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To develop a stainless steel with excellent oxidation resistance for the metallic substrate of the catalytic converter, influences of La and Zr on the oxidation resistance of 20%Cr-5%Al steel foil and toughness of the hot-rolled sheet of the steel were investigated. La addition combined with Zr increases the oxidation resistance of the steel foil more than La sole addition or La addition combined with Ti, and the Zr addition equal to 1 at Zr/(C+N) in the atomic percent ratio improves the toughness of the hot-rolled sheet of 20%Cr-5%Al-La steel. The newly developed stainless steel, RIVER LITE 20-5USR (20%Cr-5%Al-La-Zr steel) has more excellent oxidation resistance at high temperature compared with conventional steel.



The body can be viewed from the next page.

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## 1 Introduction

Ceramics have been used in the past as the substrate material for automotive catalytic converters. In 1985, a metallic honeycomb made of an Fe-Cr-Al alloy foil was used for the first time in Germany on an automobile as a catalytic substrate.[1] In Japan, Nissan Motor Co., Ltd. adopted a similar stainless steel foil in 1988,[2] and other automobile makers also began to use the stainless steel foil. Such a material for catalytic converters has now been adopted by almost all car makers.

The Fe-Cr-Al alloy used in the metallic honeycomb has long been known as a material with good oxidation resistance, and an addition of rare earth metal has been reported effective for improving the oxidation resistance.[3-6] Kawasaki Steel started many years ago to examine the effect of rare earth metals on the oxidation resistance of 20%Cr-5%Al steel and in particular developed RIVER LITE 20-5SR (20%Cr-5%Al-La-Ti steel) on the basis of a finding that La addition is the most effective.[7-10] This steel has already been adopted by Nissan Motor Co., Ltd. and many other automobile and motorcycle makers as a catalytic substrate, examples of which are shown in **Photo 1**.

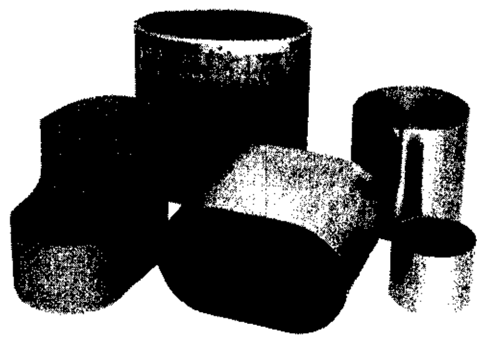

Photo 1 Metallic substrates for catalytic converters

To cope with an ever strengthening automotive emission control from the standpoint of global environmental protection, exhaust gas must be cleaned immediately after starting the engine, and to achieve this, it is necessary to move the installation position of the catalytic converter from the conventional "under the floor" position to the high-temperature zone nearer the engine. This explains why the development of a material with improved oxidation resistance is desired for use in the high-temperature zone.

Further, since Fe-Cr-Al alloys, although excellent in oxidation resistance, are generally brittle, their yield in the manufacturing process are relatively low. In improving the oxidation resistance, therefore, it is important to prevent any lowering of the toughness of the material.

We have investigated the effects of La and Zr on the

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oxidation resistance and on the toughness of 20%Cr-5%Al steel, and developed RIVER LITE 20-5USR (20%Cr-5%Al-La-Zr steel) as a material with an improved producibility and its anti-oxidation lifetime almost three times that of the conventional 20%Cr-5%Al steel. The present report describes this development and introduces the characteristics of RIVER LITE 20-5USR.

## 2 Effects of La and Zr Contents on Oxidation Resistance and Toughness

### 2.1 Experimental Procedure

The samples were 20%Cr-5%Al steel as the basic composition, with the amounts of La and Zr in the steel made to vary. **Table 1** shows the chemical compositions of the experimental heats. The La- and Ti-added steels are the same as R20-5SR used in the metallic honeycombs shown in Photo 1. These steel were cast into 10-kg steel ingots after being vacuum melted in an induction furnace, and were made into a 3-mm-thick hot-rolled sheet and a 50-$\mu$m-thick bright annealed steel foil by the process shown in **Fig. 1**.

The oxidation test was carried out by hanging downwards a coupon measuring 20 mm in width and 30 mm in length, on whose shorter side a hole of $\phi$2 mm was drilled, in a 1 200°C tubular electric furnace in the air. The mass was measured before and after heating the coupon for a certain period.

According to Kawasaki et al.,[11] the oxidation of 20%Cr-5%Al steel foil proceed in the following stages: (1) the 1st stage in which Al in the alloy is oxidized according to the parabolic law, (2) the 2nd stage in which, after the comsumption of all Al, Cr is oxidized according to the linear law, and (3) the 3rd stage in which there is a sudden mass increase and all Cr and Fe in the alloy are oxidized. This oxidation behavior is schematically represented in **Fig. 2**. In the case of metallic honeycomb, when oxidation proceeds to the "breakaway" oxidation of the 3rd stage, the entire foil becomes a brittle oxide and breaks away. Consequently, the life of the foil material ends with the start of oxidation in the 3rd stage. In the present report, the time until this oxidation start is defined as the "lifetime," and is used as an index for evaluating oxidation resistance. In addition, the theoretical mass increment was obtained, when all Al in the alloy foil had been completely oxidized into $Al_2O_3$, and the time when the mass gain curve reaches this value is defined as the "time when oxidation proceeds from the 1st stage to the 2nd stage," thereby obtaining the respective oxidation times for the 1st and 2nd stages.

The toughness of the hot-rolled sheet was evaluated by the Charpy impact test. A JIS No. 4 sub-size test specimen of 3 mm thickness was used, having been worked so that its longitudinal direction was the rolling direction. The test was carried out within a temperature range of 0 to 200°C.

In order to investigate the relationship between toughness and precipitates in the steel, the residue of

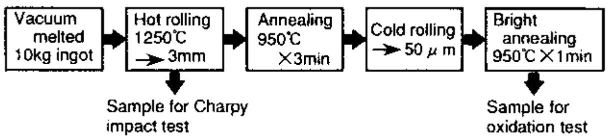


Fig. 1 Experimental procedure for sample preparation

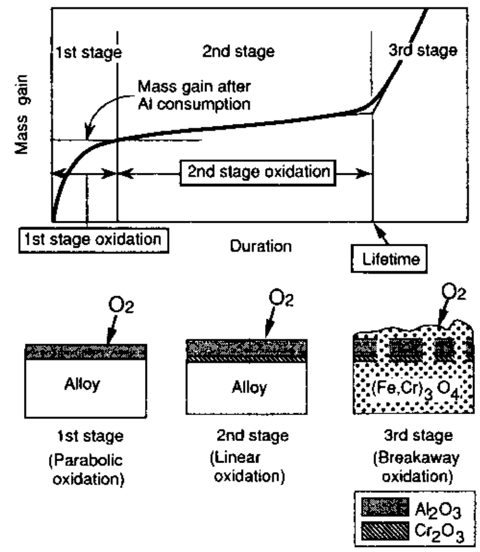


Fig. 2 Schematic representation of oxidation behavior of 20%Cr-5%Al steel foil

Table 1 Chemical compositions of experimental heats (mass %)

| | C | Si | Mn | P | S | Cr | Al | La | Zr | Ti | N |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Base steel | 0.006 | 0.12 | 0.10 | 0.025 | 0.002 | 20 | 5.7 | Tr. | Tr. | Tr. | 0.005 |
| La and/or Zr added steels | 0.006 ~0.014 | 0.10 ~0.14 | 0.09 ~0.11 | 0.021 ~0.026 | <0.005 | 19.5 ~20.5 | 5.5 ~5.9 | Tr. ~0.11 | Tr. ~0.5 | Tr. | 0.003 ~0.008 |
| La and Ti added steel (R20-5SR) | 0.007 | 0.15 | 0.10 | 0.025 | 0.003 | 20 | 5.4 | 0.06 | Tr. | 0.07 | 0.004 |

the hot-rolled sheet was sampled by the electrolytic extraction method, and the kinds of precipitates were identified by X-ray diffraction. The quantity of each precipitate was calculated from the atomic weight by a chemical analysis and from the results of precipitate identification.

## 2.2 Experimental Results and Discussion

### 2.2.1 Oxidation resistance

**Figure 3** shows the oxidation curves for the basic 20%Cr-5%Al steel foil, the La+Zr-added steel foil, and the conventional La+Ti-added steel foil at 1 200°C in the air. The basic steel foil shows a mass increment of $2 \times 10^{-2}$ kg/m$^2$ in a short time, indicating a very short lifetime of about 50 ks. The lifetime of the conventional steel foil to which 0.06% La and 0.07% Ti in mass % are added, is about 150 ks. In comparison, the lifetime of the steel foil to which 0.06% La and 0.09% Zr are added is as long as 600 ks, thereby indicating satisfactory oxidation resistance.

**Figure 4** shows the effects of La and/or Zr additions on the oxidation behavior of 20%Cr-5%Al steel foil. The lifetime of the steel foil to which 0.08% Zr is added solely is almost equal to that of the basic steel foil. However, the lifetime of the steel foil with 0.06% La solely added is more than 500 ks. This shows that the addition of La improves the oxidation resistance of the steel foil. The oxidation resistance-improving effect of La is well known,[7-9,12,13] and the effect per addition quantity is reported to surpass that of Y.[7-9] The additon of 0.09% Zr together with 0.06% La was found to further improve the lifetime to 600 ks. When the Zr content was increased to 0.25%, however, the lifetime conversely decreases by about 30% to 400 ks. This suggests that there is an optimum value for Zr addition; therefore, a more detailed investigation was made regarding the effects of La and Zr additions on the lifetime.

**Figure 5** shows the effects of La on the oxidation duration and lifetime in the 1st and 2nd stages of a steel foil to which 0.08% Zr was added. The oxidation duration of the 1st stage reaches a maximum when the La content is about 0.04%, and when the La content exceeds 0.04%, the oxidation duration becomes constant at 180 ks. On the other hand, oxidation duration of the 2nd stage increases with increasing La content when La content is less than 0.08%, and then becomes nearly constant in the vicinity of 640 ks regardless of La content above 0.08%. The lifetime is characterized by the 2nd stage, because both the variation and absolute value of oxidation duration are larger than those in the 1st stage.

**Figure 6** shows the effect of Zr content on the oxidation duration of the 1st and 2nd stages and on the lifetime of the steel foil to which 0.06% La is added. The oxidation durations of the 1st and 2nd stages were maximized by the addition of a small amount of Zr, and the oxidation duration decreases with increasing Zr content above that amount. The lifetime also reflects the characteristics of the 1st and 2nd stages. This is different from the results shown in Fig. 5, which illustrates the effect of varying La content under constant Zr content, thereby indicating that the Zr content has an optimum value with respect to the lifetime.

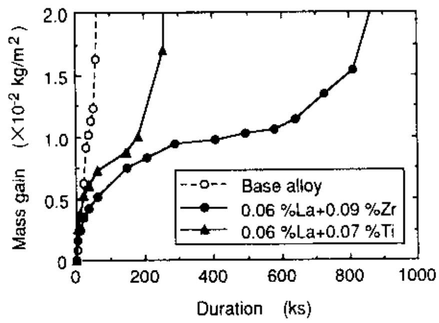


Fig. 3 Oxidation behavior of 20%Cr-5%Al steel foil, La + Zr added steel foil, and La + Ti added steel foil (thickness 50 $\mu$m, oxidized at 1 200°C in air)

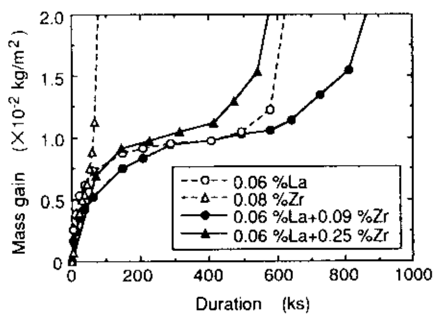


Fig. 4 Effect of La and/or Zr additions on oxidation behavior of 20%Cr-5%Al steel foils (thickness 50 $\mu$m, oxidized at 1 200°C in air)

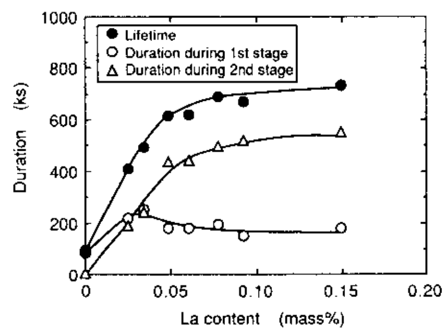


Fig. 5 Effect of La content on duration during 1st and 2nd stages and on lifetime of 20%Cr-5%Al-0.08%Zr steel foil (thickness 50 $\mu$m, oxidized at 1 200°C in air)

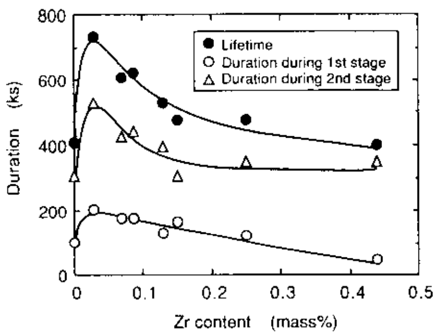


Fig. 6 Effect of Zr content on duration during 1st and 2nd stages and on lifetime of 20%Cr-5%Al-0.06%La steel foil (thickness 50 $\mu$m, oxidized at 1 200°C in air)

Table 2 X-ray diffraction analysis of surface oxides of steel foils (oxidized at 1 200°C for 10.8 ks in air)

| Steel | Strong peak | Weak peak |
|---|---|---|
| Base | $\alpha$-$Al_2O_3$ | $Cr_2O_3$ |
| La addition | $\alpha$-$Al_2O_3$ | $Cr_2O_3$ |
| La and Zr addition | $\alpha$-$Al_2O_3$ | $ZrO_2$(mono*1), $Cr_2O_3$, $ZrO_2$(tetra*2) |
| Zr addition | $\alpha$-$Al_2O_3$ | $ZrO_2$(mono*1), $Cr_2O_3$, $ZrO_2$(tetra*2) |

*1monoclinic, *2tetragonal

Lifetime is governed by the oxidation duration of the 2nd stage, regardless of the amount of La or Zr added. Oxidation of Cr, which obeys the linear law in this stage, proceeds because the oxygen atoms pass through the $Al_2O_3$ layer formed during the 1st stage and are supplied to the interface between the bulk alloy and oxide.[7-9] Consequently, the oxidation behavior of Cr in the 2nd stage is affected by the properties of the $Al_2O_3$ layer formed during the 1st stage. Then a structural analysis of the oxidized layer was carried out.

**Table 2** shows the results of a qualitative analysis by X-ray diffraction of the oxidized layer oxidized for 10.8 ks at 1 200°C in air. In all the steel samples, $\alpha$-$Al_2O_3$ and a small amount of $Cr_2O_3$ were detected. In the La-added steel foil, no oxides of La were detected, whereas, in the only Zr-added steel foil and La + Zr-added steel foil, a small amount of $ZrO_2$ was detected. The improvement in lifetime due to La + Zr addition seems to be related to $ZrO_2$ which was only detected in a small amount, although no details have yet been clarified.

The foregoing result indicates that, in order to maximize the lifetime of 20%Cr-5%Al steel foil to which both La and Zr are added, it is only necessary to increase the La content to 0.08% or above and to add a small amount of about 0.03% Zr.

### 2.2.2 Toughness

Next, the effects of La and Zr content on the toughness of the hot-rolled sheets were investigated. **Figure** 7 shows the effect of La addition on the toughness of steel to which 0.09% Zr is also added, and **Fig. 8** shows the effect of Zr addition on the steel to which 0.04% La is added. With a constant content of Zr, no effect of La content on the toughness of the hot-rolled steel sheets is apparent. However, with a constant content of La, the toughness is improved when the Zr content is increased to 0.10%, but drops when the Zr content is further increased to 0.44%.

The effects of chemical elements on the toughness of 20%Cr-5%Al steel have been reported from several studies. Koike et al.[14] have reported that precipitation of $M_{33}C_6$-type compounds at the grain boundary is the cause of a decrease in toughness. Fukaya et al.[15] have evaluated the toughness of 20%Cr-5%Al steel by the value of [Ti] ([Ti] = Ti $- \frac{48}{12}$C $- \frac{48}{14}$N) and reported that when the value of [Ti] was 0, the toughness reached a

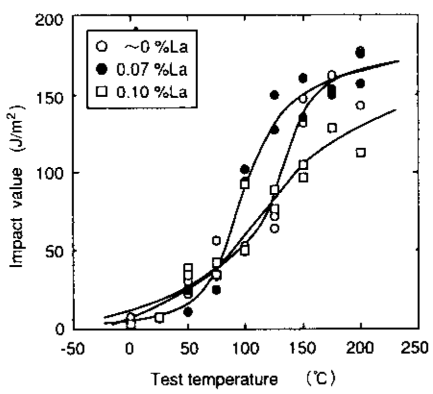


Fig. 7 Effect on La content on toughness of hot-rolled sheets of 20%Cr-5%Al-0.09%Zr steels

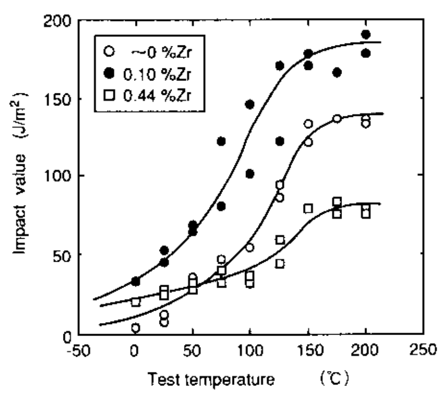


Fig. 8 Effect on Zr content on toughness of hot-rolled sheets of 20%Cr-5%Al-0.04%La steels

maximum.

Thus, in order to understand the effect of Zr content on the toughness of 20%Cr-5%Al-La steel, the temperature $_{v}T_{50}$ at which the Charpy impact value shows 50 J/m$^2$ was evaluated according to the value of Zr/(C + N), which expresses in an atomic percent ratio. The result is shown in **Fig. 9**. The $_{v}T_{50}$ value is smallest when Zr/(C + N) is about 1, and toughness becomes the most satisfactory.

**Figure 10** shows the effects of Zr content added to 20%Cr-5%Al-La steel sheets on the precipitation behavior of the Zr, Fe, Cr and Al contents. The (C + N) content of all these steel sheets is almost constant at 0.015%. In a basic steel which does not contain Zr, the amounts of Fe and Cr precipitated as $M_{23}C_6$-type carbides are very high. AlN is also detected. When a small amount of Zr was added, ZrN was precipitated, and the amounts of the carbidies of Fe or Cr and AlN decrease. When the Zr content is increased and Zr/(C + N) approaches 1, ZrC in addition to ZrN is precipitated to make the carbides of Fe and Cr smaller. Furthermore, when the Zr content is increased and Zr/(N + C) exceeds 1, a large amount of intermetallic compounds of $Fe_3Zr$ in addition to ZrN and ZrC are precipitated. Consequently, the toughness improvement by Zr addition at less than 1 for Zr/(C + N) may be due to a decrease in the precipitation of $M_{23}C_6$-type carbides. The toughness decrease at 1 or above for Zr/(C + N) may be due to a increase in the precipitation of $Fe_3Zr$.

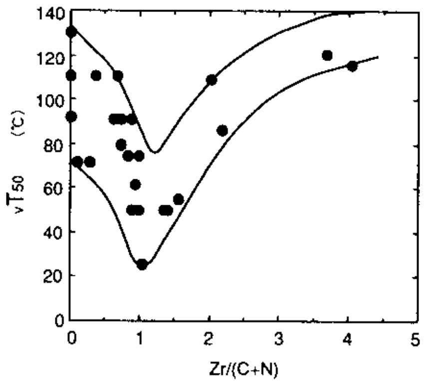


Fig. 9 Effect of Zr/(C + N) in atomic percent ratio on toughness of hot-rolled sheets

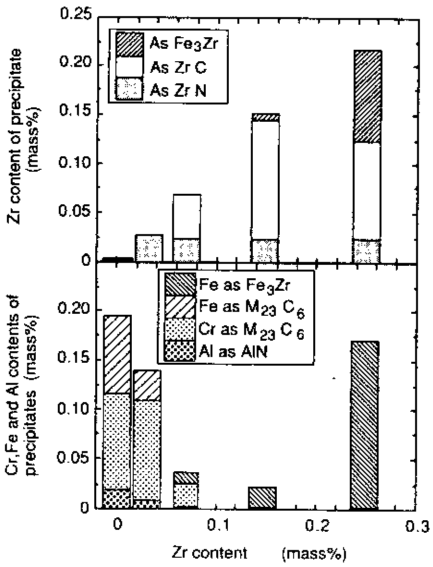


Fig. 10 Effect of Zr content on precipitation behavior of Zr, Cr, Fe and Al in hot-rolled sheets

## 3 Characteristics of R20-5USR

An investigation into the effects of La and Zr on the oxidation resistance of 20%Cr-5%Al steel foil and on the toughness of the hot-rolled steel sheet indicated that the oxidation resistance can be improved by increasing the La content to 0.08% or above, and that the toughness of the hot-rolled sheet can be improved by Zr addition so that Zr/(C + N) expressed as an atomic percent ratio will become about 1. Here, we selected the composition of the developed steel as 20%Cr-5%Al-0.08%La-0.03%Zr with a 0.01% (C + N) content by taking into consideration in current steel refining techniques.

To confirm the characteristics of the developed R20-5USR steel, we carried out a manufacturing experiment using 5-t experimental steel ingot. **Table 3** shows the representative chemical composition of the developed R20-5USR steel. The results of the experiment confirmed that $_{v}T_{50}$ for the hot-rolled steel sheet was about 70°C compared with about 100°C for conventional steel, thereby verifying satisfactory toughness.

**Figure 11** shows the oxidation resistance at 1 200°C in the air of 50-$\mu$m foil manufactured from the developed steel, and **Table 4** shows the mechanical properties and lifetimes at 1 200°C of R20-5USR and R20-5SR foils. The table indicates that the R20-5USR steel has a lifetime three times as long as that of the conventional steel R20-5SR equivalent. The mechanical properties of

Table 3 Representative chemical composition of R20-5USR (mass %)

| C | Si | Mn | P | S | Cr | Al | La | Zr | N |
|---|---|---|---|---|---|---|---|---|---|
| 0.005 | 0.13 | 0.10 | 0.027 | 0.004 | 20.1 | 5.7 | 0.10 | 0.05 | 0.0042 |

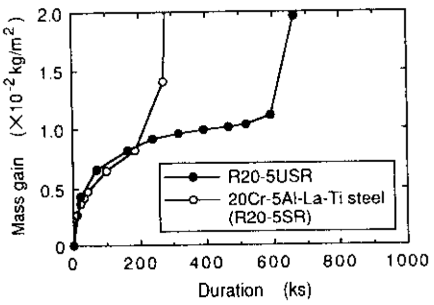


Fig. 11 Oxidation behavior of R20-5USR foil and 20%Cr-5%Al-La-Ti steel (R20-5SR) foil (thickness 50 $\mu$m, oxidized at 1 200°C in air)

Table 4 Mechanical properties and lifetime of R20-5USR and 20%Cr-5%Al-La-Ti steel (R20-5SR) foil (thickness 50 $\mu$m)

| Steel | Mechanical properties | | Lifetime at 1 200°C in air (ks) |
|---|---|---|---|
| | TS (N/mm²) | EL (%) | |
| R20-5USR | 568 | 21 | 600 |
| 20Cr-5Al-La-Ti (R20-5SR) | 588 | 24 | 200 |

the developed steel are the same as those of the conventional steel.

## 4 Conclusions

With an aim of developing a steel not only producible but highly serviceable in catalytic converters placed in the high-temperature zone near the engine, the authors have investigated the effects of La and Zr on the oxidation resistance and toughness of 20%Cr-5%Al steel. The results of this study enabled the development of a highly oxidation-resistant 20%Cr-5%Al steel "R20-5USR.", Findings obtained from this development are summarized as follows:

(1) By adding proper amounts of La and Zr in combination to the basic composition of 20%Cr-5%Al steel, high oxidation resistance can be obtained to a level exceeding that of the conventional steel to which La and Ti have been added in combination.

(2) The lifetime of 20%Cr-5%Al-Zr steel foil increases with increasing La content up to 0.08%, and then lifetime is practically constant with any further La addition above 0.08%.

(3) The lifetime of 20%Cr-5%Al-La steel foil was achieved maximum by adding a small amount of Zr. Above this level, the lifetime decreased with increasing Zr content.

(4) The toughness of a hot-rolled sheet of 20%Cr-5%Al-La steel was highest when Zr/(C + N) expressed in an atomic percent ratio was about 1.

(5) The R20-5USR developed steel has a lifetime of about three times as long as that of conventional 20%Cr-5%Al steels, and is relatively easy to produce. Its mechanical properties are as good as those of conventional steels.

The authors express their deep appreciation to Nissan Motor Co., Ltd., Showa Aircraft Industry Co., Ltd., AC Rochester GM and Honda Motor Co., Ltd. for supplying the metallic honeycombs shown in Photo 1.

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