process causes precipitation of carbides and other phases in an austenitic matrix phase for AISI 316L stainless steel. Simulations are carried out at 600, 800, and 1000 °C isothermal process temperatures, as previously mentioned, and the parameters monitored are the compositional profiles and the variation of the phase fractions. A single cell planar geometry is employed, shown in Figure 1. A planar geometry corresponds to an infinitely wide plate of a certain thickness. This reflects the substrate material geometry. The total cell size is taken equal to 20 μm after careful examination of its effect on the diffusion kinetics.

To solve the diffusion equations numerically, the matrix is discretized with a geometric grid of 90 points, so that the composition is calculated only at the grid points and it is assumed to vary linearly between the grid points. Geometric grid point demonstrates a varying density of grid points in the matrix. A geometrical factor larger than one and equal to 1.11 is selected which yields a higher density of grid points at the lower end of the cell. For the Cr coating process of AISI 316L stainless steel with halide activated pack cementation method, the matrix is set austenite and the carbides that form are set as spheroid phases dispersed in austenite matrix. The dispersed phase model assumes that diffusion takes place only in the matrix and the dispersed phases act as point sinks or sources of solute atoms; thereby the phase fraction and composition are calculated from the average composition in each node, assuming that equilibrium holds locally in each volume element.

To represent the impeding effect of dispersed phases on the diffusivity of the matrix, a labyrinth factor is introduced. In the present study, the labyrinth factor is set as the volume fraction of the

matrix phase, while the initial volume fraction of the dispersed phases is calculated according to the equilibrium conditions. Note that the dispersed phase model is appropriate for problems where diffusion occurs mainly in a continuous matrix phase and the volume fraction of dispersed phases is significantly low.

For the chromizing process, it is assumed that Cr diffuses continuously in the substrate material through the lower interface of the cell. The chromizing kinetics are controlled by the chromium activity at the interface which usually takes values in the range of 0.5-1. In this work, a value of 0.8 is selected. Therefore, the boundary conditions set on the lower interface of the cell are,

$$\alpha_{Cr} = 0.8 \tag{1}$$

$$\left. \frac{\partial c_k}{\partial x} \right|_{x=0 \mu m} = 0, k \neq Cr \tag{2}$$

where α_{Cr} is the activity of chromium, and $\frac{\partial c_k}{\partial x}$ is the concentration gradient of element k (mol/m⁴). The system is considered closed for all the elements except chromium, since the fluxes J_k (mol/m²s) are equal to zero. The fluxes can be described by Fick-Onsager law for a multicomponent system with n elements,

$$J_k = \sum_{j=1}^{n-1} D_{kj}^n \frac{\partial c_j}{\partial x} \tag{3}$$

where D_{kj}^n is the diffusion coefficient matrix (m²/s). For the upper interface, the system is considered closed for all elements and the boundary conditions are,

$$\left. \frac{\partial c_k}{\partial x} \right|_{x=20 \mu m} = 0 \tag{4}$$

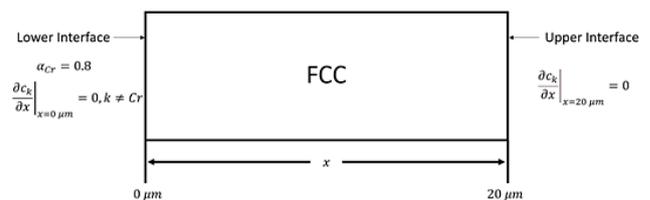


Figure 1. Schematic illustration of the cell employed in the DICTRA simulations for the chromizing processing.

3. Discussion and Results

The equilibrium phase diagram is given in Figure 2 depending on the carbon content calculated with Thermo-Calc for AISI 316L stainless steel alloy.

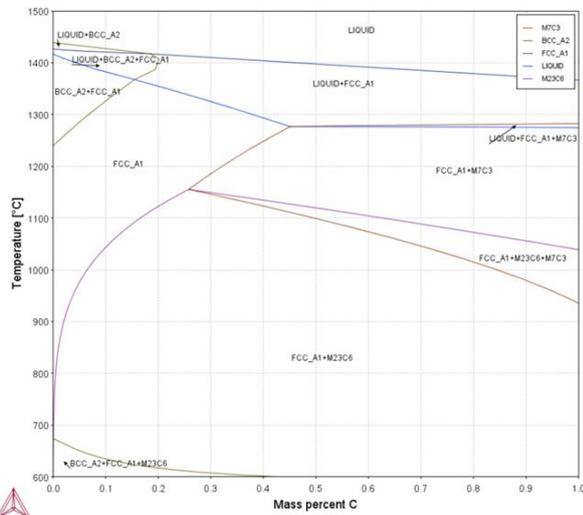


Figure 2. Equilibrium phase diagram calculated with Thermo-Calc for AISI 316L stainless steel alloy.

The phases in the AISI 316L alloy equilibrium phase diagram provide information about phases that may occur depending on the temperature during the coatings process to be made by the halide activated pack cementation method. Therefore, these phases were used as input phases in the database during Thermo-Calc calculations of coatings for AISI 316L alloy. The phase diagram with respect to Cr content

Table 2. Phase that can occur sequentially depending on the increasing Cr content at process temperatures.

For 600 °C: 9 phase fields;	Delta-ferrite+austenite+M ₇ C ₃ , Delta-ferrite+austenite+M ₂₃ C ₆ +M ₇ C ₃ , Delta-ferrite+austenite+M ₂₃ C ₆ , Delta-ferrite+austenite+M ₂₃ C ₆ +Sigma, Delta-ferrite+austenite+M ₂₃ C ₆ +Sigma+Sigma#2, FCC_A1#2+M ₂₃ C ₆ +Sigma+Sigma#2, Delta-ferrite+austenite+M ₂₃ C ₆ +Sigma + Sigma#2, Delta-ferrite+austenite+M ₂₃ C ₆ +Sigma, Delta-ferrite+austenite+M ₂₃ C ₆ .
For 800 °C: 6 phase fields;	Austenite, Austenite+M ₂₃ C ₆ , Austenite+M ₂₃ C ₆ +Sigma Austenite+M ₂₃ C ₆ +Sigma+Sigma#2, Delta-ferrite+austenite+M ₂₃ C ₆ +Sigma, Delta-ferrite+austenite+M ₂₃ C ₆ .
For 1000 °C: 3 phase fields;	Austenite,

calculated with by Thermo-Calc for the chromizing process is depicted was given in Figure 3.

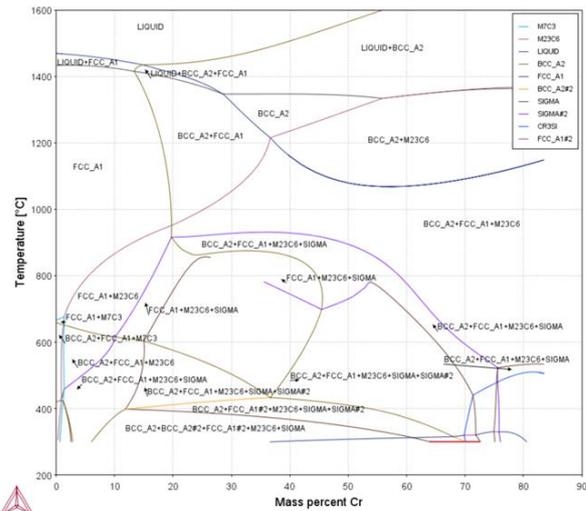


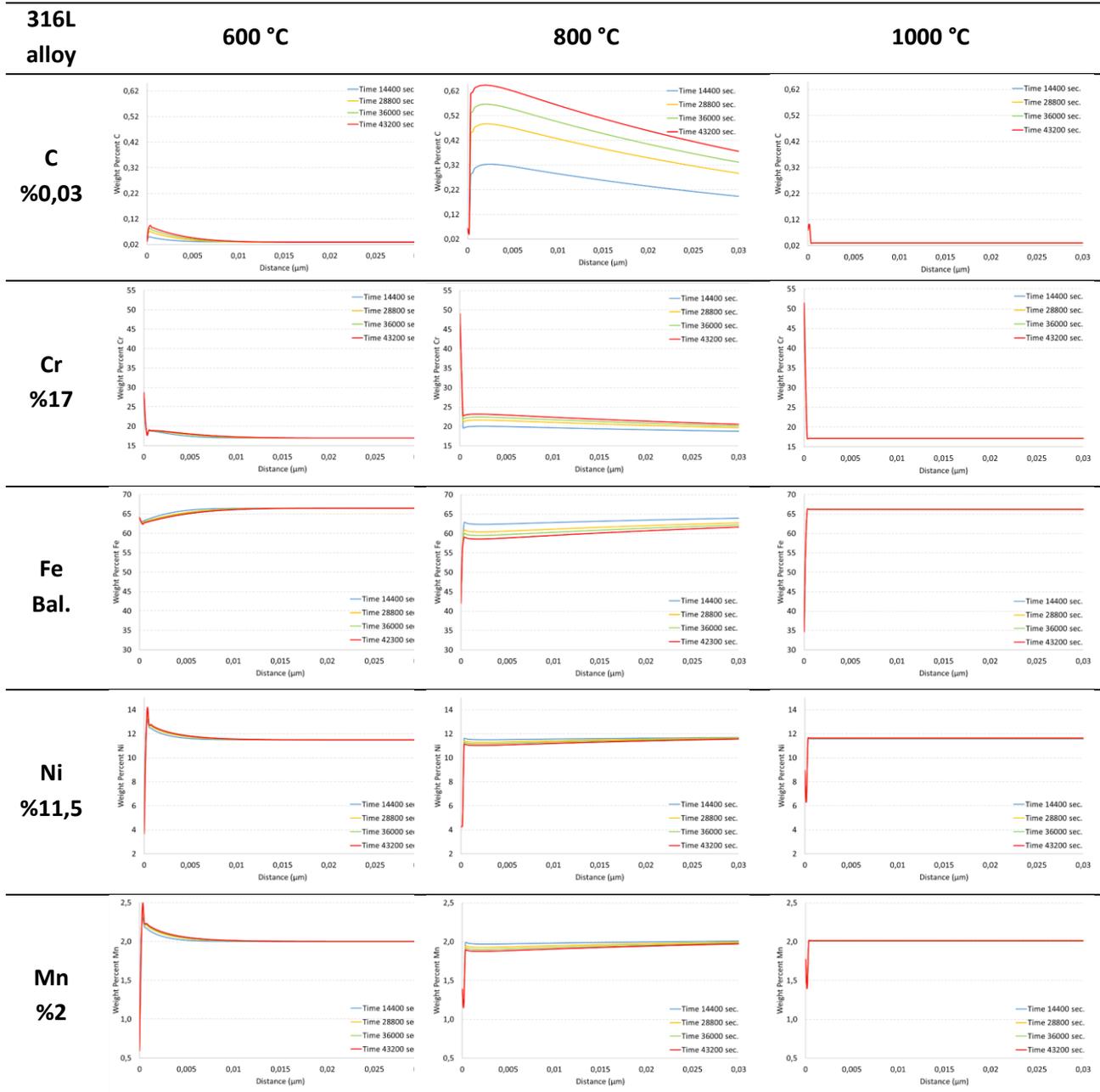
Figure 3. Calculated isopleth section by using Thermo-Calc for the chromizing processing in AISI 316L stainless steel alloy.

In this study, process temperatures were chosen as 600, 800 and 1000 °C. Therefore, in the diagram in Figure 3, the phase fields at these temperatures indicate the phases that may occur in the chromizing process for AISI 316 L stainless steel alloys. The phase fields that can occur in sequence, depending on the increasing Cr content in the processing temperatures from the diagram are given in Table 2.

Delta-ferrite+austenite,
Delta-ferrite+austenite+M₂₃C₆.

During the coating process, diffusion occurs in alloying elements (C, Cr, Fe, Ni, Mn, Si, Mo) depending on the process conditions. Figure 4 shows the compositional profiles of C, Cr, Fe, Ni, Mn, Si and Mo obtained by DICTRA simulations of diffusion for different processing times at 600, 800

and 1000 °C in the chromizing process for AISI 316L stainless steel alloy.



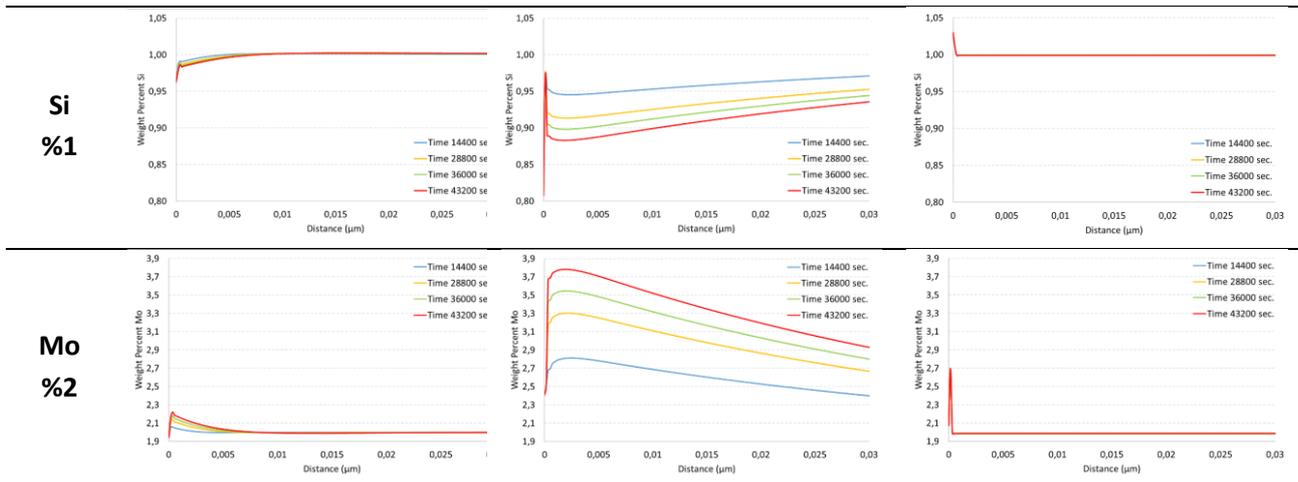


Figure 4. Compositional profiles indicating the of alloy elements for different process times at 600, 800 and 1000 °C in the chromizing processing for AISI 316L stainless steel alloy.

A magnified region of the C compositional profile at 1000 °C in the chromizing process for AISI 316L stainless steel alloy are given in Figure 5. It is observed that for the selected processing times compositional profiles are almost identical.

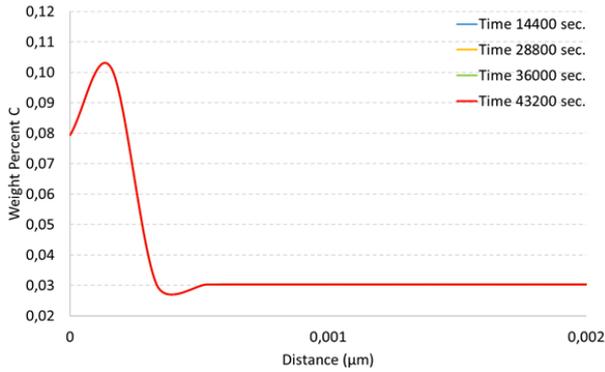


Figure 5. Compositional profile of C at 1000 °C in the chromizing processing for AISI 316L stainless steel alloy.

Evolution of integrated volume per volume (ivv) of ferrite (BCC) at 1000 °C in the chromizing process for 316L stainless steel alloy is given in Figure 6.

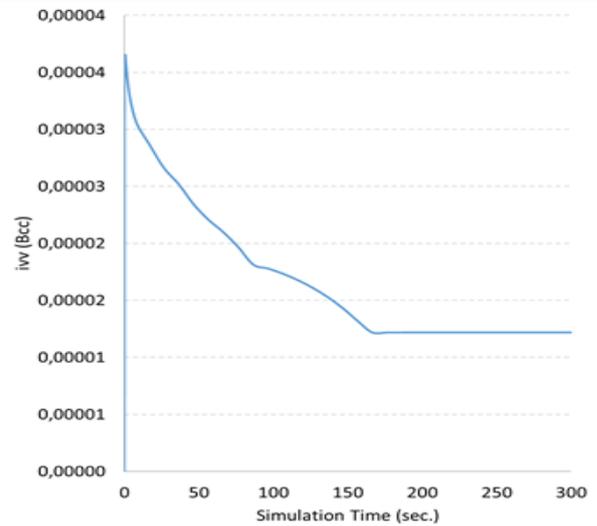


Figure 6. Evolution of ferrite (BCC) of volume fraction at 1000 °C in the chromizing processing for 316L stainless steel alloy.

Comparison of compositional profiles of Cr and Fe elements for different process times at 1000 °C in the chromizing processing for 316L stainless steel alloy are given in Figure 7.

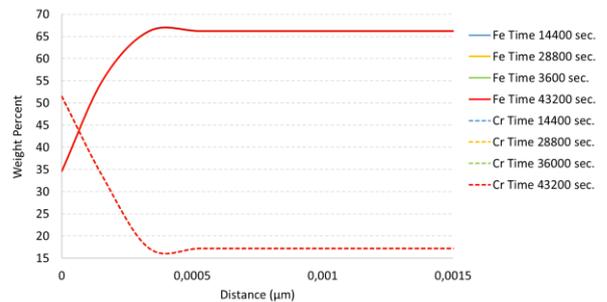


Figure 7. DICTRA simulations of diffusion of Cr and Fe elements at 1000 °C in the chromizing processing for 316L stainless steel alloy.

4. Conclusions

During the deposition of Cr on the substrate surface, a chromium carbide (Cr_{23}C_6) is formed rapidly on the surface depending on the carbon diffusion. Chromium carbide was formed due to an outward diffusion of carbon and the strong affinity of Cr towards carbon. The formation of this type of carbide layer blocks the diffusion of Cr from the substrate surface and locally carries the carbon in the steel content, causing decarburization in the steel substrate material.

Presence of this layer shows that a chromization induced ferrite layer was formed between the coating and substrate material. The presence of this ferrite layer is highest between the coating and the substrate material. This layer decreases over time.

A sharp decrease of Cr concentration appeared in the depth of 0.0005 μm , while the intensity of Fe increased rapidly at the same location, indicating the interface between chromizing induced ferrite layer and the substrate.

Acknowledgment

The authors gratefully acknowledge the financial support of the TÜBİTAK 2219-International Postdoctoral Research Fellowship Program for Turkish Citizens (Application period: 2018/2).

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