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TiC-Coating on the High Carbon Steels SK3 and SKS93 Using the Powder-pack Method

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CONTENTS

ABSTRACT

TiC coatings on high carbon steels are suggested to improve wear resistance as well as resistance to corrosive atmospheres. However, coating high carbon steels with pure TiC is technically difficult due to the rather strong affinity of Ti to N_2, O_2 or H_2. A coating reagent including mainly ferro-Ti, Al_2O_3 and small amount of NH_4Cl was applied to two high carbon steels of SK3 and SKS93 at various temperatures and time periods in a closed crucible.

The layers were inspected under the microscope and their hardness profiles determined. The TiC coatings were also identified by X-ray diffraction and EPMA.

1. INTRODUCTION

In modern technology, it is frequently necessary to strengthen the surface of metallic materials for construction parts or machinery elements for protection against mechanical stresses, heat or corrosive atmospheres. Chemical, mechanical and thermo-chemical surface treatments have been widely employed in practice.

The thermo-chemical method is characterized by the diffusion of atoms of the coating material into the base metal as well as the formation of a layer on it. This may achieve the desired surface properties.

The most common thermo-chemical surface heat treatment processes are carburization and nitriding. In these processes, carbon and nitrogen atoms play an important role. Similar treatments using other elements are also employed, for example, chromizing, aluminizing, boronizing, siliconizing and titanizing.

It is well known that steels with TiC coatings have good wear resistance as well as good corrosion resistance.

There are four processes for providing TiC protective layers on steel most frequently used: PVD, CVD, salt solution immersion and the powder-pack method. Both the PVD and the CVD processes require expensive and complicated equipment.

The powder-pack method is, on the contrary, a very simple process for providing protective coatings. There are, however, some disadvantages in its actual application. It is especially very difficult to produce a pure TiC layer on a steel surface.

The purpose of this study is to present the most suitable treatment conditions to produce a TiC coating on steel surfaces by the powder-pack method.

2. EXPERIMENTAL PROCEDURES

2.1. Test Piece

To produce a TiC layer on the steel surface, it is indispensable to supply carbon atoms from a substrate or an atmosphere which is used as a carrier gas or as an additional gas. Since carbon atoms from the substrate steels diffuse into the surface layer, high carbon steels SK3 and SKS93 were chosen as test pieces. The chemical composition of these steels is given in Table 1. All test pieces were cut to 15 x 10 x 5 mm, polished with emery paper from No. 320 to No. 1000, degreased in alkali solution and washed in an acid solution.

TABLE 1
Chemical Composition of Specimens

	C %	Si %	Mn %	P %	S %	Cr %
SK3	1.00–1.10	< 0.35	< 0.5	< 0.03	< 0.03	–
SKS93	1.03	0.39	0.98	0.024	0.018	0.44

2.2. Experimental Apparatus and Experimental Conditions

The experimental arrangement for TiC coating is shown in Figs. 1 and 2. The crucible containing the test piece was filled with spender materials, the chemical composition of which is given in Table 2.

The material was heated to 1223°K for times between 3.6 and 18 k.s. The filling percentage of the powder pack material was held constant at $17\text{–}20 \times 10^{-3}$ N/mm^3. Argon was supplied as a protective atmosphere at the rate of 5×10^4 $mm^3/60$ s. The ferro-Ti powder used (10 to 30 μm in diameter) contained 42.6 wt.% Ti. The Al_2O_3 powder was about 300 mesh in size. The NH_4Cl used as an activator to produce

TABLE 2
Chemical Composition of Spender Powder

Element	Ferro-Ti	Al_2O_3	TiH_2	NH_4Cl
Weight (grf)	120	70	6	4

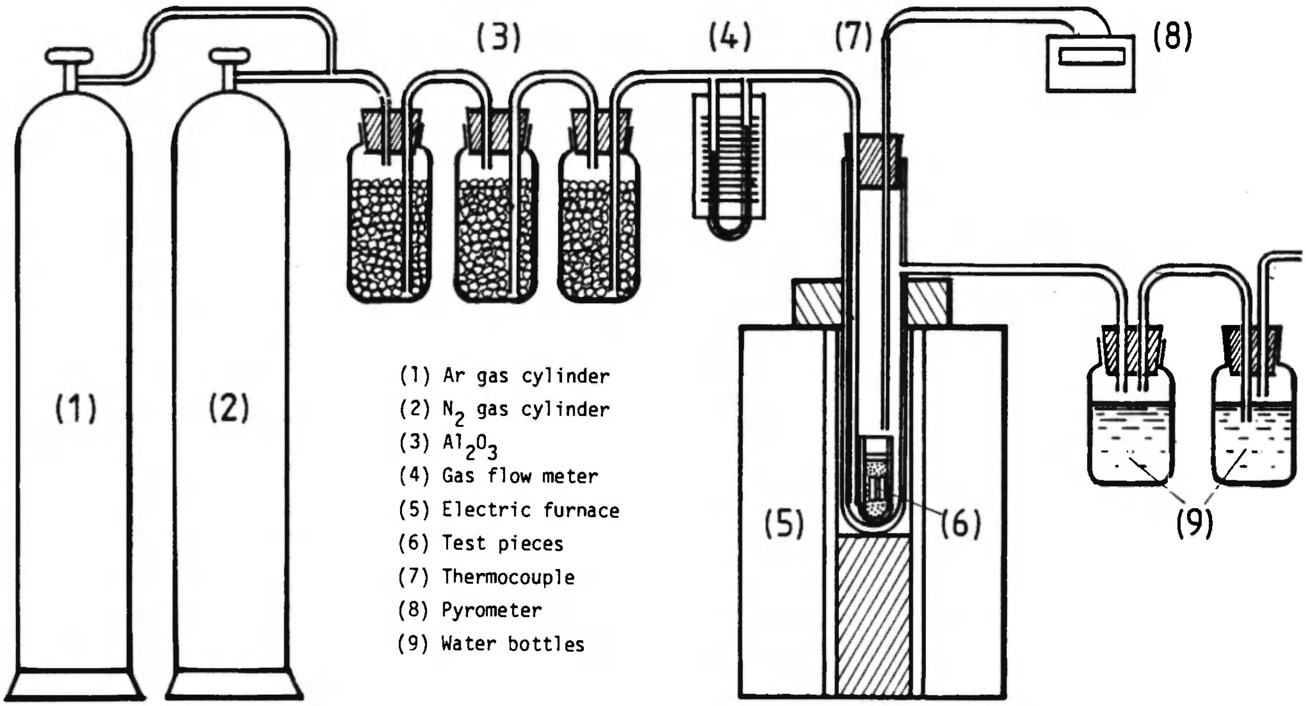

Fig. 1. Representation of experimental apparatus for TiC coating steel surfaces.

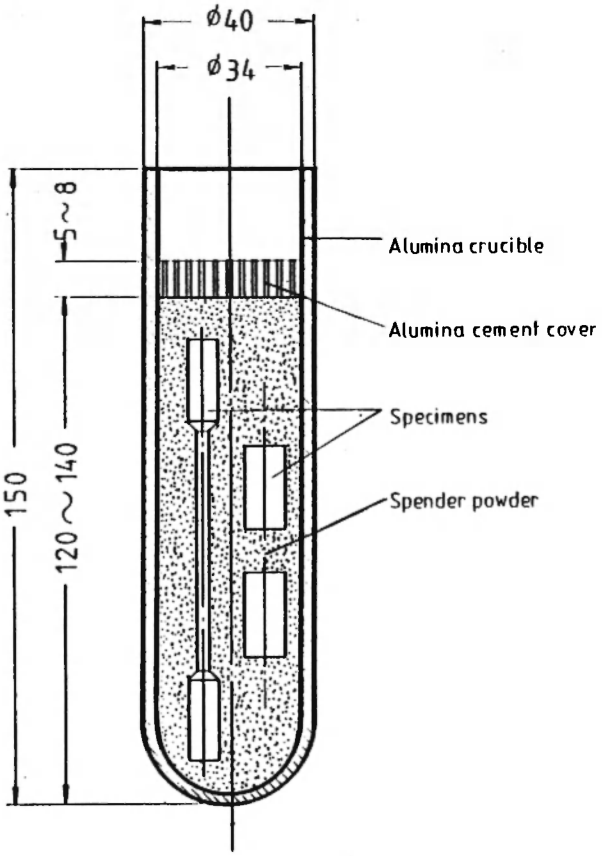

Fig. 2. Reaction crucible with the spender powder and specimens

$TiCl_4$ was a high quality industrial product. The time needed to reach the treatment was about 10.8 k.s. and the cooling time to room temperature was about 18 k.s.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Observation of TiC Coating Layers by Microscope and SEM

Fig. 3 shows the sectional microstructures of a TiC coating treated at 1253°K for 3.6 k.s. (SKS93). These sections were cut with a diamond cutter and polished with diamond paste.

Fig. 3 shows clearly that the TiC coating layer consists of two zones. The first zone includes many pores. The second zone, the actual coating zone, is free of porosity, very hard and not easily removed. The SEM micrograph in Fig. 4 shows that there are many voids or pores between the first and second zones. The cause of the exfoliation of the first zone is not only because of the porosity, but is also due to the differences in chemical composition, moduli of elasticity, linear expansion coefficients and residual stresses of these two zones. When perfectly coated sections were etched

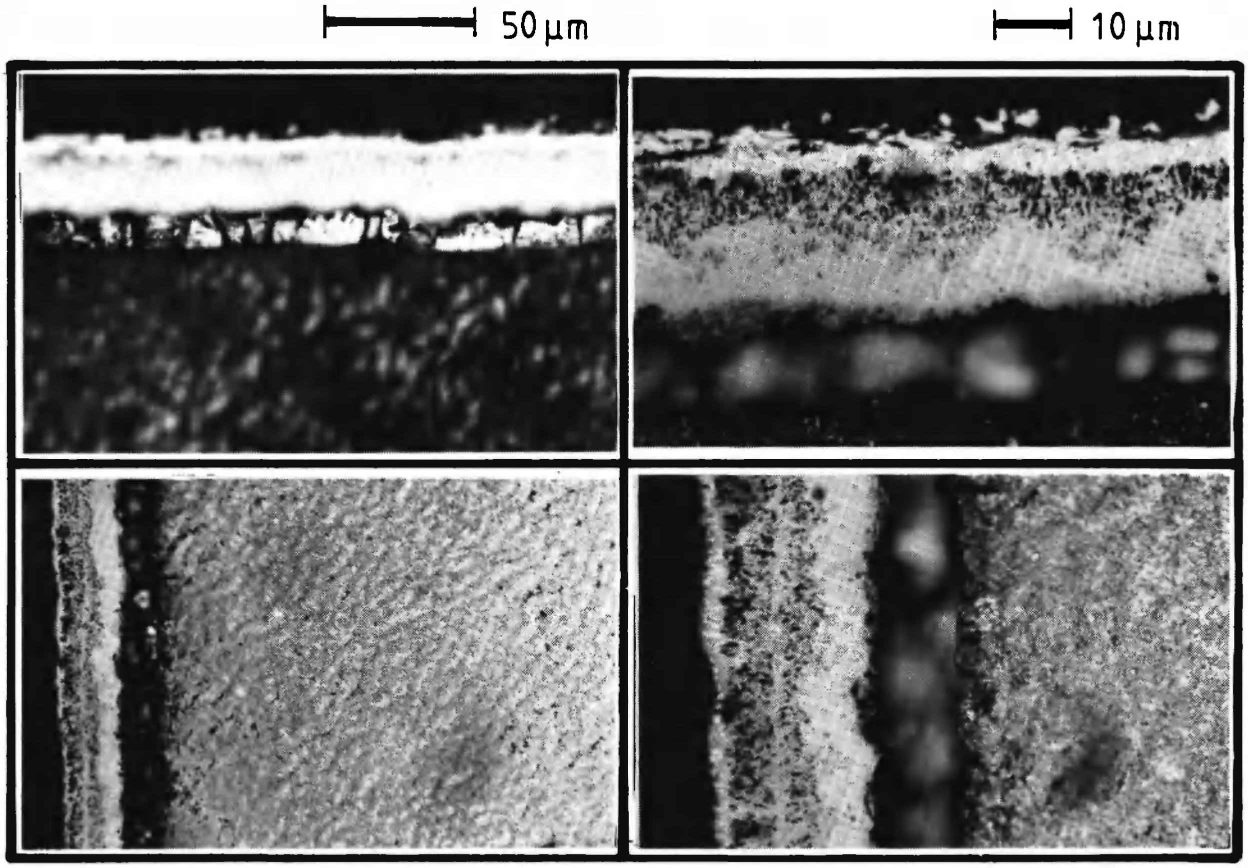

Fig. 3. Microstructures of TiC-coated layer SKS93 (Treated at 1253°K/3.6 k.s.). Etching reagent: $CuSO_4$ + HCl + H_2O

Fig. 4. SEM Micrographs of TiC-coated layer SKS93 (Treated at 1253 K / 3.6 k.s.). Not etched.

with a 5% Nital solution, they changed as illustrated in Fig. 5.

It is clear from the microstructures that the coating layer consists of three zones. A white zone, with a cloudy appearance, constitutes the third zone which is formed by decarburization due to the diffusion of carbon atoms. This decarburization process is influenced by various parameters, such as the kind of steel, the carbon concentration, the content of alloying elements with a high affinity to carbon, the chemical composition of the activator, the protective atmosphere, the filling material and its components, and the position of the test piece in the crucible /1, 2/.

According to the equilibrium phase diagram of the Fe–Ti–C system by W. Tofaute and A. Buttinghaus /3/, the present experimental condition was close to the ferrite (α-Fe) formation boundary.

Fig. 5 shows many voids between the coating layer and the base metal; this is due to the Kirkendall-effect, to the fact that the diffusion velocity of carbon is greater than that of other elements but in the opposite direction /4, 5, 6, 7/.

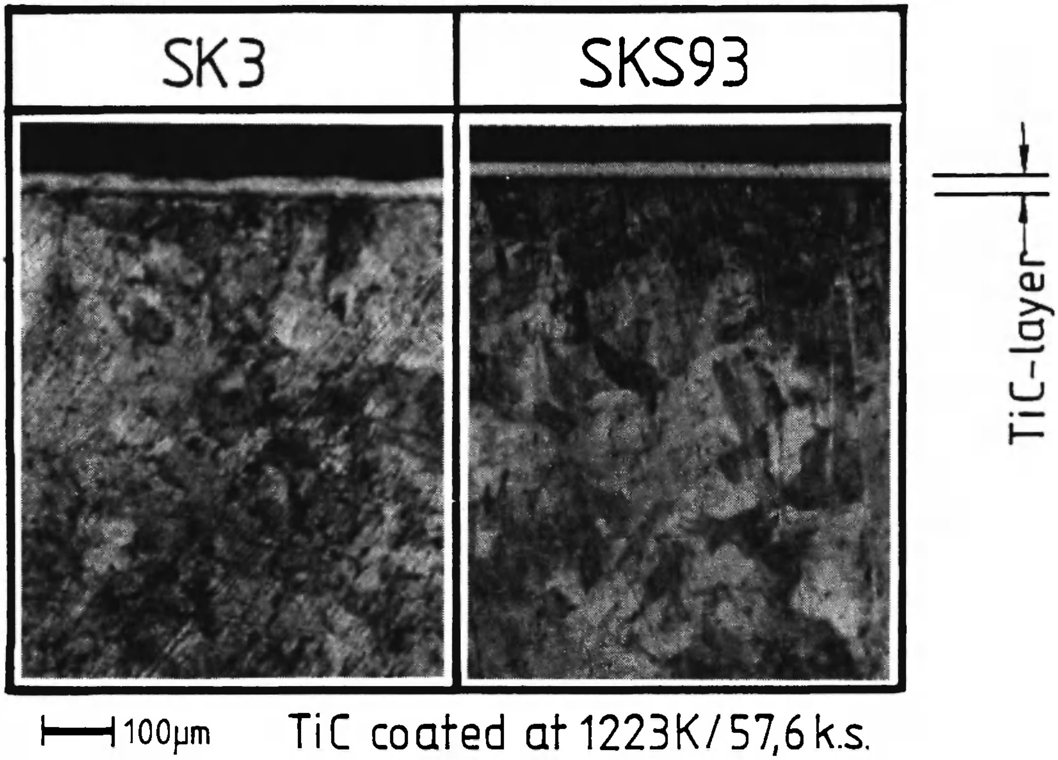

Fig. 5. Microstructure of titanium carbide coated layer. Etching reagent: 5% Nital.

3.2. Dependence of Coating Layer Thickness on Treatment Time

The relationship between treatment time and coating thickness is shown in Fig. 6. In each case, a linear relation was observed. It may also be noted that a parabolic relation was not observed, because this depends on the amount of argon gas flow as well as the ratio between the surface area of the specimen and the amount of spender material, none of which applied. If a sizeable specimen is placed in a large crucible and subjected to a high flow of argon gas during treatment, a parabolic curve with regard to the treatment time may be obtained.

3.3 Hardness of TiC Coatings

The Micro-Vickers hardness of TiC-coatings is known in the range between 3,200 and 3,800 HV. It exceeds the value of TiN layers (less than 2500 HV) /8, 9, 10, 11, 12, 13/.

Hardness distribution profiles are indicated in Figs. 7 and 8. The first zone of SKS93 steel has a hardness of about 2,200 HV and the second zone one of more than 3,000 HV. The third zone, being decarburized, has between 200 and 300 HV.

3.4. Analysis of TiC Coatings using EPMA

Intensity profiles of various elements are illustrated in Figs. 9 and 10. These show the intensity profiles of Ti–Kα and Fe–Kα, which are reflected from the coating layers of SKS steel.

As can be seen in Fig. 9, titanium is uniformly distributed to a depth of about 13 μm. The Fe–Kα distribution shows a converse concentration pattern, reaching normal level after about 18 μm of depth with titanium level less than 5%. SKS93 steel coated by TiC shows similar behaviour, as shown in Fig. 10.

Analysis by a special EPMA apparatus determining the chemical composition of a small area of the coating layer has also been carried out and the results are listed in Table 3. The analysis details conducted with this equipment were as follows:

(1) Diameter of electron beam: 1 μm
(2) Accelerating Voltage: 1 KV
(3) Sample current: 2×10^{-7} A
(4) Test piece: SK3 (treated at 1223°K/3.6 k.s.)

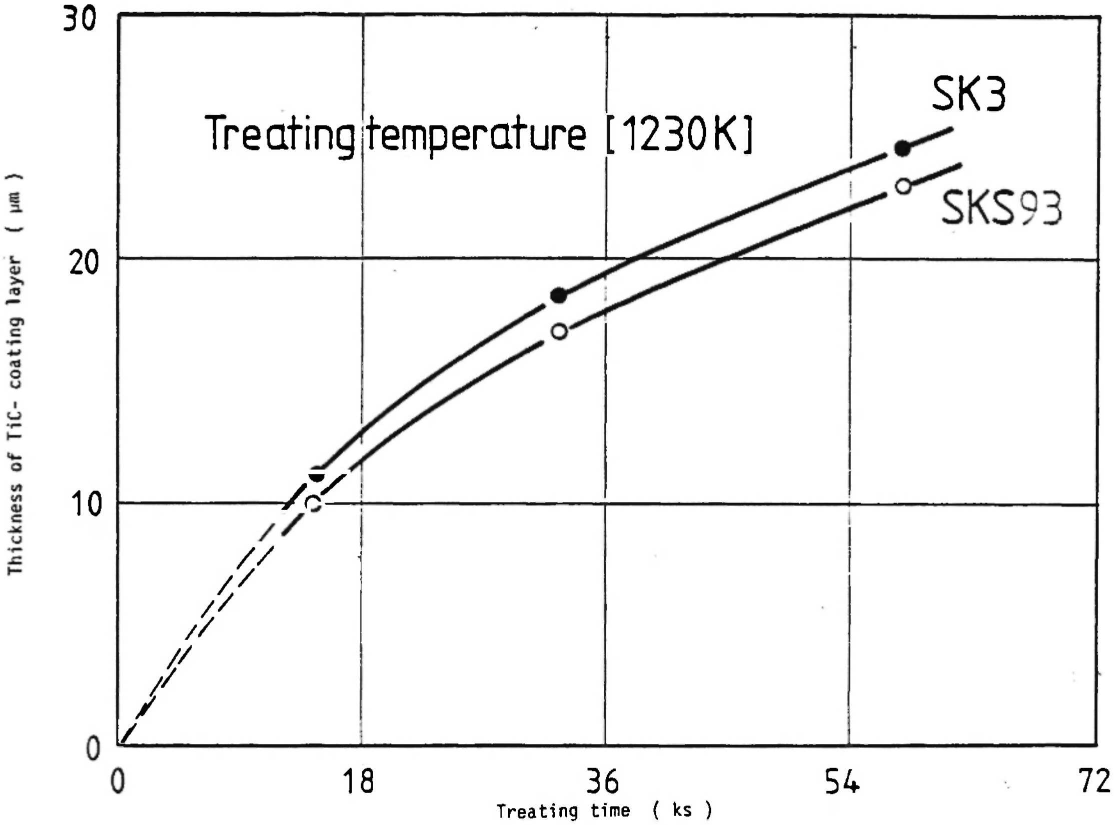

Fig. 6. Effect of treatment time on the thickness of coating layer (TiC).

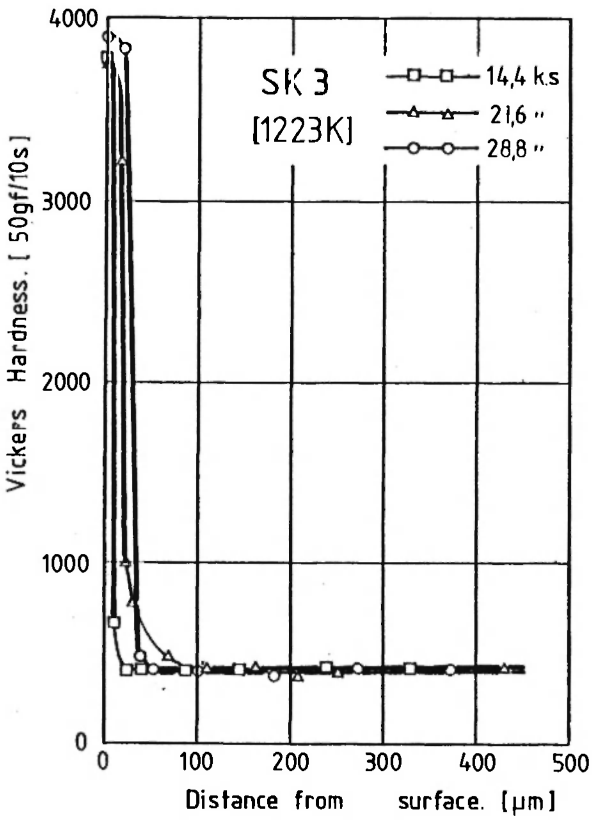

Fig. 7. Hardness profile in TiC Coatings

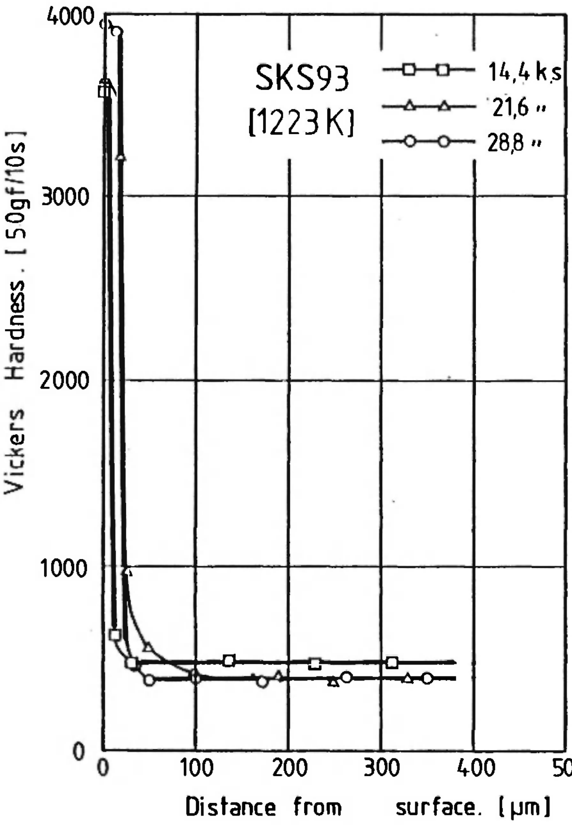

Fig. 8. Hardness profile in TiC coatings

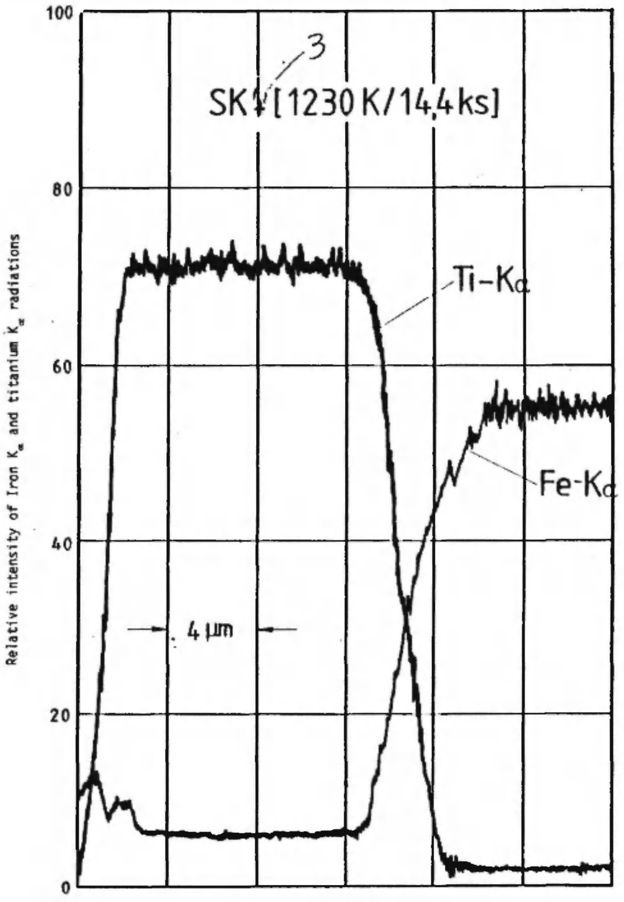

Fig. 9. Intensity profiles of various K radiations of TiC coatings.

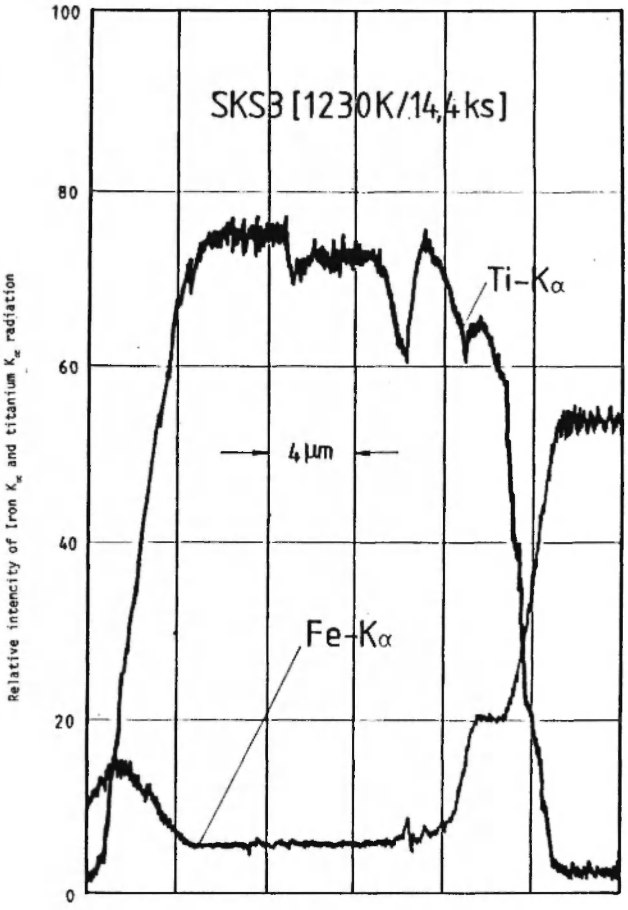

Fig. 10. Intensity profiles of various K radiations of TiC coatings

3.5. *Identification of Various Compounds in the Coating Layers by X-ray Diffraction*

Two examples of diffraction patterns are shown in Fig. 11. In steel SK3 and SKS93, TiC, α-Fe and Fe_3C were identified.

Both samples were treated at 1223°K for 3.6 k.s. and had a thickness of about 10 µm. The diffraction conditions were:

(1) Acceleration voltage: 40 KV
(2) Sample current: 30 mA
(3) Target: Co
(4) Filter: Fe

Some compounds were found in both matrix and boundary, but some of them were not detected in the coating.

ε–Ti–Fe–O, ε–TiN or FeO were detected in the first zone of both SK3 and SKS93 steels which indicated that oxygen was not purged sufficiently during treatment. It is generally accepted that oxygen has a detrimental effect upon the quality of protective coating layers. In other thermo-chemical treatments, oxygen has no significant contribution to the carburization at layer boundaries.

Since the oxygen content was not reduced sufficiently, the first zone of the protective layer could easily be removed mechanically.

Attention should be paid to the fact that both FeO and TiC compounds have a similar cubic crystal structure (NaCl-type) so that it is relatively difficult

TABLE 3
Chemical Composition of TiC Coatings Layer

Element	Ti	Fe	O	N	C
At.%	49.8	1.6	8.0	2.5	38.0
Wt.%	76.7	2.8	4.1	1.1	14.7

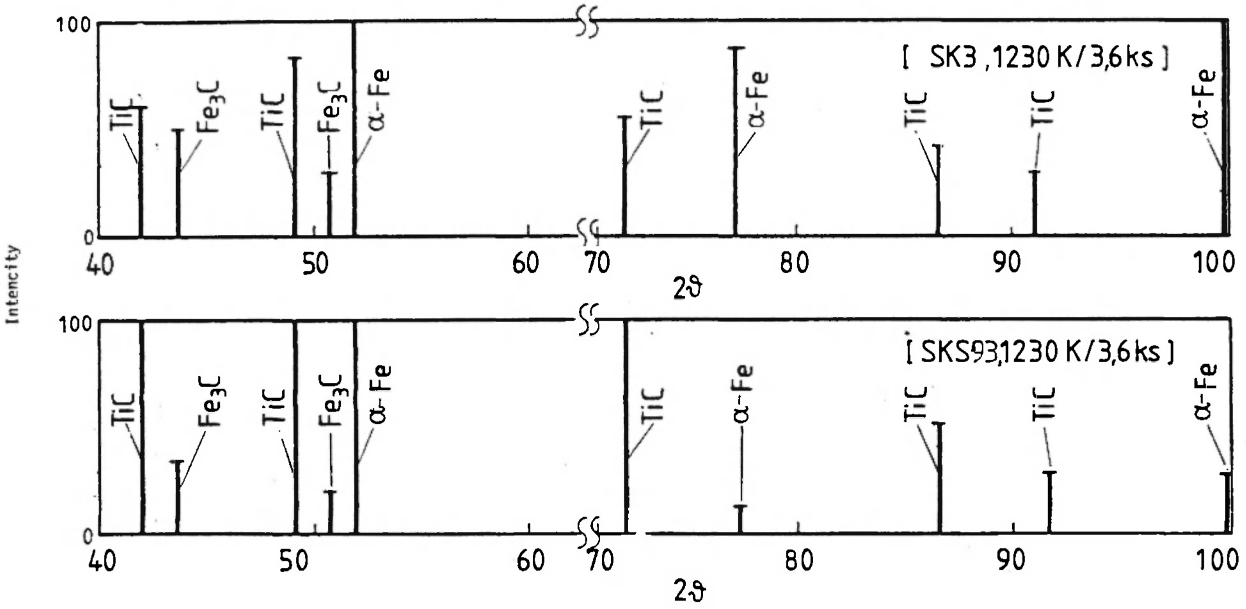

Fig. 11. X-ray diffraction pattern of TiC coated steels (40 KV, 30 mA, Co Target, Fe Filter)

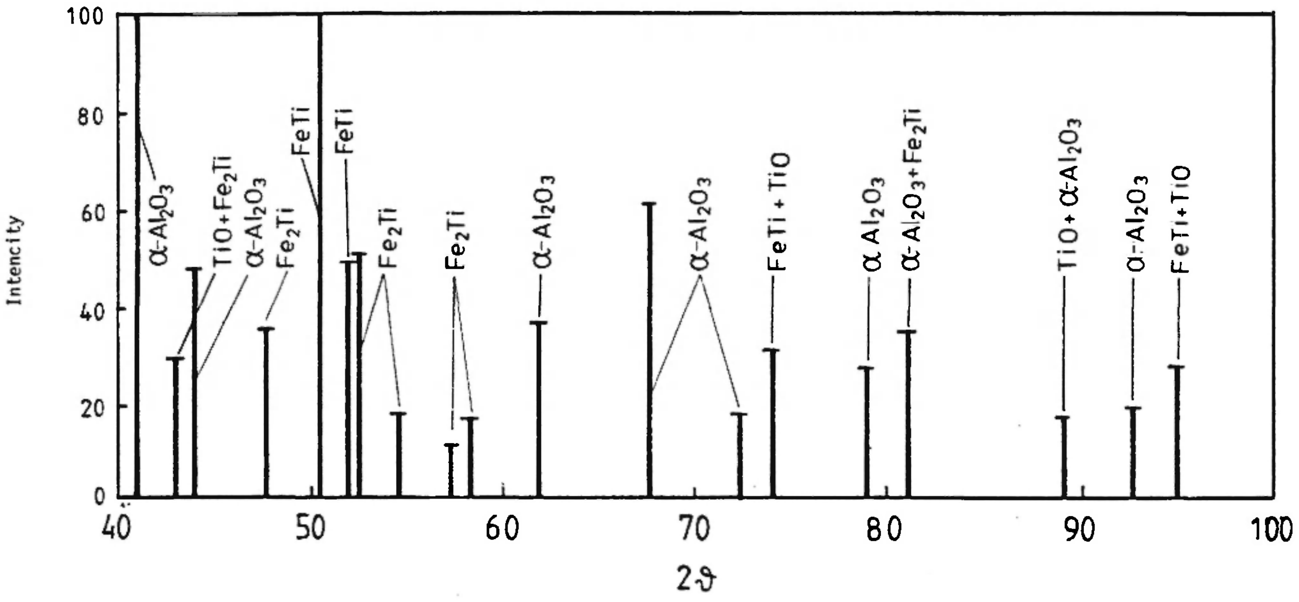

Fig. 12. X-ray diffraction pattern of spender materials after one use (1230°K, 14.4 k.s.); (40 KV, 30 mA, Co Target, Fe Filter).

to separate them by X-ray diffraction. For this purpose, chemical or EPMA analysis is required.

The residual powder used for coating was also analysed by X-ray diffraction. The results shown in Figs. 12 and 13 were for samples treated for 14.4 k.s. at 1230°K. Prior to the experiment, the chemical composition was Fe–Ti (42.6 wt% Ti) 60 wt.%, Al_2O_3 35 wt.%, TiH_2 3 wt.% and NH_4Cl 2 wt.%. After being applied, the following changes were found:

(1) Titanium oxide is formed;

(2) Titanium is used to increase the amount of intermetallic Fe_2Ti compound;

(3) Ammonium chloride is detected.

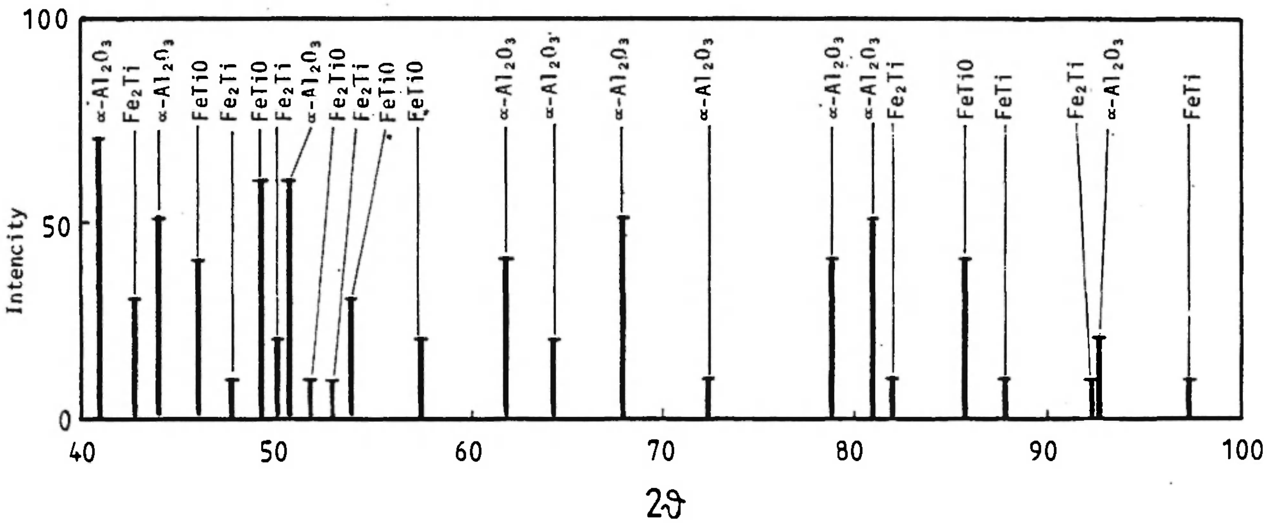

Fig. 13. X-Ray diffraction pattern of spender powder after 5 times used (1230 K/14.4 k.s.). (Voltage: 40 KV, Current: 30 mA, Target: Co, Filter: Fe, Count Full Scale: 400 cps).

CONCLUSION

This research was conducted to examine the feasability of coating high carbon steel with TiC by the powder-pack method.

It is possible to coat high carbon steel with a coating layer consisting mainly of TiC, but the treatment conditions are found to be very difficult to control. There are many factors influencing the formation of protective layers and further investigation is necessary to find optimum conditions. Of major importance appears to be the removal of oxygen from the reaction tube and the prevention of decarburization between the coating and the substrate.

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