Formation of Cr-Ti Composite Layers on Steel by Using the Pack Diffusion Process in Air

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ABSTRACT

The formation of Cr-Ti composite layers on steel and their hardness were studied by changing the powder composition and the processing condition. When using Fe-Cr powder, the formation of Fe_3C and carbides containing Cr and Fe were mainly detected on the steel surface. However, when using Cr powder, chromium carbides and/or nitrides containing Cr and Fe appeared to form on the surface. When using Fe-Ti powder, a Ti rich layer was formed on the matrix side of the layer and its Ti concentration increased with an increase of the Fe-Ti content. The surface of the composite layer shows the values of Knoop microhardness of 800 - 980 (0.245N.load).

1. INTRODUCTION

Various carbide coatings such as TiC, VC, W_2C and NbC were proposed and partly used. However, chromium carbide coating is known to be most widely used for surface hardening of high carbon steel and alloy tool steel. One reason for this is that Fe-Cr powder is cheaper than Fe-Ti, Fe-V, Fe-W and Fe-Nb materials. Although chromium carbide (hereafter referred to as Cr carbide) coating on steel is made by the molten salt process /1,2/ and by the powder pack process with fluoride /3/, the pack diffusion process has been frequently employed under a protective atmosphere such as hydrogen, argon /4-8/ or other gases /9/. This makes the apparatus and its operation more complicated.

The main purpose of this work is to study the effects of the powder composition (Cr powder, Fe-Cr, Fe-Ti) and the processing conditions (temperature and time) on the formation of Cr-Ti composite layers on steel by using the pack diffusion process in air. The structure and hardness of the layer formed are also determined.

2. MATERIAL AND EXPERIMENTAL PROCEDURES

An alloy tool steel (JIS G 4404: SKS93) was used as the specimen. Table 1 lists the contents of six elements in the specimen for convenience of discussion. The specimen was 3 mm thick with a diameter of 22

TABLE 1

Chemical composition of six elements in the specimen presently under investigation.

	C %	Si %	Mn %	P %	S %	Cr %
SKS93	1.02	0.25	0.99	0.015	0.009	0.46

mm. The specimen surface was polished using No. 180 to No. 1000 emery papers and washed using an ultrasonic washer with acetone. The following reagents were used as a source material: Fe-Cr powder (63.8% of Cr and 7.3% of C, particle size: 100 mesh under) or high purity Cr powder (99.7% purity, particle size: 100 mesh under); Fe-Ti powder (41.2% of Ti and 0.04% of C, particle size: 100 mesh under); Al_2O_3 powder (min. 80%, particle size: 200 mesh under); and a small amount of NH_4Cl. A porcelain crucible (15 ml) was used; the specimen was wrapped in a stainless steel (SUS304) net of 100 mesh and put into a covered crucible. Temperature and time were 1073 K - 1223 K and 1.8 k.s. - 57.6 k.s., respectively. The specimen was treated at the desired temperature, cooled in a muffle furnace and then taken out of the crucible at room temperature. The layers formed on the steel surface were examined with an X-ray diffractometer, an electron probe microanalyzer (EPMA) and a microhardness tester.

3. RESULTS AND DISCUSSION

3.1 Effect of Powder Composition on the Composition of the Layer

Fig. 1 shows the X-ray diffraction patterns of the top surface of steels treated at 1223 K for 57.6 k.s. using powders of 70% Fe-Cr plus Fe-Ti (I) or 70% Cr plus Fe-Ti (II) with 4% NH_4Cl and 26% Al_2O_3. As can be easily seen from the results in Fig. 1, various components were observed in the composite layers formed on the steel surface. The following comments are noteworthy: When the source material contains no Fe-Ti powder (see Ia), the layer appears to consist mainly of $(Cr,Fe)_7C_3$ with small amounts of pure Cr, Fe-Cr solid solution and $Cr_{23}C_6$ were also detected in this case. The peak intensity of $(Cr,Fe)_7C_3$ in the layer formed by using 55% Fe-Cr plus 15% Fe-Ti (see Ib) is lower than in Ia. However, the X-ray fluorescence analysis confirmed that there was no remarkable difference in the composition of Ia and Ib. Fe_3C and pure Fe were observed in the layer in Ic, in which powder containing 20% Fe-Ti was used. In this case, the Ti concentration in the layer was estimated to be 1.3% using X-ray fluorescence analysis. However, the X-ray diffraction result shows no carbide or nitride of Ti formed on the steel. The Cr concentration in the layer is consistent with the amount of Fe-Cr powder in the source material: 49% for Ia, 42% for Ib and 26% for Ic.

The Cr powder content in the source material was 70% for IIa and 55% for IIb. In these cases, the components of layers formed were attributed mainly to $(Cr,Fe)_2N_{1-x}$; limited amounts of Cr_2N and $Cr_2(C,N)$ also formed in the layer. This implies that formation of nitrides readily occurs when pure Cr powder is used rather than Fe-Cr powder as a source material, and this is consistent with the fact that the affinity of nitrogen (N) with Cr is stronger than that with Fe /10/.

In the case of IIc with 35% Cr plus 35% Fe-Ti, carbides and nitrides were no longer detected on the steel surface in the X-ray diffraction pattern, and only Fe-Cr solid solution and pure Fe were observed. The Ti concentration on this specimen was estimated to be 2.1%. However, EPMA analysis for the cross section of this layer indicated an increase in the Kα intensities for Fe, Cr, Ti, N and carbon and the formation of Cr-Fe-Ti carbonitrides. It may be worth mentioning that a carbide layer with uniform thickness was obtained when more than 55% Fe-Cr powder or more than 45% pure Cr powder was included in a source material.

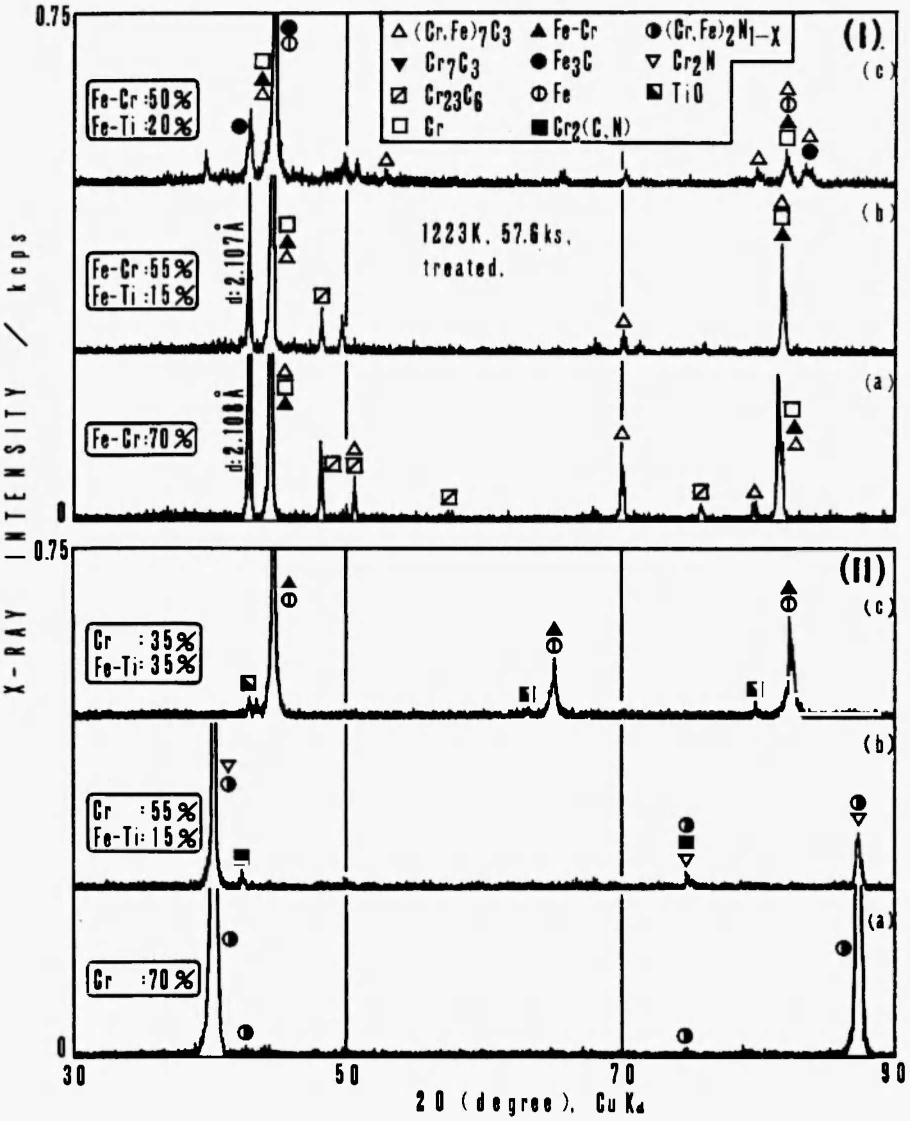

Fig. 1: X-ray diffraction patterns of the top surface of steels treated using Fe-Cr/Fe-Ti (I) and Cr powder/Fe-Ti (II) as a source material.

3.2 Effects of Powder Composition on the Variation of Elements in the Cross Section of a Layer

Fig. 2 shows the X-ray intensity profiles for various elements in the cross section of specimens treated at 1223 K for 57.6 k.s. using powders of Fe-Cr plus Fe-Ti (I, II) and Cr plus Fe-Ti (III, IV) as the source materials. When powder containing 70% Fe-Cr and no Fe-Ti (I) was used, the layer formed involved Cr, Fe and C and the concentration gradient was observed for Cr-Kα and Fe-Kα from the surface inwards. The layer component is mainly $(Cr,Fe)_7C_3$ (see Fig. 1, 1a). When using 55% Fe-Cr plus 15% Fe-Ti (II), the layer also consists of Cr, Fe and C and the Ti concentration in this layer was estimated to be 0.3%. The formation of a Ti rich

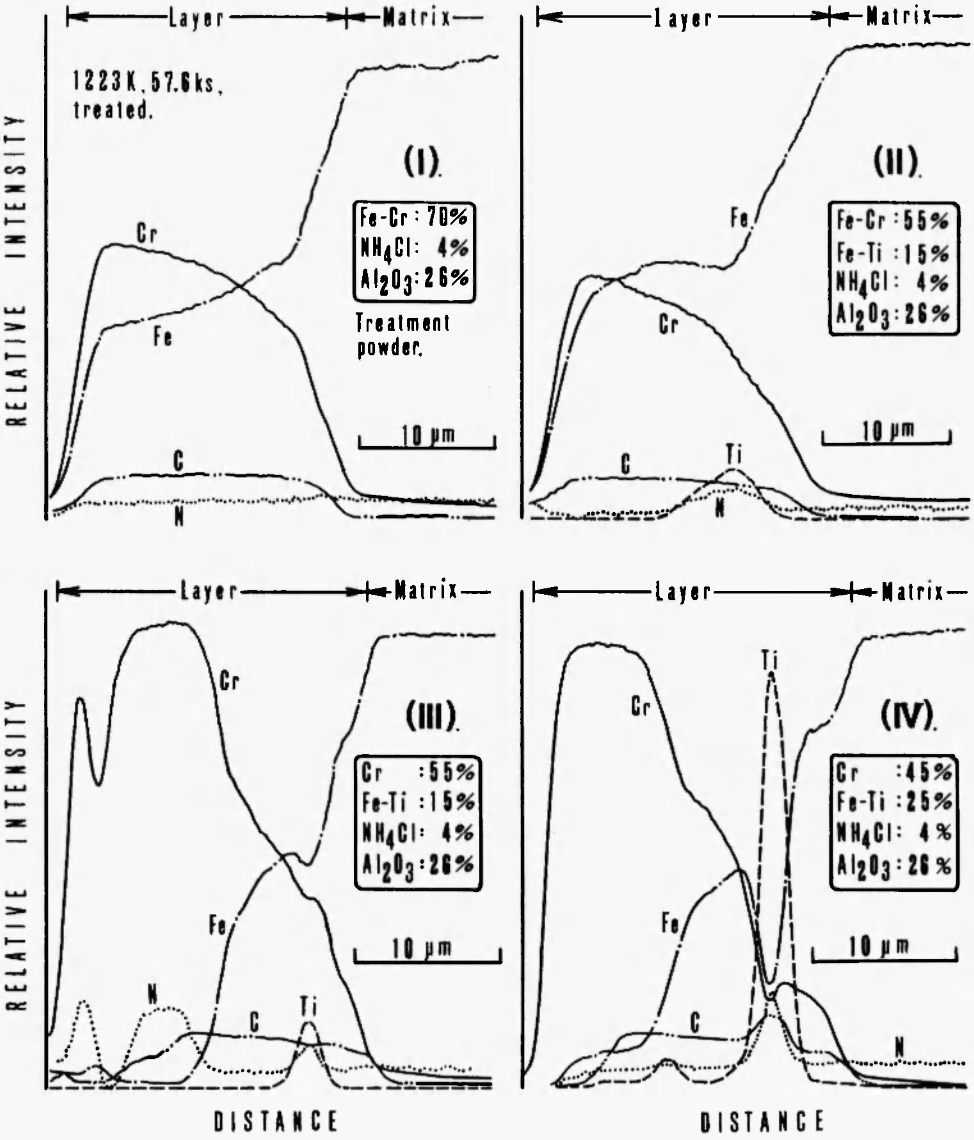

Fig. 2: X-ray intensity profiles of various elements in the cross section of the composite layers formed on the steel surface using Fe-Cr/Fe-Ti (I, II) and Cr powder/Fe-Ti (III, IV).

zone was observed on the matrix side in the layer where a slight increase in the N concentration was detected.

The EPMA results are shown in Fig. 2, III and IV, when the powder contains 55% Cr plus 15% Fe-Ti or 45% Cr plus 25% Fe-Ti, respectively. The Cr concentration in the layer surface (III: 80%, IV: 79%) formed by using pure Cr powder is higher than in the case of Fe-Cr powder (I: 49%, II: 42%). The formation of a Ti rich zone on the matrix side of the layer was clearly confirmed by the Ti-Kα intensity. As for III, the concentration of N in the layer surface is slightly higher than that of the inner part, and the formation of nitrides is quite likely to occur in the layer surface. As for IV, the concentration of C and N in the Ti rich zone is higher than those in the matrix. These results, therefore, suggest that the affinity between C and Ti or N and Ti is stronger than that of a C and Fe combination.

3.3 Effects of Temperature and Time on Layer Composition

Fig. 3 shows the X-ray diffraction patterns obtained from the composite layers formed on steel treated at 1073 K - 1223 K for 57.6 k.s. A source material is powders of 55% Fe-Cr plus 15% Fe-Ti (I) and of 55% Cr plus 15% Fe-Ti (II). As for I, the formation of Fe_3C was mainly detected on the steel surface treated at temperatures of 1073 K and 1123 K. On the other hand, in the 1223 K treatment, pure Cr, Fe-Cr solid solution and Cr-Fe carbides were formed with no Fe_3C. This suggests that Fe_3C is formed on the steel surface at relatively lower temperature (1073 K and 1123 K) when using Fe-Cr powders. The Cr concentration in the source material in I is lower than that in II, and this makes formation of the Cr composite layer more difficult for I, where C in Fe-Cr diffuses onto the steel surface at a lower temperature. As a result, the C concentration on the surface increases in order to form Fe_3C. On the other hand, at a higher temperature (1223 K), the Cr diffusion onto the steel surface readily occurs to form a Fe-Cr solid solution and/or Cr-Fe carbides. As for II, no Fe_3C was detected at 1073 K, but $Cr_2(C,N)$, $(Cr,Fe)_7C_3$ and Cr_7C_3 were identified by X-ray diffraction. The X-ray intensities of Cr_7C_3 and $(Cr,Fe)_7C_3$ formed at 1123 K appear to be lower than those formed at 1073 K, and when the treatment temperature increases further, Cr nitrides and/or Cr-Fe solid solution are formed on the steel surface.

Fig. 4 shows the X-ray diffraction patterns obtained from specimens with Fe-Cr plus Fe-Ti (I) and pure Cr plus Fe-Ti (II) treated at 1173 K for various times between 1.8 and 57.6 k.s. In I, only a little Fe_3C formed on the surface for 1.8 k.s. Formation of $(Cr,Fe)_7C_3$, Fe-Cr solid solution and Fe_3C was found for 7.2 k.s., and formation of $(Cr,Fe)_7C_3$, pure Cr and Fe_3C was detected for 57.6 k.s. The Fe-Cr powder in the source material contains 7.3% C, and then the carbon diffuses into the steel surface. This results in an increase of the C concentration on the surface to form Fe_3C. As for II, formation of Cr_2N and $(Cr,Fe)_7C_3$ was observed for 1.8 k.s., but no Fe_3C was detected. In cases where the treatment time was longer than 1.8 k.s., Cr carbides and Cr nitrides or Cr-Fe nitrides were formed. When using powder containing 15% Fe-Ti, the Ti concentration in the surface of the layer formed was found to be less than 3%, and formation of Ti carbide was not confirmed by X-ray diffraction.

3.4 Effects of Temperature and Time on the Variation Changes of Elements in the Cross Section of the Layer

Fig. 5 presents the X-ray intensity profiles of various elements in the cross section of the layer formed on the steel surface treated at 1173 K for 1.8 k.s., and at 1073 K for 57.6 k.s. In Fig. 5a at 1173 K for 1.8 k.s. with Fe-Cr powder, the layer formed on the steel surface consists mainly of Fe_3C. Formation of a Ti rich or a C rich zone slightly occurred in the layer, but the thickness of such Cr or C rich zones was not uniform. Therefore, the diffusion of Cr, C and Ti into the steel surface is feasible in this case.

When using pure Cr powder, the uniform thickness of the layers was obtained on the steel surface under conditions at 1073 K for 57.6 k.s. (Fig. 5b) and at 1173 K for 1.8 k.s. (Fig. 5c). The concentrations of Cr, C, Ti and N in the layer were found to be higher than those in the source material. It was clearly shown that when pure Cr powder is used, a carbide layer easily forms on the steel surface compared with the case of Fe-Cr powder. In addition, the Cr concentration in the layer formed when using pure Cr powder was much higher than that when using Fe-Cr, and the Ti rich zone was formed on the matrix side of the layer. It was also mentioned that the N concentration on the surface of the layer was high. When using pure Cr powder as a source material, a composite layer containing Cr, C, Ti and N of uniform thickness can be obtained on steel under conditions where temperature is relatively low (Fig. 5b) or time is short (Fig. 5c).

3.5 Structure of the Layer

Fig. 6 shows the X-ray diffraction patterns obtained from specimens with different thickness corresponding to

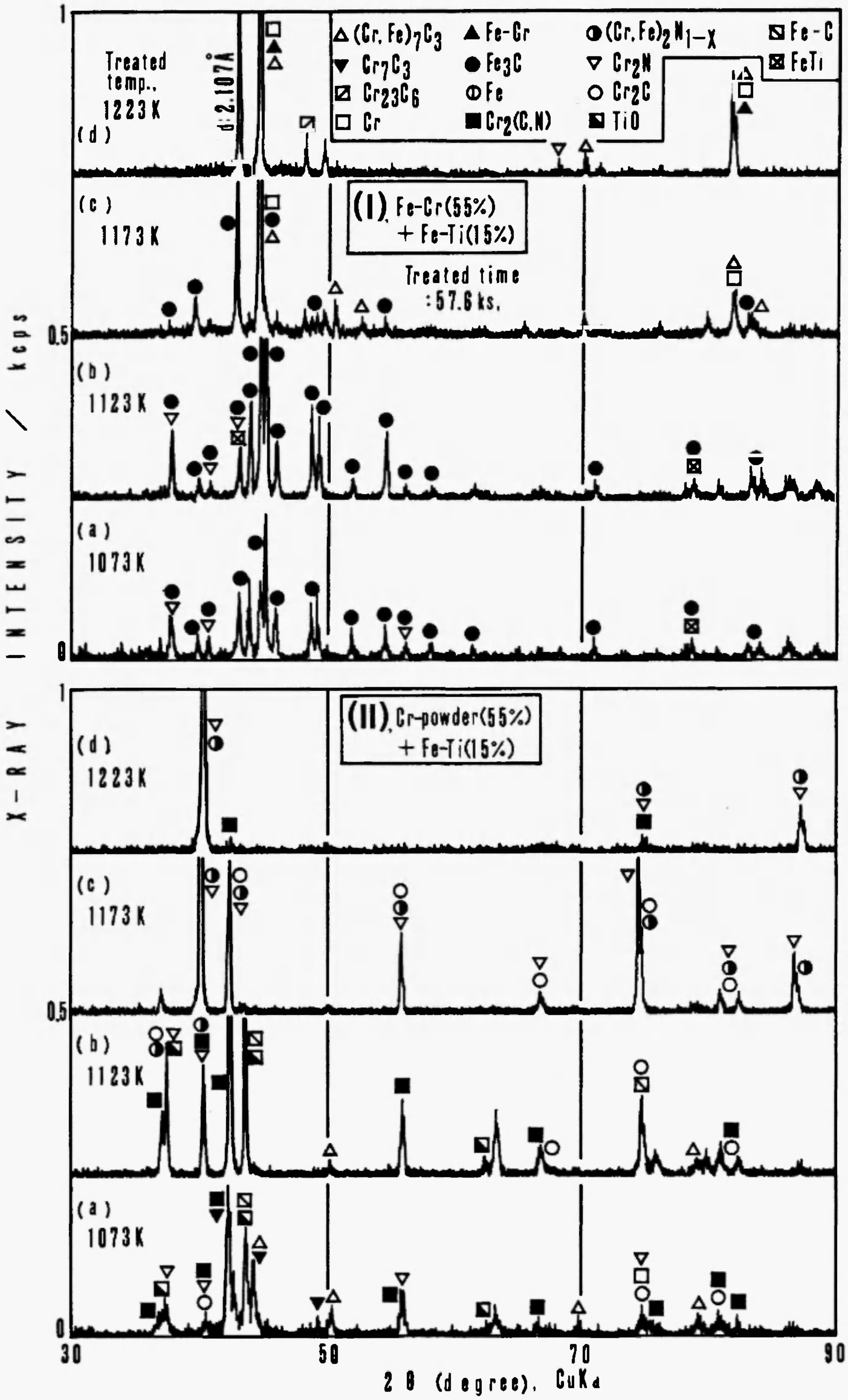

Fig. 3: X-ray diffraction patterns of layers formed on the steel surface at various temperatures for 57.6 k.s. using Fe-Cr/Fe-Ti (I) and Cr powder/Fe-Ti (II).

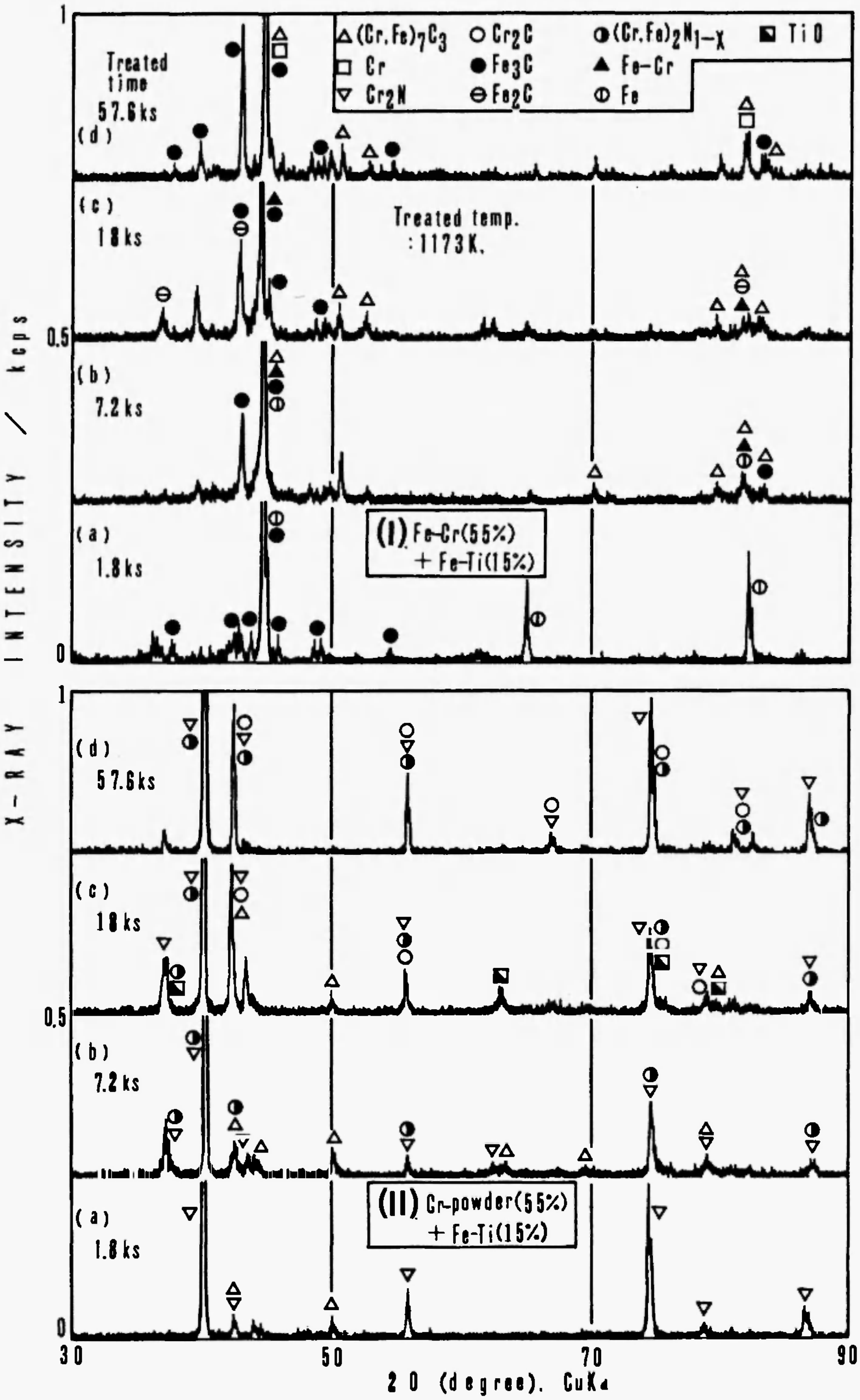

Fig. 4: X-ray diffraction patterns of layers formed on the steel surface at treatment of 1173 K for various times using Fe-Cr/Fe-Ti (I) and Cr powder/Fe-Ti (II).

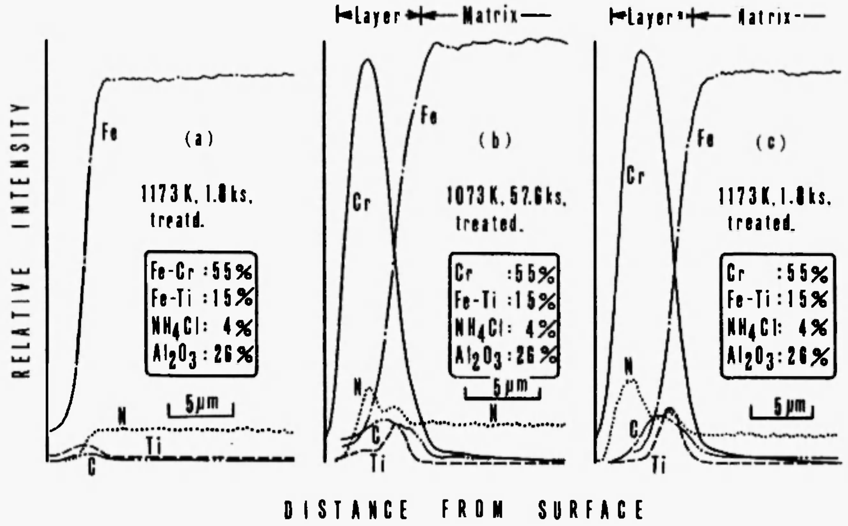

Fig. 5: X-ray intensity profiles of various elements in the cross section of the composite layers formed on the steel surface at 1173 K for 1.8 k.s. (a,c) and 1073 K for 57.6 k.s. (b).

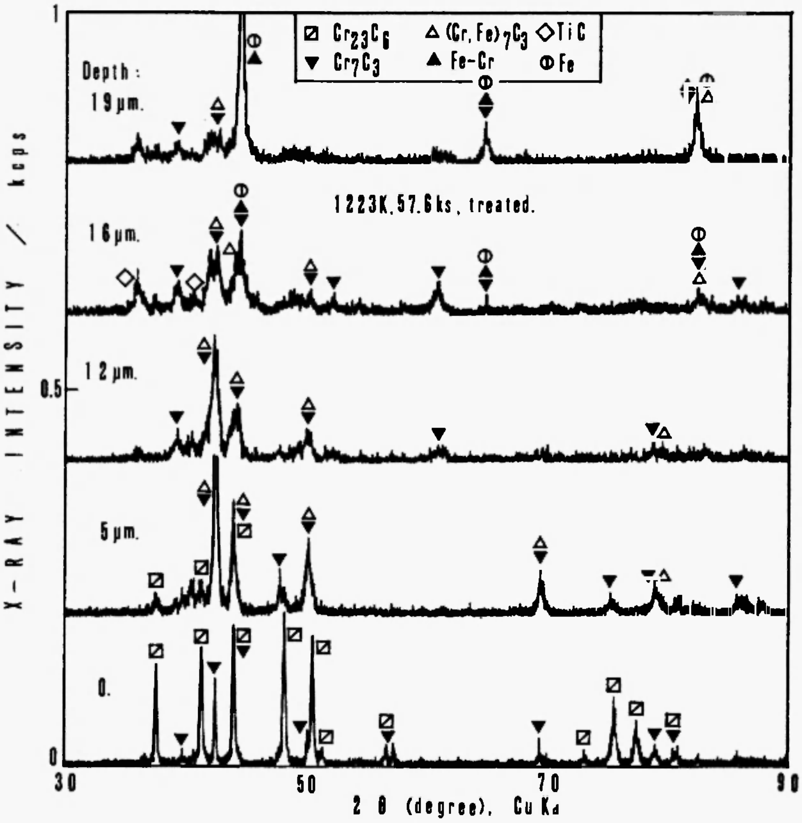

Fig. 6: X-ray diffraction patterns for specimens with different thickness corresponding to the layer shown in Fig. 2 (IV).

the layer shown in Fig. 2 (IV). From the results shown in Figs. 6 and 2 (IV), the composition of the layer formed on the steel surface was found from surface to inside to be as follows. $Cr_{23}C_6$ → Cr_7C_3 and $(Cr,Fe)_7C_3$ → carbide containing Ti, Cr and Fe → carbide containing Cr and Fe. The $Cr_{23}C_6$ layer was very thin - only a few microns thick. The Cr concentration of $(Cr,Fe)_7C_3$ on the surface of the layer was higher than that in the inner section. Carbides with higher Cr concentration were, therefore, formed on the surface rather than in the inner section of the layer. A Cr solid solution with a Cr concentration gradient was formed below the carbide layer. It also became clear from the X-ray diffraction results that no Ti(C,N) existed in the Ti rich zone.

3.6 Thickness of the Layer

Fig. 7 presents the thickness of the white layer formed on the steel surface as a function of temperature (a) or time (b). A cross section of specimens was polished in order to obtain a mirror surface and etched with a 5% Nital solution. The thickness of the layer was determined by optical microscopy. The EPMA results confirmed that the composition of the white layer formed on the steel surface was pure Cr or Cr-Fe compounds. The results at temperatures between 1073 K and 1223 K for 57.6 k.s. are shown in Fig. 7a. The thickness of the white layer strongly depends on temperature. Under the same conditions, the thickness of the white layer when using 55% pure Cr powder (II) was greater than that when using 55% Fe-Cr powder (I). When pure

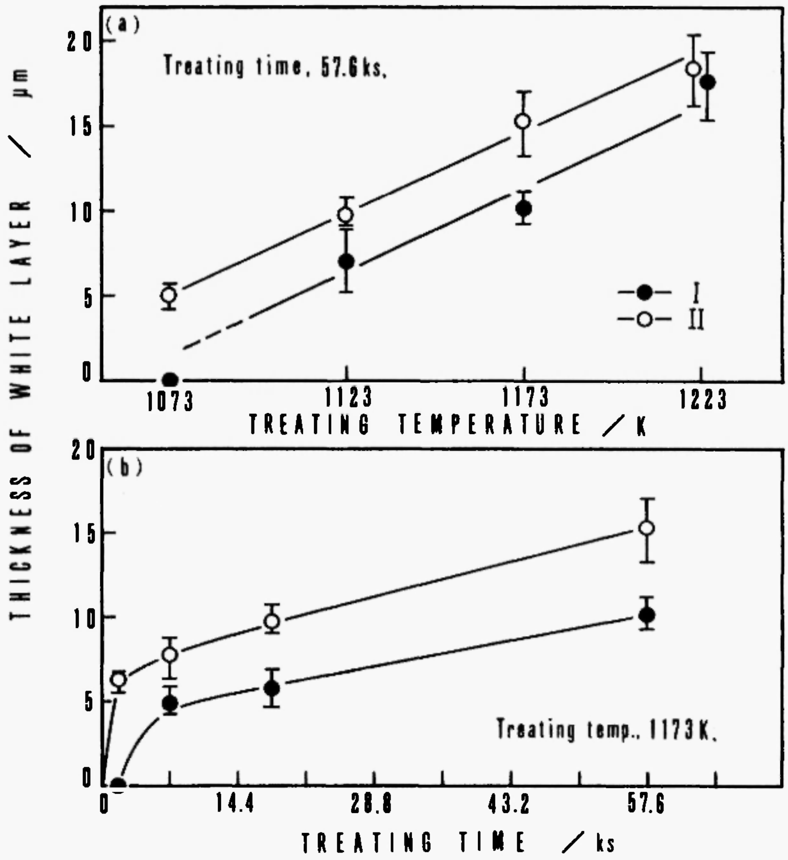

Fig. 7: Relation between the thickness of the white layer formed on the steel surface and temperature (a) or time (b). The mixture of 55% Fe-Cr (I) or 55% Cr powder (II) with 15% Fe-Ti, 4% NH_4Cl and 26% Al_2O_3 was used as a source material.

Cr powder was used, the thickness of the white layer formed at 1073 K for 57.6 k.s. was estimated to be 5 μm, and that formed at 1223 K for 57.6 k.s. was 19 μm. The results at 1173 K for the period between 1.8 k.s. and 57.6 k.s. are given in Fig. 7b. When Fe-Cr powder was used (I), the thickness of the white layer was not so great compared to II, where pure Cr powder was used. It may be worth noting that no white layer was obtained at 1173 K for 1.8 k.s. However, when pure Cr powder was used under the identical condition, formation of the white layer of 6 μm thickness was confirmed on the steel surface. This result clearly suggests that pure Cr powder is superior to Fe-Cr powder as a source material for producing a favorable composite layer on the steel surface.

3.7 Hardness of the Layer

Fig. 8 shows the profiles of Knoop hardness in the cross section of steels treated at 1223 K for 57.6 k.s. The specimen tilted by 0.1 radian was polished. The surface of the composite layer indicates the values of Knoop microhardness of 800 - 980 with a load of 0.245N. These hardness values are lower than that (Hv: 1200) /11/ of Cr carbide. As shown in Fig. 8, the hardness gradient appears from the surface to the inner section, and the hardness value markedly decreases at the distance beyond 10 μm from the surface. The values of hardness for the composite layers formed using pure Cr powder were found to be slightly higher than those of Fe-Cr powder. It was also shown that the hardness values of the composite layer appeared insignificant to the formation of Ti rich zone.

4. CONCLUSIONS

A feasibility study was made in order to coat the surface of the alloy tool steel (SKS93) with a hard layer (carbides, nitrides and carbonitrides) by means of a pack

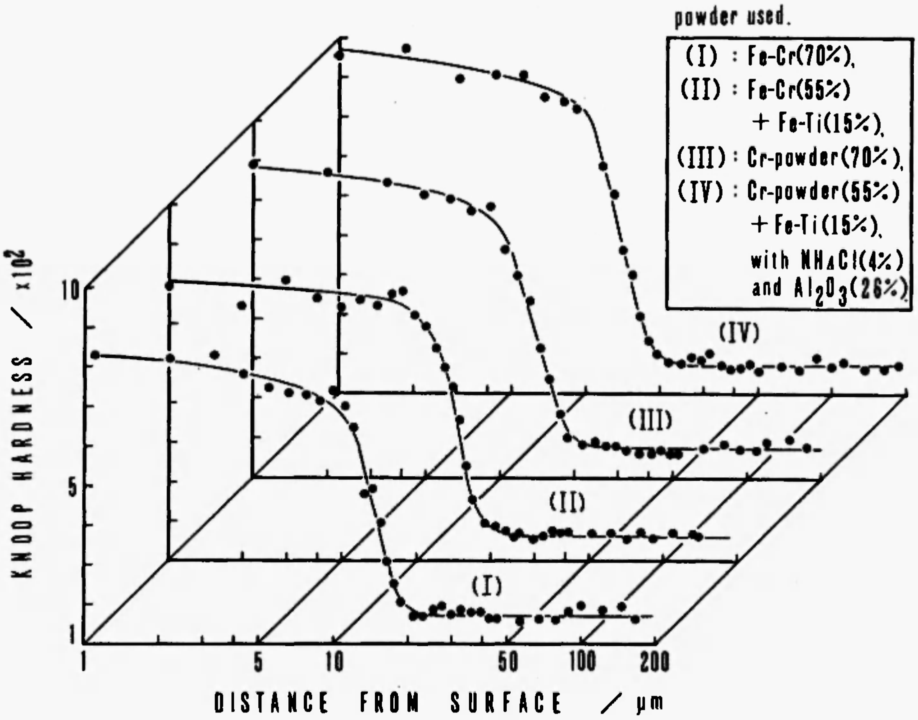

Fig. 8: Profiles of Knoop hardness in the cross section of steels treated at 1223 K for 57.6 k.s. using various powders.

diffusion process in air. The following conclusions were drawn:

(1) When a source material contained Fe-Ti powder, a Ti rich zone was formed in the layer on the steel surface, but no formation of Ti compounds was detected.

(2) When using Fe-Cr powder (63.8% Cr and 7.3% C), the surface components of the layer formed were found to be Fe_3C and Cr-Fe carbides. When using pure Cr powder, the formation of carbides and/or nitrides containing Cr or Cr and Fe was confirmed on the steel surface.

(3) When using Fe-Cr or pure Cr powder coupled with Fe-Ti powder as a source material, the formation of compounds consisting of Cr, Ti, C, N and Fe was obtained on the steel surface in cases where the temperature was relatively low and/or time was short (1073 K, 57.6 k.s.), (1173 K, 1.8 k.s.).

(4) In the case of pure Cr powder, the thickness of layers was great and its Cr concentration was higher than in the case where Fe-Cr powder was used under the identical condition.

(5) The composite layer formed on the steel surface showed the gradient in the Cr concentration from the surface to the inner section.

(6) The surface of the composite layer indicated the values of Knoop microhardness of 800 - 980 with a load of 0.245N.

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