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REACTION STEPS OF A FORMATION OF THE BLACK LAYER BETWEEN IRON NITRIDE AND TiN COATING

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Abstract

The interfacial structure of duplex treated AISI 4140 consisting of iron nitride and TiN layer was characterized by optical microscope, SEM and XRD. A black layer was formed from the decomposition of iron nitride during Ti ion bombardment. The black layer was characterized as an α-Fe phase transformed from the iron nitride by XRD.

In order to identify the formation mechanism of the black layer, a thermal analysis of iron nitride undertaken by DSC method. As an iron nitride was mostly consisted of γ'-Fe_4N and ε-Fe_3N phase after plasma nitriding, in this study, a γ'-Fe_4N and ε-Fe_3N powders were separately prepared by the different processing conditions of gas nitriding of iron powder in the fluidized bed. From the DSC thermal analysis, the phase transformation of γ'-Fe_4N, ε-Fe_3N was followed the path of transformation ; γ'-$Fe_4N \rightarrow \gamma$-$Fe \rightarrow \alpha$-Fe and of ε-$Fe_3N \rightarrow \varepsilon$-$Fe_{2.5}N + \gamma'$-$Fe_4N \rightarrow \gamma'$-$Fe_4N \rightarrow \gamma$-$Fe \rightarrow \alpha$-Fe, respectively. It explains the reason why the ε-Fe_3N phase disappeared in the first time and then γ'-Fe_4N in the formation of the black layer in the duplex coating.

Key words : *black layer, duplex coating, hard coating, TiN, nitride*

I. Introduction

A hard phase ceramic films were improved the tool life and performance. But, the tools and dies that require a high load sustaining capacity and an impact resistance can not be fulfilled by coating of a hard phase films alone. Whereas, the duplex treatment comprising an iron nitride beneath and TiN hard films has been proved an alternative technology for a disadvantage of the thin films[1-3].

The chief duplex treatment can be done with discontinuous process in which a long ion nitriding can be achieved with a low cost processing because it can be done by not only a relatively large chamber, but also its simple design, while an expansive hard phase film such as TiN which require a high vacuum, complex cathode design and numerous targets can be coated within a shorter processing time compared with that of ion nitriding. In the discontinuous duplex treatment, however, the substrate should be exposed to the atmospheric environment when the substrate was moved to the ion plating chamber after ion nitriding. In this exposure, the substrate may be contaminated with harmful substance such as an oxide or inorganic matter that reduce the adhesion property of top TiN coating. So, the contaminants should be removed before coating TiN films by bombarding the surface of an iron nitride with energetic ions. But the iron nitride was so unstable that the iron nitride may decompose to ferritic α-Fe during bombarding with energetic ions at high temperature. The most distinctive layer was an interlayer which shows black color between TiN and an iron nitride which was caused by the ion bombardment[13]. It was suggested that the formation of the layer was related to the decomposition of an iron nitride at high temperature. But, the mechanism of the decomposition of the iron nitride was not clearly studied until now. In this study, we proposed the decomposition mechanism of iron nitride in view of the formation mechanism of the black layer by DSC thermal experimental method.

2. Experimental

The interfacial structure of duplex treated AISI 4140 consisting of iron nitride and TiN layer was characterized by optical microscope, SEM and XRD.

The formation mechanism of the black layer might be closely related to the decomposition of the iron nitride. The iron nitride layer resulted from the plasma nitriding method was mostly composed of thin layer shaped iron nitride above the diffusion layer. The thin layer was not suitable for the experiment of the DSC thermal analysis for the decomposition mechanism of the iron nitride because the amount of iron nitride was too little for the experiment and the nitride layer showed a mixture of γ' or ε phase. So, in this experiment, the iron powder with the purity of 99.9% was made by gas nitriding method. The γ'-Fe_4N and ε -Fe_3N powders were separately prepared by the different processing conditions of gas nitriding of iron powder. A thermal analysis of iron nitride made by the gas nitriding was undertaken by DSC method in order to clarify the formation mechanism of the black layer.

3. Results and discussion

Fig. 1 shows a nitrided cross-sectional mor-

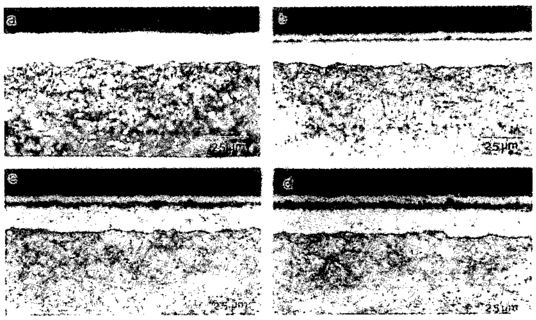


Fig. 1 The influence of Ti ion bombardment time on the ceoss-sectional optical micrographs of AISI 4140 steel prenitrided with conventional DC method and coated TiN films with different bombardment time of (a) 0 min, (b) 10 min, (c) 20 min, (d) 30 min.

phology and x-ray diffraction patterns of plasma nitrided SCM4 low alloy steel. The compound iron nitride layer was around 20 ㎛ in thickness that consisted of γ'-Fe_4N and ε-Fe_3N phases. Sun et al. suggested the decomposition of iron nitride was closely related to the destabilization of iron nitride at high temperature above 450℃[1]. As it can be seen in Fig. 1, because the iron nitride was mixed with γ'-Fe_4N and ε-Fe_3N, we cannot analyze how each iron nitride phase will decompose from the original iron nitride phases to the black layer. In the first time, the separated iron nitrides of γ'-Fe_4N and ε-Fe_3N were prepared by gas nitriding method of pure iron powder. The DSC thermal analysis method was used to study the mechanism of a decomposition of the separately synthesized iron nitride powder. Fig. 2 shows the x-ray diffraction pattern of the Ti ion bombarded surface. With the increase of the Ti ion bombardment time, the intensity of the α-Fe peak was increased. It represented the main

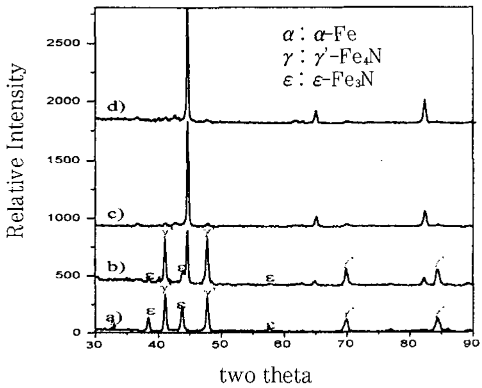


Fig. 2 The phase changes of the substrate bombarded for diffent time of (a) as-ion nitrided, (b) 10 min, (c) 20 min, (d) 30 min. As the time was increased, the intensity of α-Fe peaks was increased, while those of γ'-Fe_4N and ε-Fe_3N peaks were decreased.

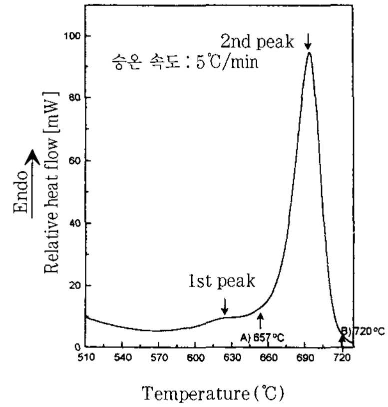


Fig. 3 DSC peak of γ'-Fe_4N powder. The peak shows two endothermic reactions. First reaction was occurred at 615℃ and the second reaction at the 698℃

constituent of the black layer is α-Fe.

Fig. 3 shows the DSC peak of the decomposition reaction of the iron nitride of a γ'-Fe_4N. The DSC result has two endothermic reaction peaks for the decomposition from the γ'-Fe_4N to α-Fe. The amount of heat related to the 2nd peak was much greater than that related to the first peak. In order to identify each peak of the DSC reaction of the decomposition of the iron nitride, x-ray diffraction experiment was conducted for the specimen that was quenched from the temperature of the finished reaction of the peak. Fig. 4 shows the X-ray diffraction results of the specimen that was quenched from the temperature as indicated to the temperature in the Fig. 3. Fig. 4(a) shows the x-ray diffraction peak of the as-gas nitrided powder. It consisted of mostly γ'-Fe_4N phase and a small amount of ε-Fe_3N included. The small amount of the ε-Fe_3N phase was disappeared through the first peak of the iron nitride decomposition reaction as shown in Fig. 4(b). Finally, the γ'-

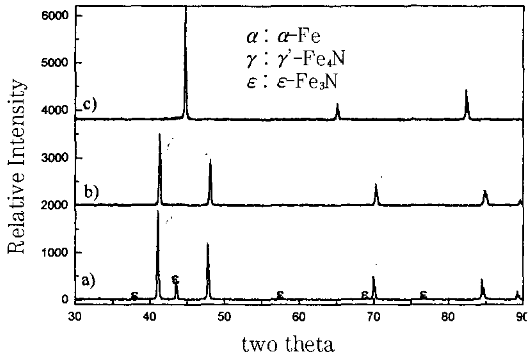


Fig. 4 X-ray diffraction pattens of γ'-Fe_4N iron nitride after DSC.
(a) As-gas nitrided powder,
(b) After first reaction (quenched A in Fig. 3)
(c) After full reaction (quenched from B in Fig. 3)

Fe_4N phase was decomposed to the α-Fe phase that is the main composition of the black layer of the duplex coating process by the reaction of the 2nd peak.

In a similar way with the decomposition of a γ'-Fe_4N phase, an ε-Fe_3N iron nitride powder was synthesized for the DSC experiment. The purity of the ε-Fe_3N showed very high compared with that of the γ'-Fe_4N phase. Fig. 5 shows the DSC peak of the decomposition reaction of the ε-Fe_3N iron nitride. The DSC result showed three peaks of endothermic reactions for the decomposition of the ε-Fe_3N to α-Fe, a final composition of the black layer. The heat related to the 3rd peak was much greater than that of the other two reactions. Similar to the method of analysis of γ'-Fe_4N phase, to identify each peak of the DSC peak of the decomposition of the ε-Fe_3N iron nitride, x-ray diffraction analysis was conducted for the specimen that was quenched from the temperature of the end point of the reaction of the each peak.

Fig. 6 shows the x-ray diffraction results of the specimen that was quenched from the temperature as indicated into the peaks during the DSC experiments as shown in the Fig. 5. The single phase of ε-Fe_3N was decomposed to the ε-$Fe_{2.5}N$ and γ'-Fe_4N through the reaction of 1st peak. A formation of ε-$Fe_{2.5}N$ phase from the ε

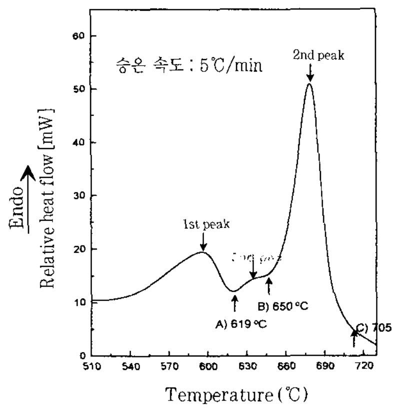
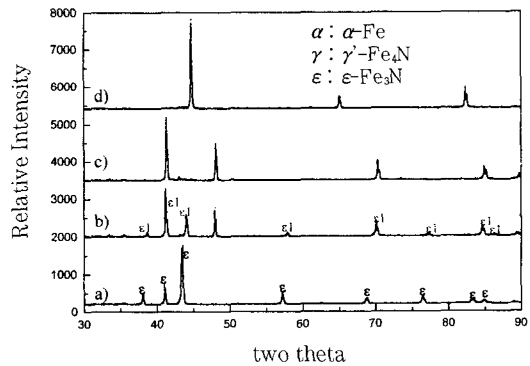


Fig. 5 DSC peak of ε-Fe_3N powder. The peak shows three endothermic reactions. First reaction was occurred at 594℃ the second reaction at the 638℃ and the third reaction at 681℃



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(b) After first reaction (quenched A in Fig. 3)
(c) After full reaction (quenched from B in Fig. 3)

-Fe_3N was thought to be not possible to be taken place because ε-$Fe_{2.5}N$ was a phase having higher content of nitrogen compared with the phase of the ε-Fe_3N. The nitrogen content had to be increased from the outside if the phase of ε-Fe_3N had changed to the ε-$Fe_{2.5}N$. But, because the DSC thermal experiment was conducted in the environment of an Ar gas, an additive reaction of nitrogen might be not possible. The increase of the nitrogen could be explained by the phenomena that the reaction of the ε-Fe_3N to the ε-$Fe_{2.5}N$ was always happened with that of ε-Fe_3N to the γ'-Fe_4N phase. The nitrogen that came from the decomposition of the ε-Fe_3N to the γ'-Fe_4N would recombine with the ε-Fe_3N to become a ε-$Fe_{2.5}N$.

The 2nd peak showed the phase change of ε-$Fe_{2.5}N$ to γ'-Fe_4N from the analysis of the x-ray diffraction. The ε-$Fe_{2.5}N$ that had transformed from the ε-Fe_3N through the first peak, transformed to the γ'-Fe_4N by the 2nd reaction. After all, ε-Fe_3N phase completely transformed to the γ'-Fe_4N, finally, which would be decomposed to transform to the α-Fe. The phase transformation procedure explains reason why the ε-Fe_3N phase disappeared in the first time and then γ'-Fe_4N in the formation of the black layer in the duplex coating consisted of the plasma nitriding and PVD coating process.

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