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Application of Low Temperature Liquid Sulfurization Catalyzed with Rare Earth on Cr12 Impacting Die

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Abstract: One kind of quenched Cr12 steel dies for impacting stainless steel wire rope (SSWR) was treated by low temperature liquid sulfurization catalyzed with rare earths, in order to extend their service life for assuring the continuity of production line, and simultaneously improve the surface quality of SSWR obtained. After immerged into the melting sulphur containing 4% (mass fraction) of LaF_3 and 1% of $CeCl_3$ at 463 K for 4 h, the sulfurized dies were very smooth and black, with little distortion and hardness loss. They exhibited a certain extent of corrosion-resistance in air due to the coexisting rare earths in the sulfurized layer. Optical observations showed that the sulfurized layer was uniform and had scale-like structure. The trail of machined SSWR indicated that the production capacity of sulfurized dies had been doubled and the replacing period on line was postponed. SEM morphology also proved that the wear extent of cavities on sulfurized dies decreased greatly and the surface quality of SSWR obtained was improved markedly.

Key words: application; sulfurization; Cr12; die; stainless steel wire rope; rare earths
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In recent years, stainless steel wire ropes (SSWR) have been used in many fields of industry owing to their excellent properties, such as good corrosion and heat resistance, high plasticity and tensile strength, and long fatigue life, etc.[1,2] As is known, SSWR can be obtained by deep drawing, twisting, folding and impacting in a variety of dies and accessory equipments[3]. Among them, the drawing dies, through which steel wires are drawn to reduce their diameters, and the impacting dies, through which steel ropes are twisted and impacted to avoid wires loosening, are the main tools which should possess prominent wear resistance. Therefore, with the rapid increase in their demand, the new lubrication technology integrated into the drawing processes is required for the improvement of production efficiency and surface quality of SSWR.

Our recent studies have demonstrated that a new sulphurizing process, termed as low temperature liquid sulfurization catalyzed with rare earths (LTLS)[4], possesses some virtues such as low distortion and hardness loss of machined units, without the potential CN^- pollution problem existing in the traditional sulfurizing processes[5], and easy operation. The sulfurized layers thus obtained exhibit certain extent of corrosion-resistance in air due to rare-

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earth additions[4]. Besides, tribological characteristics of sulfurized steel are very good[6], similar to some other metal sulfides such as MoS_2, WS_2, etc.[7~10]. Considering that excellent lubrication is usually required for high quality SSWR and the new sulfurizing processing technique can be united with tempering procedure for Cr12 impacting dies, it should be particularly suitable for solid lubrication of the impacting die cavity. The attempt of this work was to ameliorate quenched Cr12 impacting dies with the new sulfurizing processing technique instead of conventional tempering. The improvement extent of machining capacity for the sulfurized dies on the production line of SSWR was also evaluated, in which the surface quality of SSWR and the lifetime of dies were supposed to be enhanced simultaneously, in order to keep the continuity of production line.

1 Experimental

The stainless steel wire ropes of $\Phi\ 7 \times 7 - 1.59$, made of 0Cr18Ni9, and the Cr12 impacting dies were from Fasten Group of China. The compositions and hardness of the materials are shown in Table 1. After interception from the production line, all samples of SSWR and impacting dies were ultrasonically cleaned in acetone for subsequent scanning electron microscope observation (SEM).

The SSWR of $\Phi\ 7 \times 7 - 1.59$ consists of six facial bunches and one core bunch with hexagonal cross section. Every facial bunch includes six facial wires and one core wire, 0.20 and 0.22 mm in diameter, respectively. Another core bunch contains seven wires with a diameter of 0.22 mm. The wires were deep-drawn from wire rods of 4 mm in diameter. Compared with the original wire rods ($HV_{0.05}$ 188 ~ 204), the formed stainless steel wire ropes were much harder with a Vickers hardness of $HV_{0.05}$ 584 ~ 613, i.e., the SSWR were greatly deformed and work-hardened. Hence, impacting dies with high hardness ($\geqslant$HRC55), highly finished and anti-corrosive surface, are required for continuous production of high quality stainless steel wire ropes.

Conventional impacting dies are made of quenched and low-temperature tempered Cr12 with a hardness of approximately HRC57-62. In our present study, low temperature liquid sulfurization (LTLS) was adopted to substitute for low-temperature tempering in order to get better friction-reducing behavior. It is practicable and economical since low-temperature tempering and new sulfurizing processing for Cr12 can be performed at approximately the similar temperature range. That is to say, new sulfurizing processing can be compatible with the machining process of Cr12 impacting dies.

Hereon, referred to our recent study[4], the quenched Cr12 dies were sulfurized at 190 ℃ for 4 h using a melting liquid containing 95% of S, 4% (mass fraction) of LaF_3 and 1% of $CeCl_3$, and then placed in a solution of 15% (mass fraction) MoS_2 at 100 ℃ for 0.5 h. Prior to sulfurization, Cr12 dies were dipped into an acid solution for 30 min and subsequently rinsed by water for 10 min. A sulfurized layer of uniform thickness was believed to be formed on the quenched Cr12 substrate. The morphology and composition of this layer were analyzed by scanning electron microscopy (SEM) equipped with energy-dispersive X-ray (EDX) spectrometry. Additionally, phase analysis of sulfurized coating on the quenched Cr12 substrate was performed by X-ray diffractometry (XRD). Hardness of sulfurized Cr12 samples were obtained from Rockwell hardness tester and HX-200 micro-hardness tester with Vickers indenter. After sulfurization, the sulfurized impacting dies were installed on the production line to impact the stainless steel wire ropes. Furthermore, sulfurized dies were studied on the trail of operation with a wire-moving rate of 8 $mm \cdot min^{-1}$, contrasted with unsulfurized dies. The morphology of sulfurized die cavities and wire surface were examined by SEM to evaluate the improvement in machining-ability of sulfurized-die.

2 Results and Analysis

2.1 Morphology and characteristics of sulfide-coated impacting die

The surface macro-and micro-morphology of sulfurized Cr12 impacting dies are shown in Figs. 1 (a)

Table 1 Compositions and hardness of 304 stainless steel ropes and sulfide layer on Cr12 substrate

Materials	Alloy chemical composition/(%, mass fraction)								Hardness
	C	Si	Mn	P	S	Cr	Ni	Fe	
304 stainless steel	$\leqslant$0.07	$\leqslant$1.00	$\leqslant$2.00	$\leqslant$0.035	$\leqslant$0.030	17.00 ~ 19.00	8.00 ~ 11.00	Bal.	Rod: $HV_{0.05}$ 188 ~ 204, SSWR: $HV_{0.05}$ 584 ~ 613
Cr12 steel	2.00 ~ 2.30	$\leqslant$0.40	$\leqslant$0.40	$\leqslant$0.030	$\leqslant$0.030	11.50 ~ 13.00	–	Bal.	Quenched: HRC 59-63, Sulfurized: HRC 57 ~ 62
Sulfide layer	–	–	–	–	50.67	4.98	–	42.35	$HV_{0.05}$ 67 ~ 72

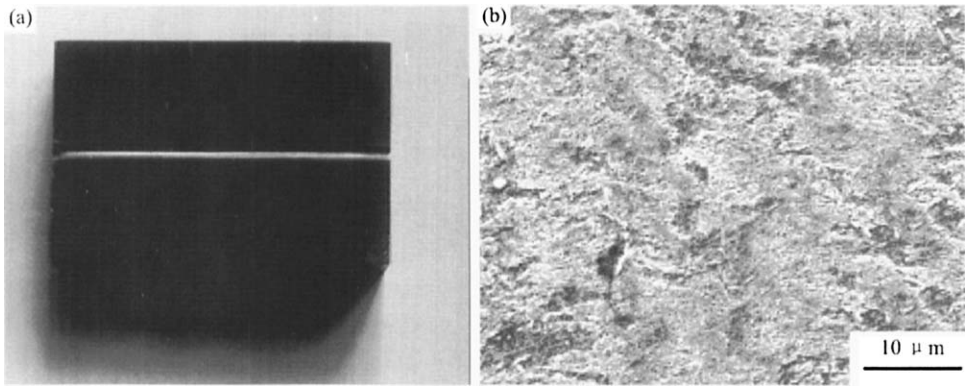

Fig. 1 Surface morphology of a Cr12 impacting die after hybrid sulfudizing
(a) Macroscopic morphology; (b) Microscopic morphology by SEM

and (b), respectively. It shows that the surface of the sulfurized die is very smooth and black in color, while a scale-like sulfide structure is distributed over the whole surface. As is shown in Ref. [4], the sulfurized layer on the surface of Cr12 steel die was uniform with a thickness of over 10 μm. X-ray diffraction spectrum of the sulfurized Cr12 sample followed by immersed in MoS_2 is shown in Fig. 2, which dominantly consisted of FeS and MoS_2 phases. A facial scanning with EDAX gave the composition of sulfurized layer on the treated Cr12 die, as shown in Table 1. The content of S in this result is rather high due to the coexistence of MoS_2 and it is very difficult to distinguish Mo from S by electron probe (their diffraction peaks are nearly overlapped).

The hardness of sulfurized Cr12 dies and tempered dies are shown in Table 1. Hardness tests proved that sulfurized Cr12 die maintained a hardness of about HRC59 with little hardness-loss. Moreover, optical observations showed that sulfurized dies exposed to workshop air at room temperature for four weeks still kept clear surface without corrosive pits, probably, owing to the addition of rare earths[4]. Obviously, sulfurized dies, treated by low temperature

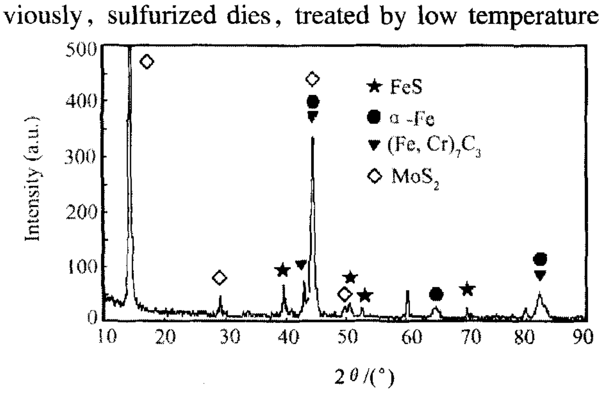

Fig. 2 X-ray diffraction spectrum of a hybrid sulfurized Cr12 die

liquid sulfurization catalyzed with rare earths, completely satisfy the essential requirements of industrial applications.

2.2 Surface state of employed sulfide-coated dies

A sulfurized impacting die was installed at the production line to impact the stainless steel wire ropes with a length of 1500 m. The representative sections of unsulfurized Cr12 die (UD) and sulfurized Cr12 die (SD) were observed and the results are presented in Figs. 3 and 4, respectively. The samples of dies were numbered referred to the quantity of SSWR machined by them, such as UD-1 (unsulfurized Cr12 die after machining SSWR for about 1.5 km long), SD-20 (sulfurized Cr12 die after machining SSWR for about 30 km).

As is shown in Fig. 3, the trumpet mouth on the unsulfurized die, which had machined SSWR for about 1.5 km, was worn more seriously than other sections. Therefore, the morphology of the trumpet mouth on the sulfurized die and the unsulfurized die were compared to evaluate the lubricant effects of sulfurization (Fig. 4). It can be seen that, under the same working conditions, there is slight difference between them for the first batch of SSWR because the cavities have been only worn lightly at the initial stage of usage. The cavity of unsulfurized die for 30 km of SSWR (marked UD-20) was worn rather seriously, while that of sulfurized die for 82.5 km of SSWR (marked SD-55) was worn relatively slight. Obviously, sulfurization processing can improve solid lubricant condition for Cr12 impacting dies and reduce their cavity wear extent. The results on the trail of operating proved that the service life of sulfurized Cr12 dies was double and the replacing interval was prolonged in favor of ensuring continuous production of SSWR.

2.3 Surface morphology of steel wires

SEM revealed the surface morphology of stainless steel wires intercepted from SSWR before impacting (Fig.5) and after impacting by sulfurized die or unsulfurized die (Fig.6). Herein, samples of SSWR were numbered referred to the impacting die and the sequence they were machined, such as UW-1 (the first batch of SSWR machined by unsulfurized Cr12 die), and SW-20 (the twentieth batch of SSWRs machined by sulfurized Cr12 die).

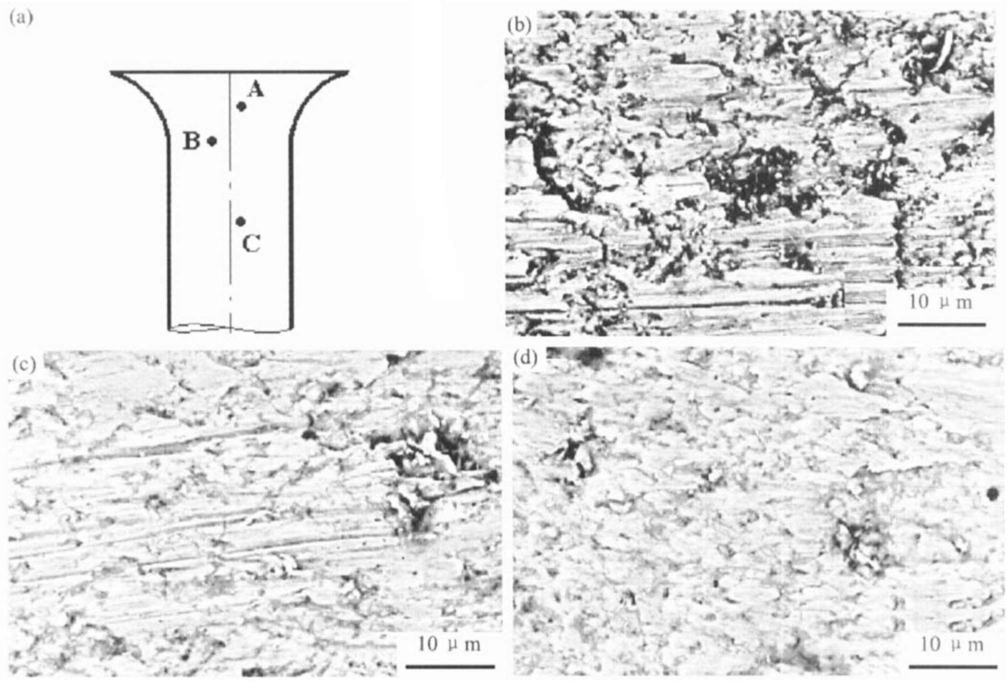

Fig.3 SEM morphology of working face on an unsulfurized Cr12 impacting die
(a) Observation points; (b) Trumpet mouth near A point; (c) Transition area near B point; (d) Coral area near C point

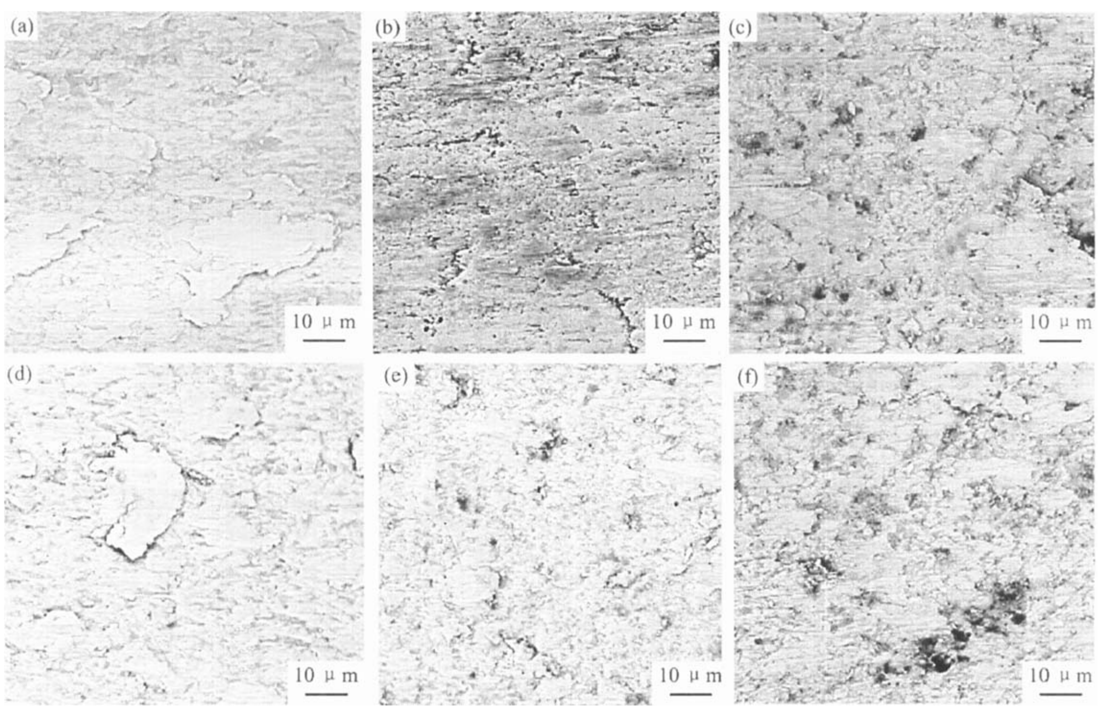

Fig.4 SEM morphology of trumpet mouth on sulfurized die and unsulfurized die at different running time
(a) UD-1; (b) UD-20; (c) UD-50; (d) SD-1; (e) SD-20; (f) SD-55

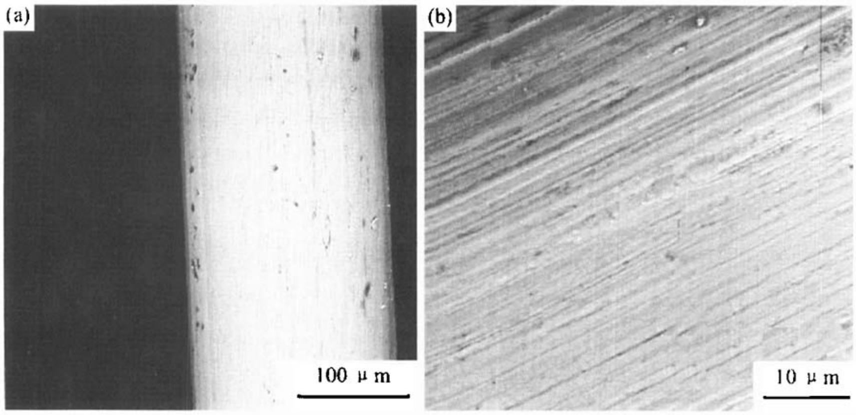

Fig.5 Surface morphology of stainless steel wire before impacting
(a) At a low magnification; (b) At a higher magnification

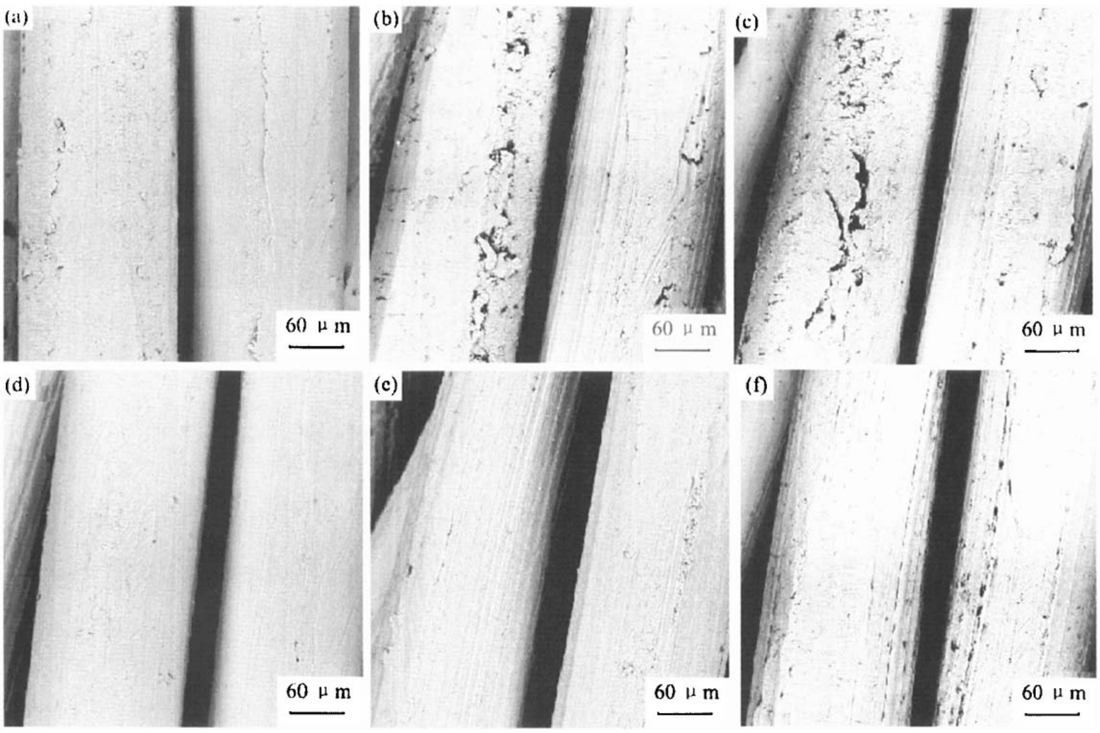

Fig.6 Morphology of SSWRs impacted by sulfurized die or unsulfurized die
(a) UW-1; (b) UW-20; (c) UW-50; (d) SW-1; (e) SW-20; (f) SW-55

As is shown in Fig.5, there are a lot of traces parallel to the drawing direction on the wire surface, which were formed during the drawing process. These are unavoidable common defects. As shown in Fig.6, some grinding traces, which are evidently different from the drawing defects in Fig.5, can be seen on the surface of the first and twentieth batches of SSWR machined by unsulfurized die. These traces have a certain degree of relation to the drawing direction. On machining the fiftieth batch of SSWR, the unsulfurized die had to be changed due to serious grinding traces (Fig.6(c)). Whereas, when impacting by sulfurized die, the grinding traces of the fifty-fifth batch of SSWR are still shallow. The SSWR shows clear cylinder surface with trivial scrapes. Especially, the surface quality of SW-55 is better than that of UW20. It is obvious that the surface quality of SSWR impacted by sulfurized dies is improved greatly.

3 Discussion

As shown above, the new sulfurizing processinvg is highly compatible with the machining process of Cr12 impacting dies. This processing could substitute for low-temperature tempering due to their approximate treatment temperature. Apparently, the hybrid sulfurizing technology could improve greatly the lifetime of Cr12 impacting dies and increase the performance-cost ratio. While the raw material and technological processes keep unchanged, the surface quality and productivity of SSWR will be improved markedly.

The sulfurized Cr12 dies have a good friction-reducing effect on the impacting process of SSWR due to the lubricating function of sulfurized layer, which has been proved by on-line operating results. The phenomenon can be explained referring to the theory of adhesion wear. As is shown in Fig. 7, when a stainless steel wire rope passes through Cr12 die, it is subjected to the action of friction force (T), drawing force (Q) and lateral pressure (P)[11]. According to the traditional Amontous friction formula: $T = \mu P$[12], it is feasible to reduce the friction force between the die and wire ropes by decreasing the friction coefficient (μ) or lateral pressure in order to improve the surface quality of SSWR. As is shown in Table 1 and referred to Ref. [4], the sulfurized layer on Cr12 substrate is extraordinarily soft and difficult to adhere to substrate, which would lead to obvious decrease in the friction force between the sulfurized Cr12 die and SSWR. Therefore, the service life of Cr12 impacting dies and surface quality of SSWR have been improved markedly due to light wear rate between them.

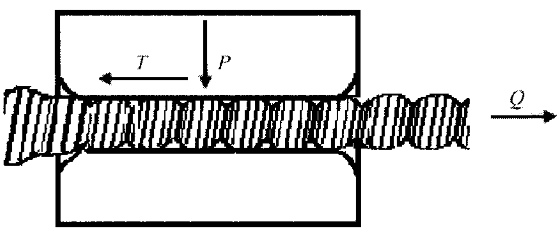

Fig. 7 Schematic illustration for stress state of SSWR through Cr12 die

Furthermore, LTLS can be widely used to produce other kinds of steel wire ropes beside SSWR. However, further research linked with its service condition should be done in order to quantitatively evaluate the improving effect of solid lubricating on the impacting dies and to guide its optimization design. Therefore, some questions still need to be solved at present. For example, the online measurement of friction coefficient between steel wire ropes and impacting die. According to Amontous law, it could be obtained by measuring the drawing force (Q) and lateral pressure (P) of steel wire ropes passing through the impacting die. Then, the appropriate thickness of sulfurized layer might be designed to improve its economic benefits. Besides, the sulfurizing technology could be tried to apply to other important wear-resistant parts including the drawing dies and wire-disk couples.

4 Conclusions

1. With the catalyzing of rare earths, uniform sulfurized layer was obtained on quenched Cr12 dies by low temperature liquid sulfurization. The treatment was performed at 463 K for 4 h using a melting liquid containing 95% (mass fraction) of S, 4% of LaF_3 and 1% of $CeCl_3$.

2. The sulfurizing processes, in substitution for the tempering procedures, are compatible with machining technique of Cr12 dies without remarkably increasing the production cost. The sulfurized dies have very smooth and black surface, little distortion and hardness loss, even a certain extent of corrosion-resistance in air.

3. The surface quality of SSWR, machined with sulfurized Cr12 die, was improved remarkably due to decrease in deformation resistance during impacting course. Meanwhile, the service life of Cr12 impacting dies was doubled in favor of SSWR continuous production.

4. The low temperature liquid sulfurization technique possessed some virtues (such as low cost, safety, easy control, etc.) and would find wide industrial applications in the drawing production line, with Cr12 impacting die as a representative.

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