Isothermal Precipitation Behavior of Copper Sulfide in Ultra Low Carbon Steel

Zhongzhu LIU, Mamoru KUWABARA and Yoshihisa IWATA

Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8603 Japan.

(Received on June 20, 2007; accepted on August 16, 2007)

Copper and sulfur are typical residual elements or impurity elements in steel. Sufficient removal of them during steelmaking process is difficult for copper and costly for sulfur. Utilization of copper and sulfur in steel, especially in steel scrap, has been an important issue for a long period for metallurgists.

Copper and sulfur may combine to form a copper sulfide, which may provide a prospect to avoid the detrimental effects of copper and sulfur in steel. Unfortunately the formation mechanism of a copper sulfide in steel has not been completely clarified so far. In the present paper, solution treatment of samples containing copper and sulfur are firstly performed at 1623 K for 2.7×10^4 s followed by quenching into water. The samples are then isothermally heat-treated at 673 K, 873 K, 1073 K, 1273 K and 1373 K for different time followed by quenching into water again. The size, morphology, constituent and crystallography of sulfide precipitates in these samples are investigated by SEM and TEM equipped with EDS. Fine copper sulfides (less than 100 nm) are observed to co-exist with silicon oxide in samples even isothermally heat-treated at 1373 K for 1.44×10^4 s; Film-like copper sulfides are generally observed to co-exist with iron sulfide in all samples; Plate-like copper sulfides are observed especially in sample isothermally heat-treated at 1073 K for 1.44×10^4 s. The formation mechanisms of these copper sulfides have been discussed in detail.

KEY WORDS: copper sulfide; isothermal precipitation; morphology; crystallography; ultra low carbon steel.

1. Introduction

Copper is one of the major residual elements in steel because it is difficult to remove it during the steelmaking process. The concentration of copper in steel has been increasing gradually due to the continuous recycling of scrap steel. Copper may cause hot shortness at high temperatures since it is harder to be oxidized than the iron matrix. However, it could be used as an alloying element in some steels to improve the corrosion resistance and to enhance the mechanical properties.1–3)

Sulfur is an undesirable impurity in steel since it may lead to low toughness and poor weldability. Sulfides in steel also cause problems due to their size and morphology. Large sulfides usually result in bad mechanical properties, and non-spherical sulfides cause some properties with anisotropy. However, the removal of sulfur from steel results in a large quantity of slag and CO₂ exhaust.

A lot of attention has been given to the strengthening effects from the copper solid solution or the copper particle precipitates in steel.1–3) However, copper and sulfur in steel may form various copper sulfides with different morphologies.4–7) For example, the present authors have reported four kinds of copper sulfide in steel5); copper sulfide coexisted with oxide inclusion, plate-like copper sulfide, shell/film-like copper sulfide and nano-scale copper sulfide. These copper sulfides may have great influences on the microstructure and properties of steel. The nano-scale copper sulfides may increase the strength and work hardening ability of steel.4,5) The shell/film-like copper sulfide may nucleate the acicular ferrite during gamma/alpha transformation and then refine the microstructure of steel.7) The shell/film-like copper sulfide may also improve the corrosion resistance of steel.7) In addition, copper sulfides, unlike copper, does not wet or penetrate the grain boundaries and therefore may inhibit hot shortness.

Unfortunately, compared with MnS and FeS, people have been paying little attention on the formation mechanism of copper sulfide in steels. Although some papers reported the existence of copper sulfides in steel or iron previously,10–15) few papers discussed the formation mechanism of copper sulfide in detail. On the other hand, mineralogists have carried out extensive investigations on the thermodynamics and phase relations in the Cu–S system.16) The results show that the copper bearing sulphides are very complex in this system as shown in Table 1 summarized by Fleet,17) in which the original list of eleven minerals and phases by Craig and Scott18) in 1974 is expanded to fourteen with the original list of eleven minerals and phases by Craig and Scott18) in 1974 is expanded to fourteen with the introduction of iron into the Cu–Fe–S system.19) The new minerals roxbyite, geerite, and spionkopite. There have been no studies on the stability of these new minerals. In addition, the introduction of iron into the Cu–S system makes it more complicated since there are twenty one minerals and phases in the Cu–Fe–S system.17)

According to the phase diagram of the Cu–S system,19) the high Digenite (Dg) has a broad phase field, with the new minerals roxbyite, geerite, and spionkopite. There have been no studies on the stability of these new minerals. In addition, the introduction of iron into the Cu–S system makes it more complicated since there are twenty one minerals and phases in the Cu–Fe–S system.17)
up to 780 K at 36.60 at% S and down to 345 K at 35.65 at% S. Therefore, the high Digenite is the most probable phase that is expected in steel at high temperature. But people have confusedly presumed and reported several crystal structures and phases, for example cubic Cu$_{1.8}$S or Cu$_{1.6}$S or CuS 2, hexagonal CuS and rhombohedral Cu$_{1.6}$S and so on, for copper sulfide in steel.

In the previous papers, the authors found that copper sulfides could be formed in strip casting steel. Differently from the formerly reported copper sulfides in steel/iron, which usually coexisted with MnS, almost pure copper sulfides with various morphologies were found in the previous strip casting steels. In the present paper, the formation mechanism such as precipitation temperature, stability and crystallography of various copper sulfides have been investigated during isothermal heat treatment process.

2. Experimental Procedures

2.1. Materials and Heat Treatment Conditions

The chemical composition of the present steel is shown in Table 2. The steel is firstly prepared in an induction heating furnace under flowing argon gas. About 350 g of electrolytic iron is melted at 1873 K. After the alloying elements (Cu, S) are added to the melted iron, the melt is cooled to room temperature with the furnace. An ingot with size of 40×50 mm (hereafter named as sample H00) then could be obtained for the following heat treatment.

The solution treatment of the ingot is held at 1623 K for 2.7×10$^3$ s followed by quenching into water (sample H16Q). The sample H16Q is then cut into pieces with thickness of about 5 mm and isothermally heat-treated at 673 K, 873 K, 1073 K, 1273 K and 1373 K for 2.7×10$^3$ s and 1.44×10$^4$ s, respectively, followed by quenching into water again. The sample number and the detail heat treatment history of samples are listed in Table 3.

2.2. Analysis Methods

The size, morphology, constituent and crystallography of sulfide precipitates in the samples are investigated by SEM and TEM. Carbon extraction replicas are prepared for TEM observation. The sample is firstly cold mounted, grinded and mirror polished. It is then etched by 3 vol% Nital to expose the precipitates. After vacuum evaporation, the sample is dipped into 3 vol% Nital again to lift the replica. The replicas are floated on Ti or Al or Nylon grids, and a carbon specimen holder is used to avoid a possible detection of Cu from the grid and the specimen holder. The TEM observation is performed on a Hitachi-800 microscope operated at 200 kV and equipped to an Energy Dispersive X-Ray Spectroscopy (EDS).

3. Experimental Results and Discussion

3.1. Sulfides in Samples Isothermally Treated at 1373 K

3.1.1. Copper Sulfide Coexisted with Silicon Oxide in Sample H13L

There are two kinds of typical precipitates observed in sample H13L, as shown in Fig. 1. One is fine sulfide with size less than 100 nm, and it is always coexisted with silicon oxide. The EDS spectrums show that these fine sulfides...
are mainly copper sulfide (Cu\textsubscript{x}S) and usually include a little of iron or iron sulfide. The atomic rations of these sulfides, (Cu+Fe)/S, are among a wide range, that is from 0.6 to 1.8, although most of it is closed to 1.1.

It is interesting that the oxide inclusion which coexisted with Cu\textsubscript{x}S is almost pure silicon oxide, as shown in Fig. 2. It has been thought that complex silicate oxide, which has low melting point and high sulfur capacity, could nucleate the sulfide precipitation in steel\textsuperscript{21}; while pure silicon oxide has no such ability since its high melting point and low sulfur capacity. Although Holzheld has reported that copper has some solubility in silicate melts irrespective of the presence of sulfur,\textsuperscript{22} there has no such report for copper in pure silicon oxide. On the other hand, Wakoh has investigated the effect of sulfur content on the MnS precipitation with oxide nuclei in steel deoxidated by Mn–Si, Mn–Ti, Al and Zr, respectively.\textsuperscript{23} It is found that the precipitation ratio of MnS on oxide is large in almost all oxides when the content of sulfur is higher than 0.01 mass% in steel. The present precipitation of Cu\textsubscript{x}S on pure silicon oxide may be also that case. That is the pure silicon oxide works as the precipitation site of Cu\textsubscript{x}S.

3.1.2. Copper Sulfide Coexisted with Iron Sulfide in Sample H13L

In sample H13L another typical precipitate is sulfide with size from 0.2 to 1.5 \(\mu\)m. The EDS spectrums show that these large sulfides are mainly iron sulfide and they are always accompanied with a little of copper sulfide (thereafter named as “free-standing” iron sulfide since it is not coexisted with oxide) as shown in Fig. 1.

The iron sulfide coexisted with silicon oxide is also observed in sample H13L. In the case that if iron sulfide and silicon oxide are just contacted with each other (Fig. 3(a)), its size is usually smaller than “free-standing” iron sulfide while larger than the Cu\textsubscript{x}S coexisted with silicon oxide; while if silicon oxide is huggd or covered by iron sulfide (Fig. 3(b)), its size is similar to the “free-standing” iron sulfide. The diffraction pattern shows that the iron sulfide has a hexagonal structure, which is closed to the Joint Committee on Powder Diffraction Standards (JCPDS) card 37-0477, as shown in Fig. 4.

Although it is not clear that the little iron accompanying with the Cu\textsubscript{x}S coexisted with silicon oxide is solid solution one in Cu\textsubscript{x}S or just an attachment on it, the little copper sulfide accompanying with iron sulfide seems just a shell/film attached on the iron sulfide, as shown in Fig. 5. The STEM-EDS spectrums show the Cu concentration at the edge of the iron sulfide particle is quite higher than that of the interior part, which means that the iron sulfide is covered by a copper sulfide shell/film.

The interesting point is that this is a popular phenomenon in all of the present samples, whether the iron sulfide may have different morphologies as introduced above or later as shown in Figs. 7 and 13. That means all the iron sulfides are accompanied by a copper sulfide film in the present samples. Ishiguro\textsuperscript{20} has reported that the shell/film-
like copper sulfide could also be precipitated even during a short time in water quenching, which seems could be supported by present results. The precipitation temperature of film-like copper sulfide in his samples, hot rolled and water quenching ultra low carbon steel containing residual level of copper, is speculated between “below 1 023 K” and 893 K.

3.1.3. Precipitates in Sample H13S

The precipitates in sample H13S is shown in Fig. 6. Free-standing iron sulfides with various sizes are popular in it. Some of them are seems to be precipitated along the prior austenite grain boundary (Fig. 6(c)). Even the sulfide is less than 100 nm, its composition is mainly iron sulfide including some copper sulfide (Fig. 6(d)). In addition, almost no Cu$_x$S and iron sulfide coexisted with silicon oxide are observed in this sample. It seems that the pure silicon oxide in H13L sample is formed during the long time isothermal treatment process, and after it precipitates copper sulfide and iron sulfide then precipitate on it.

3.2. Sulfides in Samples Isothermally Treated at 1 273 K

Iron sulfides coexisted with silicon oxide (Fig. 7(a)) and free-standing iron sulfides (Fig. 7(b)) are observed in sample H12L and H12S. No obvious difference is detected between these two samples except that the number of sulfide in H12L is larger than that in H12S. In addition, there is no obvious difference observed for these two kinds of sulfides in samples heat treated at 1 373 K and 1 273 K.

3.3. Sulfides in Samples Isothermally Treated at 1 073 K

3.3.1. Plate-like Sulfide in Sample H10L

There are at least three kinds of precipitates observed in sample H10L, they are free-standing iron sulfide, plate-like sulfide and free-standing fine sulfide, as shown in Fig. 8. Universally existed plate-like sulfide is the typical character of sample H10L. These plate-like sulfides are usually parallel or vertical with each other as shown in Fig. 8(b) even when they precipitate along the grain boundary. The main composition of the plate-like sulfide may be iron sulfide including some copper sulfide, or copper sulfide including a little of iron sulfide as shown in Fig. 9. For the plate-like copper sulfide, the atomic ratio Cu/S is about 1.3–1.7 while the (Cu+Fe)/S is about 1.6–1.80. The diffraction patterns have shown that the plate-like iron sulfide has the same structure as the free-standing iron sulfide in Fig. 5; while the plate-like copper sulfide has a cubic structure and is close to digenite (JCPDS: 24-0061) or geerite (JCPDS: 33-0491) as shown in Fig. 10.

The plate-like copper sulfide has been speculated to be precipitated in austenite phase in a previous paper. In the present samples, plate-like copper sulfide is only observed in samples heat treated at 1 073 K, at which both gamma and alpha phase may exist. Further direct evidence is necessary to confirm from what phase that plate-like copper sulfide is precipitated.
3.3.2. Free-standing Fine Copper Sulfide in Sample H10L

The fine sulfide (Fig. 8 and Fig. 11) in sample H10L also has a small size as less than 100 nm as the fine copper sulfide in sample H13L. No obvious silicon oxide could be observed along with these fine sulfides, although sometimes low concentration of silicon is detected by EDS analysis (Fig. 11). These fine sulfides are mainly copper sulfide including some iron.

3.3.3. Precipitates in Sample H10S

Some free-standing iron sulfide (with large size) and copper sulfide (with fine size) are also observed in sample H10S as shown in Fig. 12. Plate-like sulfides are also observed but with fewer number.

3.4. Sulfides in Samples Isothermally Treated at 873 K and 673 K

There seems no obvious character for the precipitates in samples isothermally treated at 873 K and 673 K even for different times. The iron sulfides, free-standing and coexisted with silicon oxide, are observed in these samples. Copper sulfide film is, as the same in other samples, covered on these iron sulfides as shown in Fig. 13. In addition, the sulfide has smaller size in sample H673L compared with that in sample H873L, which may be due to the low isothermal temperature.

The characters of sulfides in all the present samples as summarized in Table 4. In brief, fine copper sulfide coexisted with silicon oxide and the free-standing copper sulfide is too fine to obtain.
perfect diffraction patterns. Such difficulty also exists for shell/film-like copper sulfide since it is usually too thin. In addition, Cu–S system is a quite complicated system. Identification based only on the diffraction pattern is generally difficult since a lot of kinds of copper sulfide are present and the patterns of different crystals often coincide with each other with errors of measurement of diffraction spot distance and angle.

The crystal structure and phase of copper sulfide in iron and steel reported in literatures has been summarized in Table 5. Since the experimental procedure may have great effect on the crystal structure and phase of copper sulfide, it is briefly introduced as following.

The diffraction patterns of the shell-like copper sulfide obtained by Nosach in Bessemer type transformer steel indicate the presence of Cu₉S₅, which may be the earliest report on the crystal structure of copper sulfide in steel.

Harbottle has reported the observation of discrete particles of copper sulfide, positively identified as Cu₁.₈S (Digenite I), and found only in the matrix of the mild steel weld specimens but not in the plate material.

Sakai has investigated the sulfides in hot rolled grain-oriented silicon steel containing Cu. Fine particles with size 20–50 nm are indicated as (Cu, Mn)₁.₈S with lattice parameter in the range 0.539 to 0.552 nm.

Dowling has reported copper-sulfur rich patch, similar to shell-like copper sulfide, on oxide inclusion in submerged arc welds in high strength low alloy steels. Diffraction patterns from TEM and STEM have indicated that the copper-sulfur rich patch has a cubic structure with lattice parameter in the range 0.55 to 0.59 nm. This value is believed consistent with the structure of Cu₂S₀.₂, and CuS₂.

Kejian has investigated the copper containing sulfide present in controlled rolled niobium–titanium bearing high strength low alloy steels. Disc-like copper containing sulfides, having a thicker ring-like edge, are frequently observed and mainly occur close to and/or within the pearlite banding. The diffraction patterns of these sulfides are found to be very close to those from covellite, although there are some which can match other copper bearing phases. After heated at 973 K and 1 173 K, soaked for 1 h, and quenched in water, the associated copper bearing sulfides are still observed and their diffraction patterns are similar to those obtained from digenite.

Madariaga has reported shell-like CuS with h.c.p.
structure (B18 type, covellite) in medium carbon microalloyed steel. Cubic samples of 10 mm side are austenitized for 45 min at 1523 K in an inert argon atmosphere followed by direct quenching into a bath at 723 K for different times, followed by water quenching.

Recently Ishiguro has investigated the copper sulfide in hot rolled ultra low carbon steel. The atomic ratio of Cu/S of film-like copper sulfide is determined to be 1.8 by EDS, and the phase is determined to be Cu₄S₅ (JCPDS card 33-491, gerrite, also Cu₁.₆S) from X-Ray Diffraction (XRD) of the extracted precipitates.

The main confusion of the crystal structure of copper sulfide in steel is among digenite, gerrite and covellite phases. Some of the crystal plane distances obtained by XRD and their indices are listed in Table 6, which shows several crystal plane distances for these three phases are so close to each other that identification only based on SAED patterns seems very difficult. Identification based on XRD data which includes the intensity of the peaks seems more reasonable compared with that only based on the SAED patterns. That is why although the SAED pattern similar to cubic is observed in Fig. 10, it is still difficult to decide the phase is Cu₁.₆S or Cu₁.₄S in present research.

As discussed above, digenite is the most possible phase formed above 780 K in Cu–S system, but at 780 K and 708 K it may change into covellite and chalcocite, respectively. In addition, at temperature below 388 K, several transformations occur among digenite, chalcocite, djurleite, covellite and anilite phases. If a sample is hot mounted before grinding, the peak temperature for the sample undergoing is usually higher than 388 K. Furthermore, some of these transformations may also occur during grinding and polishing of the sample, as well as during the TEM observation due to the heating from electron irradiation. Considering these factors, the Cu₁.₆S phase identified by XRD of the extracted precipitates seems to be the original phase in steel; while the other phases reported by most researchers may be a mixture of the original phase in steel and the one produced during sample preparation (such as hot mounting, grinding...) and electron irradiation when conducting TEM observation. Unfortunately, gerrite is a

---

Table 5. Brief summary of the reported crystal structure of copper bearing sulfide in iron and steel in literatures.

| Sample                        | Morphology                      | Ratio of Cu/S | Crystal structure     | Identification method | Phase          | Ref. |
|-------------------------------|---------------------------------|---------------|----------------------|-----------------------|----------------|------|
| Hot rolled low carbon steel   | Free standing; shell-like       | 1.8±0.3       | Cubic/ pseudocubic   | XRD                   | Cu₁.₄S        | 20   |
| Strip casting low carbon steel| Free standing; shell-like; plate-like | cubic         | Cubic                | SAED                  | Cu₁.₆S        | 6    |
| Medium Carbon steel, 1523K+45 min - 723 K×10s/20min-quench | Shell-like | h.c.p. | SAED | CuS | 26, 27 |
| HSLA steel, controlled rolled | Shell-like; Free standing       | 1.0 (Cu+Mn)/S | h.c.p.; cubic        | SAED                  | Cu₁.₄S        | 15   |
| HSLA steel, submerged arc welds | Shell-like | cubic | SAED | Cu₁.₆S; Cu₂S₅ | 25 |
| 3% Si steel, hot rolled       | Free standing                   | cubic         | SAED                 | (Cu,Mn)₁.₄S         | 14 |
| Mild steel weld               | Free standing                   | cubic         | SAED                 | Cu₁.₄S        | 13   |
| Bessemer type transformer steel, cold rolled | Shell-like | cubic | SAED | Cu₁.₄S | 24 |

Note: SAED - Selective Area Electron Diffraction; XRD- X-Ray powder Diffraction.

---

Table 6. Some crystal plane distances and their indices for gerrite (Cu₁.₄S), digenite (Cu₁.₆S) and covellite (CuS).

| Cu₀.₄S | Cu₁.₆S | CuS |
|-------|--------|-----|
| d, Å  | hkl    | hkl | d, Å  | hkl    | hkl |
| 3.1200 | 100 | 22 1; 5 5 5 | 111 | 3.2160 | 40 | 111 | 3.2200 | 10 1 |
| 2.7120 | 10 | 3 3 4 | 200 | 2.7850 | 68 | 2 0 0 | 2.7240 | 00 6 |
| 1.9180 | 50 | 7 7 6 | 22 0 | 1.9693 | 100 | 2 2 0 | 2.0430 | 00 8 |
| 1.6370 | 30 | 1 1 3; 8 8 9 | 3 1 1 | 1.6794 | 14 | 3 1 1 | 1.6340 | 2 0 1 |
| 1.5760 | 10 | 4 4 2; 10 10 10 | 2 2 2 | 1.5720 | 2 0 3 | 1.3925 | 3 | 4 0 0 | 1.3900 | 1 1 8 |
| 1.2470 | 10 | 9 9 7; 15 15 15 | 3 3 1 | 1.2270 | 2 1 2 | 1.0710 | 2 | 5 1 1 | 1.0946 | 3 0 0 |

* with Rhombohedral indices.  
** with Cubic indices.
new mineral just reported by Goble in 1980.28) The structure and its stability have not been determined, to say nothing of its relationship with other copper sulfide phases. It is quite possible that digenite is firstly formed at high temperature and transforms into other Cu–S phase during following cooling in steel. At room temperature, it is also possible that several Cu–S phases exist in the copper bearing sulfide particle in steel. Anyway, on the crystal structure and phase of copper sulfide in steel, further comprehensive investigation is necessary.

5. Conclusions

Fine copper sulfide with size less than 100 nm is mainly observed in samples isothermal treated at 1 373 K and 1 073 K for $1.44 \times 10^4 \text{s}$. At 1 373 K it is coexisted with pure silicon oxide while at 1 073 K almost free-standing particle. Plate-like copper sulfide with cubic structure and iron sulfide with hexagonal structure are mainly observed in samples isothermally treated at 1 073 K. Iron sulfides with various sizes are widely existed in all of the samples treated at different temperatures. A copper sulfide film is always covered with these iron sulfides. It is of a great probability that digenite copper sulfide firstly precipitates in steel at high temperature and transforms into other Cu–S phase at low temperature.

Acknowledgement

The authors would like to thank Dr. S. Arai and Mr. T. Sato, Eco Topia Science Institute, Nagoya University, for their fruitful discussion.

REFERENCES

1) J. Syarif, T. Hoshino, T. Tsuchiyama and S. Takaki: *Tetsu-to-Hagané*, 86 (2000), 558.
2) A. Takahashi and M. Iino: *ISIJ Int.*, 36 (1996), 241.
3) S. W. Thompson and G. Krauss: *Metall. Mater. Trans. A*, 27A (1996), 1573.
4) A. Guillet, E. Es-sadiqi, G. Lesperance and F. G. Hamel: *ISIJ Int.*, 36 (1996), 1190.
5) Z. Liu, Y. Kobayashi and K. Nagai: *Mater. Trans.*, 45 (2004), 479.
6) Z. Liu, Y. Kobayashi, K. Nagai, J. Yang and M. Kuwabara: *ISIJ Int.*, 46 (2006), 744.
7) Z. Liu, Y. Kobayashi, K. Nagai, J. Yang and M. Kuwabara: *CAMP-ISIJ*, 19 (2006), 743.
8) Z. Liu, Y. Kobayashi and K. Nagai: *ISIJ Int.*, 44 (2004), 1560.
9) T. Haru, R. Uemori, H. Tamehiro and C. Kato: *Zairyo-to-Kankyo*, 49 (2000), 150.
10) H. Morrogh: *J. Iron Steel Inst.*, 154 (1946), 399.
11) N. F. Dubrov, I. A. Gorlach and M. V. Lyasko: *Stal*, 7 (1960), 517.
12) D. A. Melford: *J. Iron Steel Inst.*, 200 (1962), 290.
13) J. E. Harbottle and S. B. Fisher: *Nature* (London), 299 (1982), 139.
14) T. Sakai, T. Shimazu, K. Chikuma, M. Tanino and M. Matsoo: *Tetsuto-Hagané*, 70 (1984), 2049.
15) H. Kejian and T. N. Baker: *Mater. Sci. Technol.*, 8 (1992), 1082.
16) M. Posfai and P. Buseck: *Am. Mineral.*, 79 (1994), 308.
17) M. E. Fleet: *Rev. Min. Geo.*, 61 (2006), 365.
18) J. R. Craig and S. D. Scott: *Rev. Min.*, 1 (1974), CS-1.
19) T. B. Massalski: Binary Alloy Phase Diagrams, Vol. 1, American Society for Metals, Metals Park, OH, (1986), 953.
20) Y. Ishiguro, K. Sato and T. Murayamma: *Mater. Trans.*, 46 (2005), 769.
21) M. Wakoh, T. Sawai and S. Mizoguchi: *Tetsuto-Hagané*, 78 (1992), 1697.
22) A. Holzheid and K. Lodders: *Geo. Cos. Acta*, 65 (2001), 1933.
23) M. Wakoh, T. Sawai and S. Mizoguchi: *ISIJ Int.*, 36 (1996), 1014.
24) V. F. Nosach and V. Y. Goldshteyn: *Fiz. Met. Metalloved.*, 44 (1977), 288.
25) J. M. Dowling, J. M. Corbett and H. W. Kerr: *Metall. Trans. A*, 17A (1986), 1611.
26) I. Madariaga and I. Gutierrez: *Sce Mater.*, 37 (1997), 1185.
27) I. Madariaga and I. Gutierrez: *Acta Mater.*, 47 (1999), 951.
28) R. J. Goble: *Can. Mineral.*, 18 (1980), 519.
29) R. J. Goble: *Can. Mineral.*, 23 (1985), 61.
30) N. Morimoto and G. Kullerud: *Am. Mineral.*, 48 (1963), 110.
31) Natl. Bur. Stand. (U.S.), Circ. 539, IV (1955), 15.
32) N. Morimoto: *Mineral. J.*, 3 (1962), 338.
33) A. Putnis: *Am. Mineral.*, 62 (1977), 107.