Effects of the Carbon Content on the Properties of WC-TiC-Co Alloys*

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The effects of the binder composition in the cemented carbides have been investigated, and it is known that the binder composition or the carbon content of the alloys has a remarkable effect on the properties of the two-phase WC-Co alloys. However, no research has so far been carried out on WC-TiC-Co alloys.

In the present experiment, ordinary WC-TiC-10%Co alloys which contain 6~25% titanium carbide in carbides and consist of (WC + β + γ) three phases were vacuum-sintered. The carbon contents of the specimens were strictly controlled. The relation between the properties of the sintered alloys and the carbon content or the titanium carbide content was examined. The results obtained were as follows: (1) The lattice parameters of the β and γ phases showed a regular change in the three-phase region due to the change in composition in both phases. (2) The tungsten content in the binder phase of the three phase alloys varied from 2~3% in minimum to 9~10% in maximum depending on the carbon content. The amount of tungsten dissolved in the binder phase corresponded to the values in the WC-Co alloys. (3) The addition of titanium carbide resulted in an extreme extension of the three phase range owing to the change in carbon content in the β phase. (4) The properties, such as transverse-rupture strength, magnetic saturation, etc., varied regularly within the three-phase region.

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I. Introduction

The relations between the properties and the carbon content or the binder composition for the WC-Co alloys have been studied in detail by Suzuki et al. (1)~(4), with the finding that the properties of the two-phase alloys, consisting of the same grain size of tungsten carbide, are decisively affected by the carbon content, because the composition of the binder phase is sharply affected by a small change in carbon content.

However, the effects of carbon content have not so far been investigated for alloys of the WC-TiC-Co system. Therefore, the present study was undertaken to make clear the relations between the properties of these alloys and their carbon contents.

II. Specimens and Experimental Procedures

Commercially available Co, WC and WC-TiC (70/30) mixed carbide powder were used. The titanium carbide content in the carbides was set in the range of 6~17% or 25% if necessary. The cobalt content was always kept constant at 10%. After the mixed powder was wet-ball milled and compacted, the WC-TiC-10%Co alloys, i.e., the (WC + β + γ) three-phase alloys (β = WC-TiC mixed carbide phase and γ = Co phase), were vacuum-sintered at 1400°C for 1 hr. The carbon content of each alloy was carefully controlled by means of varying the carbon content of the starting carbide materials. The
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III. Experimental Results and Discussions

The lattice parameters of γ and β phases in the specimens containing 6, 11 and 17% titanium carbide were first measured, using FeKα and CoKα X-ray, respectively. As shown in Fig. 1, the parameter of the γ phase of the alloys showed constant values of ~3.574 Å and ~3.552 Å in the four-phase regions which contain the γ phase and the free carbon phase, respectively; and it decreased with increase in carbon content in the three-phase region. The constant values and the change of the parameter were just the same as those in the straight WC-Co alloys. The lattice parameter of the β phase also reached constant values of ~4.314 Å and ~4.321 Å in each region. In this case, however, it increased with increase in carbon content in the three-phase region. From these results, it was obvious that within the three-phase region the parameter of the γ phase varied regularly in connection with that of the β phase. The three-phase regions in Fig. 1 were determined by finding the range of changes in the lattice parameters of γ and β phases. The result was naturally found to correspond to that by the microscopic determination.

The reason why the lattice parameter of the γ phase varied with the carbon content will be described. As seen from the results(5) by the authors on the WC-TiC-10% Co alloys containing a small amount of titanium carbide, the β phase was clearly observed even in the alloys containing a very small amount of titanium carbide (0.15%). Therefore, the titanium dissolved in the binder phase does not appear to cause abrupt changes in the parameter of the γ phase. X-ray micro-analysis was made on the surface of the coarse binder phase, especially formed in the alloys containing titanium carbide. The results obtained were as follows. The amount of titanium dissolved was hardly measurable regardless of the carbon content of the alloys, while the amount of tungsten was much larger especially in the low carbon alloys. Therefore, it is considered that the changes in the parameter of the γ phase in Fig. 1 result from the dissolved tungsten. The dissolution amount of tungsten is independent of the titanium carbide content in the alloys, and it is estimated to be in the range between 2~3% and 9~10% in the three-phase region, as observed in the WC-Co alloys. These results indicate that the binder composition of the (WC+β+Co) three-phase alloys depends on the tungsten carbide phase, due to the thermodynamical stability of the WC phase and the β phase. These relationships are also seen in WC-TaC-Co alloys(6)(7).

On the other hand, changes in the lattice parameter of the β phase may be well explained by the Ti–W–C equilibrium diagram of Nowotony et al.(8), in Fig. 2. However, the temperature of 1900°C at which the diagram was established is too high to discuss the changes. Supposing a diagram at a lower temperature of about 1400°C (i.e., sintering temperature), an inter-phase relationship similar to that at 1900°C can also be found, but the boundary between the β and (WC+β) phase regions will shift to the TiC side, which will bring some changes in the iso-parameter lines. Thus, the carbide composition of the specimens should be within the bounds of the (WC+β) region. It seems reasonable that the above changes in the parameter of the β phase are due to the changes in the carbon content of the β phase itself. Because, titanium, as mentioned above, was hardly dissolved in the binder phase and also it was confirmed by other experiments that cobalt was hardly dissolved in the β phase. So, the changes in the lattice parameter of the β phase in cemented carbides can be explained from the Ti–W–C diagram, just in the case of alloys having no binder phase.

It is clearly shown in Fig. 1 that the range of the (WC+β+γ) phase region increases with increase in titanium carbide content. The relation between the phase range and the titanium carbide content is represented in

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Fig. 3 by using the specimens having various contents of titanium carbide up to 25% in carbides. The fact that the three-phase region widely extends owing to the increase of titanium carbide, will be explained by the wide change in the carbon content of the \( \beta \) phase.

Because, the variation of the carbon content in the three-phase alloys is considered to be the sum of the variations in the \( \beta \) and binder phases; the value in the latter phase is known to be as small as about 0.18% C, according to the results\(^{(1)(2)}\) obtained previously for the WC-10% Co alloys.

The extension of phase range due to the addition of the titanium carbide appears to be favorable to the preparation of the alloys, but at the same time it is apt to lead the ignorance of the close controlling of the carbon content. In addition, it must be pointed out that the stoichiometric carbon content of the alloys would shift to an excess carbon range when the titanium carbide content exceeds a definite value, i.e., about 4% in carbides.

The relation between specific gravity and carbon content is shown in Fig. 4. The specific gravity decreased with increase in carbon content; however, the change is not so simple as compared with the straight alloys. The reason can be explained by the fact that the specific gravity of the \( \beta \) phase increases, but that of \( \gamma \) phase decreases with increase in carbon content. However, the specific gravity decreases relatively with increase in titanium carbide content.

The relation between magnetic saturation and carbon content is shown in Fig. 5. From the above-mentioned results, it is clear that the change in magnetic saturation...
depends on the amount of the tungsten dissolved in the binder phase. Each alloy shows a same maximum saturation value in the excess carbon range; this corresponds to the fact that all the lattice parameters of the $\gamma$ phase show a certain minimum value in that range. Hence, the carbon content at which the saturation value reaches a maximum indicates the phase boundary between three- and four-phase regions. The maximum saturation value is in good agreement with that of the straight alloys.

The hardness and the coercive force are illustrated in Fig. 6. The decrease in the coercive force with increase in titanium carbide content may be attributable to the increase in the amount of the coarse $\beta$ phase as shown in Photo. 1. The reason why the value of the coercive force is higher than that of the straight alloys may be explained as follows. The grain refinement of tungsten carbide takes place in the high titanium carbide specimens in a similar way to the alloys containing a small amount of titanium carbide (5). At the same time, the volume fraction of the binder phase decreases with increase in titanium carbide content, because the specific gravity of titanium carbide is lower than that of tungsten carbide. It may be due to coarsening of the $\beta$ phase that the hardness of the alloys does not always increase with the amount of titanium carbide.

The relation between transverse-rupture strength and carbon content is shown in Fig. 7. The fact that the strength of the alloys decreases with increase in titanium carbide content corresponds to the results obtained by many workers(9) (10). A number of factors can be considered as for the reason of the decrease in strength. However, the factors such as the increase of the mean grain size of the carbides and the decrease of the volume fraction of the binder phase are probably not essential. The grain refinement of tungsten carbide and the skeleton formation of the $\beta$ phase (due to the poor wettability between the two phases) are considered as more important factors. The curves representing the relation between strength and carbon content become more gentle with increase in titanium carbide content. It may be associated with the extension of the three-phase region. A maximum strength in each alloy lies almost at the point of the highest carbon content in each three phase region indicated in the figure. Based on the previous results(7) (4) on the relation between strength and grain size, the above result may be regarded as a natural consequence, because the mean grain size of the carbides is about 2 $\mu$ even in the specimen containing 17% titanium carbide. However, strictly speaking, the maximum strength in the alloys relating to the carbon content must be further discussed, from the viewpoint of the strength of $\beta$ phase and of the characteristics or the amount of the $\beta$ skeleton.

The structures of the alloys were examined microscopically. The occurrence of the $\gamma$ type compound in the low carbon alloys and the free carbon phase in the high carbon alloys is similar to that in the straight alloys. However, the higher the content of titanium carbide, the finer the tungsten carbide. This may be explained by the fact that the tungsten carbide powder in mixture is more easily crushed in the ball-mill with increase in titanium carbide content and the grain growth of tungsten carbide is hindered in the alloys containing titanium carbide during the sintering process. The skeleton formation of the $\beta$ phase is promoted with increase in titanium carbide content.

**IV. Conclusion**

The properties of the sintered WC-TiC-10%Co (WC-$\beta-\gamma$) alloys containing 6-25% of titanium carbide have been studied in relation to their carbon contents. The results obtained were summarized as follows:

1. The lattice parameters of $\gamma$ and $\beta$ phases in the alloys change regularly with their carbon content in the three-phase region, and they show constant values when the carbon contents of the alloys are beyond the above range. Changes in the lattice parameter of the $\gamma$ phase are mainly based on changes in the solid solubility of tungsten in the binder phase and have no relation to the solubility of titanium. The amount of tungsten dissolved...
in the binder phase is in the range between 2~3% and 9~10%. The parameter changes in the $\beta$ phase are caused mainly by changes of the carbon content in the phase range.

(2) The three-phase range is extended by the addition of titanium carbide. This can be explained by the composition change of the $\beta$ phase due to the carbon content in the alloys. The degree of extension must be studied further as a function of the amount of the binder phase.

(3) The stoichiometric carbon contents of the alloys are within the bounds of the excess carbon range, when the titanium carbide content increases more than about 4% in carbides.

(4) Strength of the three-phase alloys attains a maximum on the high carbon side in the phase range. Magnetic saturation of the alloys increases with increase in carbon content and attains a constant maximum value in the excess carbon range. The specific gravity, hardness and coercive force of the alloys have also been studied.