Effects of copper content on the machinability and corrosion resistance of martensitic stainless steel

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Abstract The effects of copper addition on the machinability and corrosion resistance of martensitic stainless steel 4Cr16Mo are presented in the article. The results showed that the machinability of stainless steel 4Cr16Mo was obviously improved by adding Cu. When the content of copper in the stainless steel was 1.4%, the machinability of stainless steel was optimal. With the increase in the content of copper, the corrosion resistance of stainless steel 4Cr16Mo was improved. From the observation of the electron backscattered diffraction (EBSD) and high resolution electron microscopy (HREM), it can be seen that Cu-rich phases were dispersed in the stainless steel, and determined to be about 10 nm.

Introduction

Development of new materials and manufacturing technologies has enabled the manufacturers to adopt new conditions in production and production strategies [\[1](#page-4-0)]. Stainless steels are typically difficult-to-machine materials. Many attempts have been made to improve the machinability of these steels by adding free-machining elements, such as sulfur, lead, selenium and tellurium [[2,](#page-4-0) [3\]](#page-4-0). In recent years, environmental considerations have been forcing industries to take measures to reduce the amount of elements, such as Pb, Se, and Te in these steels, which may cause health concerns [\[4](#page-4-0)]. Though sulfur is an effective

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element to improve the machinability of steels [[5\]](#page-4-0), sulfide inclusions have been recognized as preferential sites for localized corrosion, and cause the decrease in corrosion resistance [\[6](#page-4-0)]. In order to avoid these disadvantages, copper has been adopted to improve the machinability of austenite stainless steels [\[7](#page-4-0)].

In this article, the effects of addition of copper on the machinability, and corrosion resistance of martensitic stainless steel 4Cr16Mo are presented. Both the machinability and corrosion resistance of stainless steel 4Cr16Mo were both obviously improved by adding Cu. In addition, by means of electron backscattered diffraction (EBSD) and high resolution electron microscopy (HREM), the distribution and size of Cu-rich phases in the steel were also studied.

Experimental procedures

Metal samples preparation

The chemical compositions of the steels used, are shown in Table [1](#page-1-0). The specimen were 4Cr16Mo, 4Cr16MoCu1.1, 4Cr16MoCu1.4, and 4Cr16MoCu1.9. The ratio of Ni and Cu was approximately 1/2 in order to avoid copper brittleness. Specimen with dimensions $90 \text{ mm} \times 60 \text{ mm} \times$ 60 mm were used for the milling test, which were annealed at $1,050$ °C for 2 h, and then quenched. In order to produce the same hardness, specimen without copper were aged at 580 \degree C for 5 h, while those with copper were aged at 650 °C for 5 h. The corrosion specimen were cut from milling specimen. Specimen with dimensions 10 mm \times 10 mm \times 5 mm were used for electrochemical measurements. To create working electrodes, an electrical contact to each sample was provided by a length of copper wire,

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Table 1 Chemical compositions of studied materials $(wt, \%)$		C	Cr	Mo	Ni	Cu	Fe
	4Cr16Mo	0.42	15.70	1.17	0.17	-	Bal.
	4Cr16MoCu1.1	0.40	15.65	1.11	0.60	1.1	Bal.
	4Cr16MoCu1.4	0.41	15.55	1.13	0.87	1.4	Bal.
	4Cr16MoCu1.9	0.42	15.62	1.14	0.94	1.9	Bal.

connected to the back of each specimen mounted in an epoxy resin. Then the specimen were ground on a series of silicon carbide papers from 240 grit to 600 grit, degreased in acetone, washed with sterile distilled water, and dried in a desiccator until use.

Milling tests

Milling tests were carried out under dry conditions on the MH600C machining equipment using carbide milling-tools coated with AlTiN. The feed speed and milling speed were 800 mm/min and 75 m/min, respectively. The flank wear (VB) of the tools was measured. A Bruel & Kjaer 4368 sensor and Labview program were used to analyze the vibration signal in the milling test. Specimen for TEM observation were prepared by standard methods involving mechanical grinding, polishing and dimpling, followed by ion milling of foils to perforation on a liquid nitrogencooled specimen stage, to eliminate further aging during the thinning period. Microstructure studies were performed in a JEM-2010F operating at an accelerating voltage of 200 KV. The microscope used for EBSD was a JSM-6460LV SEM fitted with a tungsten filament operating at 20 Kev, and equipped with the Oxford INCA software package. EBSD scans were carried out in random position along the steel.

Electrochemical measurements

Immersion corrosion test was carried out in a closed capsule, which contained 10 wt.% HCl. The time and temperature of immersion corrosion test was 24 h and 25 °C , respectively. Then the corrosion rates were measured. Anodic polarization curves were measured in order to investigate the effect of Cu on corrosion resistance. All electrochemical tests were carried out in the solution containing 0.5 M NaCl, with a three-electrode system. The M283 potentiostat was used to measure anodic polarization curves. Working electrode potentials were referred to a saturated calomel electrode (SCE). The counter electrode was a Pt-plate. Polarization curves were determined with a scan rate of 1.666 mV/s. All measurements were carried out at 25 °C .

Results and discussions

Milling tests

The vibration amplitude and the flank wear of steel in the milling test was decreased by adding Cu. Figure 1 shows the variation of the vibration amplitude of the steels. It is clear that the vibration amplitudes of 4Cr16Mo with copper were lower than that of 4Cr16Mo without copper, and the vibration amplitude of 4Cr16MoCu1.4 was the lowest. In Fig. [2](#page-2-0), the relationship between the flank wear and the cutting length indicated that the tool wear of 4Cr16Mo with copper was less than that of 4Cr16Mo without copper, especially 4Cr16MoCu1.4.

The aging–strengthening effect of copper increased the aging temperature of steels as shown in Fig. [3](#page-2-0). In order to get the same hardness, steels, with copper should be aged in a higher temperature. With the increase in aging temperature, the yield strength of steel was decreased. When the hardness of specimen was all 36 HRC, the yield strengths of steels were showed in Table [2.](#page-2-0) It was obvious that the yield strength of steels with copper was lower than that of steel without copper. So the steels with copper would be easier to generate shear plastic deformation under the extrusion of the rake face and cutting edge in the milling test.

Fig. 1 The vibration amplitude in milling test

Fig. 2 The flank wear of steels in milling test

Fig. 3 Effects of aging temperature on hardness

By means of EBSD and HREM, the size and distribution of Cu-rich phases in the steel were studied. Cu-rich phases were dispersed in the steel, as Fig. 4a showed. In Fig. 4b, different colors indicate different orientations of copper precipitation. It can be seen that copper precipitated in a random orientation. The resolution of SEM is correspondingly low. In fact, these so called ''Cu-rich phases''

Table 2 The tensile results of steels

	4Cr16Mo	4Cr16Mo Cu1.1	4Cr16Mo Cu1.4	4Cr16Mo Cu1.9
Yield Strength	955 MPa	841 MPa 857 MPa		865 MPa
Break strength		1,100 MPa 1,080 MPa 1,086 MPa 1,097 MPa		
Percent Elongation 13.9%		15.4%	15.7%	15.1%

Fig. 4 Phase map (a) and orientation map (b) of 4Cr16MoCu1.4 by EBSD

in micrometer magnification consist of many real Cu-rich phases, which may be several nanometers. It is necessary to use HREM to identify Cu-rich phases clearly. Figure [5a](#page-3-0) gives the distribution of the Cu-rich particles by HREM, which were marked by ellipses. The copper-rich phase was to be approximately 10–100 nm, as Fig. [5](#page-3-0)b shows, and Fig. [5](#page-3-0)c indicated that the concentration of copper in these copper-rich phases was above 30%. When the average diameter of copper particles was to be about 10–100 nm, the copper particles served as plastic binders and solid lubricants, which provided a considerable reduction and compensation of wear of friction pairs [\[8](#page-4-0)]. By means of EBSD and HREM, the diameter of Cu-rich phases in 4Cr16Mo with copper was determined to be about 10–100 nm, as Figs. 4 and [5](#page-3-0) showed. In the milling test, the cutting tool and material by cutting can be seen as a couple of friction pairs. Cu-rich phases served as solid lubricants to lubricate the cutting tool. As a result, lubricant reduced cutting-tool wear, improved machinability, and increased service life of cutting-tool.

Fig. 5 The distribution (a), shape (b), and energy spectrum analysis (c) of copper-rich phase by HREM

Corrosion resistance analysis

The corrosion resistance of steel 4Cr16Mo was improved by adding Cu. Figure 6 shows the variation of the corrosion rate with increasing content of Cu in the solution containing 10 wt.% HCl at 25 \degree C for 4Cr16Mo stainless steels. Addition of Cu reduced the corrosion rates of 4Cr16Mo stainless steels in HCl solution. With the increased content of Cu, the corrosion rates of 4Cr16Mo stainless steels in HCl solution decreased. Figure 7 shows the anodic

Fig. 6 Corrosion rates of stainless steels

Fig. 7 Polarization curves of stainless steels

polarization curves of 4Cr16Mo, 4Cr16MoCu1.1, 4Cr16MoCu1.4, and 4Cr16MoCu1.9. It was clear that the equilibrium potential of 4Cr16Mo increased with the increase in the content of Cu. In addition, nickel increased the solubility of copper in the steel; the role of nickel is an assist elect of copper for the improvement of the corrosion resistance [[9\]](#page-4-0). The results showed that the corrosion resistance of stainless steel with copper was better than that without copper.

Conclusions

Both the machinability and corrosion resistance of stainless steel 4Cr16Mo were obviously improved by adding Cu. The vibration amplitude of 4Cr16Mo with copper was lower than that of 4Cr16Mo without copper, and the vibration amplitude of 4Cr16MoCu1.4 was the lowest. The tool wear of 4Cr16Mo with copper was less than that of 4Cr16Mo without copper, especially stainless steel 4Cr16MoCu1.4. So, when the content of copper in the stainless steel 4Cr16Mo was 1.4%, the machinability of stainless steel was optimal. With the increase in the content of copper, the corrosion rate of stainless steel 4Cr16Mo decreased, and the equilibrium potential of stainless steel increased. In addition, from the observation of EBSD and HREM, it can be seen that Cu-rich phases were dispersed in the stainless steel and determined to be about 10 nm.

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