A composition-modulated Co–Ni laminated plating has been developed to prolong the lifetime of molds to be employed in continuous steel casting. We have investigated the relationship between the laminated structure and the mechanical properties of the plating films. The tensile strength of as-plated film was enhanced by the thinned thickness of the constituent layers, while the elongation received no effect of the thickness change of the constituent layer and remained almost stable in the range from 3 to 5%. Heat treatment at 400°C have brought about the improvement both in the tensile strength and the elongation. The improvement in the elongation was as remarkable as reached 13% in the film composed of layers with a thickness of 0.8 μm. The layer with low Ni content had an hcp structure, and that with high Ni content produced two phases of the hcp and fcc structures in the as-plated state. By the heat treatment, the high Ni-content layer turned into the single fcc phase, while the low Ni-content layer kept the hcp phase, and accordingly, the film structure changed into the one where the lattice of the hcp and fcc layers was distinct. The fact that the fcc layers, which was easily deformed, were formed continuously in the lateral direction, was seemed to contribute to the significant improvement in the elongation after heat treatment.

KEY WORDS: Co–Ni alloy plating; composition-modulation; elongation; continuous casting mold.

1. Introduction

In recent years, the employment environment in the continuous steel casting mold (hereinafter called “Mold”) have become severer due to application of electromagnetic stirring technology for improving steel quality and high-speed casting for productivity improvement.1–3) Particularly, in the meniscus portion which is the upper part of the Mold, the flow of the molten steel increases, so that the thermal shock to the Mold becomes strong, and cracks occur in the plating film which is the protective layer applied to the inner surface of the Mold. The occurrence of crack brings about peeling of the plating film, which presents a serious problem for the quality and production efficiency of the cast steel piece. Also, the proceeding of the cracks to the substrate of copper alloy of the Mold shortens the life of the Mold itself.

Therefore, we have commenced the research activities of cobalt-nickel (Co–Ni) alloy plating films that have excellent elongation properties at high temperatures against thermal shock. As a result, we have developed the composition-modulated Co–Ni laminated plating with laminating the alloy layers having different composition alternatingly by micrometer level thickness. 4,5) This composition-modulated Co–Ni laminated plating is available to produce by periodically varying stirring conditions during film formation in a single bath. Many of the studies6–12) have been reported on the plating films consisted of the conventional metal multilayer films, but laminated structure producing required lamination in the plural different tanks or pulse electric plating as well as due to complicated manufacturing process, so that they are difficult to be put into industrial practice. In addition, there are many studies on the thickness of the constituent layers at the nanometer level, but there are few reports on thick films laminated with micrometer-level layers.

This composition-modulated Co–Ni laminated plating that we have produced this time capitalizes on the difference of electrodeposition rates between Co and Ni in plating conditions. Consequently, the minimum thickness that can be laminated in a state where the alloy composition of the constituent layers clearly differs is about 0.2 μm, and the total plating thickness that can be formed is not limited. Its manufacturing method is simple, and thick film formation on the order of several millimeters is available. 5) Since we have discovered that it also has excellent mechanical proper-
ties and corrosion resistance as compared with the conventional Co–Ni plating, when we have applied this film to the Mold, it showed crack resistance and the life of the Mold has been drastically prolonged which was already reported.5) It is interesting that the multilayer structure of the composition-modulated Co–Ni laminated plating gives effect to the mechanical properties of the coating, and when this coating is heat-treated, it displays remarkable improvement in elongation which is available for the industrial use. The change in the mechanical property produced by the heat treatment has been regarded as coming from the crystal structure change in each layer.

In this paper, we have conducted research activities of the film properties before and after heat treatment by means of changing the thickness and composition of each layer to be laminated and have investigated the effect of the crystal structure of the constituent layer on the mechanical properties of the film.

2. Experiments

The composition-modulated Co–Ni laminated plating, same as in the previous report,3) had been formed by using a plating solution consisting of cobalt sulfate, nickel sulfate and boric acid and by bringing about the disparity of nickel content in the constituent layers by stirring the plating solution strongly and less alternately during plating. The stirring control of the plating solution had been carried out by switching the power of air at constant intervals by using a timer device. The constituent layer had been aimed to be laminated and have investigated the effect of the crystal structure of the constituent layer on the mechanical properties of the film.

For the production of the tensile test piece, a SUS 304 plate (100 × 40 mm² and 3 mm in thickness) had been used as a cathode to form a plating film having a thickness of 0.5 mm. The plating film alone had been mechanically peeled off and had been processed into a dumbbell type tensile test piece with a width of 5 mm and a gauge distance of 17 mm by electric discharge machining. The picture of the test piece appearance has been shown in Fig. 1.

As for the heat treatment of the plating film, an electric furnace had been used, keeping the temperature at 400°C for one hour in an air atmosphere, after that the furnace had been cooled off. The oxide film formed by the heat treatment had been removed by the waterproof paper of No. 400 and then the piece had been applied for testing.

The tensile test for which a universal material testing machine (MODEL 4206 manufactured by Instron Co., Ltd.) had been employed and the measurement had been conducted at a cross head speed of 0.25 mm/min at room temperature. The elongation had been obtained from the maximum strain displacement at the time when the test piece had fractured.

The cross-sectional observation and the composition analysis of the plating film had been carried out by using a scanning electron microscope (SEM) (ERA-8900FE manufactured by Elionix Corporation) with an energy dispersive X-ray analyzer (EDX). Crystal structure analysis of the plating film had been performed using the electron beam backscatter diffraction (EBSD) system (TSL Solutions Co., Ltd.) attached to the previously mentioned SEM.

The crystal grain size obtained by the EBSD analysis has been indicated by the diameter of a circle having the same area as the measured crystal grain. There exist Number method and Area Fraction method to calculate the area of the crystal grain, the Number method shows a value obtained by dividing the total area of object by the number of crystal grains, while the Area Fraction method shows the average value of the values worked out in multiplying the ratio of each crystal grain area out of the total crystal grain area by each crystal grain area. This time the average crystal grain size has been calculated by Area Fraction method.

3. Results and Discussion

3.1. Changes in Mechanical Properties by the Heat Treatment

As reported in the previous report,3) the composition-modulated Co–Ni laminated plating, in the as plated state has not exhibited much difference in the elongation from the conventional single layer Co–Ni alloy plating. However, when heat-treated, the composition-modulated Co–Ni laminated plating has shown elongation of 10% or more, remarkably improved as compared with the elongation (3%) of the conventional Co–Ni alloy plating. In this section, we have tried to compare the stress-strain curves before and after the heat treatment and to examine the behavior of mechanical properties.

Figure 2 has shown the stress-strain curves before and after the heat treatment of the composition-modulated Co–Ni laminated plating (constituent layer thickness 3.4 μm at regular intervals). In the as plated state, the tensile stress
has risen linearly up to about 600 N/mm², and then has changed into mild rise and has fractured at a tensile strength of 730 N/mm², about 4% elongation. On the other hand, the heat-treated sample at 400°C has behaved similarly to the as plated sample at the initial stage of the test, but after that, the elongation has markedly improved while exhibiting mild stress rise, and the tensile strength has been 840 N/mm², and has fractured at an elongation of about 10%. Also, in the region where the stress has risen linearly, the stress has been higher in the heat-treated sample at 400°C than in the as plated state. Note that the stress-strain curves before and after the heat treatment has shown the same tendency even in the other composition-modulated Co–Ni laminated plating in which the thicknesses of the constituent layers and the spacing ratio have been changed.

3.2. Influence of the Changes in Thickness of Constituent Layers on the Properties of the Film

In the composition-modulated Co–Ni laminated plating, it is possible to arbitrarily change the thickness of the constituent layer by controlling the plating conditions. We have investigated the influence on the mechanical properties of the film by changing the thickness of the constituent layers to be laminated. First, the relationship between the thickness of the constituent layers and the tensile strength when the constituent layers have equally spaced has been shown in Fig. 3(a), and the relationship between the thickness of the constituent layers and the elongation has been shown in Fig. 3(b). The tensile strength was higher as the thickness of the constituent layer has been smaller, and it has displayed, at the maximum 780 N/mm² when the constituent layer thickness was 0.8 μm in as plated state. As the thickness of the constituent layer went up, the tensile strength went down and it reached to about 700 N/mm² at about 6 μm or more. By the heat treatment at 400°C of samples, the tensile strength was about 150 N/mm² higher than the as-plated one. The fact that thinner constituent layer brought about the higher tensile strength has possibly been regarded as the effect of grain refinement. But this subject will appear later in this paper.

The elongation of the as plated sample has had nothing to do with the thickness of the constituent layer, and it had stayed almost stable as 3 to 5%. However, the samples being heat-treated at 400°C showed significant elongation improvement, especially 13% improvement for the samples with a constituent layer thickness of 0.8 μm. As can be seen from the stress-strain curves shown in Fig. 2, improvement of elongation has greatly contributed to improvement of tensile strength.

Next, we have investigated the mechanical properties when the constituent layers to be laminated had been placed alternately with irregular intervals each other. The tensile strength in the irregularly spaced constituent layers has been shown in Fig. 4(a), and the changes of elongation has been
shown in Fig. 4(b). The horizontal axis has indicated the abundance ratio of the “high Ni-containing layer” which has been a layer obtained by weakening the agitation. We have produced the test piece of the arbitrary abundance ratio by means of increasing the thickness alone of high Ni containing layer in order to have the higher abundance ratio, while increasing the thickness alone of low Ni containing layer to have the lower abundance ratio, based upon the standard as 50% abundance ratio of high Ni containing layer having constituent layer thickness of 3.4 μm with even intervals.

In the as plated sample, the tensile strength has risen mildly as the abundance ratio of the high Ni-containing layer has increased. In the sample being heat-treated at 400°C, the tensile strength has increased in accordance with the increment of the abundance ratio of the high Ni-containing layer, but it has shown a local maximum at 67%, and after that point it has tended to be slightly lower. On the other hand, the elongation has been about 4% in the as plated sample regardless of the abundance ratio of the high Ni containing layer. In the sample being heat-treated at 400°C, it has increased in accordance with the increment of the abundance ratio of the high Ni-containing layer and have shown a tendency to saturate at the abundance ratio of 67% or more. At the abundance ratio of 80%, although the elongation has been somewhat improved, the tensile strength has been slightly lowered, and the effect of the laminated structure has been reduced. In addition, the heat-treated sample has been more affected by the abundance ratio of the high Ni-containing layer than the as-plated sample.

3.3. Effect of Film Composition and Metal Structure on Mechanical Properties

The factor of the change of the mechanical property which has been brought about by heating the plating film can be regarded as the influence of the mutual diffusion that took place among the layers whose composition ratio vary each other. Figure 5 has shown the composition line analysis results of Ni and Co in the cross section of the composition-modulated Co–Ni laminated plating. It can be recognized that this film has periodically modulated the composition at intervals of about 3 μm. We have acknowledged no substantial difference of modulated composition between as plated test piece and heat-treated sample at 400°C. It has therefore become evident that the composition change caused by diffusion has not been the factor of mechanical property change.

Generally, it is known that the metal materials have a correlation among hardness, tensile strength and elongation, and that the higher the hardness, the higher the tensile strength, and the lower the hardness, the better the elongation. As previously reported, although the composition-modulated Co–Ni laminated plating has been harder than the conventional Co–Ni alloy plating, the elongation has been greatly improved as compared with the conventional Co–Ni alloy plating.5) As mentioned before, since the change factor of the mechanical property caused by the heat treatment of the composition-modulated Co–Ni laminated plating has not been a composition change, it is conceived that some structural changes might have occurred in each layer which have greatly affected the mechanical property. As shown

![Cross-sectional SEM image and composition line analysis of composition-modulated Co–Ni laminated alloy plating.](image)
in Fig. 3(b), the elongation had almost no correlation with the thickness of the constituent layer, while the effect of the heat treatment has been extremely large to the elongation. In order to investigate this factor, we have made the fracture surface observation after the tensile test. Figure 6 has shown the SEM image of the fracture surface observation and the line analysis result of Ni of specimens modulated at different intervals with the abundance ratio of the high Ni containing layer as 67%. Figure 6 also has shown the uneven images of fracture surface by three-dimensional roughness analysis. From the SEM image, it has been confirmed that the sample heat-treated at 400°C had a larger deformed portion at constant intervals with respect to the vertical direction of the film thickness. From the results of the line analysis, it has been found that highly deformed portions have been in the high Ni content area and in the layer with the high Ni content. By the inspection of the three-dimensional roughness image, we could not recognize any distinct constant deformation phenomenon in the as plated sample, as had been seen in the sample heat-treated at 400°C.

3.4. Influence of Crystal Structure on Mechanical Properties

The composition-modulated Co–Ni laminated plating that we have produced have consisted of being a layer of a low Ni content (17 to 20 wt%) and a layer of a high Ni content (35 to 40 wt%). Fukumuro et al.\(^\text{13}\) have confirmed that, in the Co–Ni alloy electrodeposited film, the \(\alpha\) phase being the fcc structure has been formed in the entire composition range, and the \(\varepsilon\) phase being the hcp structure with the Ni content in the range of 0 to about 40 at% has been formed. In the composition-modulated Co–Ni laminated plating which have been prepared this time, the existence of two phases of \(\alpha\) phase and \(\varepsilon\) phase in both as plated samples and the samples heat-treated at 400°C has been confirmed by the X-ray analysis.

In order to investigate the crystal structure changes by the heat treatment for further details, the crystal structure analysis by EBSD method in the film cross section direction has been conducted. Figure 7 has shown an EBSD analysis image that analyzes the distribution of crystal grains when the constituent layer thickness has been changed. The vertical direction of the EBSD analysis image has shown the plating film growth direction. In the as-plated sample, crystal grains have grown in a columnar state in the film growth direction, which has been inconsistent with the periodic change of the composition shown in Fig. 5. In particular, when the layer thickness has been small (less than 3.4 \(\mu\)m), the said tendency has been large, and it is considered that columnar growth has occurred in line with a certain crystal orientation. On the other hand, in the sample heat-treated at 400°C, it can be seen that a layered structure has been formed in the direction perpendicular to the film growth direction inside the large columnar crystal grains as has been observed in the as plated sample.

Figure 8 has shown the result of the EBSD analysis results before and after heat treatment as has been shown in Fig. 7, focusing on fcc structure and hcp structure. In the as-plated sample, the layer with a low Ni content has exhibited the hcp structure, and the layer with a high Ni content has a columnar growth keeping the hcp structure as it is, and

![Fig. 6. SEM image of fractured surface of composition-modulated Co–Ni alloy plating.](image-url)
the hcp structure and the fcc structure have coexisted. On the other hand, in the sample heat-treated at 400°C, the layer with high Ni content has changed to fcc structure, while the layer with low Ni content has kept the same hcp structure as before heat treatment. As a result, the hcp structure and the fcc structure have been clearly separated and changed to an alternately laminated structure. As described above, in the sample heat-treated at 400°C, a layered structure had been formed in the direction perpendicular to the film growth direction inside large crystal grains as being found in the as plated sample. It is considered that the layer with high Ni content, which has made columnar growth keeping the hcp structure as it is, has changed into the fcc structure by heat treatment. In this way, it is considered that the layer having the easily deformable fcc structure has periodically formed as a continuous layer, has contributed to the improvement in elongation.

Next, **Fig. 9** has shown the results of our investigation of the relationship between the average grain size analyzed by EBSD method and the constituent layer thickness. In the case of the as-plated sample as the constituent layer thickness is small (3.4 μm or less), the average crystal grain size has been larger than each layer thickness. This is due to the effect of columnar growth keeping the hcp structure as it
is. On the other hand, when the constituent layer thickness has been large (7 μm), the average grain size has become small because the crystal grains have a crystal structure according to the composition in each layer. Also, comparing the average grain size before and after heat treatment, the grain size of the sample heat-treated at 400°C has been smaller. It is considered that this is because each layer has a thermodynamically stable structure, and the grain size has changed depending on the thickness of each constituent layer.

In the sample heat-treated at 400°C, the average grain size also has increased gradually with the increment of the layer thickness. The reason that high tensile strength can be obtained when the layer thickness is small as shown in Fig. 3 is considered to be the effect of grain refinement. On the other hand, in the as plated sample, although the average crystal grain size analyzed by the EBSD method is relatively large, the tensile strength is high when the constituent layer thickness is small. It is considered that a substructure such as dislocation concentration is formed at the interface where composition change occurs in the crystal grain regarded as one crystal grain in EBSD analysis, and this becomes deformation resistance.

According to the binary phase diagram of Co–Ni, there are regions where the hcp phase and the fcc phase coexist when the Ni content is in the range of 20 wt% to 40 wt%. In this region, the temperature at which the hcp phase transforms to the fcc phase and the temperature at which the fcc phase transforms to the hcp phase differ greatly. In the layer with high Ni content (about 38 wt% Ni) in the composition-modulated Co–Ni laminated plating prepared for this study, hcp phase and fcc phase were mixed as it was plated, but it is thought that it changed to a thermodynamically stable fcc single phase at 400°C. It is considered that the fcc structure is maintained because this composition region does not pass through the transformation point at which the fcc phase changes to the hcp phase even when it is cooled to a normal temperature state.

Normally, when the metal material is heat-treated and gradually cooled, the crystal grain size increases and the strength tends to decrease. However, the composition-modulated Co–Ni laminated plating produced this time showed the opposite tendency. It is inferred that the heat treatment of the composition-modulated Co–Ni laminated plating at a proper temperature changes the crystal structure into a stable crystal structure in each constituent layer, and the crystal grains are refined.

As described above, it is considered that the formation of the fcc phase which is easy to deform as a continuous layer largely contributes to the improvement of the elongation. In the sample with constituent layer thickness of 7 μm shown in Fig. 8, the thickness of the high Ni content layer is also thick, and it appears that the fcc phase exists as a continuous layer even when it is plated. However, even in this sample, the elongation is greatly improved by the heat treatment, and it is thought that the abundance of the fcc phase is not the only factor of the elongation improvement. Therefore, the crystal orientation in the fcc phase and the hcp phase was investigated. Figure 10 shows the relationship between the elongation and the abundance ratio of each crystal plane observed from the cross section. The abundance ratio of each crystal plane is the ratio to all fcc phase or all hcp phase in the EBSD measurement plane. There was no clear tendency to the crystal orientation in the state of low elongation before heat treatment. On the other hand, in the state of high elongation after heat treatment, the abundance ratio of each oriented plane tends to show a substantially constant value, and in particular, the abundance ratio of the...
hcp (0001) plane tends to decrease. Since the slip plane of the hcp structure is only the (0001) plane, plastic deformation hardly occurs. When the specimen subjected to tensile deformation was viewed from the cross-sectional direction, the slip plane (0001) had a random orientation in the as-plated condition. Due to the heat treatment, the (0001) plane perpendicular to the tensile direction decreases, and it is considered that the (0001) plane close to parallel to the tensile direction relatively increased and became easy to deform. It is considered that this contributes to the elongation. Although this point is interesting, since it is beyond the scope of the present research purpose, we will consider it as a future study subject.

4. Conclusion

We have conducted the investigation of the film properties before and after the heat treatment of the composition-modulated Co–Ni laminated plating, and have examined the influence of the crystal structure of the constituent layer on the mechanical properties of the film, and so obtained the following results.

1) The tensile strength was higher as the thickness of the constituent layer was smaller, and it exhibited maximum 780 N/mm² when the constituent layer thickness was 0.8 μm as plated. By heat treatment at 400°C, the tensile strength went up by about 150 N/mm² higher than the as plated one.

2) The elongation was not affected by the thickness of the constituent layer in the as plated sample, being almost constant as 3 to 5%. However, in the sample heat-treated at 400°C, the elongation has been greatly improved, especially 13% in the sample with the constituent layer thickness of 0.8 μm.

3) When the constituent layers were laminated to have different intervals, the tensile strength gradually went up as the abundance ratio of the high Ni-containing layer increased in the as plated sample. In the sample heat-treated at 400°C, the tensile strength went up according to the increasing of the abundance ratio of the high Ni-containing layer, showing the maximum value at 67%. On the other hand, the elongation was about 4% in the as plated sample irrespective of the abundance ratio of the high Ni-containing layer, but in the sample heat-treated at 400°C, the elongation rose as the abundance ratio of the high Ni-containing layer increased, and showed a tendency to be saturated at the abundance ratio of 67% or more.

4) In the sample heat-treated at 400°C, the crystal grain size showed the tendency to become small as the thickness of each layer was reduced. It is considered that the cause of the increase in tensile strength made by the reduction of the constituent layer thickness is the refinement of crystal grains.

5) In the sample heat-treated at 400°C, the layer with high Ni content changed only to fcc structure, while the layer with low Ni content stayed in the same hcp structure as before heat treatment. Thus, the hcp structure and the fcc structure were clearly separated and changed to an alternately laminated structure.

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