

KINETIC STUDY OF NIOBIUM CARBIDE COATING FORMATION ON AISI L2 STEEL USING THERMO-REACTIVE DEPOSITION TECHNIQUE

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Abstract In the present study, Thermo-Reactive Deposition method (TRD) in a molten bath was used to form niobium carbide coating on AISI L2 steel. The coating was formed in five different composition of borax ($\text{Na}_2\text{B}_4\text{O}_7$), boric acid (B_2O_3), and ferro-niobium. For all of the five compositions of molten bath, niobium carbide coating treatment was carried out at 1173 K, 1273 K, and 1373 K for 2, 4 and 8 hours. The thickness of coating ranged between $3.6 \pm 0.1 \mu\text{m}$ to $33.6 \pm 0.5 \mu\text{m}$ depending on the bath composition, treatment time, and temperature. Kinetic study of the formation of NbC coating demonstrated that for the molten baths containing 10 wt.% ferro-niobium or more, growth of the coating is under the controlled of by diffusion. For such molten baths, the activation energy of the process was estimated to be 122.5 kJ/mol. A practical formula to estimate the coating thickness in these molten baths has been suggested.

Keywords Surfaces, Niobium Carbide, Thermo-Reactive Diffusion, Kinetic

چکیده در این تحقیق برای تشکیل پوشش کاربید نایوبیوم بر سطح فولاد AISI L2 از روش نفوذ فعال حرارتی استفاده شد. پوشش دهی در پنج ترکیب مختلف از بوراکس، اسید بوریک و فرونایوبیوم انجام شد. برای هر ترکیب حمام، فرایند پوشش دهی در دماهای ۱۱۷۳، ۱۲۷۳ و ۱۳۷۳ درجه کلوین و زمان های ۲، ۴ و ۸ ساعت انجام شد. بسته به دما، زمان و ترکیب شیمیایی حمام، ضخامت پوشش بین $۳/۶ \pm ۰/۱$ میکرومتر تا $۳۳/۶ \pm ۰/۵$ میکرومتر متغیر بود. بررسی سینتیکی تشکیل پوشش کاربید نایوبیوم نشان داد که برای حمام های مذاب شامل ۱۰ درصد وزنی فرونایوبیوم و بیشتر، تشکیل پوشش تحت کنترل نفوذ می باشد. برای این گونه حمام های مذاب، انرژی فعال سازی فرایند $۱۲۲/۵$ kJ/mol است. برای تعیین ضخامت پوشش در چنین حمام هایی یک رابطه ریاضی ارائه شده است.

1. INTRODUCTION

Hard coating with carbide of transition metals is a common method for improving resistance to wear, seizure, and corrosion. These kinds of coatings are required to enhance the life of mechanical components such as forming and machining tools [1,2]. Thermal Diffusion (TD) process, which is also referred to as Thermo-Reactive Deposition/diffusion (TRD) process and Toyota Diffusion process, is a high temperature surface modification process that forms a hard, thin, wear-resistant layer of carbides on steels as well as other carbon-containing materials such as nickel and cobalt alloys, cemented carbides, and steel-bonded carbides [3].

TRD coatings have applications similar to those of coatings produced by chemical vapor deposition (CVD) or physical vapor deposition (PVD) [4]. In this treatment, carbide forming elements (CFE's) are resolved in molten borax or boric acid or a mixture of them. Then, carbon containing specimens are immersed in the molten bath comprising carbide forming elements (CFE's). The CFE atoms are deposited on the surface by a thermochemical process and react with carbon that diffuses to the surface from the substrate. The chemical combination of carbon atoms present in the substrate with the CFE atoms dissolved in the bath results in the formation of carbide layer [5-7].

Niobium carbide (NbC) coatings exhibits high

hardness [8], high toughness, and Young's modulus, and high melting point, together with excellent wear and friction properties [9,10], what which is are highly desirable for a coating in high temperature or abrasive environments. There are a number of reports methods of producing making niobium carbide coatings such as pack method [11], filtered vacuum cathodic arc deposition method [12], and laser alloying method [13]. The aim of this study is depositing thin layers of niobium carbide on steel substrates using TRD method and investigating the kinetics of formation of this carbide layer.

2. MATERIALS AND METHODS

Cylindrical samples 10 mm in diameter and 15 mm in height were prepared from AISI L2 steel. The chemical composition of this steel is shown in Table 1. Coating was performed by immersing samples in a molten bath consisting of borax ($\text{Na}_2\text{B}_4\text{O}_7$), boric acid (B_2O_3), and ferro-niobium. The ferro-niobium used in this work contained 65 wt.% niobium. Five different compositions of molten bath were used (Table 2). Treatment was carried out at 1173 K, 1273 K, and 1373 K for 2, 4, and 8 hours in an electrical resistance furnace. To

prepare the molten bath, mixture of borax and boric acid was melted in a graphite crucible. Then, ferro-niobium powder with particle size below 149 μm (nominal 100 mesh) was added to the molten bath. The molten bath was kept in the furnace for 30 minutes to let niobium dissolve in borax. Then, samples were immersed in the molten salt bath. After TRD treatment, samples were cooled in air and cleaned in boiling water to remove the remaining salt. Samples were sectioned, polished and etched with 2% nital. Microstructural details of the samples were investigated by NEOPHOT32 Optical Microscope (OM), and TESCAN VEGAIXMU Scanning Electron Microscope (SEM) equipped with Energy Dispersive X-ray Spectrometry (EDS). The thickness of coating was measured by means of a micrometer attached to the optical microscope. The values reported for thicknesses are the average of at least ten measurements. The coating phases were analyzed by JOEL-JDX-8030 X-Ray Diffraction (XRD) using $\text{Cu-K}\alpha$ radiation.

3. RESULTS AND DISCUSSION

3.1. Coating Properties Optical micrographs and SEM images of the cross-section of the coated

TABLE 1. The Chemical Composition of the Used Steel (AISI L2).

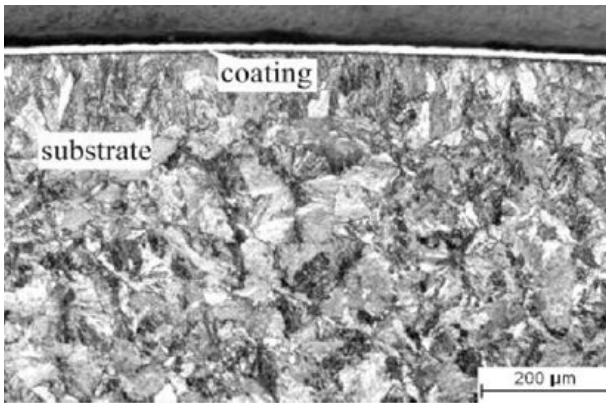
Element	C	Mn	Cr	Mo	Si	V	Fe
wt.%	1.1	0.45	0.58	0.08	0.12	0.06	Bal.

TABLE 2. Different Compositions of the Molten Bath.

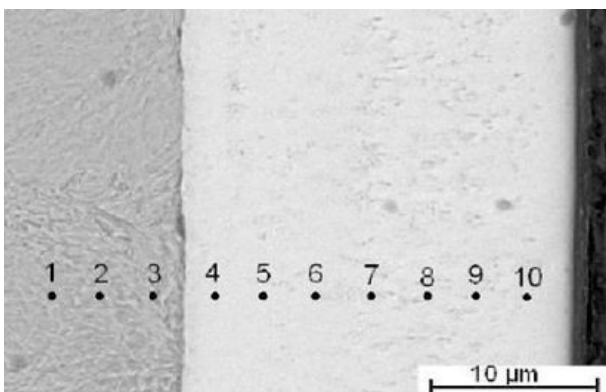
Molten Bath No.	Ferro-Niobium (wt.%)	Boric Acid (wt.%)	Borax (wt.%)
1	5	5	90
2	7	5	88
3	10	5	85
4	20	5	75
5	30	5	65

samples revealed that the coating formed on the steel substrate was smooth, compact, and uniform in thickness all over the surface (Figure 1). Depending on the treatment time, molten bath composition, and temperature, thickness of the coating varied from $3.6 \pm 0.1 \mu\text{m}$ to $33.6 \pm 0.5 \mu\text{m}$. There are two distinct regions in Figure 1; (a) the dark region which is the steel substrate; and (b) the bright region which XRD analysis confirmed that it was NbC phase (Figure 2).

Figures 2a-c show respectively the XRD pattern of the coated samples; (a) in a bath comprising 10% ferro-niobium for 4 hr at 1173 K, (b) in a bath comprising 20% ferro-niobium for 8 hr at 1273 K, and (c) in a bath comprising 7% ferro-niobium for 2 hr at 1373 K. The result of EDS analysis at

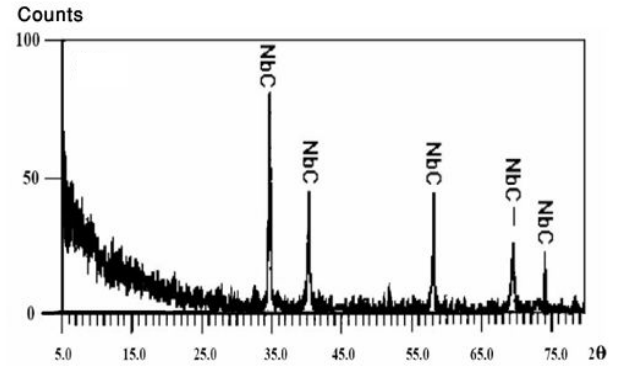


(a)

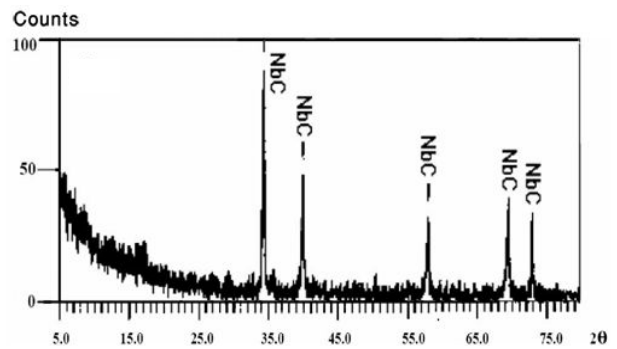


(b)

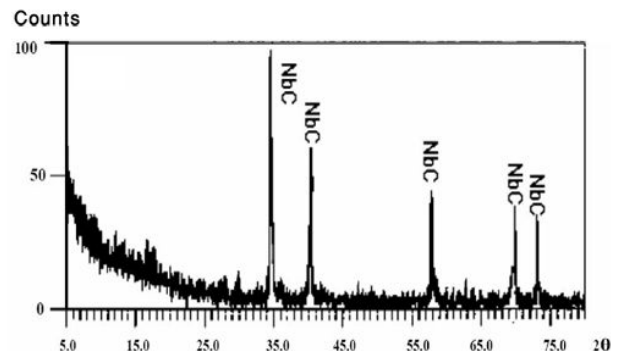
Figure 1. Image of section from the treated sample in a molten bath containing 20 wt.% ferro-niobium for 8 hours at 1273 K, (a) optical micrograph and (b) BE, SEM micrograph.



(a)



(b)



(c)

Figure 2. X-Ray diffraction pattern of niobium carbide layer formed on the AISI L2 steel substrate: (a) in a bath comprising 10 wt.% ferro-niobium for 4 hr at 1173 K, (b) in a bath comprising 20 wt.% ferro-niobium for 8 hr at 1273 K and (c) in a bath comprising 7 wt.% ferro-niobium for 2 hr at 1373 K.

points 1 to 10 which are delineated in Figure 1 is shown in Table 3. It is seen that the amounts of niobium at points 1, 2, and 3 which are within the substrate are insignificant. Also, the quantities of

detected iron at points 4-10 were small. Carbon was detected at all of these 1-10 points, but because of the apparatus error, the reported carbon content was not accurate. However, the formation of NbC on the substrate proves that carbon has diffused outward to the coating. The elements concentration profile is seen in Figure 3. It is seen that, diffusion of iron atoms from substrate to the coating and diffusion of niobium atoms from the coating to the substrate are limited.

3.2. Coating Growth Kinetics Presuming that diffusion is the primary factor affecting the coating layer thickness and carbide layer growth occurs perpendicular to the substrate, then on the basis of the classical kinetic theory the squared thickness of the carbide layer (l^2) as a function of treatment time (t) is described by the following equation [15]:

$$l^2 / t = k \quad (1)$$

Where l is the thickness of coating (m), t is time (s), and k is the growth rate constant (m^2/s).

It should be noted that if the coating growth is controlled by diffusion, it grows according to Equation 1, otherwise, it does not. The effect of treatment time on the square of coating thickness at different temperatures and different molten bath compositions is shown in Figure 4. Figures 4a-e belong to the molten baths containing 5, 7, 10, 20, and 30 wt.% ferro-niobium respectively. It is observed that for the molten baths comprising of less than 10 wt.% ferro-niobium, namely 5 wt.% and 7 wt.% ferro-niobium (Figures 4a and 6b), the square of the coating thickness versus treatment time plots are not linear and the growth of carbide layer does not follow Equation 1. The amount of niobium in this type of molten baths is low and supply of niobium to form coating is limited. Therefore, diffusion of elements from niobium carbide coating to substrate and elements from

TABLE 3. Amount of Iron and Niobium, Determined by EDS, at the Points 1-10 (Shown in Figure 1).

Point	1	2	3	4	5	6	7	8	9	10
Niobium (wt.%)	0.04	0.07	0.1	90.6	90.7	91.1	91.2	92.1	92.5	92.9
Iron (wt.%)	95.1	94.9	94.7	0.9	0.8	0.7	0.5	0.3	0.2	0.1

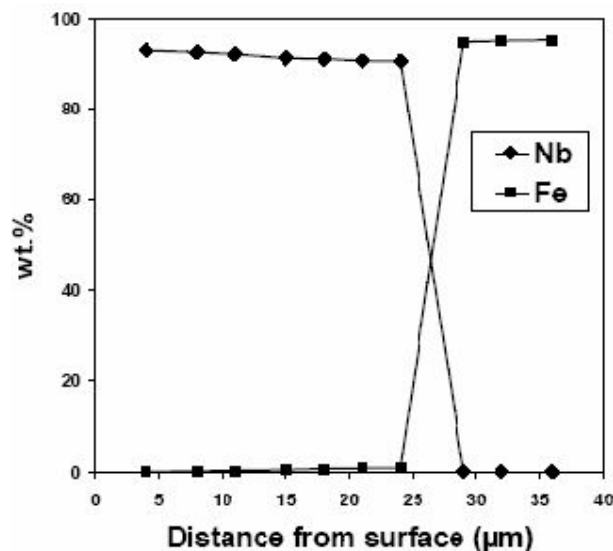
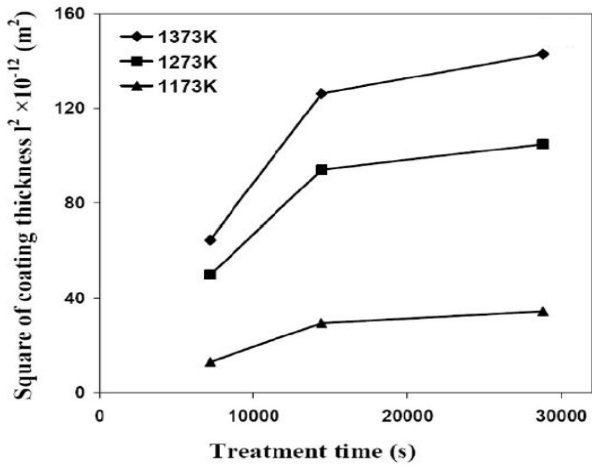
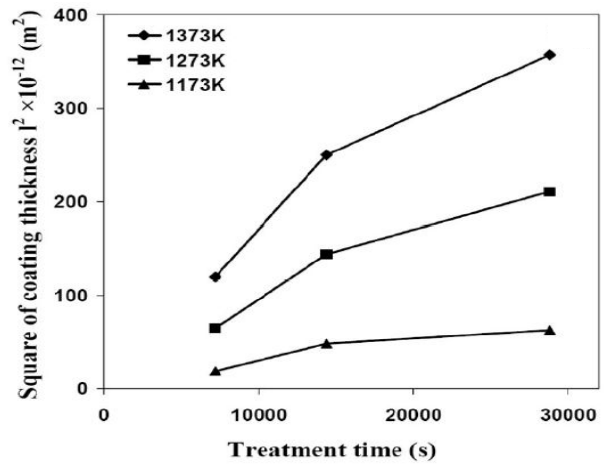


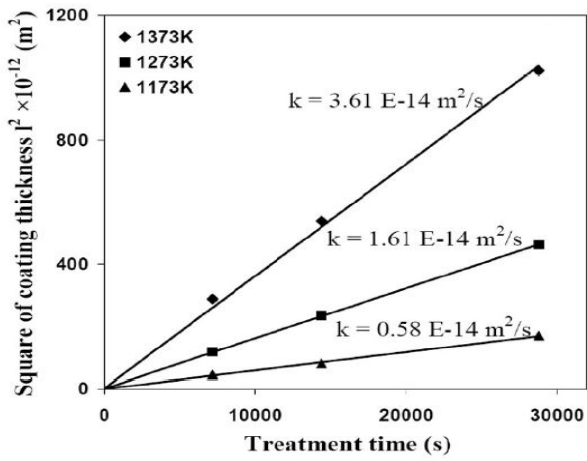
Figure 3. Concentration profiles, determined by EDS, for iron and niobium across the thickness of the coating from outer surface of coating (point 10) to substrate (point 1).



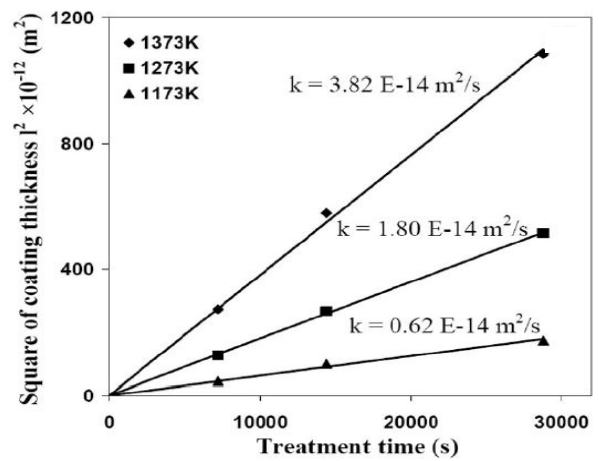
(a)



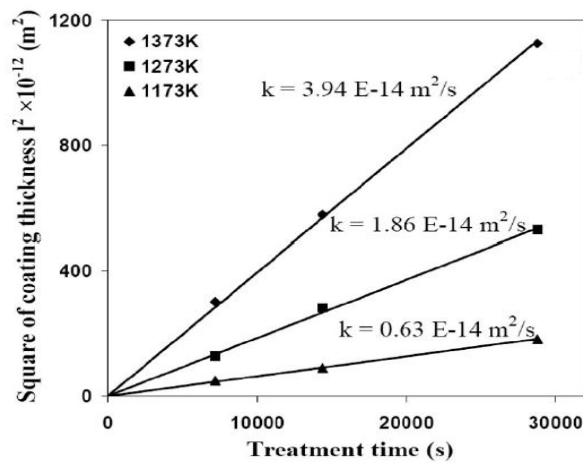
(b)



(c)



(d)



(e)

Figure 4. Square of the coating thickness versus niobium carbide coating time for a molten bath containing: (a) 5 wt.%, (b) 7 wt.%, (c) 10 wt.%, (d) 20 wt.% and (e) 30 wt.% ferro-niobium.

substrate to the coating does not control the kinetics of growth, or is not the only phenomenon which controls the kinetics of the coating growth.

As it is seen in Figure 4, for the molten baths containing 10 wt.% or more ferro-niobium (Figures 4c-e), the niobium carbide layer growth follows the pattern suggested by Equation 1. In other words, diffusion of elements through the carbide coating controls the carbide layer growth kinetics. In these molten baths the quantity of niobium is high enough and diffusion becomes the controlling parameter in the coating growth kinetics.

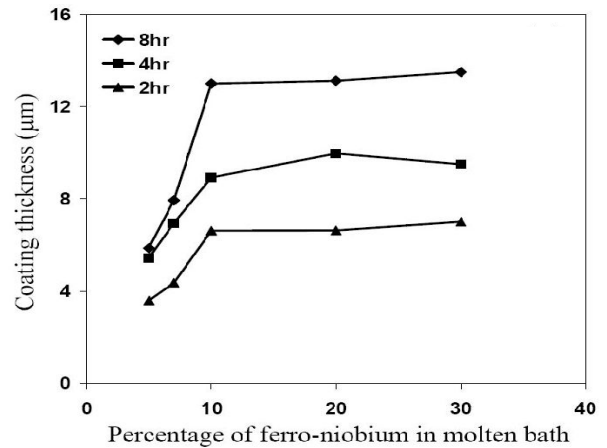
The relationship between coating thickness and amount of ferro-niobium in the molten bath for different treatment times and at different temperatures is shown in Figure 5. It is observed that the variation of coating thickness with the increased concentration of niobium in the molten bath is the same for three temperatures 1173, 1273, and 1373 K. It is seen that at the beginning, the thickness of coating increases considerably with the increased concentration of ferro-niobium in the molten bath. But, increasing the amount of niobium in the molten bath beyond 10 wt.% ferro-niobium does not have a great influence on the coating thickness. That is, for the molten baths comprising of 10 wt.% ferro-niobium or more, the niobium carbide coating growth rate is out of control of niobium concentration in the molten bath and diffusion is what controls the coating growth kinetics. Moreover, it is observed that the thickness of coating increases significantly with increasing treatment time.

For the molten baths containing 10 wt.%, 20 wt.%, and 30 wt.% ferro-niobium in which diffusion controls the growth kinetics, the relationship between growth rate constant (k) and treatment temperature (T) has been suggested as [3-5]:

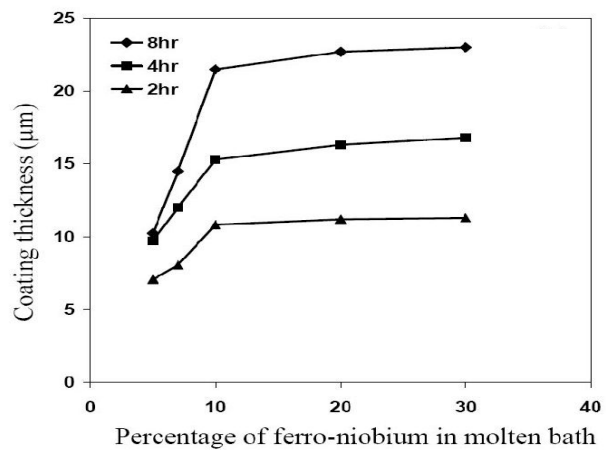
$$k = k_0 \exp\left(\frac{-Q}{RT}\right) \quad (2)$$

Where Q is the activation energy (J/mol), T absolute temperature (K), R universal gas constant (8.314 J/mol.K), and k_0 the constant term of k (m^2/s). Equation 3 is expressed from the natural logarithm of Equation 2 as follows:

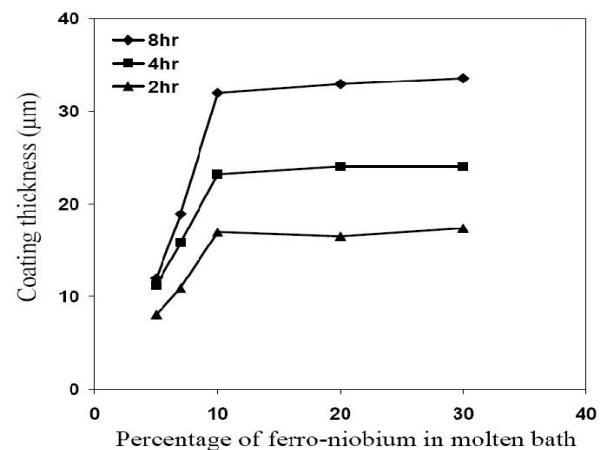
$$\ln k = \ln k_0 - \frac{Q}{R} \frac{1}{T} \quad (3)$$



(a)



(b)



(c)

Figure 5. The thickness of coating versus percentage of ferro-niobium in the molten bath at: (a) 1173 K, (b) 1273 K and (c) 1373 K.

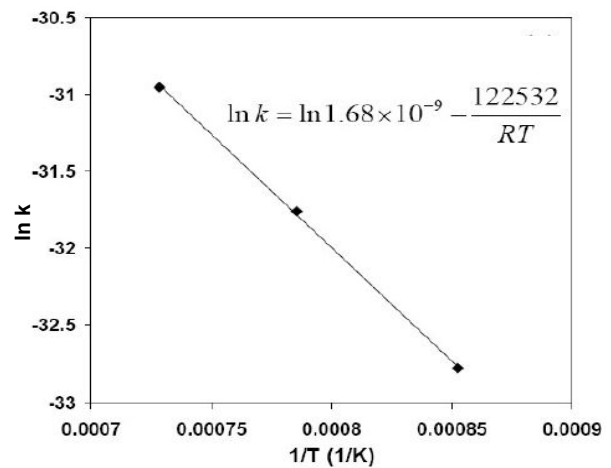
Activation energy is the energy required to cause a particular reaction to occur. In diffusion, the activation energy is related to the energy required to move an atom from one lattice site to another. The atom is originally in a low-energy, relatively stable location. In order to move to a new location, the atom must pass an energy barrier. This energy barrier is the activation energy. Heat supplies the atom with the energy needed to exceed this barrier [16]. Where the coating growth kinetics is under the control of diffusion, activation energy of the process can be determined from the slope of plots in Figure 6. Figures 6a-c belong to the molten baths comprising 10, 20, and 30 wt.% ferro-niobium in sequence. The activation energy for each of these molten baths was 122.5, 122, and 123.1 kJ/mol respectively. Also, for these molten baths the constant terms of k (k_0) were estimated to be 1.68×10^{-9} , 1.73×10^{-9} and 1.96×10^{-9} m²/s in sequence. It is observed that for these molten baths the activation energies (Q) and the constant terms of k (k_0) are very close to each other. The activation energy and k_0 of the process can be regarded as the average of these calculated values. Hence, For the molten baths containing 10 wt.% ferro-niobium or more, the activation energy (Q) and k_0 can be estimated as 122.5 kJ/mol and 1.79×10^{-9} m²/s respectively. Based on Equations 1 and 2, Equation 4 can be written as follows:

$$l = \sqrt{k_0 \cdot t \cdot \exp\left(\frac{-Q}{RT}\right)} \quad (4)$$

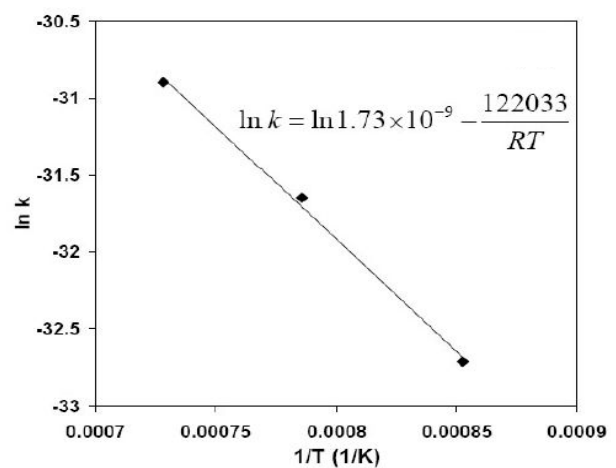
From Equation 4, a practical formula to estimate coating thickness for the molten baths containing 10 wt.% ferro-niobium or more, can be written as follows:

$$l = \sqrt{1.79 \times 10^{-9} \cdot t \cdot \exp\left(\frac{-14739}{T}\right)} \quad (5)$$

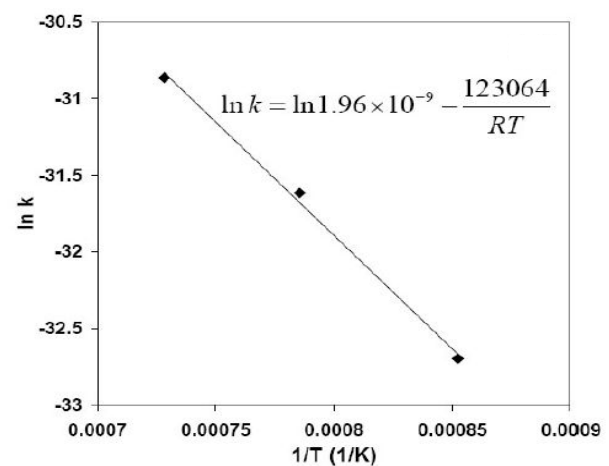
In Figure 7, coating thickness estimated by Equation 5 has been compared with the experimental results of the tests for the molten bath containing 10, 20, and 30 wt.% ferro-niobium. It is seen that the estimated and experimental results are very close to each other and the practical formula has a very good reliability.



(a)

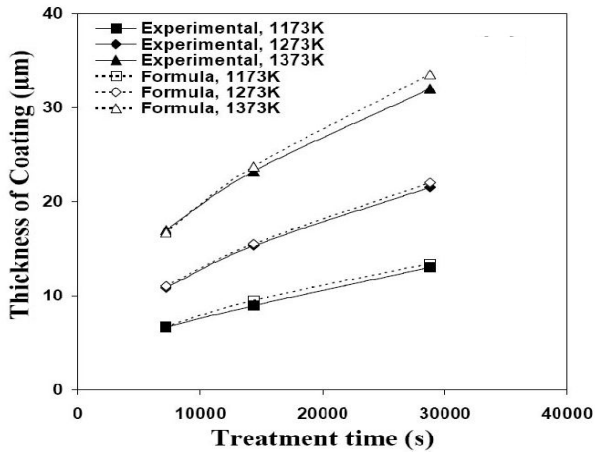


(b)

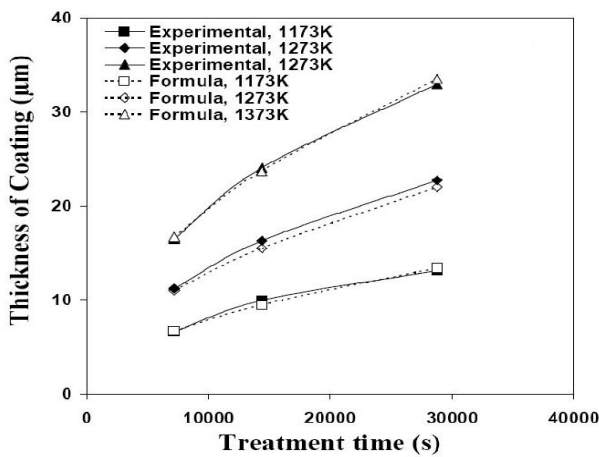


(c)

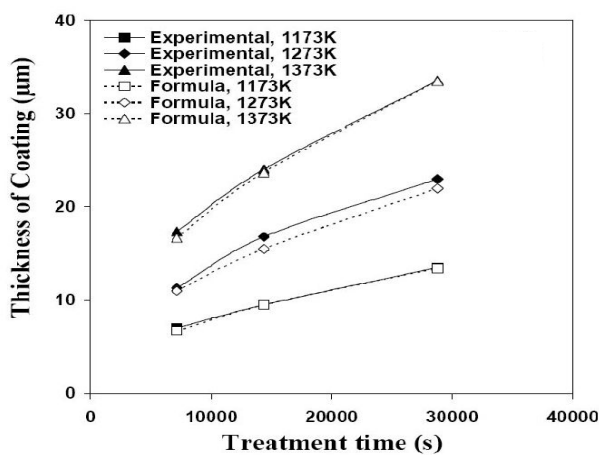
Figure 6. In k versus $1/T$ for a molten bath containing: (a) 10 wt.%, (b) 20 wt.% and (c) 30 wt.% ferro-niobium.



(a)



(b)



(c)

Figure 7. The thickness of coating versus percentage of ferro-niobium in the molten bath at: (a) 1173 K, (b) 1273 K and (c) 1373 K.

4. CONCLUSIONS

Niobium carbide can be formed on AISI L2 steel by TRD method in a molten bath comprising of borax, boric acid, and ferro-niobium. The formed carbide coating has a dense and compact morphology with a smooth interface with, and a good bonding to the substrate. Diffusion of elements from niobium carbide coating to the steel substrate and elements from substrate to the coating controls the kinetics of growth for the molten bath containing 10 wt.% or more ferro-niobium. For the molten baths containing less than 10 wt.% ferro-niobium, the growth kinetics is not under the control of diffusion. For the molten bath containing 10 wt.% ferro-niobium or more, the activation energy (Q) and constant of k (k_0) of the process are estimated to be 122.5 kJ/mol and 1.79×10^{-9} m²/s respectively. A practical formula was calculated to estimate the coating thickness, l (m), of a sample treated in a molten bath containing 10 wt.% ferro-niobium or more, at the treatment temperature, T (K), and for the treatment time, t (s).

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