FORMATION OF NIOBIUM CARBIDE COATING ON AISI L2 STEEL USING THERMO-REACTIVE DIFFUSION (TRD) TECHNIQUE

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Abstract

In this study, a thin layer of niobium carbide was thermochemically formed on AISI L2 tool steel substrates using the thermo-reactive diffusion (TRD) method. Five different compositions of salt bath were selected and for each composition the treatment was performed at three different temperatures (900, 1000, 1100 °C) for three different times (two, four, eight hours). The morphology of the coating was characterized through optical and scanning electron microscopy (SEM), and the crystalline structure was studied through X-ray diffraction (XRD). The reaction layer of niobium carbide formed was uniform all over the surface and had a smooth interface with the substrate. The thickness of the coating varied from 3.6 to 33 μm depending on the chemical composition of the salt bath, process time and temperature. The chemical composition was evaluated via Energy-dispersive X-ray Spectroscopy (EDS) and the atomic distribution map of the coating and substrate was prepared. The hardness value of the coated samples was 2450±50 HV 0.05 which was much higher than the hardness of the uncoated sample (280 HV). Corrosion properties of NbC coated samples in 3% NaCl solution were studied and the results showed that coated samples had better corrosion resistance in comparison to the uncoated steel.

Introduction

Since the 1960s, hard coatings have been applied as an effective solution to decrease wear and improve friction characteristics of tool steels, especially in cutting tools [1]. Niobium carbide (NbC) coatings have been attracting considerable attention owing to their excellent properties. In addition to the high melting point (3610 °C), excellent chemical stability, high toughness, excellent wear and friction properties [2,3], it possesses extremely high hardness [4].

Physical vapor deposition (PVD) and chemical vapor deposition (CVD) are the techniques which are used to produce NbC coatings on an industrial scale. These methods have advantages and disadvantages. For instance, both techniques require expensive and complicated equipment that must be operated under high-vacuum conditions [5]. The thermo-reactive diffusion technique (TRD), also known as TOYOTA Diffusion process (TD) [6] is another technique used to achieve NbC coatings. The main advantage of the TRD process appears to be its low cost, because the treatment is performed at atmospheric pressure and it does not require such expensive equipment as the high-vacuum techniques [7].

In the TRD process, one of the carbide or nitride forming elements such as Nb, Cr, V, Ti diffuses into the surface by a thermochemical process at elevated temperatures (800-1200 °C) and forms a carbide or nitride layer on the surface [8,9]. Most carbon-containing materials such as steels, cast irons, cobalt alloys, cemented carbides, carbide-metal cermets, carbide ceramics, and carbon may be used as the substrates for carbide coating [10]. The best applications for TRD coatings are tools that have demanding wear requirements and galling problems. This includes many types of forming and cutting tools, and die components. Examples of the applications of NbC coating include: draw-dies for sheet metal working, squeeze-rolls for pipe and tube manufacturing, die-casting cores and sleeves for aluminum and zinc casting, extrusion punches and dies for cold forging and warm forging, press-forging dies for hot forging, form dies for rubber and plastic forming, cutting tools and knives [11].

The aim of this study is the forming of thin reaction layers of NbC on AISI L2 tool steel using the TRD method and assessing its properties in addition to investigating the effect of some parameters including temperature, treatment time and chemical composition of the molten bath on the coating.

Experimental Method

Five different compositions of molten salt bath comprising borax ($Na_2B_4O_7$), boric oxide (B_2O_3, added as boric acid) and ferroniobium (65 wt.% niobium) were selected according to Table I. Cylindrical samples of AISI L2 tool steel (φ 10 mm × height 15 mm) were prepared for the TRD process. Forty-five specimens were coated by immersing in the molten bath. For each composition of the bath, treatment was performed at 900 °C, 1000 °C and 1100 °C for two, four and eight hours. Then samples were cooled in air and were cleaned of the remaining salt using boiling water.

Table I. Compositions* of Molten Salt Bath

Composition Number	**Ferroniobium Concentration (wt.%)**	**Borax Concentration (wt.%)**	**Boric Acid Concentration (wt.%)**
Composition 1	5	90	5
Composition 2	7	88	5
Composition 3	10	85	5
Composition 4	20	75	5
Composition 5	30	65	5

*Compositions refer to the additions at room temperature

The microhardness of the coating was measured by means of the BUEHLER Micro Met instrument. The applied load of the microhardness test was 50 g for 15 seconds. Samples were sectioned, polished and etched with 2% nital. Microstructural details of the samples were studied using the Optical Microscope (OM), and the TESCAN VEGAIIXMU Scanning Electron Microscope (SEM) equipped with Energy Dispersive X-ray Spectrometry (EDS). The atomic distribution profile in the coating and substrate was studied by X-ray Spectrometry. The thickness of the coating was measured by means of a micrometer attached to the optical microscope. The values reported for thickness were the average of at least ten measurements. The coating phases were analyzed by JOEL-JDX-8030 X-Ray Diffraction (XRD) using Cu-Kα radiation. The Tafel potentiodynamic polarization test was carried out to assess corrosion resistance of the coated samples in 3 wt.% NaCl solution.

Results and Discussion

Characterization of the Coating

Optical and SEM micrographs of the cross-section of the treated samples showed that a uniform layer of NbC was formed all over the surface with a dense and compact morphology. The coating had a smooth interface with the substrate for all of the treated samples. In Figure 1, the optical micrograph of the cross section of the sample treated for four hours at 1100 °C in bath composition 4, Table I, is shown. The NbC coating (light region) is clearly distinguished in this image, uniformly covering the substrate (dark region). The XRD analyses of the coated samples revealed that the composition of the coating was NbC for all the treatment temperatures and times, Figure 2. However, it has been reported that NbC coating treatment by the TRD method in a solid medium forms NbC/Nb_2C multiphase [12]. In Figure 3, the SEM image of the section from the treated sample in a molten bath containing 20 wt.% ferroniobium for two hours at 1100 °C is shown.

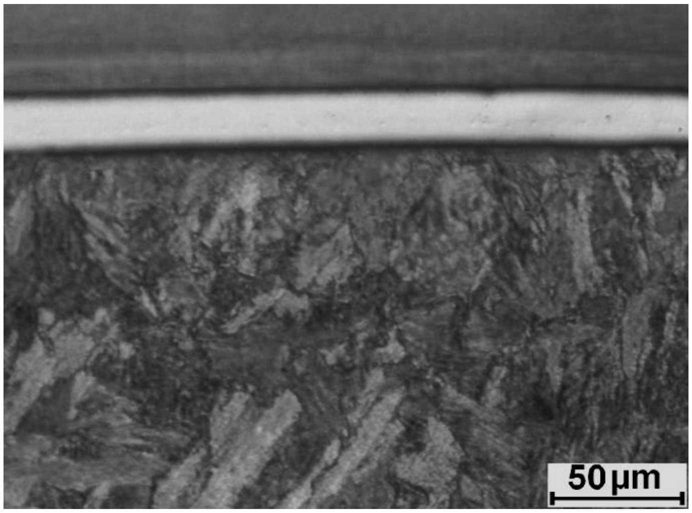
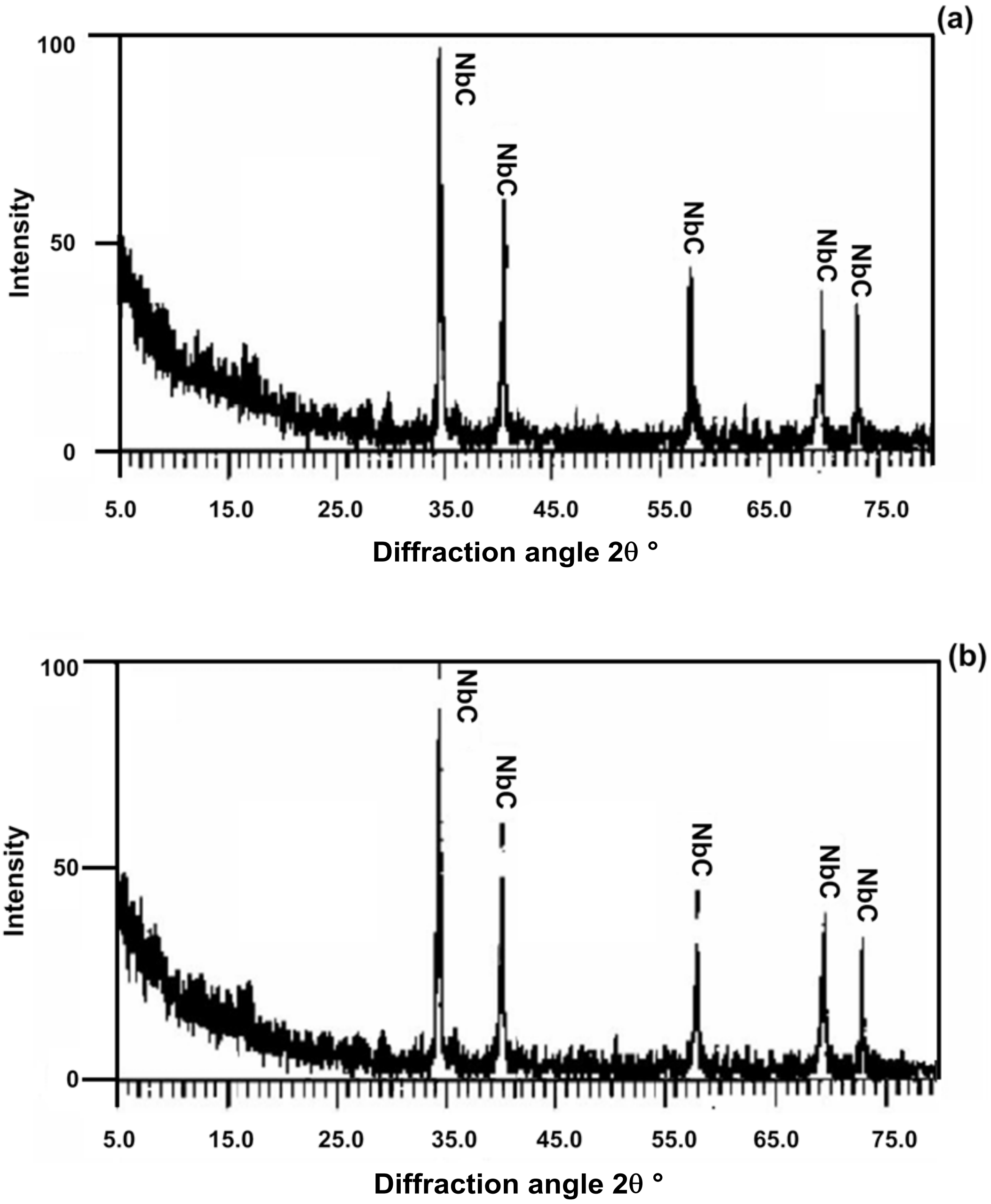


Figure 1. Optical micrograph of the section from the sample treated in a molten bath comprising 20 wt.% ferroniobium for two hours at 1100 °C.


(a)
100
50
0
Intensity
NbC
NbC
NbC
NbC
NbC
5.0
15.0
25.0
35.0
45.0
55.0
65.0
75.0
Diffraction angle 2θ °
(b)
100
50
0
Intensity
NbC
NbC
NbC
NbC
NbC
5.0
15.0
25.0
35.0
45.0
55.0
65.0
75.0
Diffraction angle 2θ °

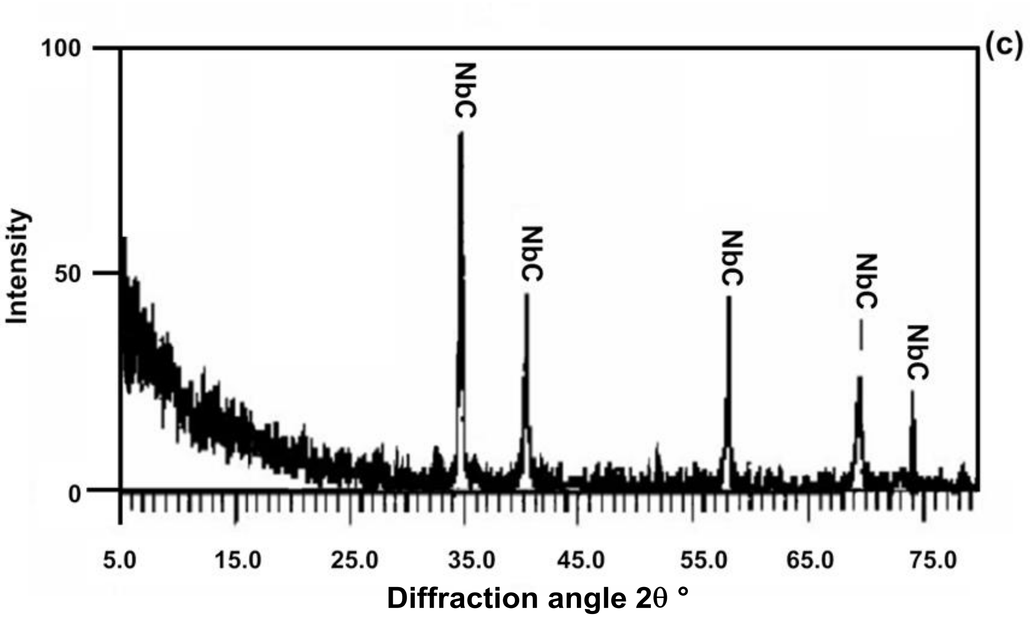


Figure 2. X-ray diffraction spectra of specimens; (a) treated in composition two for two hours at 1100 °C, (b) treated in composition four for eight hours at 1000 °C, (c) treated in composition three for four hours at 900 °C .

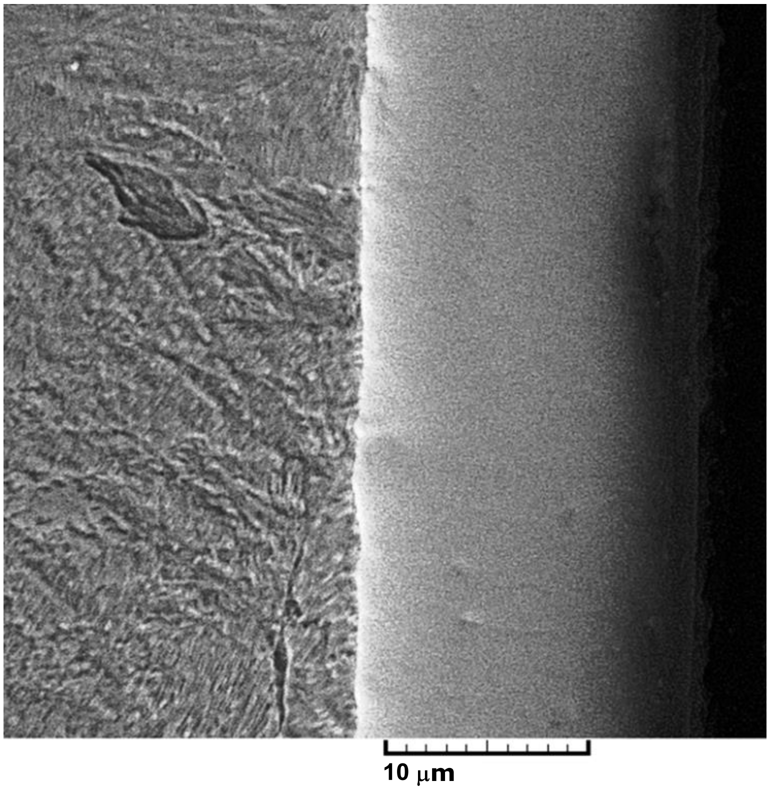


Figure 3. SEM micrograph of the cross section of the sample treated in a molten bath containing 20 wt.% ferroniobium for two hours at 1100 °C.

The result of point EDS analysis showed that the concentration of iron within the coating at different distances from the coating/substrate interface was insignificant (maximum 0.9 wt.%). In addition, the concentration of niobium within the substrate was a maximum of 0.1 wt.%. Carbon was detected in the coating and substrate, but because of apparatus error, the reported concentration of carbon was not accurate. However, the formation of NbC on the substrate confirms the outward diffusion of carbon to the coating. The linear distribution map of the elements Nb, C, Fe is shown in Figure 4. It is observed that diffusion of iron atoms from the substrate to the coating, and diffusion of niobium atoms from the coating to the substrate are limited. This intermixing generates an interface assuring a metallurgical bond. The distribution map of elements confirms the presumed mechanism that the dissolved niobium in the salt bath is adsorbed on the surface of the steel and carbon diffuses outward to the coating and combines with niobium and forms the NbC coating [13].

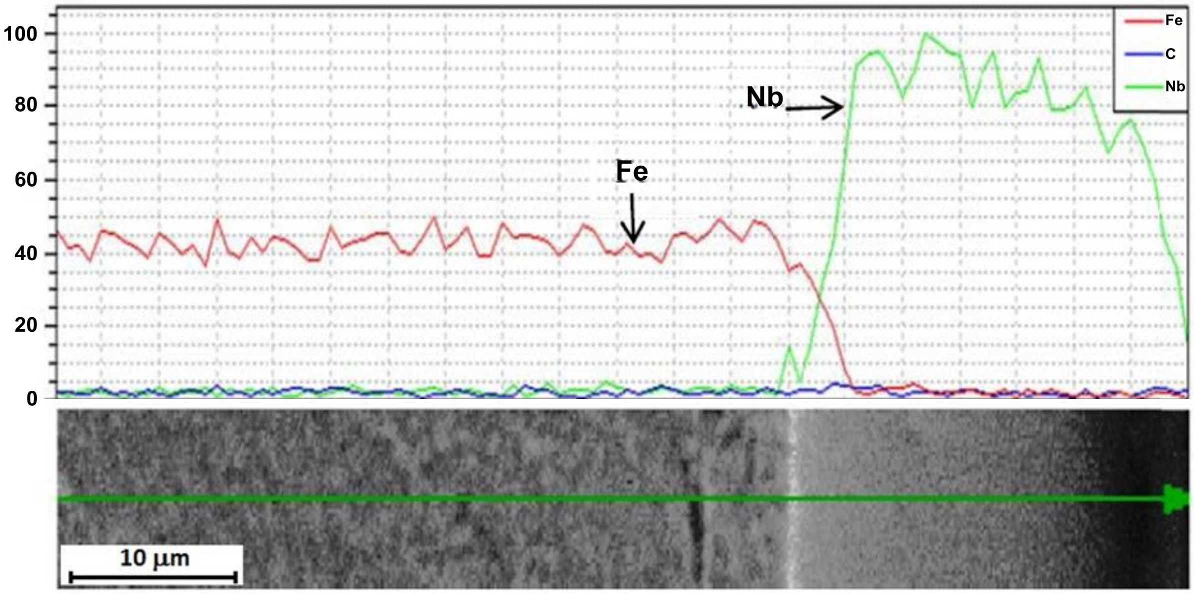
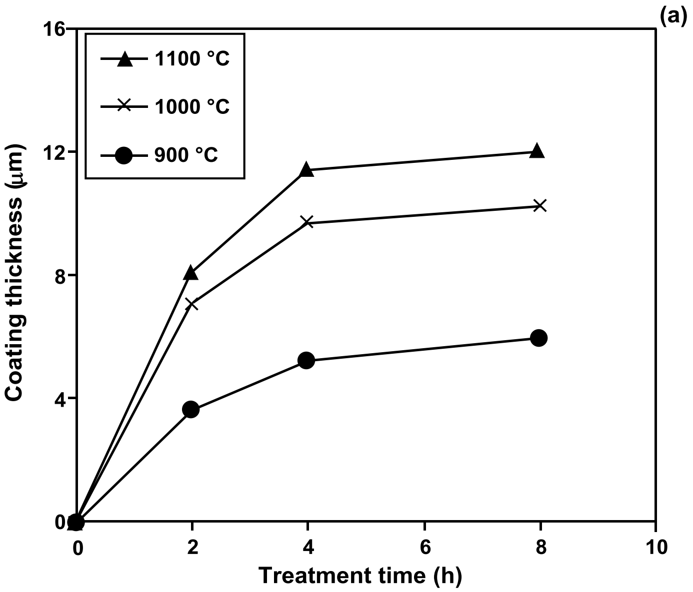
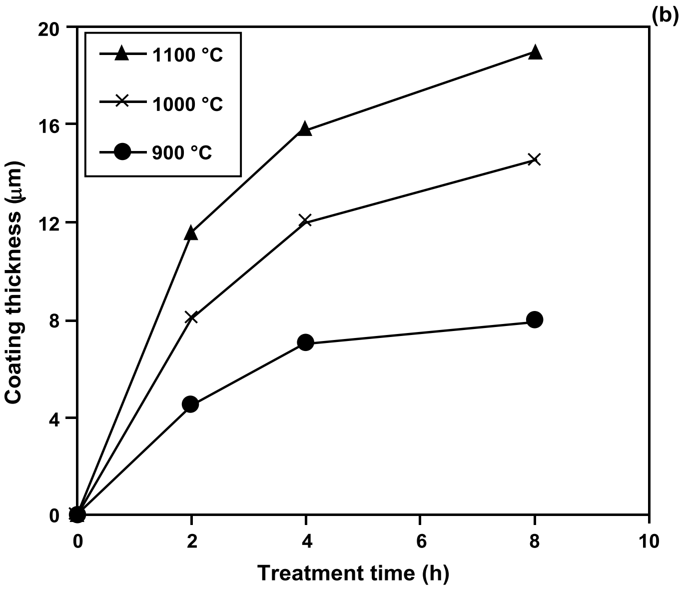


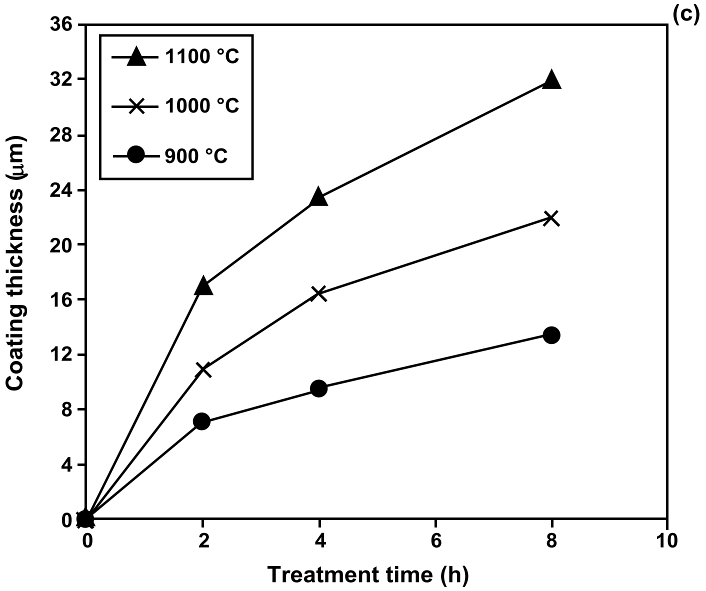
Figure 4. EDS line scan analysis of the section from the sample treated in a molten bath containing 30 wt.% ferroniobium for four hours at 1100 °C.

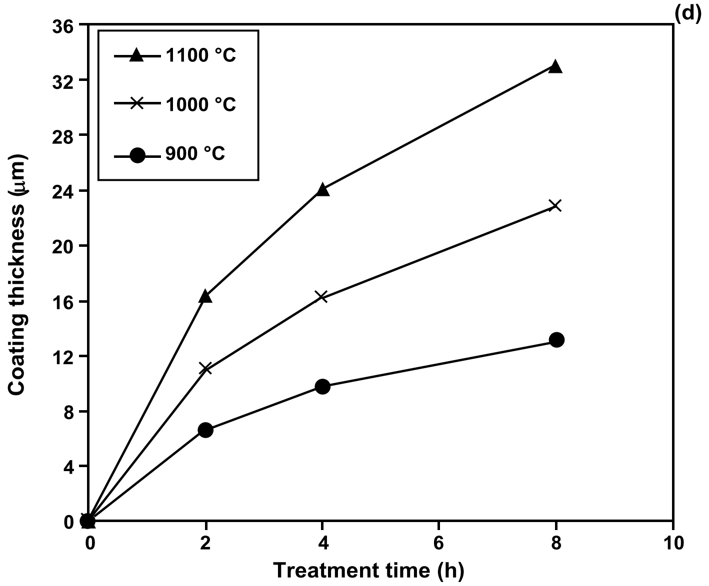
Effect of the Parameters on the Coating Growth

The thickness of the coating varied from 3.6 to 33 μm depending on process time, temperature and the chemical composition of the salt bath. The effect of treatment time on the thickness of the coating at different temperatures and different molten bath compositions is shown in Figure 5. Figures 5(a)-(e) exhibit the thickness of coating versus treatment time plots for the molten baths containing 5, 7, 10, 20, and 30 wt.% ferroniobium respectively. It is observed that for all of the molten bath compositions the thickness of the coating increases significantly with increasing time of treatment. In addition, the graphs show greater thicknesses at higher treatment temperatures. It shows the considerable effect of temperature on the rate of coating growth.


(a)
1100 °C
1000 °C
900 °C
Coating thickness (μm)
0
4
8
12
16
Treatment time (h)
0
2
4
6
8
10


(b)
1100 °C
1000 °C
900 °C
Coating thickness (μm)
0
4
8
12
16
20
Treatment time (h)
0
2
4
6
8
10


(c)
1100 °C
1000 °C
900 °C
Coating thickness (μm)
36
32
28
24
20
16
12
8
4
0
0
2
4
6
8
10
Treatment time (h)


(d)
1100 °C
1000 °C
900 °C
Coating thickness (μm)
36
32
28
24
20
16
12
8
4
0
0
2
4
6
8
10
Treatment time (h)

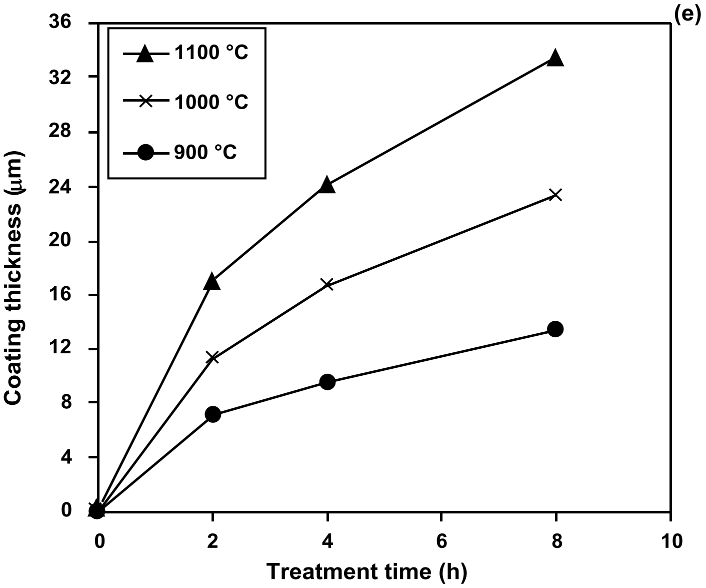
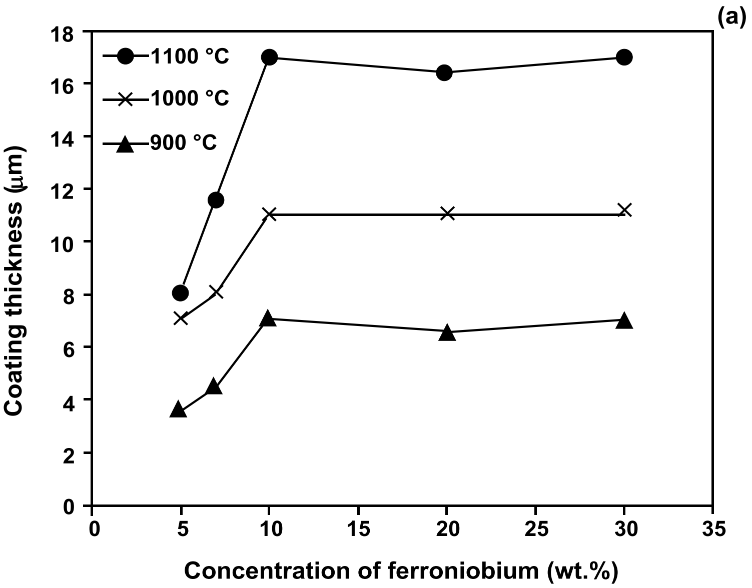
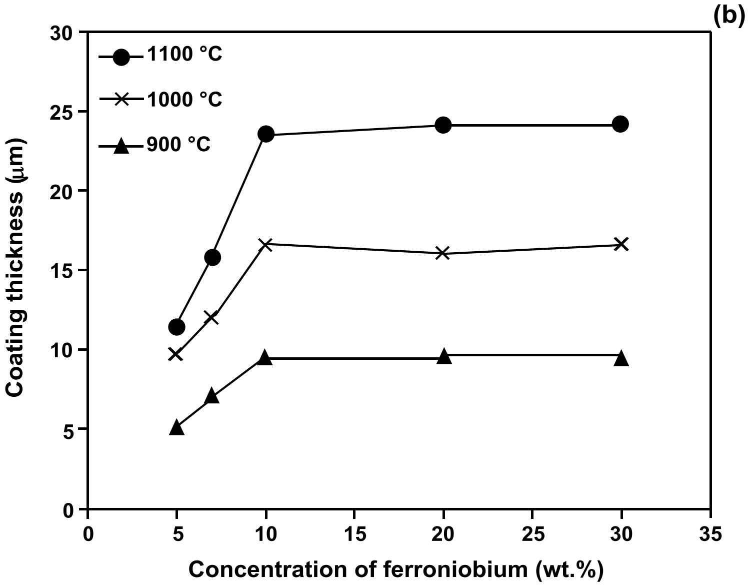


Figure 5. Coating thickness versus treatment time for different compositions of salt bath (Table I); (a) composition 1, (b) composition 2, (c) composition 3, (d) composition 4, (e) composition 5.

In Figure 6 the effect of chemical composition of the molten bath on the thickness of the coatings at different treatment temperatures is shown. It is observed that for the molten baths containing less than 10 wt.% ferroniobium, an increase in the concentration of niobium in the bath results in an increase in the thickness of the coating. However, for the molten baths containing more than 10 wt.% ferroniobium the concentration of niobium has an insignificant effect on the thickness of the coating. It is assumed that for the molten baths which contain a small amount of ferroniobium (less than 10 wt.%), the adsorption of niobium atoms on the surface of samples is the rate controlling step. However, for the molten baths comprising more than 10 wt.% ferroniobium, there are sufficient quantities of dissolved niobium and the growth kinetics of the coating are not under the control of the adsorption of niobium atoms on the surface.


(a)
Coating thickness (μm)
0
2
4
6
8
10
12
14
16
18
1100 °C
1000 °C
900 °C
0
5
10
15
20
25
30
35
Concentration of ferroniobium (wt.%)


(b)
Coating thickness (μm)
0
5
10
15
20
25
30
1100 °C
1000 °C
900 °C
0
5
10
15
20
25
30
35
Concentration of ferroniobium (wt.%)

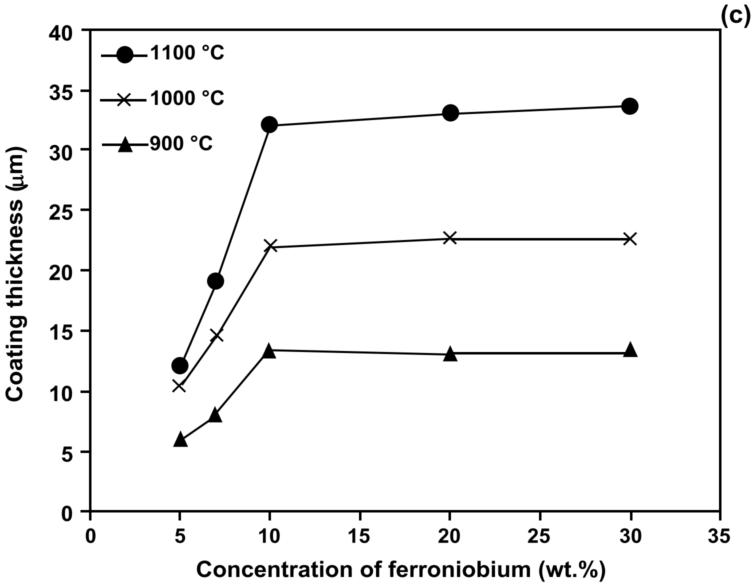


Figure 6. Coating thickness versus concentration of ferroniobium in the molten bath; (a) treated for two hours, (b) treated for four hours, (c) treated for eight hours.

Hardness

The results of the microhardness tests on the coated samples reveal a great increase in the hardness compared with the uncoated samples (280 HV). The microhardness of all the coated specimens was almost the same ranging from 2400 to 2500 HV. Figure 7 shows the microhardness test traverses and the hardness profile on the cross-section of the specimen treated in a molten bath comprising 10 wt.% ferroniobium at 1000 °C for four hours. In order to increase the number of readings, the hardness traverses were taken at an angle to the surface. The hardness profile shows that the hardness of the coating remains almost the same at all distances from the coating/substrate interface, but, it drops dramatically at the interface and within the substrate. Owing to the fact that the Vickers indentation imposed in the coating/substrate interface does not show the formation or propagation of cracks at the interface, it can be concluded that there is a strong metallurgical bond between coating and substrate.

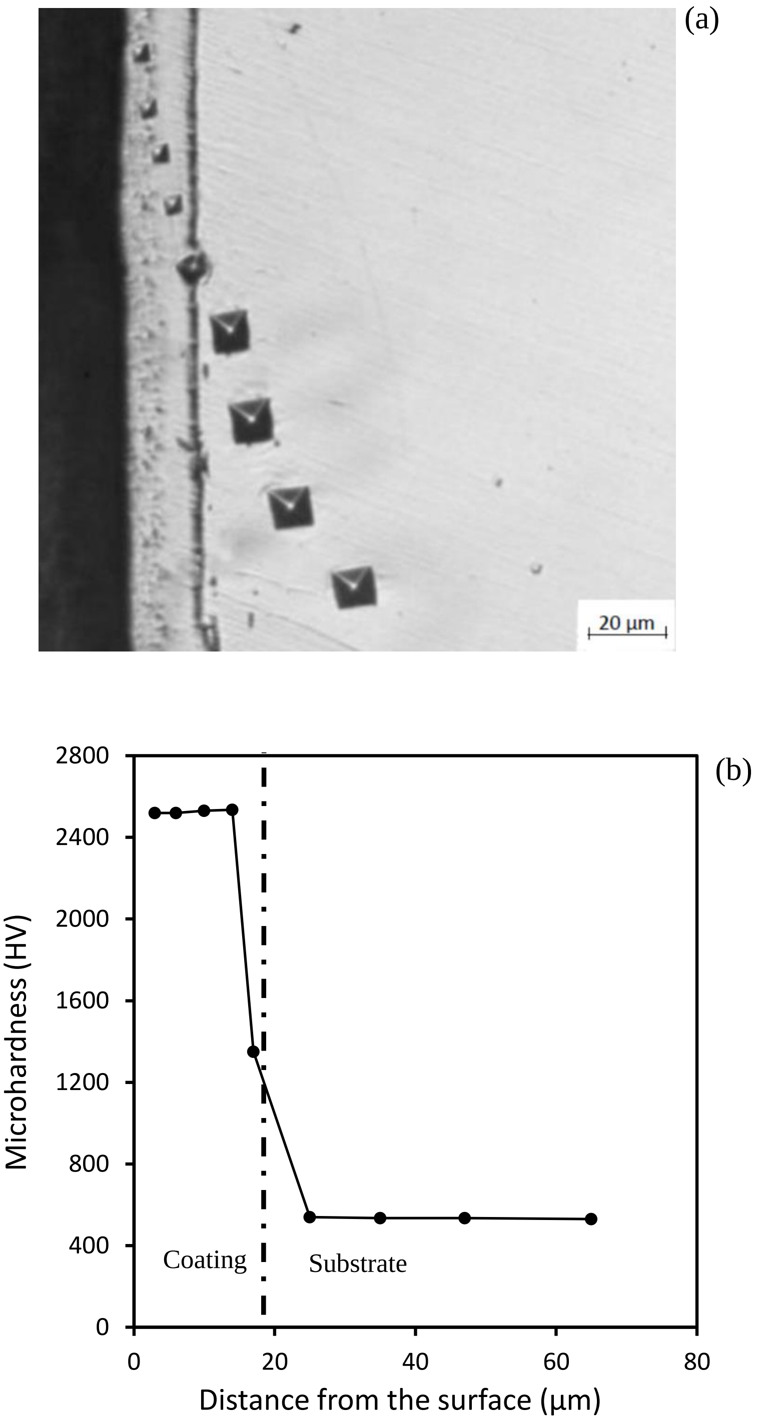


Figure 7. Microhardness versus distance from surface of the coated sample treated in a molten bath comprising 10 wt.% ferroniobium at 1000 °C for four hours; (a) image from microhardness test traverses, (b) microhardness profile.

The hardness of the NbC coating which is produced by the TRD technique is almost the same as the hardness of vanadium carbide TRD coatings (2430-2700 HV) [14] and higher than the hardness of other TRD coatings including chromium carbide (1350±30 HV) [15], chromium nitride (1780±58) [16], vanadium carbonitride (2220±40) [17], and boronized steel (1600-1900 HV) [10].

Corrosion Properties

Figure 8 shows polarization curves of the Tafel potentiodynamic polarization test in 3 wt.% NaCl solution of three coated specimens treated in a molten bath containing 10 wt.% ferroniobium for four hours at three different treatment temperatures (900, 1000, 1100 °C) and the uncoated specimen. A positive shift in corrosion potential has occurred due to the application of the coating. It is observed that the corrosion potential of the coated samples at different treatment temperatures is almost the same. Polarization curves of coated samples exhibit a passive behavior which can be affected by treatment temperature. In summary, coated specimens show better corrosion resistance in comparison with the uncoated specimen.

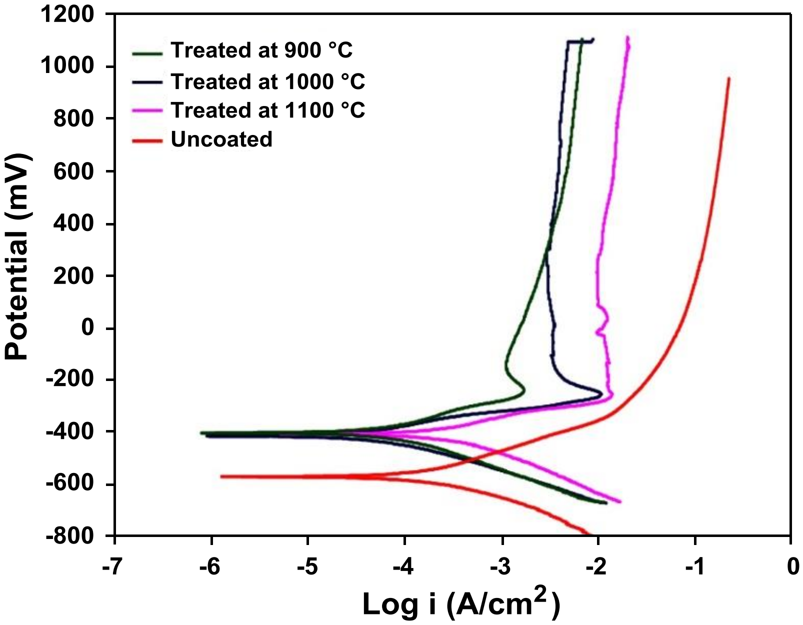


Figure 8. Potentiodynamic curves of three coated specimens treated in the molten bath containing 10 wt.% ferroniobium for four hours and the uncoated specimen.

Conclusions

The thermo-reactive diffusion technique has been employed to produce NbC coatings on AISI L2 tool steel, using different salt bath chemistries, temperatures and times.

1. NbC coating has a dense and compact morphology and good metallurgical bonding with the substrate.

2. The coating thickness increases with time (0-8 hours) and temperature (900, 1000, 1100 °C).

3. For the molten baths comprising less than 10 wt.% ferroniobium, an increase in the concentration of niobium in the bath results in an increase in the thickness of the coating for a given time and temperature. However, for the molten baths containing more than 10 wt.% ferroniobium the concentration of niobium has an insignificant effect on the thickness of the coating. It is assumed that for the molten baths which contain less than 10 wt.% niobium, the adsorption of niobium atoms on the surface of samples is the rate controlling step. However, for the molten baths containing more than 10 wt.% ferroniobium, there is a sufficient quantity of dissolved niobium and the growth kinetics of the coating are not under the control of the adsorption of niobium atoms on the surface.

4. The hardness value of the TRD coated samples is 2450±50 HV 0.05 which is much higher than the hardness value of uncoated steel (280 HV). Comparing other TRD coatings, it is similar to vanadium carbide (2430-2700 HV) and higher than chromium carbide (1350±30 HV), chromium nitride (1780±58), and vanadium carbonitride (2220±40).

5. NbC coating improves the corrosion resistance of steel in 3 wt.% NaCl solution.

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