Communications

Spinel Crystals in Tuyere Coke

STANISLAV GORNOSTAYEV and JOUKO HÄRKKI

A number of dodecahedral and octahedral spinel crystals were found in tuyere coke. The possibility of spinel formation from a gas phase in the tuyere coke can be considered for dodecahedral crystals. The octahedral spinels may have been formed by annealing of precursor mineral aggregates followed by crystallization of new phases. Investigations into spinel crystals can be important for further interpretations of the conditions of origin and subsequent behavior of mineral matter during coke degradation.

The amount and nature of the mineral phases in metallurgical coke can be regarded as important factors affecting its properties and behavior in the blast furnace (BF).[1,2] Data on the mineral phases in BF coke are still scarce, however,[2–5] and their behavior during coke degradation is still poorly understood. Under natural conditions, the composition, morphology, and textures preserve a record of the means by which the minerals were formed, and these data can be used to estimate the conditions of formation of their synthetic analogues,[6] including those originating in coking processes and during the evolution of coke in the BF.

The changes that take place in the mineral phases of BF coke can be regarded as either structural or chemical.[2] The structural changes in particular include[2] expansion of metaclays and the swelling and balling-up of aluminosilicates, while the chemical changes are more complex and include (but are not limited to) mineral phase decomposition, alkalization, and the formation of new crystalline and glass phases. Various gases circulating in the BF change the composition of the existing mineral phases and cause the formation of new phases acting as agents for the transport of components through pores.

The synthetic equivalents of minerals that have so far been found in tuyere coke but are not observed in primary coke are gupeiite, Fe_3Si; xifengite, Fe_5Si_3; schreibersite, Fe_3P; barringerite, Fe_2P; oldhamite (Ca, Mg, Fe, Mn)S; Al_2O_3 (corundum crystals); spinel, $MgAl_2O_4$; and fersilicite, FeSi.

We describe here a case study of spinel crystals, which represents the first report on the occurrence and crystalline features of this mineral in tuyere coke.

A number of coke samples were selected from drill core 130,303,203, obtained using a mobile tuyere rig from the tuyere zone of the BF at Rautaruukki Steel Works (Raahe, Finland). The samples were cut into pieces about 20-mm long, 20-mm wide, and 5-mm thick, preserving one original surface. The cut pieces were fixed to 28 × 48 × 1-mm glass plates and studied with a JEOL* JSM-6400 scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS), which was also widely used for observing and identifying the minerals and other phases reported here.

A number of small (3 to 15 μm) crystals and aggregates of almost pure spinel, $MgAl_2O_4$ (EDS spectrum data), were found in two samples of the coke, selected from the 150- and 210-cm levels (from the beginning of the tuyere) in the drill core. The spinels occur as euhedral, equidimensional crystals of dodecahedral and octahedral habit, as twins of octahedral and prism habit and as irregular crystals and their aggregates. Combination of forms should also be mentioned. The euhedral, equidimensional crystals of dodecahedral habit occur inside deep pores attached to their walls (Figures 1(a) and (b)), or in areas adjacent to the pore throat (Figure 1(a)), while the octahedral crystals with clearly visible {111} faces (Figures 1(d) and (f)) are found mainly on the coke surface, where they are located near the pores (Figures 1(c) and (d)) or along the cracks (Figures 1(e) and (f)). In the latter case, they often constitute parts of complex aggregates with less well-shaped crystals and form twins and various intergrowths (Figure 1(f)). The occurrence of two shapes of spinel, which were also found in different environments, indicates different conditions of formation.

The formation of the mineral phase during coking and in BF coke can be compared to some extent with pyrometamorphic processes that occur during the spontaneous burning of coal spoil-heaps.[7,8,9] These unique systems have generated 209 mineral species (including spinel), and it has been suggested that the gas phase may play an important role in the formation of minerals in them.[7,8,9] The authors of the article[9] mentioned a temperature range of 1200 °C to 1500 °C in the coal heaps, so that such conditions would be available in a tuyere zone. They also pointed out that "gas transport synthesis was achieved" and concluded "that a decisive control on the process of Ca, Mg and Fe separation and formation of their minerals is exerted by the types of complex metal compounds containing S, C, and H that are responsible for gas transport."[9] The reaction for the formation of spinel from a gas phase can be found in[10]

$$Al_2O_3\,(s) + Mg + H_2O \rightarrow MgAl_2O_4\,(s) + H_2$$

The amounts of Mg and Al in a coke, and consequently in the BF, may vary in any given case and are greatly dependent on the mineral composition of the original coal blends. The main sources of Mg in coals are dolomite, $CaMg(CO_3)_2$, magnesite, $MgCO_3$, various silicates, and clays, while Al is often associated with silicates and clay minerals[2] (*e.g.*, kaolinite $Al_2Si_2O_5[OH]_4$).

The possibility of spinel formation from a gas phase in the tuyere coke can be considered for dodecahedral crystals attached to pore walls (Figures 1(a) and (b)). Although there is no solid evidence for this model at present and it should be approached with caution, there are some signs and indirect comparisons that may favor such a hypothesis. The facts that no traces of precursor phases were found near the spinels and that their crystals have compositions close to the ideal

*JEOL is a trademark of Japan Electron Optics Ltd., Tokyo.

STANISLAV GORNOSTAYEV, Research Scientist, and JOUKO HÄRKKI, Professor, are with the Laboratory of Process Metallurgy, University of Oulu, FIN-90014, Finland. Contact e-mail: ssg@cc.oulu.fi

Manuscript submitted April 26, 2004.

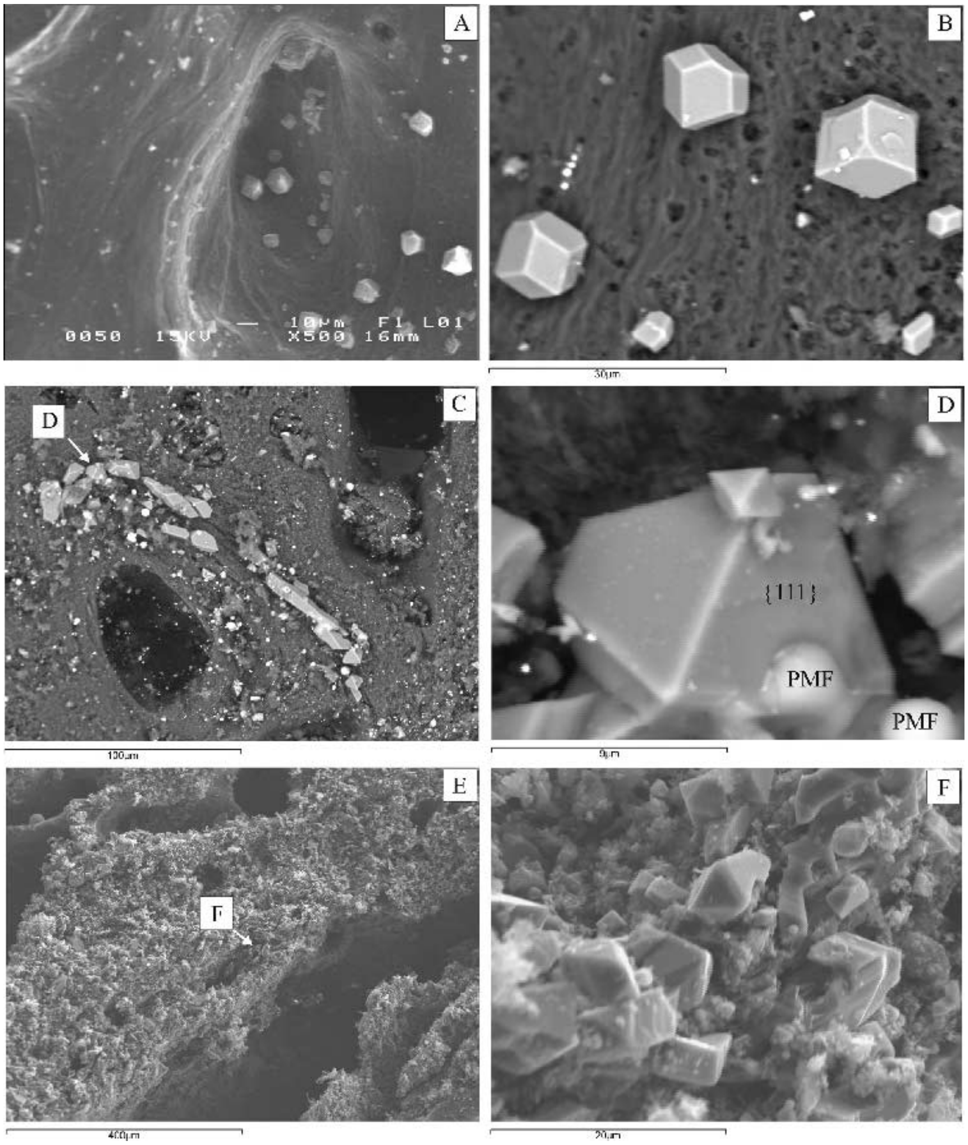

Fig. 1—Photographs by SEM of various spinel occurrences in the tuyere coke (PMF—precursor mineral phase).

spinel stoichiometry—$MgAl_2O_4$, support this suggestion.[9] If this is the case, then the temperature in this area should have been about 2100 K, as was reported for spinel from chondritic meteorites[10,11] originated from solar nebula (a gaseous cloud parental to the solar system). Also, the formation of Al-rich spinel ". . . seems best understood in terms of the evaporation of a refractory liquid followed by rapid crystallization."[11]

Octahedral crystals and their intergrowths are common under conditions of rapid crystallization of diamonds from oversaturated systems, for example,[12] which has the same crystal system (cubic) as spinel. The octahedral spinel crystals and their intergrowths were encountered on the tuyere coke surface, which may also be a place for more rapid spinel crystallization than inside the pores, where conditions (temperature and gas composition) were probably more stable. The octahedral spinels may have been formed by annealing of precursor mineral aggregates, resulting in the decomposition of minerals to the point of an amorphous state and the crystallization (recrystallization) of new phases from an amorphous matrix, as also reported for pyrometamorphic rocks in the heaps.[9] This was certainly the case for the crystals shown on plates C through F of Figure 1. This conclusion is supported by the observed textural relationships of the aggregate of mineral matter to the coke matrix (Figure 1(c)) and by the association of the spinel crystal (Figure 1(d)) with the remnants of an O-Al-Si-K-Mg-Na (EDS spectrum data) precursor phase. In the latter case, the precursor phase aggregate was probably a sheeted silicate that was annealed and transformed to spinel but partly retained its elongated shape. The temperature of the spinel appearance in this case was limited by the properties of the precursor phase, the composition of which could not be determined quantitatively. The "mixture" of the underdeveloped spinel crystals (Figure 1(f)) is also a sign of rapid *in-situ* recrystallization.

Investigations into spinel crystals in tyuere coke can be important for further interpretations of the conditions of origin and subsequent behavior of mineral matter during coke formation and its degradation in a BF, as they can give us a better understanding of how the minerals alter the chemical and physical properties of the coke. Our preliminary data (subject to further research) have shown, for example, that the sharp edges of octahedral spinel crystals formed by the annealing of precursor phases cause cracks to appear that weaken the coke strength. On the other hand, the dodecahedral crystals observed here occur in nondestructive relationships with the coke matrix. The revealing of mechanisms for the transformation of complex silicates (*e.g.*, the O-Al-Si-K-Mg-Na phase reported on here) to spinel, $MgAl_2O_4$, can also be important for understanding the behavior of alkalis in the BF.

This research was supported financially by the TEKES Foundation (Finland), Rautaruukki Ltd., and the Academy of Finland. Helpful comments were provided by a Key Reader and anonymous referees.

REFERENCES

1. D.A. Tsikarev: *Coke Chem.*, 1993, vol. 4, pp. 30-32.
2. O. Kerkkonen: *Coke Making Int.*, 1997, vol. 9 (2), pp. 34-41.
3. K. Kojima, T. Nishi, T. Yamaguchi, H. Nakama, and S. Ida: *Trans. Iron Steel Inst. Jpn.*, 1977, vol. 17, pp. 401-09.
4. H. Haraguhi, T. Nishi, Y. Miura, M. Ushikubo, and T. Noda: *Trans. Iron Steel Inst. Jpn.*, 1985, vol. 25, 190-97.
5. G.P. Huffman, F.E. Huggins, R.W. Shoenberger, J.S. Walker, F.W. Lytle, and R.B. Greegor: *Fuel*, 1986, vol. 65, pp. 621-32.
6. E.H. Nickel: *Can. Mineralogist*, 1995, vol. 33, pp. 689-90.
7. B.V. Chesnokov: *Uralian Mineralogical Vol.*, 1997, vol. 7, pp. 3-16.
8. B.V. Chesnokov, E.V. Sokol, and E.N. Nigmatulina: *Uralian Mineralogical Vol.*, 2001, vol. 11, pp. 288-96
9. E. Sokol, N. Volkova, and G. Lepezhin: *Eur. J. Mineralogy*, 1998, vol. 10, pp. 1003-14.
10. H.-P. Gail: *Astron. Astrophys.*, 1998, vol. 332, pp. 1099-1122.
11. H. Yurimoto, A.E. Rubin, S. Itohand, and J.T. Watson: *Lunar Planetary Sci.*, 2001, vol. XXXII, Abs. 1557 (CD-ROM).
12. M.D. Evdokimov, M.Y. Ladygina, and A.R. Nesterov: *The Uralian Mineralogical School—2000*, Ekaterinburg, 2000, Uralian Branch, Russian Academy of Sciences, pp. 1-380.