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Bar and Wire Steels for Gears and Valves of Automobiles —Eco-friendly Free Cutting Steel without Lead Addition—†

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Abstract:

Free cutting steel consists of two types, one for machine structural use and the other based on low carbon steel for hard cutting, such as SAE 12L14. Conventionally, Pb has been added to free cutting steels to improve their machinability, but Pb in steel is thought to have a harmful effect on the human body. Therefore, as alternatives to Pb addition in free cutting steels, JFE Steel and NKK BARS & SHAPES studied graphite precipitation in the steel and control of the sulfide morphology by the chemical composition and developed new Pb-free free cutting steels based on these respective concepts. In the graphite-type free cutting steel for machine structural use, JFE Steel realized machinability equal to that of the Pb-added steel by controlling the state of existence of C in the steel, and achieved an excellent balance of cold workability and high fatigue strength after quenching and tempering. As a substitute for the low carbon Pb-added free cutting steel (SAE 12L14), NKK BARS & SHAPES developed a steel with improved machinability by crystallizing large sulfide inclusions, which is realized by increasing S addition while also adding Cr on the basis of the estimation from the calculated phase diagrams.

1. Introduction

Free cutting steels with Pb addition are widely used as materials for automobile and industrial machinery parts. However, in recent years, the use of Pb has been considered a problem from the viewpoint of environmental protection.

Free cutting steels can be broadly classified into two types, (1) a free cutting steel for machine structural use, in which cold forgeability and high strength, are required simultaneously with machinability, and (2) so-called low carbon free cutting steels, in which machinability with a low carbon composition is the primary requirement, as represented by SAE 12L14.

As alternatives to Pb addition for improving machinability, JFE Steel and NKK BARS & SHAPES developed free cutting steels by utilizing graphite precipitation in the steel and controlling the sulfide morphology by the chemical composition of the steel, corresponding to these respective applications. This paper introduces these steels.

2. Graphite-Precipitation-type Pb-free Free Cutting Steel for Machine Structural Use

2.1 Background of Development

The steel for machine structural use is required to possess machinability, fatigue strength after quenching and tempering, cold forgeability, and so on. Because inclusions, including Pb added to improve machinability, impair fatigue strength and cold forgeability, it had been considered difficult to satisfy these property requirements simultaneously. Therefore, the development of a steel which could satisfy the requirements of machinability, fatigue strength after quenching and tempering,

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and cold forgeability without Pb addition to the steel has been desired.

Based on this background, a free cutting steel which possesses high fatigue strength and does not require Pb addition had been strongly desired. The key point for realizing a material with these features was to discover some means of improving machinability without reducing fatigue strength.

In this development, as an alternative to Pb addition and inclusion control by free cutting additives, control of the state of C existing in the steel was studied as a completely unprecedented factor for improving machinability. The most important feature of this development is that C which normally exists in steel in the form of cementite is changed to graphite. However, in steels for machine structural use, which have a hypoeutectoid composition, industrial use of graphite had been difficult with the conventional technology.

This chapter describes the chemical composition for enabling industrial graphite precipitation and its effect on the properties of steel for machine structural use.

2.2 Concept of Development

2.2.1 Use of graphite to improve machinability-fatigue strength balance

The concept of utilizing graphite in the developed steel is shown schematically in **Fig. 1**. Changing hard cementite to graphite makes it possible to soften the steel and thereby improves machinability. Machinability is also substantially improved by the lubricating action of the graphite on the tool surface. On the other hand, because graphite particles are redissolved into the matrix by heating in the quenching process after machining, graphite which can become a stress concentrator is eliminated, avoiding deterioration in fatigue strength. The dissolved C also improves the hardenability of the steel, resulting in improved strength.[1)]

Although there are examples of graphitization of the C content in high carbon steels and cast iron,[2)] the application of these materials to machine structures is difficult from the viewpoint of toughness. On the other hand, because an extremely long time is required for graphitization of the cementite in steels for machine structural use which have a hypoeutectoid composition, shortening of the graphitization treatment time is essential for industrial use of graphite.

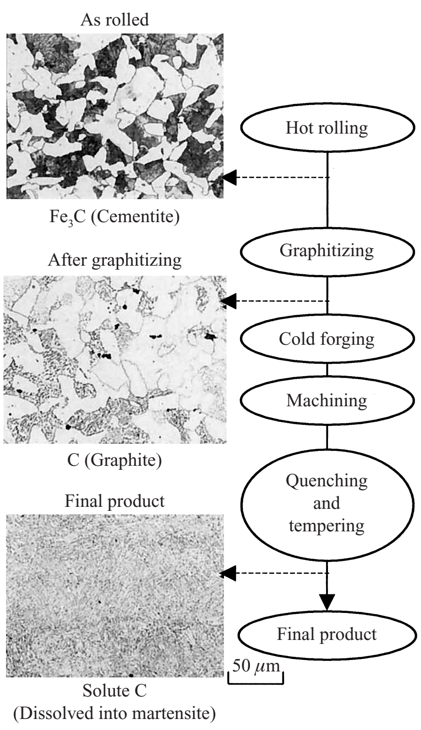

Fig. 1 A concept of utilizing graphites in the steel to achieve workability together with high strength

2.2.2 Thermodynamic stability control of cementite

Si and Cr are the main alloying elements in steel for machine structural use. Therefore, in order to shorten the graphitization time, the effects of Si and Cr on the stability of cementite in steel were studied using a thermodynamic database, Thermo-Calc. **Figure 2** shows the results of a calculation of the equilibrium atomic fraction of the cementite phase at 700ºC with the addition of these alloying elements to the base composition of Fe-0.45 mass%C. In a pure Fe-C alloy, cementite does not exist in an equilibrium phase. However, when Cr is added, cementite exists as an equilibrium phase, and its equilibrium atomic fraction increases with Cr addition. On the other hand, with the Fe-0.45C-0.6Si base composition, the equilibrium atomic fraction of cementite at a given Cr content is reduced by Si addition. Like Cr, Mn is an element which increases the stability of cementite in steel.[1)] In the field of cast iron, Yamanaka et al.[2)] reported that Cr and Mn increase the stability of cementite by replacing Fe atoms in the cementite, whereas Si reduces cementite stability by dissolving in trace quantity in the cementite. The same tendency was also confirmed in the hypoeutectoid steels.

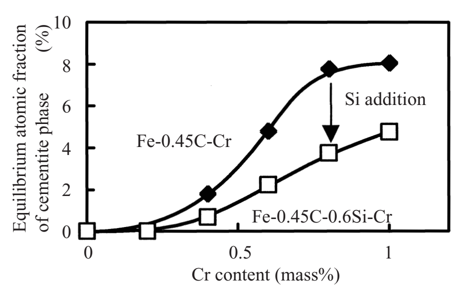

Fig. 2 Effects of Cr and Si on stability of cementite phase at 700°C

Table 1 An example of chemical composition of the developed steel (mass%)

	C	Si	Mn	Cr	B	N
Developed steel	0.45	0.6	0.3	trace	0.002 0	0.004 0
JIS S45C	0.45	0.25	0.8	0.15	–	0.005 0

2.2.3 Increase in number of graphite nucleation sites utilizing BN

Fine dispersion of graphite particles in steel is effective both for preventing deterioration of fatigue strength and for shortening the graphitization time. To achieve fine dispersion of graphite particles, it is necessary to increase the number of nucleation sites. In this development, acceleration of graphite nucleation by precipitates in the steel was studied. Although nucleation of graphite particles was accelerated by the existence of various types of precipitate in the steel, BN was an extremely effective nucleation site.[3,4)]

In addition to the crystallographic structure of the precipitates, graphite and BN also bear an extremely close resemblance in terms of their precipitation modes. Therefore, epitaxial formation and growth of graphite on the surface of BN are easy, and BN in steel can be used very effectively as a graphite nucleation site.

Based on these results, a chemical composition with the following features was selected for the developed steel. First, in order to destabilize cementite, the contents of Mn and Cr were reduced and that of Si was increased in comparison with the conventional steel for machine structural use. To increase the amount of BN which can serve as a nucleation site for graphite, the contents of B and N were optimized. An example of the main chemical composition of the developed steel is shown in **Table 1** in comparison with the JIS S45C as a steel for machine structural use.

Because graphitization of all cementites in steel is not necessarily required, the necessary properties are obtained by a combination of the reduction in the amount of cementite, accompanying partial graphitization of cementite, and shape control of the remaining cementite. Utilizing a three-phase structure consisting of ferrite, graphite, and spheroidized cementite, refinement of graphite particles simultaneously with a further simplification of softening annealing is possible.

2.3 Features of Developed Steel

Figure 3 shows the balance of machinability and cold forgeability for the developed steel and a conventional steel. As for machinability, the machining time before flank wear of a sintered carbide tool reaches 0.2 mm in the turning test was defined as tool life. Cold forgeability was defined as the compressibility (limit upset ratio) at which cracking occurred in 50% of the sampled steel.

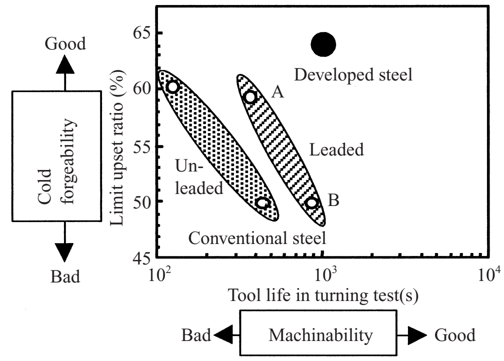

Fig. 3 Balance of machinability and cold forgeability of the developed steel in comparison with the conventional ones

Conventionally, it had been difficult to achieve both machinability and cold forgeability. However, it is possible to realize both properties with the developed steel, which shows an excellent balance of cold forgeability and machinability in comparison with the conventional steel.[3)] For example, in comparison with a steel (A in the figure) with the same cold forgeability, the developed steel showed more than 2 times longer tool life in the turning test, while in comparison of deformation capacity during cold forging with a steel (B in the figure) having an equal tool life, the developed steel showed an excellent limit upset ratio, that is, more than 10 points higher.

The excellent machinability of the developed steel is attributed to the reduction in cementite accompanying graphite precipitation and the lubricating action of the graphite.

Figure 4 shows the relationship between machinability and fatigue strength after quenching and tempering of the respective steels. The developed steel possesses machinability equal or superior to that of the conventional free cutting steel, while it also displays the fatigue

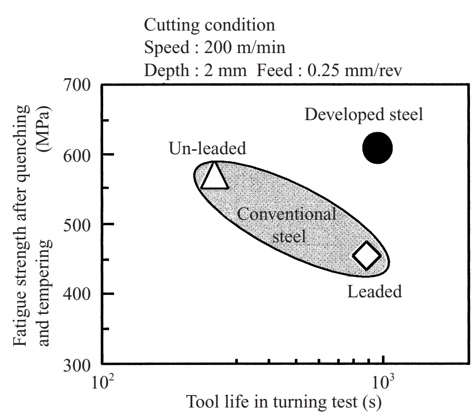

Fig. 4 Tool life obtained in the turning test and fatigue strength of the developed steel in comparison with the conventional ones

strength exceeding 500 MPa after quenching and tempering. In comparison with the size of the inclusions in the conventional free cutting steel, which is on the order of several 10s of micro meter, the graphite particles are fine, at several micro meter, due to the increase in the number of nucleation sites using BN. Furthermore, the graphite in the steel dissolves into the steel matrix due to heating during quenching. It should be noted that, although unsolved BN also exists in the developed steel, its size is about 1 μm. Thus, because the graphite and BN used in the developed steel are both fine, unlike the conventional inclusions, they are thought to have no negative effect on fatigue strength.

The developed steel can be used in a wide range of applications in steel for machine structural use, centering on parts where the conventional Pb-added steel had been used and cold forging applications where machinability is a problem and high strength had been difficult to realize.

3. Sulfide Morphology Control-type SAE 12L14-substitute Pb-free Free Cutting Steel

3.1 Background of Development

SAE 12L14 (JIS SUM24L) is a free cutting steel containing 0.3% Pb and 0.3% S. In automotive applications, it is used in large quantities in transmission oil hydraulic control valves and oil hydraulic hose connectors. Because this free cutting steel has a remarkably high oxygen content, on the order of 150 ppm, it was considered difficult to improve its machinability by adding Ca[5)] or B[6)], which is already used in the steel for machine structural use. Therefore, because it was necessary to conceive a different method, the authors studied S, which is added in large quantity as an element which improves machinability. It has long been known that the machinability of S-added free cutting steels is improved as the size of sulfide inclusions becomes larger.[7)] Therefore, the improvement of machinability by forming large sulfide inclusions was studied from this viewpoint. Because the construction of thermodynamic databases for sulfides has proceeded rapidly accompanying a progress in microalloying technology, this type of database was effectively used in this study.

For the developed steel, first, a phase diagram was obtained by the phase equilibrium calculation of a multicomponent alloy system, and the alloy composition with which large sulfide inclusions could be expected was predicted. Based on the results, confirmation tests were actually conducted, including melting and machinability tests, to decide the alloy composition, and a new Pb-free free cutting steel was developed. The authors wish to note that this new material was developed jointly with Prof. Kiyohito Ishida of Tohoku Univ. and Senior Researcher Katsunari Oikawa of AIST Tohoku: National Institute of Advanced Industrial Science and Technology.

3.2 Concept of Developed Steel

3.2.1 Prediction by phase diagram calculation

The sulfide inclusions which contribute to machinability are crystallized by a monotectic reaction during solidification of the molten steel.[8)] When considering the methods for securing large sulfide inclusions, the following methods are conceivable:

(1) Crystallization of large sulfide inclusions in the solidification stage

(2) Reduction of the forging ratio after crystallization

In case of (1), the reduction of solidification rate is a general method, and increasing the casting cross-sectional profile or slow cooling during casting is conceivable. However, in both methods, it is difficult to effect large changes in the current continuous casting process. On the other hand, in case of (2), if the production of rolling materials of the same size is considered, the reduction of forging ratio by using a smaller casting cross-sectional profile is conceivable. However, as mentioned previously, adoption of a small casting cross-sectional profile results in the reduction in the size of inclusion during casting, and thus would have little effect. The authors therefore believed that a composition system which expands the temperature range in which sulfide inclusions crystallize from the liquid phase would be effective for securing large sulfide inclusions with the existing continuous casting equipment.

Study of the composition system focused on Cr for the following reasons:

(1) Because Cr dissolves in MnS, the increase in the size of sulfide can be expected.

(2) (Cr, Mn) S also improves machinability.

(3) Cr is not harmful to the environment.

In quantifying the composition, a phase diagram was obtained by calculation and used to predict the crystallization temperature range for sulfide inclusions. In calculating the phase diagram, a thermodynamic database for Fe-C-S-Cr-Mn system phase diagrams was constructed[9)] using the CALPHAD (calculation of phase diagrams) method. The Thermo-Calc was used in the phase diagram calculations. Although calculation was done for various compositions, it was found that a large increase in the crystallization temperature range cannot be obtained with a simple increase in S or addition of only Cr; rather, the crystallization temperature range is only expanded by "Cr addition + increase in S content." **Figure 5** shows an example of the calculated phase diagram of the developed steel in comparison with the calculated

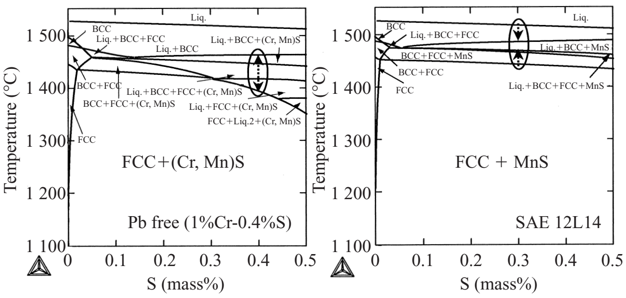

Fig. 5 Examples of calculated phase diagrams

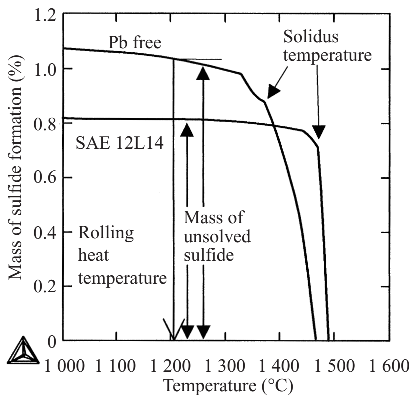

Fig. 6 Mass of unsolved sulfide of Pb free steel in comparison with SAE12L14 steel

result for the conventional steel, SAE 12L14. The crystallization temperature range for sulfide inclusions with SAE 12L14 is 19ºC, but in contrast, the crystallization temperature range for the developed steel is expanded by more than four times, to 93ºC.

In the study process, the amount of precipitated sulfides in the developed steel was also calculated. The amount of sulfide precipitates is obtained, as shown in **Fig. 6**. It can be understood that the amount of sulfides unsolved during reheating for rolling is far larger in the developed steel than in SAE 12L14. It was predicted that this fact would suppress austenite grain growth during reheating and, by functioning as nuclei for the ferrite transformation, would contribute to refinement of the microstructure of the rolled material. The refinement of microstructure improves machinability in the same manner as increasing the size of sulfide inclusions.[10] This is presumably the first time that such new knowledge could be predicted by calculation.

3.2.2 Confirmation experiments with experimental melting furnace steel

Among the compositions which were studied by calculation, test melting and machinability test were actually conducted with the systems which were considered to be candidates for a new Pb-free free cutting steel, and the confirmation tests for the final alloy composition were performed.

The samples were melted in a 150 kg vacuum melting furnace and cast. After the ingots were heated to 1 200ºC, hot forged to the diameter of 85 mm, and annealed at 950ºC, machinability test was performed. The surface cracking condition of the hot-forged materials was observed, and hot ductility was evaluated. **Figure 7** presents examples summarizing machinability and hot ductility in terms of the relationship of the concentrations of Cr, Mn, and S. The figure also shows the results for a comparison steel which was tested at the same time. As has long been known, the composition systems which produce large sulfide inclusions show good machinability. Therefore, as predicted from the phase diagram calculation, it was necessary to add Cr and increase the content of S in order to crystallize large sulfide inclusions. Moreover, with respect to the hot ductility predicted from the solidus temperature, hot forging cracking occurred frequently in the low-Mn, low-Cr region, showing a good agreement with the prediction made by calculation. To examine the microstructure, the ferrite grain size of wire rod produced by heating to 1 200ºC and rolling to a diameter of 11.5 mm was observed. **Photo 1** shows the microstructures. In comparison with SAE 12L14, the ferrite grain size of the developed steel is small. As predicted from the calculated results of the mass of sulfide precipitates in Fig. 6, the mass of unsolved sulfides in the developed steel, when heated to 1 200ºC, is extremely large in comparison with SAE 12L14, and it is therefore considered that the difference in the mass of sulfides is a causative factor in suppressing austentite grain growth in the devel-

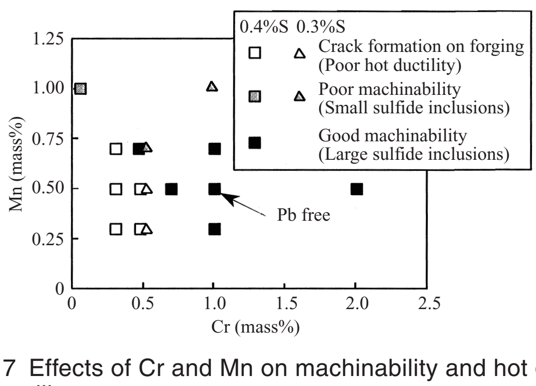

Fig. 7 Effects of Cr and Mn on machinability and hot ductility

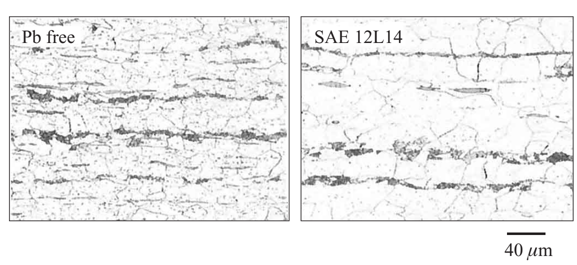

Photo 1 Micro structure of Pb free steel in comparison with SAE12L14 steel

oped steel.

As described above, the 1%Cr-0.4%S steel was adopted as the Pb-free free cutting steel as a result of confirmation tests with experimental melting furnace steel conducted based on predictions from the phase diagram calculations.

3.3 Features of Developed Steel (Steel Melted in 125 t Electric Furnace)

3.3.1 Examples of chemical composition and mechanical properties

An example of the chemical composition and the mechanical properties of the developed steel are shown in **Table 2** and **Table 3**, respectively. The mechanical properties of the developed steel are substantially the same as those of SAE 12L14.

3.3.2 Comparison of sulfide inclusions

Photo 2 shows the micrographs of sulfide inclusions. As examined thus far, the size of the sulfide inclusion is larger in the developed steel.

Photo 3 shows the EPMA element mapping for the sulfide inclusions in the developed steel. Although S, Cr, and Mn were detected in the inclusions as a whole, spots indicating high Cr concentration and high Mn concentration were observed.

3.3.3 Machinability

The machinability equal or superior to that of SAE 12L14 was confirmed under the following conditions:[11)]

Table 2 Chemical composition

(mass%)

Steel	C	Si	Mn	P	S	Cr	Pb
Pb free	0.05	trace	0.58	0.076	0.385	1.00	trace
SAE 12L14	0.07	trace	1.05	0.070	0.340	0.08	0.24

Table 3 Mechanical properties (⌀85 mm)

Steel	YS (MPa)	TS (MPa)	El (%)	RA (%)
Pb free	298	401	36	57
SAE 12L14	289	409	30	43

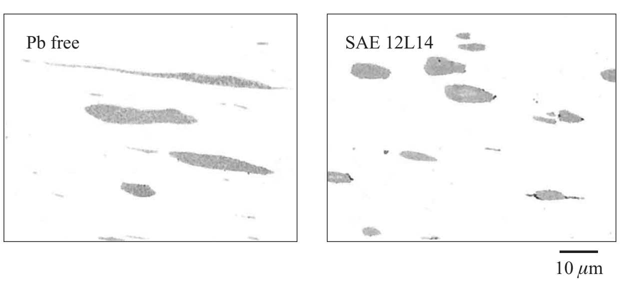

Photo 2 Size of sulfide inclusions of Pb free steel in comparison with SAE12L14 steel

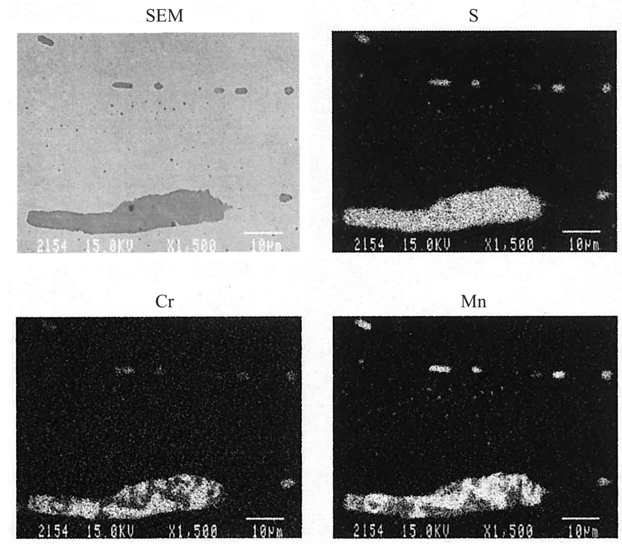

Photo 3 Elements mapping of sulfide inclusions

(1) Turning machinability with carbide, coated carbide, and cermet tools (tool life and machined surface roughness)
(2) Turning machinability with high speed steel tool (tool life and machined surface roughness)
(3) Drilling machinability with high speed steel tool (tool life)
(4) Shape of chip

The relationship between tool wear (flank wear) and the cutting time in turning and the relationship between machined surface roughness (maximum roughness) and the cutting velocity, in both cases with a carbide tool (JIS P20) are shown in **Fig. 8** and **Fig. 9**, respectively. In comparison with SAE 12L14, the progress of tool wear is gradual and the tool life is satisfactory for the developed steel. Similarly, the machined surface roughness of the developed steel is equal to or smaller than that of SAE 12L14 at all cutting velocities, and is therefore satisfactory.

Figure 10 shows the relationship between drill wear and the number of holes drilled with a 10 mm diameter high speed steel drill (JIS SKH51). As for the turning machinability, the progress of drill wear was rapid for SAE 12L14. Abnormal sound was heard when drilling exceeded approximately 1 450 holes, and it became impossible to continue drilling. In contrast, no such phenomena were noted with the developed steel, and it was possible to drill more than 1 500 holes, showing good drilling machinability.

3.3.4 Other properties

Figure 11 shows an example of carburization characteristics. Both carburization property and case depth were similar to those of SAE 12L14.

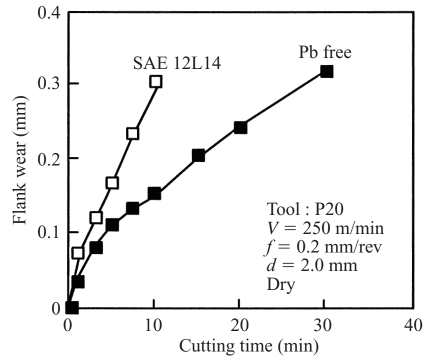

Fig. 8 Flank wear of Pb free steel in comparison with SAE12L14 steel

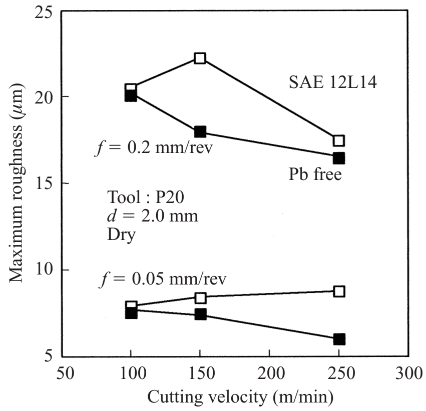

Fig. 9 Maximum roughness of Pb free steel in comparison with SAE12L14 steel

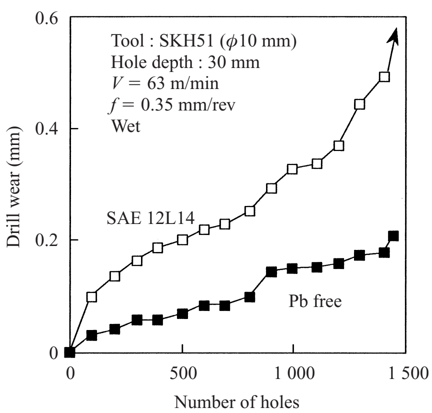

Fig. 10 Drill machinability of Pb free steel in comparison with SAE12L14 steel

4. Conclusion

This paper has introduced two new Pb-free free cutting steels, a free cutting steel for machine structural use and a substitute for SAE 12L14, which were developed in response to customers' needs from the viewpoint of global environmental problems.

The graphite-precipitation type Pb-free free cutting steel for machine structural use contains no substances which are harmful to the environment and possesses excellent machinability and cold forgeability, amply sat-

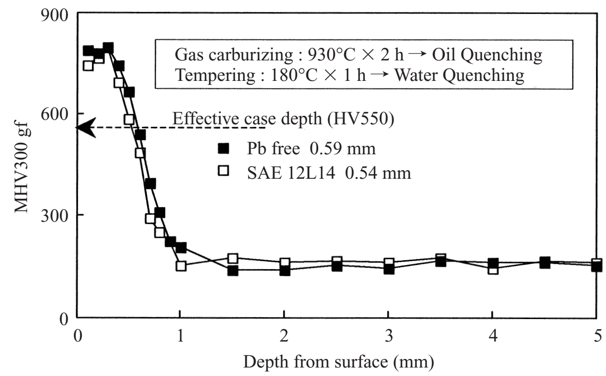

Fig. 11 Carburization characteristics of Pb free steel in comparison with SAE12L14 steel

isfying the property requirements of steel for machine structural use.

The SAE 12L14-substitute Pb-free free cutting steel features improved machinability by large sulfide inclusions. This was possible for the first time by adding Cr and further increasing the S content based on the estimation from the calculated phase diagrams.

With the increasing trend toward green procurement in all industries, there is a tendency to reduce the use of Pb. To meet this need, JFE Steel and its group companies will continue to develop new products to ensure that these Pb-free free cutting steels can be used in a variety of fields.

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