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Chromium carbide laser-beam surface-alloying treatment on stainless steel

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In order to improve the resistance to wear, oxidation and corrosion of a stainless steel die, chromium carbide surface-alloying treatment was carried out on a 12% Cr stainless steel using a CO_2 laser. Cr_3C_2 powder slurry was coated on the stainless steel and then a 3 kW CO_2 laser beam was used to irradiate the specimen. The thickness of surface-alloyed layer was about 0.3 mm and the chromium concentration was about 40% throughout the alloyed-region. Large amounts of Cr_3C_2 and Cr_7C_3 were also distributed in this alloyed layer. From the results of the isothermal oxidation test at 960 °C for 100 h, it was found that the surface-alloying treatment improved the oxidation resistance by about 100 times due to the distribution of chromium carbides and the increase in the chromium concentration. The results of the cyclic oxidation test revealed that the oxidation layer was very stable on the chromium carbide surface-alloyed region, while it scaled off very easily from the substrate region due to porous oxidation products. The microhardness was about 1100 H_V due to the dispersion and precipitation of chromium carbides in addition to the martensitic structure in the surface-alloyed region. The microhardness did not decrease much, despite heating at 960 °C for 100 h. The chromium carbide surface-alloying treatment improved the wear-resistance greatly, and the results of the wear-resistance test were very consistent with those of the microhardness test.

1. Introduction

Television Brown tubes and cathode-ray tubes are produced by pressing melted glass. In such cases the surface of the pressing die is degraded due to oxidation and wear erosion, because it is subject to high temperature ($\sim$ 700 °C) and high pressure for long times. There are also various active elements, such as sodium and potassium, in the glass, and these elements accelerate the surface corrosion by reaction with some elements in the die steel at high temperature. Therefore, martensitic stainless steel is used for pressing die materials in mass production of glassware at high temperature. In such circumstances it is common not only that the life of the stainless steel die is reduced, but also that the surface of the products is not flat enough to meet the required conditions due to the roughness of the die surface. The die must then either be repaired on the surface, or replaced by a new one. Such a die should, therefore, have good wear, corrosion and oxidation resistance at high temperature, and also a good releasing property of the pressed products.

If the life of a die is extended by the formation of a wear- and oxidation-resistant surface layer on the die steel, the die cost can be reduced. In addition, the cost of manufacturing products can be lowered further, because the idle time of the processing line is reduced by the avoidance of frequent replacement of the dies. In order to develop a new method to extend the life of a press die which is used for mass production of glassware at high temperature, a chromium carbide surface-alloying treatment was carried out on stainless steel using a CO_2 laser. Chromium carbide is chemically stable and oxidation resistant. It also has a relatively high hardness and good wear resistance at high temperature [1]. However, it is still decomposed at high temperatures, yielding elemental chromium which is the main alloying element in stainless steel. Thus it will minimize property changes and enhance the corrosion resistance of the die material.

It was reported that the chrome tool steel (H-13) had been surface-alloyed with Hastelloy C and Hastelloy X in order to extend the life of forging and pressing dies [2]. In such work, surface-alloying methods were carried out by pulsed gas metal arc welding (GMAW-P), submerged arc welding (SAW), shielded metal arc welding (SMAW) and plasma spraying treatment. It was also reported that the chromium carbide surface-alloyed layer, which was formed by the arc-coating method, has good wear resistance and enhances the erosion corrosion resistance at high temperature [1]. Although such methods can produce a thick surface-alloyed layer, it is difficult to suppress distortion and to obtain a thin layer on a local area due to the large heat input in the substrate. On the other hand, the laser-beam surface-alloying method can suppress the distortion of substrate and form a thin and accurate alloyed layer on the desired area, because this method can concentrate the laser energy on a localized area. The present work formed the basic research to improve wear and oxidation

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resistance on a surface layer while maintaining the toughness in the substrate of the stainless steel die using the chromium carbide surface-alloying treatment with a high power CO_2 laser.

TABLE I Chemical composition (wt %) of the stainless steel

	C	Si	Mn	Ni	Cr	Mo	Co	Fe
SUS 420 J2	0.290	0.638	0.821	0.241	11.760	0.075	0.050	bal.

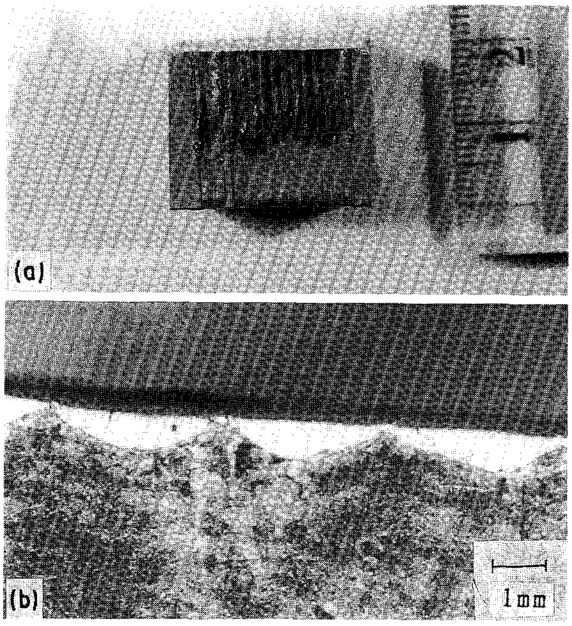

Figure 1 Photographs of the chromium carbide surface-alloyed region: (a) surface morphology, (b) cross-section (3 kW, 1 m min^{-1}).

2. Experimental procedure

2.1. Specimen preparation and laser irradiation

The specimen used for this experiment was the martensitic stainless steel (SUS420J2) which was used as the die material in glassware pressing, and its composition is shown in Table I. The dimensions of the specimen were 55 mm × 35 mm × 13 mm and its surface was finished flat by grinding before laser irradiation. The chromium carbide used was Cr_3C_2 powder (86 % Cr, 13 % C, 1 % others) which had average size of 3–5 μm and a polygonal shape near to spherical. Chromium carbide was suspended in a solution of alcohol and a small amount of methyl cellulose to produce a slurry which was coated on the specimen and then dried.

The power of the CO_2 laser was 3 kW and its focused spot size was chosen as 1.5 mm on specimen surface. The scanning speed was fixed at 1 m min^{-1}, and argon was used as the shielding gas.

2.2 Oxidation-resistance test and specimen analysis

The oxidation-resistance test consisted of two kinds of experiment. One was an isothermal oxidation test which could estimate the life of a surface-alloyed layer, and the other was a cyclic oxidation test which could examine the stability between the surface-alloyed region and the oxidized layer. These experiments were carried out in an atmospheric environment in order to match the real situation of a stainless steel die. Each specimen was heated in a furnace at 960 °C, and then its weight change was measured every 10 h for the isothermal oxidation test and every hour for the cyclic oxidation test.

After laser irradiation and the isothermal oxidation test, the microstructure of each specimen was observed under an optical microscope. In order to determine the components of the chromium carbide surface-alloyed layer and oxidized products, an X-ray diffraction test was performed by using CuK_α line of 0.15406 nm. For each specimen a microhardness test was carried out using a 200 g load, and a wear-resistance test was performed with laboratory-made equipment.

3. Results and discussion

3.1. Formation and composition of the surface-alloyed layer

Fig. 1 shows the surface morphology and a sectioned profile of a surface-alloyed layer after laser irradiation on the stainless steel (SUS420J2) with a Cr_3C_2 powder coating. The enlarged microstructure of the surface-alloyed region revealed that dendritic structures were formed due to rapid cooling, and that they consisted of martensitic structure. Contrary to the usual laser-irradiated carbon steel, which showed a clear heat-affected zone between the melted region and the pearlitic matrix, this stainless steel did not show a heat-affected zone as shown in Fig. 1b. In carbon steels, rapid cooling does not allow normal phase transformation from austenite to pearlite, but martensitic structure is formed and this structure distinguishes the melted region from the matrix region. However, the stainless steel matrix in this experiment consisted of martensite and ferrite. Thus the heat-affected zone, where the martensitic structure is formed due to rapid cooling, cannot be distinguished from the matrix structure. Table II presents the electron probe microanalysis (EPMA) spot analysis of elemental chromium in the surface-alloyed layer. As shown in this table, elemental chromium was distributed quite homogeneously and its concentration was about 40% throughout the alloyed region of 0.3 mm. This result is fairly consistent with previous chromium-, tungsten-, tungsten carbide and titanium carbide surface alloying treatments by CO_2 laser, where alloying elements were distributed homogeneously in alloyed layer [3–6].

Fig. 2 shows the X-ray diffraction patterns for the matrix of SUS420J2 stainless steel and the chromium carbide surface-alloyed layer. As the matrix material was composed of martensite and ferrite, only the α-peak appeared, as shown in (a). However, in the chromium carbide surface-alloyed layer, Cr_3C_2 and Cr_7C_3 peaks were observed in addition to the α-peak

TABLE II EPMA spot analysis of alloying elements in the surface-alloyed layer (3 kW, 1 m min^{-1})

Depth (mm)	Fe (at %)	Cr (at %)
0.1	56.610	39.014
0.2	53.248	42.647
0.3	48.496	42.456
0.4	87.625	12.274
0.5	88.209	11.683

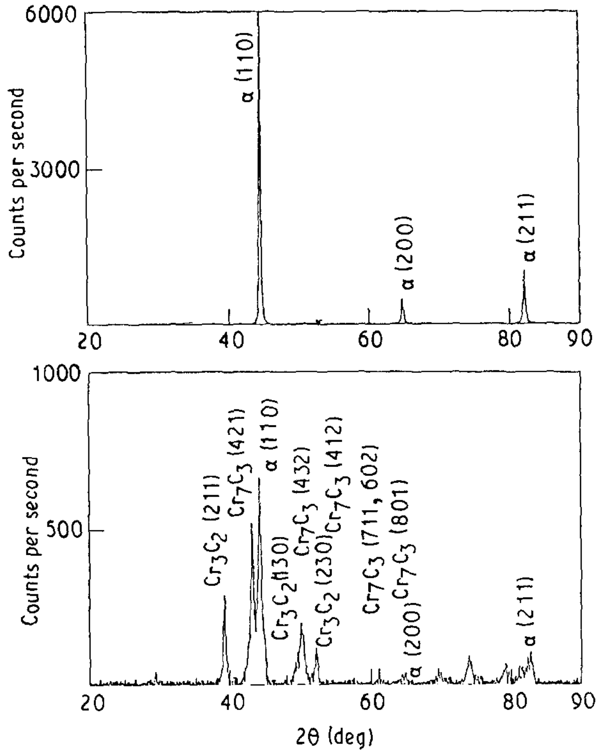

Figure 2 X-ray diffraction patterns of (a) the matrix specimen and (b) chromium carbide surface-alloyed specimen. Target: copper.

as shown in (b). The reason is believed to be that some undissolved Cr_3C_2 powders were retained and a large amount of Cr_7C_3 was precipitated from the melted region.

When the surface layer was observed carefully, a rippling effect and surface cracks were frequently revealed. The rippling effect and ruggedness of the surface layer are caused by vapour pressure, keyholing effect, shear stress due to surface tension and a temperature gradient [7], and the effect of the shielding gas on the melted region. There are several means of controlling this surface ruggedness, i.e. reduction of vapour pressure on the melted region, the addition of some alloying element to reduce the surface tension coefficient, or heating the substrate during melting.

In the present experiment, a multimode laser beam was used and the focused spot size was fixed at 1.5 mm on each specimen, in order to reduce the keyholing effect by applying a relatively uniform heating to the specimen's surface. Nevertheless, contrary to mild steel, some small cracks were observed on the surface-alloyed layer. During the solidification process, a thin liquid phase, which has a low melting point, is left in the grain-boundary region between the primary eutectic structures. When this liquid phase is finally solidified, its volume contracts and microcracks may be developed in that region. It has been reported that surface cracks could result from the propagation of such microcracks [8, 9]. In addition to the above reasons, a large amount of tensile stress was retained in the surface layer due to volume contraction during rapid cooling, and this effect would be added to the development of surface cracks. Therefore, it is necessary to avoid or suppress such cracks in order to obtain a good surface-alloyed layer. If a specimen is held at high temperature during laser irradiation and then slowly cooled, it is expected that much of the retained tensile stress may be relieved and microcracks may be reduced due to the gradual contraction of the surface-alloyed layer.

3.2 Oxidation resistance of the surface-alloyed layer

In the development of heat-resistant materials, the most important points are the environment of the working condition, the selection of materials, and the design of the protective coating on the substrate [10]. Because a stainless steel die is used in atmospheric conditions, its surface is corroded and oxidized due to melted glass. With the lapse of time the surface layer is worn off due to repeated heat and stress cycles. Then its surface becomes too rough and it must be repaired or replaced by a new one. Therefore, an oxidation-resistance test was carried out in an open furnace at 960 °C for 100 h. For both the isothermal oxidation test and the cyclic oxidation test [10, 11], weight changes were measured every 10 h and every hour, respectively, as mentioned earlier.

In the isothermal oxidation test, the usual weight change process consists of two stages: the initial stage during which the substrate is oxidized, but further oxidation is suppressed due to the formation of stable oxidation layer, and the propagation stage during which the oxidation layer is destroyed and then oxidation occurs in the substrate region. Thus the typical tendency shows that the weight of a specimen increases gradually up to a certain level and maintains this weight in the initial stage, and then it increases considerably due to oxidation of the substrate in the propagation stage. The cyclic oxidation test was carried out to examine the stability between the oxidation layer and the substrate matrix. The usual weight change process again consists of two stages: the initial stage during which the oxidation layer is formed on the surface, and the propagation stage during which the oxidation layer is scaled off due to repeated heat and stress cycles. Thus there is a typical tendency for the weight of the specimen to increase slightly in the initial stage, and then to decrease drastically due to scaling-off of the oxidation layer in the propagation stage.

Fig. 3 shows the specimen profiles of the chromium carbide surface-alloyed layer and the substrate matrix after the isothermal oxidation test in air at 960 °C for

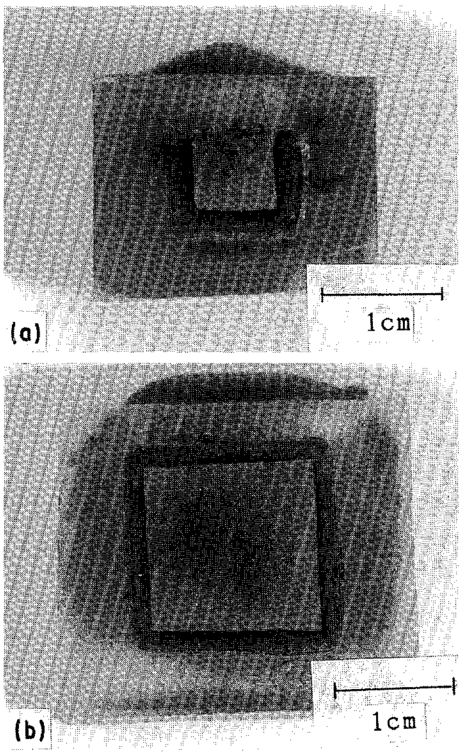

Figure 3 Photographs of specimens after the isothermal oxidation test at 960 °C for 100 h: (a) specimen with chromium carbide surface-alloying treatment on top side, (b) matrix specimen.

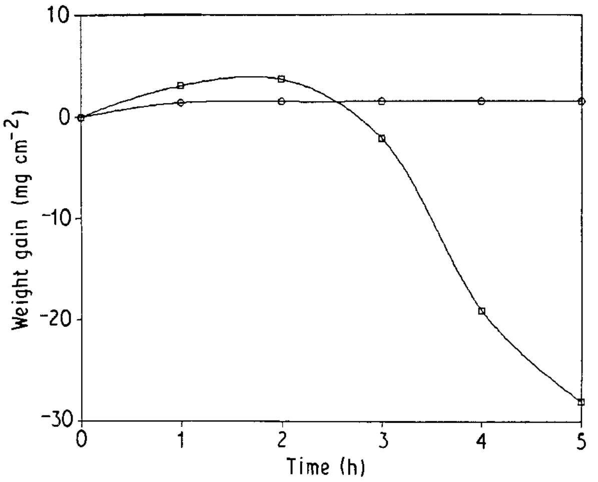

Figure 4 Results of the cyclic oxidation test. (□) Uncoated surface; (○) chromium carbide coated surface.

100 h. The upper part of Fig. 3a is the surface-alloyed layer which revealed a superior oxidation-resistance property. In order to calculate the weight change due to oxidation per unit area, the following formulae were applied.

For the matrix

$$(\text{weight change/area}) = \frac{(TW)}{(TA)} \qquad (1)$$

For the surface-alloyed layer

$$(\text{weight change/ area}) = \frac{(TW) - (SA) \times (AW/A)}{(SAL)} \qquad (2)$$

where TW is the total weight change, TA the total surface area of the specimen, SA the surface area except for the surface-alloyed layer, AW/A the average weight change of matrix/area, and SAL the area of the surface-alloyed layer.

Fig. 4 shows the results of the cyclic oxidation test for the matrix and surface-alloyed layer. According to this figure, the matrix specimen shows typical results of the cyclic oxidation test, where the specimen weight increased slightly due to oxidation and then decreased drastically due to the scaling-off of the oxidation layer. Meanwhile, the chromium carbide surface-alloyed specimen shows that the specimen weight increases very slightly and then becomes stable. This result shows that the chromium carbide surface-alloyed layer proved to have superior oxidation resistance. The reasons are believed to be that there are large amounts of chromium carbides in the alloyed region and also a dense chromium oxide layer is formed on the surface. Therefore, the stable chromium oxide layer prohibits the penetration of oxygen into the alloyed region and prevents the scaling-off of the surface layer even in repeated heat cycles. But, in the case of the matrix, the result is quite different. Because dense chromium oxide does not cover all the surface area, although the chromium concentration was 12 % in this steel, porous iron oxide was formed on the surface area and then oxygen penetrated into the matrix continuously. This porous oxidation surface layer was unstable, and thus it was scaled off due to repeated heat cycles.

Fig. 5 illustrates the results of the isothermal oxidation test in air at 960 °C for 100 h. It is seen that the specimen weight increased continuously in case of the matrix, because the surface layer was oxidized and the penetration of oxygen continued into the matrix through the porous oxide layer. Meanwhile, in the chromium carbide surface-alloyed layer, the specimen weight was maintained at an almost constant level, except for some increase for a certain period. Initially, heat-resistant chromium carbides and a thin chromium oxide layer protected the surface-alloyed layer from oxidation. However, the specimen should be cooled after 10 h to measure its weight, and rapid cooling might then cause the formation of microcracks on the surface-alloyed layer. During the second cooling and heating, these microcracks could propagate further into the matrix region, and then oxygen could penetrate into this region where large amounts of iron oxides were formed. Thus the specimen weight increased suddenly after about 20 h. However, if much iron oxide was formed inside the cavity, the crack walls suppress further formation of porous oxides, and the cavity would be sealed off. Thus, further passage of oxygen would be difficult and the specimen weight would not increase. It is speculated that if the more cracks were formed on a specimen, a greater weight gain would be obtained. Oxidation rates were calculated for both specimens by measuring weight changes after the isothermal oxidation test at 960 °C for 100 h. According to the calculated results, it was 4.5–5mg cm^{-2} h^{-1} for the matrix specimen and 0.005–0.006

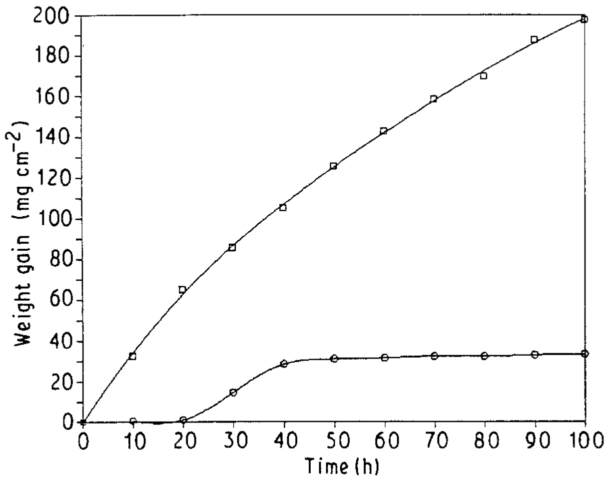

Figure 5 Results of the isothermal oxidation test. (□) Uncoated surface;(○) chromium carbide coated surface.

mg cm^{-2}h^{-1} for the chromium carbide surface-alloyed layer. This means that the chromium carbide surface-alloying treatment improved the oxidation-resistance by 100 times. If the surface-alloyed layer was perfect without any crack formation, the oxidation-resistance might be improved further.

Fig. 6 shows the profiles of oxidation layers for the surface-alloyed region and the matrix specimen after the isothermal oxidation test at 960 °C for 100 h. It can be seen that the thickness of the oxidation layer was about 100 μm for the surface-alloyed region and 1.3 mm for the matrix specimen, respectively. The oxidation layer was much thicker in the matrix specimen than in the surface-alloyed region. In order to determine the structure and composition of the oxidation products, X-ray diffraction (XRD) patterns were obtained from oxidized layers for both specimens. Fig. 7 shows XRD for both oxidized layers after the isothermal oxidation test at 960 °C for 100 h. For the matrix specimen (Fig. 7a), most oxidation products were identified as $(Fe_{0.6}Cr_{0.4})_2O_3$, $FeCr_2O_4$ and Fe_2O_3. Meanwhile, in the surface-alloyed region (Fig. 7b), most X-ray peaks were identified as α-, $FeCr_2O_4$, Cr_7C_3 and $Cr_{23}C_6$ peaks, but Fe_2O_3 and $(Fe_{0.6}Cr_{0.4})_2O_3$ peaks did not appear. These results confirm that contrary to the matrix, much more chromium and chromium carbides were present in the surface-alloyed region, and they contributed to the improvement of the oxidation resistance. Thus the dense chromium oxide on the surface prevented the penetration of oxygen into the interior. Meanwhile, because the iron concentration was much higher in the matrix, a porous Fe_2O_3 layer was formed in the matrix region and more oxygen could penetrate into the interior to give a thicker oxidation layer. Even in the formation of compound iron-chromium oxidation products, it was the $(Fe_{0.6}Cr_{0.4})_2O_3$ which had the greatest iron concentration for the matrix specimen, but it was the $FeCr_2O_4$ which had the greatest chromium concentration for the surface-alloyed region. Among the identified chromium carbides, a large amount of $Cr_{23}C_6$ was present in the surface-alloyed region. It is speculated that large amounts of Cr_3C_2 and Cr_7C_3 were dissociated during heating at 960 °C,

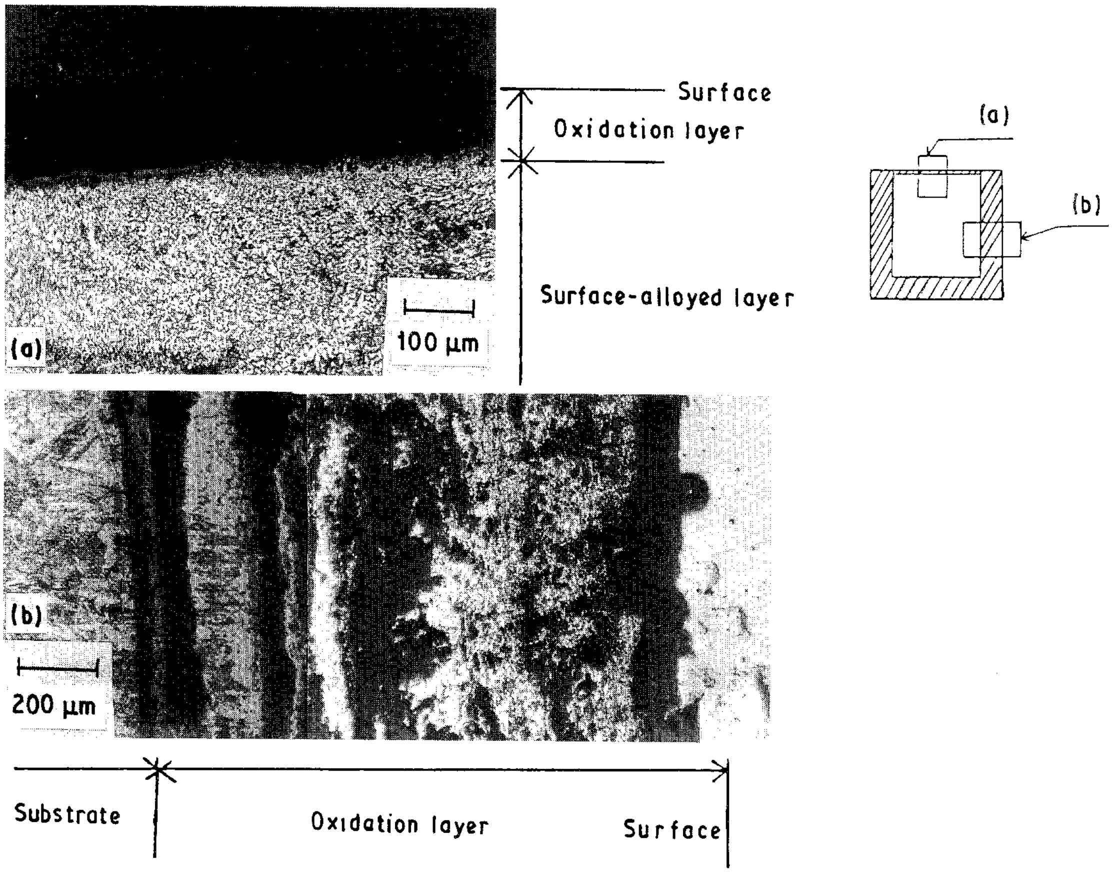

Figure 6 Photographs of the oxidized layers after heating at 960 °C for 100 h.

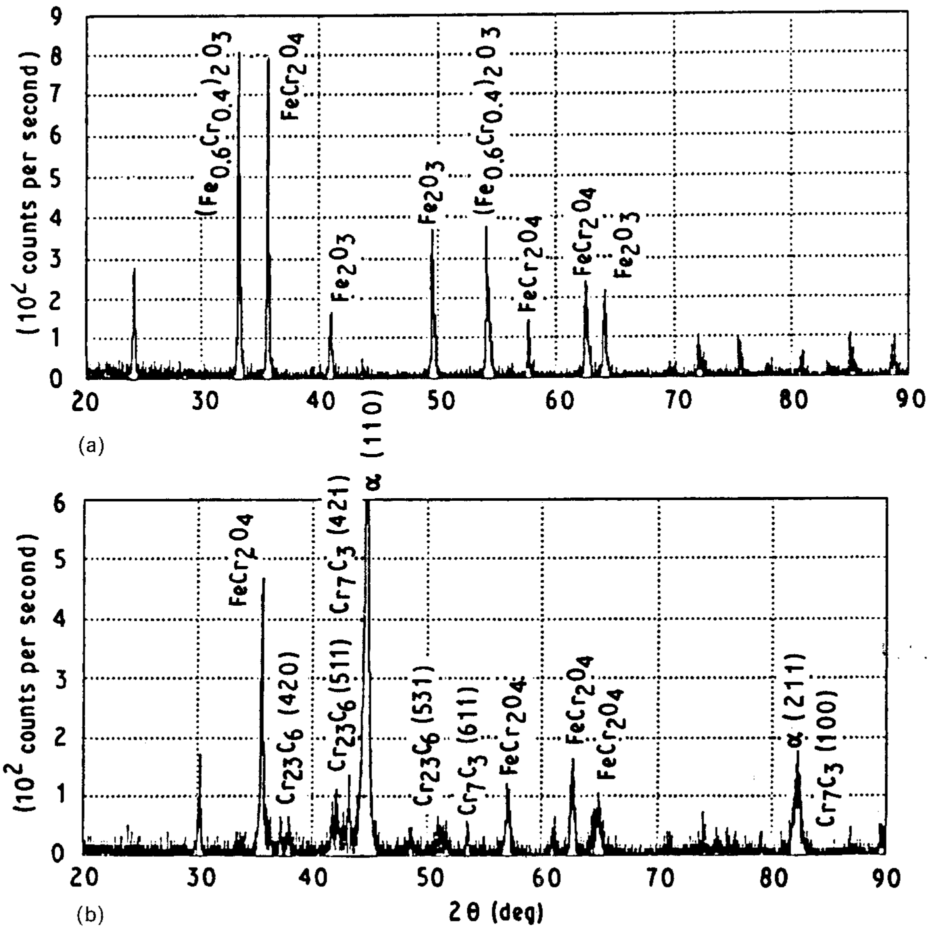

Figure 7 X-ray diffraction patterns of (a) the matrix specimen and (b) the chromium carbide surface-alloyed specimen after heating at 960 °C for 100 h. Target: copper.

and then carbon was dissolved in an alloyed region and also diffused into the matrix region. Because the chromium concentration had already been increased to 40% in the alloyed region, the stoichiometry of the chromium carbide might be changed when they were precipitated again in this region. Thus the relative carbon concentration might become lower in the surface-alloyed region after heating at high temperatures for long times, and thus $Cr_{23}C_6$ was formed during rapid cooling.

3.3. Microhardness and wear resistance of the surface-alloyed layer

Conventional heat-treatment of this stainless steel (SUS420J2) is by oil-quenching from 920–980 °C to obtain the martensitic structure. Therefore, rapid cooling due to laser irradiation resulted in the martensitic structure in the surface-alloyed layer. In addition to this martensitic structure, the strengthening mechanism was further reinforced by the dispersion and precipitation of chromium carbides. Because the cooling rate was too fast, the precipitated chromium carbides did not have enough time to grow, and it was advantageous for the dispersion of fine carbides. Thus the microhardness reached 1100 H_V near the surface region as shown in Fig. 8, which illustrates the microhardness profile for the chromium carbide surface-alloyed layer. It is seen that the microhardness of the

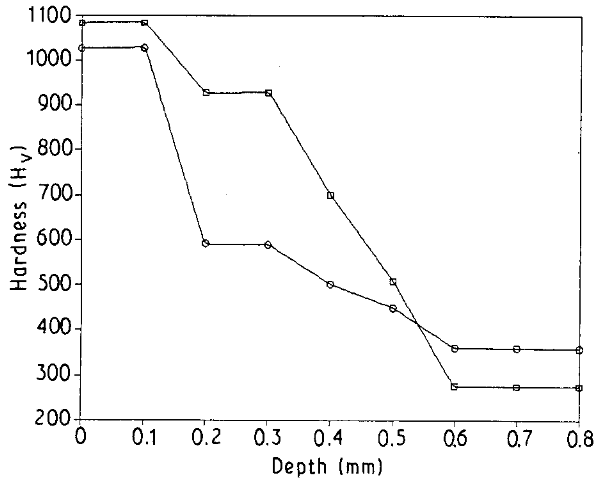

Figure 8 Microhardness of the chromium carbide surface-alloyed layer, (□) before, and (○) after heat treatment at 960 °C for 100 h.

alloyed region became slightly lower, and that of the matrix region became higher after heating at 960 °C for 100 h. This was believed to be due to the retained stress being relieved and the growth of precipitated particles during heating.

In order to examine wear resistance, various specimens were tested and their wear-losses were measured periodically. During this test, the specimen contact area was fixed at 1 cm², applied load 290 g,

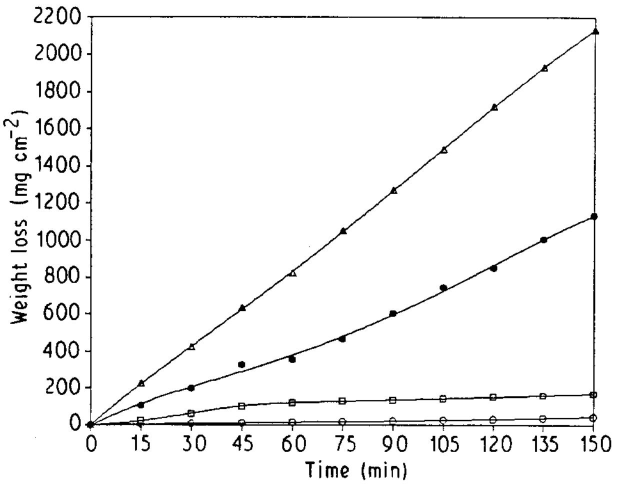

Figure 9 Results of the wear-resistance test for various specimens (wear area 1 cm^2, load 290 g, Emery paper no. 80). Uncoated surface: (△) before and (●) after heat treatment at 960 °C for 100 h. Chromium carbide coated surface: (○) before and (□) after heat treatment at 960 °C for 100 h.

and Emery paper no. 80 was used as an abrasive paper. In order to ensure the same experimental conditions, each specimen was measured every 15 min and then the abrasive paper was replaced by a new one. Fig. 9 shows the weight loss for various specimens as a function of time. The slope is very small for the surface-alloyed specimens. This means that the surface-alloying treatment improved the wear-resistance greatly. However, the isothermal oxidation test resulted in a slight increase of the slope up to 45 min. The reason why the wear-loss of the surface alloyed specimen increased after this test was believed to be due to the breakdown and wear of the dense chromium oxide layer on the surface. Once the oxidation layer was removed, the slope was equivalent to that of the normal surface-alloyed specimen. In the case of the matrix specimen, the structure became martensitic due to air cooling after the isothermal oxidation test, and thus the wear resistance was increased compared with that of the matrix region before heating. These results were very consistent with the microhardness test results.

In general, die and moulds require a very hard surface and very tough internal structure. If a die is made of SUS420J2 stainless steel, it should be heat-treated, after which its hardness is quite high due to the martensitic structure, but its toughness is deteriorated. However, if the chromium carbide surface-alloying treatment is applied to this stainless steel using a CO_2 laser, the surface area will be modified to be very hard while maintaining a relatively tough internal structure compared with the heat-treated specimen. Because wear and corrosion resistance are improved greatly even at high temperatures, the die life can be extended, especially for glassware pressing at high temperature.

4. Conclusions

When 12 % Cr stainless steel was surface-alloyed with Cr_3C_2 powders using a CO_2 laser, the thickness was about 0.3 mm and the chromium concentration was about 40 % throughout the alloyed region. Large amounts of Cr_3C_2 and Cr_7C_3 were distributed in this region. From the results of the isothermal oxidation test at 960 °C for 100 h, the surface-alloyed layer was found to improve the oxidation-resistance compared with that of the substrate by about 100 times, due to the distribution of chromium carbides and the increase in chromium concentration. Results of the cyclic oxidation test also revealed that the oxidation layer was very stable in the chromium carbide surface-alloyed region, while it was scaled off very easily from the matrix region due to the porous oxidation product. The microhardness was about 1100 H_V due to the dispersion and precipitation of chromium carbides, in addition to the martensitic structure in the surface-alloyed region. It did not decrease much, despite heating at 960 °C for 100 h. The chromium carbide surface-alloying treatment vastly improved the wear resistance, and this result was very consistent with that of the microhardness test. Although microcracks were observed on the surface-alloyed layer due to rapid heating and cooling, these defects may be prevented if the surface-alloying treatment is carried out at high temperature and the alloyed region is cooled slowly.

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