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The formation of gold metal fibers during the production of E-glass fibers

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Abstract—We first examined the relation between the solubility of gold and the reduction-oxidation (redox) condition of E-glass, but it was difficult to find a universal relation between the gold solubility and the redox of the glasses. Next, we examined in relation between the solubility of gold and the theoretical optical basicity of the glass and found that the theoretical optical basicity of the glasses was closely related to the gold solubility. We considered ways of increasing the solubility of the gold, probably through the formation of some complex with oxide ions. In the industrial process, no metal fiber was formed when glass composition of theoretical optical basicity larger than about 0.601 was spun.

Keywords: Glass fiber; E-glass; metal fiber; gold; basicity.

1. INTRODUCTION

The quality requirements for E-glass fibers, which are widely used as electrical insulator parts such as printed circuit boards in microcomputers, have been getting more rigorous each year with the developments in the electronics industry. One important demand is to avoid the inclusion of electrically conductive materials, especially metals, in the spun fibers. Figure 1 shows a schematic illustration of the incorporated so-called ‘metal fiber’, which usually consists of gold or NiS; it consists of a metal fiber into the glass fiber. We have already taken some measurements of NiS metal fibers and now we have never seen NiS metal fiber; but we have never studied gold metal fibers.

It is generally known that natural sources for the composition of E-glass contain at least several ppb of gold, so that the formation of gold metal fibers in E-glass fiber

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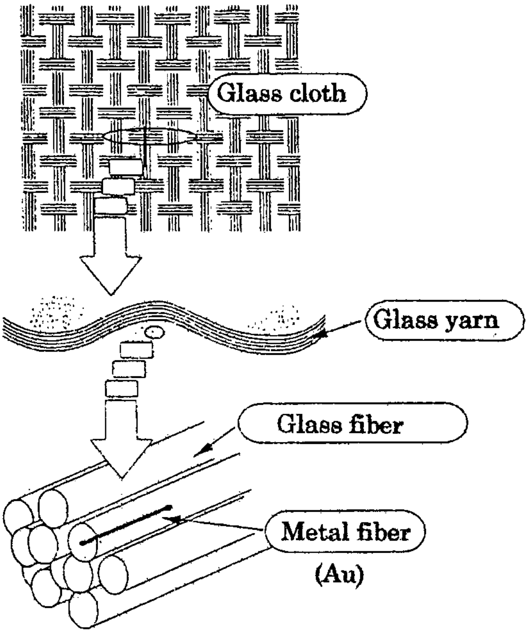

Figure 1. Illustration of gold metal fiber formed in E-glass fibers.

products is considered to be inevitable to some extent even by using modern fiber-spinning systems and techniques. The manufacturers, therefore, have had to develop a mechanical system [1, 2] to inspect the formation of metal fibers during the fiber-spinning process, and to remove every particle of gold metal fiber that remains in the glass fiber produced. Because of the large production losses involved in such a method, the manufacturers have been seeking basic countermeasures to avoid metal fiber formation and hence reduce production costs. A possible approach may be to increase the solubility of gold in the E-glass.

In the present study, the solubility of gold in various molten E-glass compositions was examined in relation to the redox condition or the optical basicity of the glass with the aim of avoiding metal fiber formation by enhancing the solubility of gold.

2. EXPERIMENTAL

As shown in Table 1, the glass composition used in the present study was in the category of ‘E-glass’. A fifty gram batch added with 0.2 wt% of gold powder (average diameter, 5 μm) was melted in alumina crucibles from 1350 to 1500°C in the air for different numbers of hours. In several runs, different amounts of carbon powders (carbon black) were successfully added to the glass batches in order to change the redox ratio during melting. The melts were poured onto a steel plate in the air. The glass samples obtained were subjected to measurements of amount of dissolved gold and the redox ratio.

Table 1.
E-glass composition used in this study

Components	wt%
SiO_2	55
Al_2O_3	14
Fe_2O_3	0.2
TiO_2	0.4
CaO	23
MgO	0.3
Na_2O	0.45
K_2O	0.15
B_2O_3	6
CaF_2	0.5

The solubility of gold in the oxide glass is generally small. Then the excess gold is precipitated as minute particles already in the melt. Some fraction of gold is vaporized in the form of a complex with fluorine included in the batches and deposited at the surface of the melts to form minute particles through decomposition. Other fractions of gold dissolved in the melt sometimes tend to be precipitated as metal colloids during cooling (or at lower temperatures for fiber drawing, surrounding 1200°C) due to supersaturation. These gave different colors to the glass, depending on the amount and size of the colloidal particles.

The gold particles remaining undissolved or precipitated in the resultant glasses were so large as to be observable under an optical microscope or even by the naked eyes. Colloid formation was detectable from coloring or by using UV-VIS absorption spectrometry. Then, the sections of glass in which no gold particles or colloids were detected were isolated and used in the measurements of gold solubility.

The amount of gold dissolved in the glass was analyzed by atomic absorption spectrometry according to the conventional manner as described below. The apparatus used was a Shimadzu AA-6700F atomic absorption spectrometer.

The fraction of ferrous ions, Fe^{2+}, to total iron included in the composition was determined in the form of $FeO/(FeO + Fe_2O_3) \times 100$ (hereafter called 'redox'). The measurement was carried out as follows. First, sulfuric acid and hydrofluoric acid were added to the powdered sample and mixed thoroughly, followed by masking the fluorine with boric acid. Into this mixed solution, 1,10-phenanthrene solution was added, and the pH was adjusted to 3.5 by adding ammonia-water and/or hydrochloric acid. The amount of ferrous ion was determined from the absorption coefficient at 510 nm using a calibration curve made beforehand. Then, ascorbic acid powder was added into that solution and the amount of the total ferrite was determined.

Further, the gold fiber formation during the commercial fiber-production run was examined for various glass compositions, which were still in the E-glass category, as listed in Table 2. Each batch was prepared by using natural raw materials which

Table 2.
Glass compositions for the metal fiber detection

	No. 1	No. 2	No. 3	No. 4	No. 5
SiO_2	54.1	54.5	55.0	54.9	54.9
Al_2O_3	13.6	13.6	14.1	14.2	14.2
TiO_2	0.6	0.2	0.3	0.4	0.4
CaO	23.0	22.5	22.3	23.0	23.0,
MgO	0.6	0.2	1.1	0.2	0.2
Na_2O	0.9	0.3	0.3	0.4	0.4
K_2O	0.1	0.2	0.2	0.2	0.2
B_2O_3	6.2	8.1	5.8	5.9	5.9
SrO	0.1	0.2	0.2	0.1	0.1
CaF_2	0.6	0.05	0.5	0.4	0.4
FeO	0.14	0.1	0.06	0.05	0.06
Fe_2O_3	0.4	0.23	0.2	0.14	0.13
basicity	0.60213	0.60182	0.60099	0.60083	0.60085

should contain at least several ppb of gold. The melting was carried out at 1500°C for 3 h and the temperature of the nozzle for fiber-drawing was set to 1200°C. The diameter of the fiber was adjusted to 10 μm. A metal fiber detector system was used to check the gold metal precipitation in the glass fiber.

3. RESULTS AND DISCUSSION

3.1. Gold solubility and redox of the glasses melted under different conditions

Figure 2 shows the redox, and the gold solubility of the glass melted at different temperatures for 1 h. Both the redox and gold solubility are increased as the melting temperature is raised. In Fig. 3, the melting time dependence on the redox and gold solubility at 1500°C are shown. It is seen that the redox and gold solubility are increased with the increase of melting time in Fig. 3. There is a point that we must be careful of here. In these runs, we used the melting condition that produces lower values of redox, achieved by shortening the melting time. In other words, we must find the conditions such that no metal fiber can be retained at this short melting time. Therefore, experiments were carried out to establish optimal conditions for this short melting time.

The effect produced on the redox and gold solubility at 1500°C by the addition to the glass batches of carbon black as a reducing reagent is shown in Fig. 4. The addition of carbon is seen to lead to increase both the redox and gold solubility. However, compared with the results given in Figs 2 and 3, the increase produced in the redox seems smaller than that expected from the increase in gold solubility.

The results of redox and gold solubility in the glass are presented as a function of analyzed FeO content in Fig. 5. In this run, the FeO content in the glasses was changed by adding some different excess amounts of FeO to the glass batch composition given in Table 1. However, the change in amounts in FeO and/or Fe_2O_3

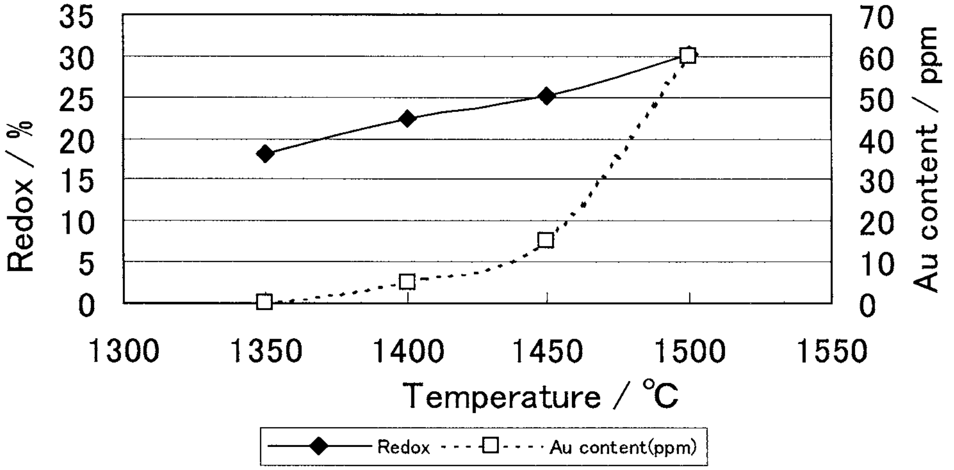

Figure 2. Change of redox and Au content with melting temperature (melting time was 1 h).

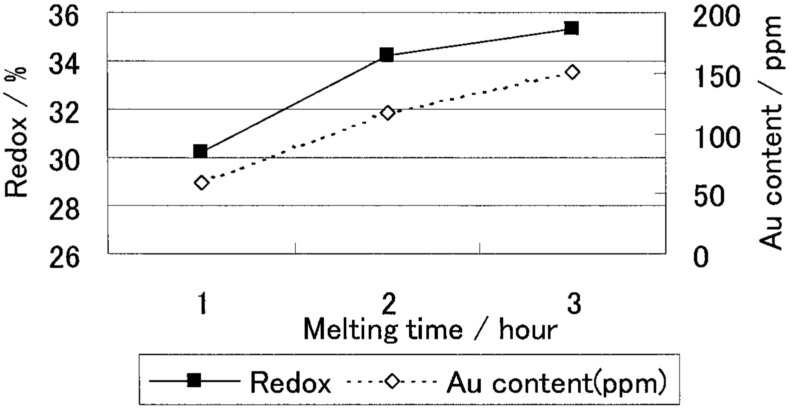

Figure 3. Change of redox and Au content with melting temperature at 1500°C.

content was so small that the resultant composition glasses were still in the category of E-glass. Moreover, all the compositions were changed by addition of carbon (3 wt%). Glass batches were melted at 1500°C for 1 h. As shown in Fig. 5, the gold solubility increased with the increase of FeO content while the redox decreased.

The gold solubility of the glasses melted under different temperatures for different times is summarized as a function of the redox in Fig. 6 by using the data given in Figs 2 to 4. The gold solubility shows a general increase with increase in redox, which suggests that the redox may be applicable as a measurement of the gold solubility of the E-glass. However, this seems peculiar, since it has been accepted that a larger redox value or a reducing environment forces the gold ions to be reduced to elemental gold with formation of colloidal particles in the glass, as has been experienced in the manufacture of gold–ruby colored glasses. So, before accepting the parallelism between the redox and gold solubility shown in Fig. 6,

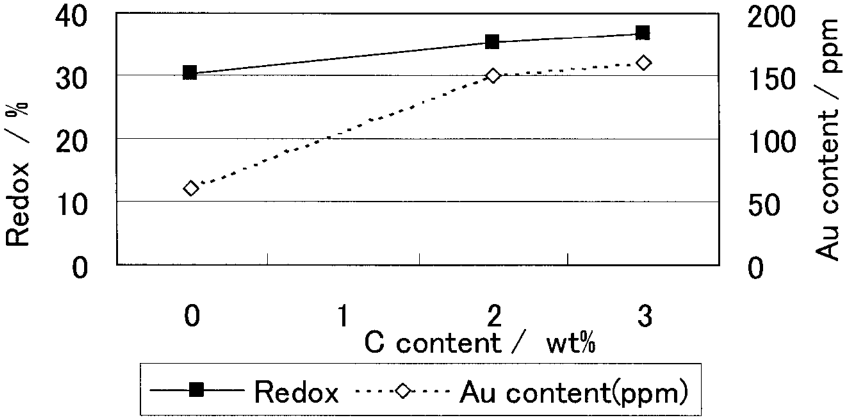

Figure 4. The relationship between the content of added C and redox or/and Au content melted at 1500°C for 1 h.

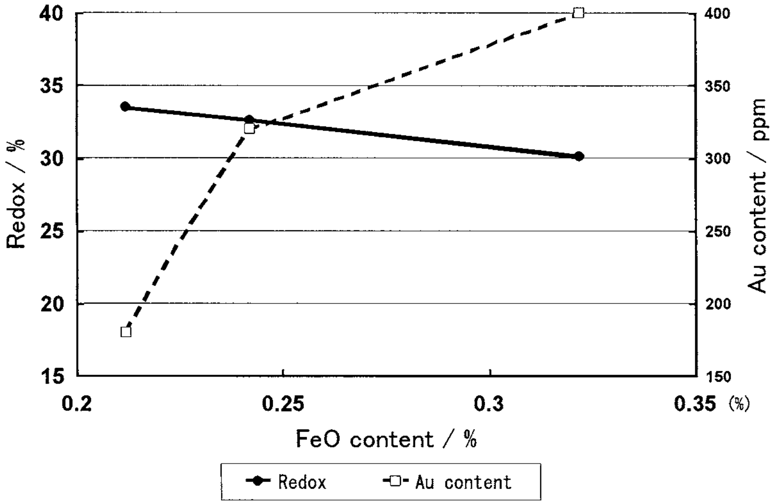

Figure 5. The relationship between FeO content and redox or/and Au content for the E-glass melted at 1500°C for 1 h.

we have to take the following facts into consideration; (1) both the redox and gold solubility are dynamic parameters, in other words, melting temperature and/or time dependent parameters; (2) the dependence of the redox is not always the same as that of the gold solubility, for an example, as suggested from the data shown in Fig. 3; (3) optimal redox and gold solubility may not have been reached within the experimental conditions employed in the present work for the short melting time to make it suitable for actual fiberglass manufacturing conditions. Therefore, the reasonability of the application of the redox as a measure of the gold solubility will be discussed further.

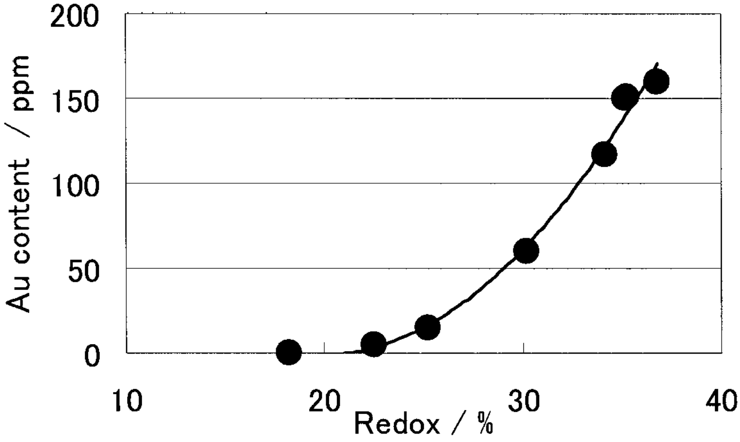

Figure 6. The relationship between the redox and Au content for E-glass melted under different conditions (summary of the data shown in Figs 2 to 4).

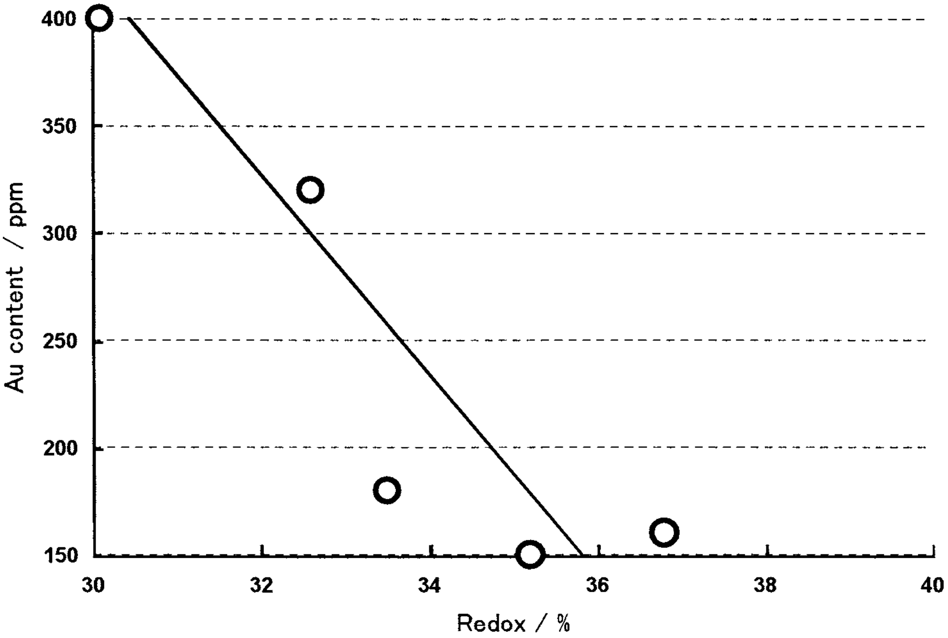

Figure 7. The relationship between redox and Au content for the glass melted at 1500°C for 1 h.

Next, the redox *vs.* gold solubility relation is examined for the glasses melted under a unique temperature-duration condition. Glasses with different amounts of carbon or FeO added and melted at 1500°C for 1 h were used in this examination. The gold solubility is plotted against the redox for those glasses in Fig. 7. As shown in Fig. 7, the relation is much different from that given in Fig. 6: the gold solubility is decreased with the increase of redox. It was considered that the difference in FeO content was too small to account for the difference in gold solubility. Accordingly, the conflict of the redox–solubility relation seen in Figs 6 and 7 indicates that the redox of the glass cannot be a universal measure of the gold solubility. Generally, it may be difficult to find some universal relation between two dynamic parameters such as solubility of gold and the redox, if the measurement conditions are not identified, and the parallelism between solubility of gold and the redox found in Fig. 6 is, now, considered just accidental.

3.2. Gold solubility related to the optical basicity of the E-glass

It has been generally known that many physical and chemical properties of the glasses and/or corresponding melts are reliably interpreted in terms of the optical basicity parameters [3–5]. Duffy and Ingram [6] suggested how to calculate the optical basicity of the other oxide by the optical basicity of CaO and H_2O and by the Pauling electronegativitites of Ca and H. Building on the ideas of Duffy and Ingram, Nakamura *et al.* [7] suggested that the electron supply capacity of the anion depended on the polarization capacity of the anion. They showed how to calculate the theoretical optical basicity of oxides that contain elements with variable oxidation number by means of the concept of the average electron density from the interionic distance between anion and cation as a new scale parameter. We should take a difference in the redox into consideration because the redox and gold solubility equilibria may not have been reached under the unique melting condition in this series of experiments. We must also consider that the gold solubility in the actual fiberglass production will change under different melting conditions even of the same batch. So we decided to use the equation of Nakamura *et al.* that was established to develop the theoretical optical basicity of Duffy and Ingram. Then we used the glass compositions from analysis of the glass after melting to take the differences in redox into consideration.

The theoretical optical basicity (Λ) proposed by Nakamura *et al.* was calculated by using the theoretical optical basicity factor of the constituents given in Table 3 and the next equation for the glasses melted under at 1500°C for 1 h.

$$\Lambda = \sum \Lambda_i X_i,$$

$$X_i = (V_i/2) \cdot n_i \cdot N_i \Big/ \sum (V_i/2) \cdot n_i \cdot N_i,$$

where Λ_i theoretical optical basicity factor of the ith element; V_i value of the ith element ion; n_i number of the ith element ion; N_i mole fraction of the ith element.

For example, the number 'n_i', which we take to be the number of oxygens in the oxide, will be 3 for aluminium oxide.

In the calculation, the Fe^{2+}/Fe^{3+} ratio was taken into account, in other words, the difference of the theoretical optical basicity among glasses under consideration arises from the difference in the Fe^{2+}/Fe^{3+} ratio and total amount of FeO.

In Fig. 8, the gold solubility is plotted against theoretical optical basicity (Λ) thus calculated. It is seen in the figure that there is a relatively good positive correlation

Table 3.
Theoretical optical basicity factors for glass constituents

	Λ		Λ
SiO_2	0.47	TiO_2	0.65
Al_2O_3	0.66	Na_2O	1.11
CaO	1.66	K_2O	1.16
MgO	6.92	B_2O_3	0.42
FeO	0.94	SrO	1.04
Fe_2O_3	0.72	CaF_2	0.67
		BaO	1.08

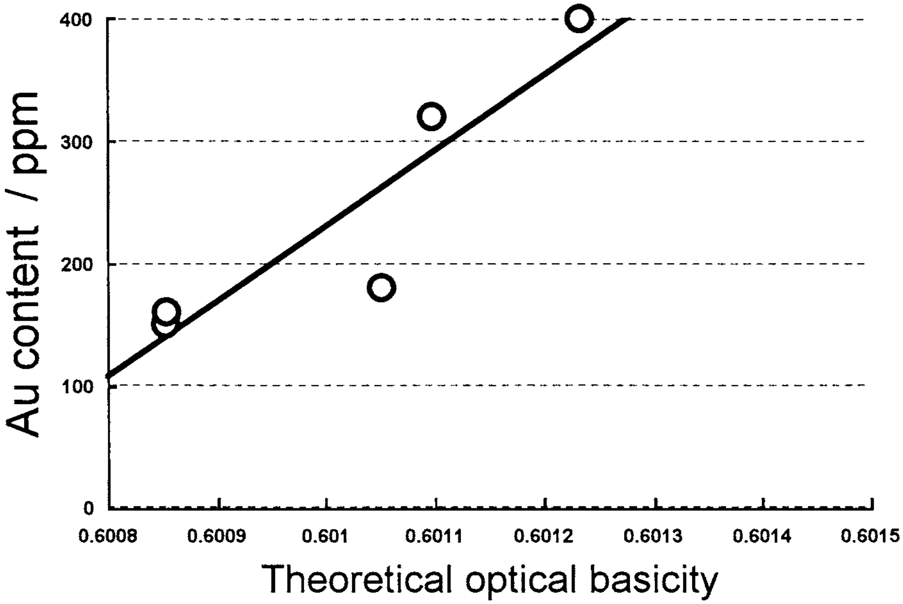

Figure 8. The relationship between theoretical optical basicity and Au content for glasses melted at 1500°C for 1 h.

between Λ and gold solubility, so it is shown that more gold is dissolved in the glass when Λ is increased.

It has been reported in several papers [8–12] that platinum is dissolved into molten glasses through the reaction with oxide ions and dissolved oxygens to form some complex ion as follows:

$$\mathrm{Pt} + m\mathrm{O_2} + n\mathrm{O}^{2-} \rightarrow \mathrm{PtO}^{2n-}_{(2m+n)}. \qquad (1)$$

It is considered very probable that gold is also dissolved in molten glass by a similar reaction:

$$\mathrm{Au} + m\mathrm{O_2} + n\mathrm{O}^{2-} \rightarrow \mathrm{AuO}^{2n-}_{(2m+n)}. \qquad (2)$$

Under the equilibrium condition, equation (2) can be expressed as follows:

$$\log\left(\text{mol\% AuO}^{2n-}_{(2m+n)}\right) = n \log a_{\text{O}^{2-}} + m \log P_{\text{O}_2} - \log \gamma\text{Au} + \text{K}_1, \tag{3}$$

where $a_{\text{O}^{2-}}$ is the activity of the oxide ion, P_{O_2} the partial pressure of oxygen, γAu the activity coefficient of Au and K_1 the equilibrium constant. Equation (3) implies that the concentration of the complex ion or gold solubility is large when the activity or the concentration of oxide ions is related to the basicity (or optical basicity) of the glass, leading to the statement that there is a positive correlation between the theoretical optical basicity and gold solubility, as in Fig. 8.

An example of the enhancement of the gold solubility is found in the manufacturing process of gold–ruby colored glasses, in which some Na_2SO_4 is added to the glass batches. The observed increase in the gold solubility is also explained in terms of the optical basicity. First, Na makes a contribution to the increment of the optical basicity to some extent. Secondly, the dissolved SO_4^{2-} ions are decomposed to O^{2-} ion and SO_3 gas (which may act as a refining reagent for the glass) in the melt as follows:

$$\text{SO}_4^{2-} \rightarrow \text{O}^{2-} \text{ (in the melt)} + \text{SO}_3 \text{ (gas)}. \tag{4}$$

The increase of the oxide ion concentration or activity contributes to the increase of the basicity of the melting and/or the corresponding glass. These lead to the increased gold solubility through equation (3). It is also possible that SO_4^{2-} ions partly react with Au directly to form a complex as follows:

$$\text{Au} + n\text{SO}_4^{2-} \rightarrow \text{AuO}_n^{2n-} + n\text{SO}_3 \uparrow \tag{5}$$

Another empirical method which has often been used practically in E-glass fiber production in order to increase the gold solubility is the addition of F^- ions as one of the glass constituents. It is believed that the added F^- ions shift the redox equilibrium toward the reduction side and increase the gold solubility. On the other hand, the addition of F^- ions should cause a decrease of the optical basicity due to the smaller basicity factor of F^- than O^{2-}. Such a conflict with our above-mentioned conclusion may be overcome by taking into account the high tendency of F^- ions to form a complex with metal ions. It is probable that F^- ions combine with O^{2-} ions in the formation of the complex with Au ions in the melts or glasses, and increases the gold solubility.

3.3. Au metal fiber formation in the E-glass fibers spun from several different compositions

The volume of Au found in the E-glass fibers conventionally spun on the commercial scale from the compositions given in Table 2 is shown in Fig. 9 as a function of the theoretical optical basicity. The difference in the optical basicity among glasses is mainly due to the difference in FeO and Fe_2O_3 contents. The figure shows that

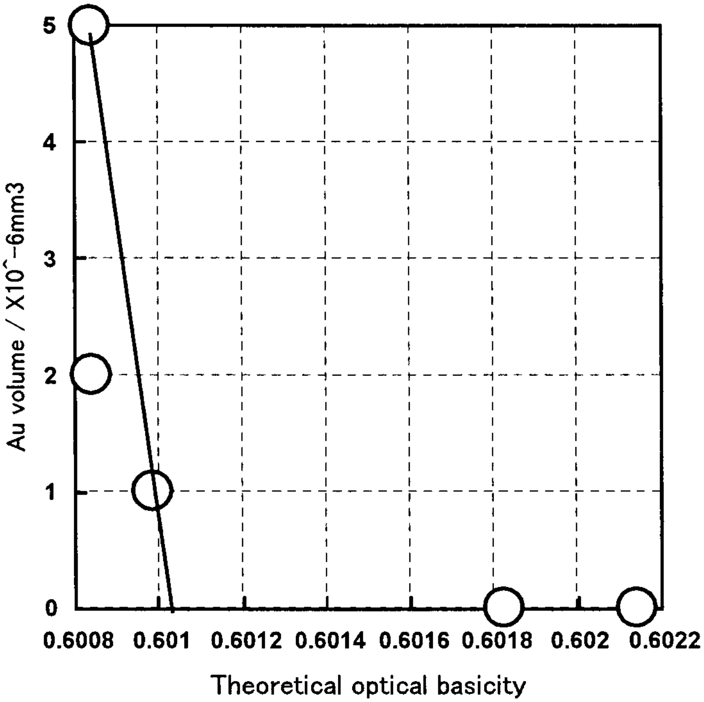

Figure 9. The relationship between theoretical optical basicity and Au volume found by metal detector in the practical production runs.

no Au metal fibers are detected in the glass fibers if the theoretical optical basicity is larger than about 0.601. This result indicates that the theoretical optical basicity of the glass is a very useful and convenient parameter to design a composition in which the Au metal fiber formation is much depressed or completely suppressed during fiber-drawing.

4. CONCLUSION

The solubility of gold in E-glass was examined in relation to the redox and the optical basicity, with the aim of avoiding gold-metal fiber formation in the E-glass fibers. The following results were obtained.

(1) The solubility of gold was increased in one case, and decreased in another case with increase of redox, depending on the melting schedule. Thus it was considered to be difficult to find a universal relation between the gold solubility and the redox of glass.

(2) Theoretical optical basicity of the glasses was closelr related to the gold solubility. The gold solubility or the concentration of the complex ion consisting of Au and oxide ions was large when the activity or the concentration of oxide ions or the optical basicity of the glass was large.

(3) In practical runs for drawing E-glass fibers from several different compositions, no metal fiber formation was encountered when the glass composition of theoretical optical basicity larger than about 0.601 was spun.

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