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Phase Equilibria of Al_2TiO_5–Ti_3O_5 Pseudobrookite Solid Solution in the Al_2O_3–TiO_x System under Various Oxygen Partial Pressures

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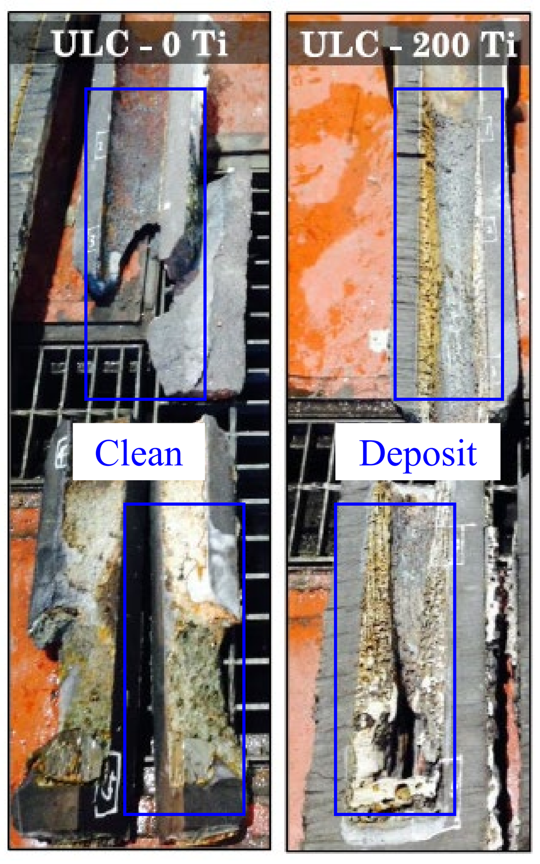
Abstract

The phase equilibria in the Al_2O_3–TiO_x system were investigated in wide ranges of temperature and oxygen partial pressure: 1300 - 1600 °C and $10^{-16.6}$ ~10^{-8} atm, respectively. The equilibrium phases and their compositions were identified using X-Ray Diffraction (XRD) and Electron Probe MicroAnalysis (EPMA), respectively. Most noticeably, a wide range of pseudobrookite solid solution was found in equilibrium with almost pure alumina. At each temperature, the cationic ratio expressed as $R_{Ti} = n_{Ti}/(n_{Al} + n_{Ti})$ of the pseudobrookite solid solution showed a noteworthy dependency on the oxygen partial pressure. This resulted in the formation of a broad range of pseudobrookite solid solutions, ranging from Al_2TiO_5 (R_{Ti} = 1/3) to Ti_3O_5 (R_{Ti} = 1.0). Complete miscibility within the pseudobrookite solid solution was observed at 1600 °C, with only a minor miscibility gap becoming evident below 1500 °C. Based on the results obtained in the present study, the behaviuors of Al_2TiO_5 pseudobrookite have implications in two key domains: (1) understanding changes in the physical properties of the materials and (2) elucidating the evolution of Al–Ti complex oxide inclusions in liquid steel which can deteriorate the steel cleanliness.

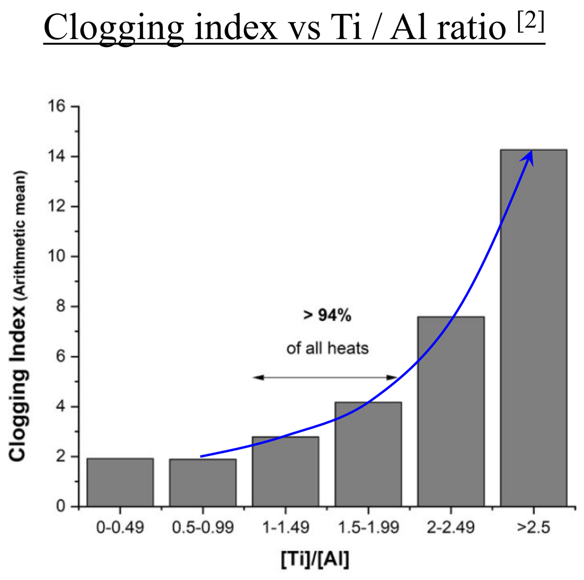
1 Introduction

- Ti-added Ultra-Low C (ULC) steel: Stability and role of Al-Ti complex inclusions

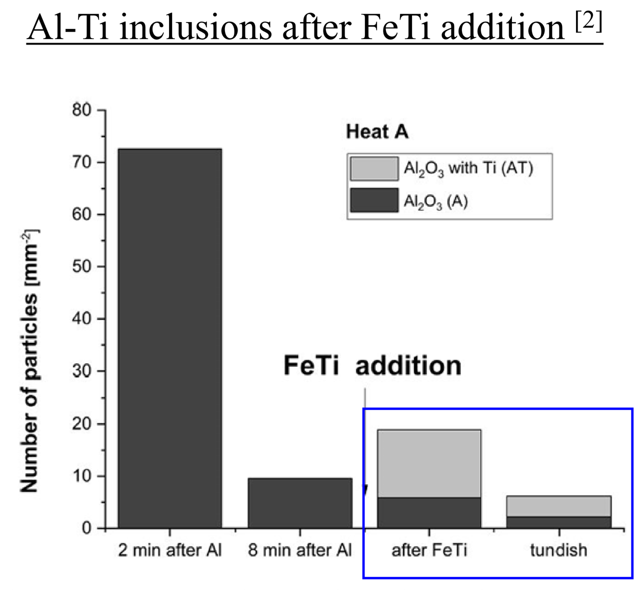
Cross sectional view of SENs [1]



Clogging index vs Ti / Al ratio [2]



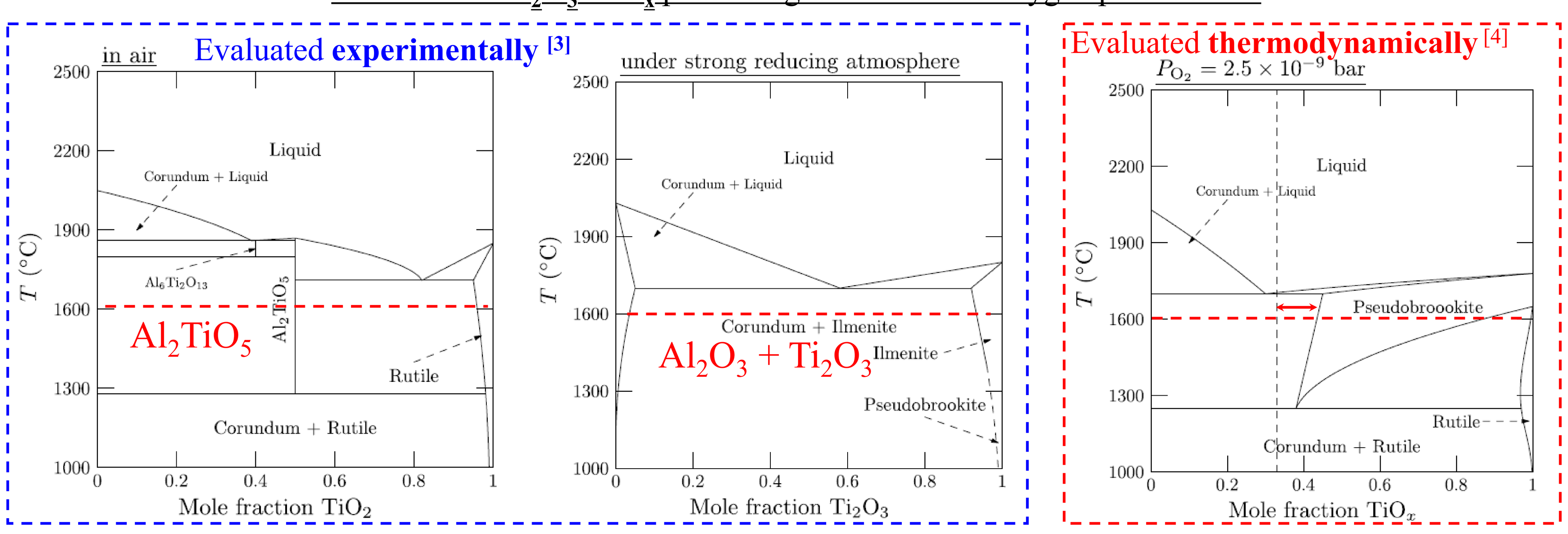
Al-Ti inclusions after FeTi addition [2]



- More clogging occurs in Ti-added ULC steel production than in ULC steel
- This clogging behaviuor is critical to productivity and many researchers have investigated this behaviour
- Presence of Ti-containing inclusion is treated as the main cause of the problem

- Importance to investigate the phase equilibria of Al_2O_3-TiO_x system

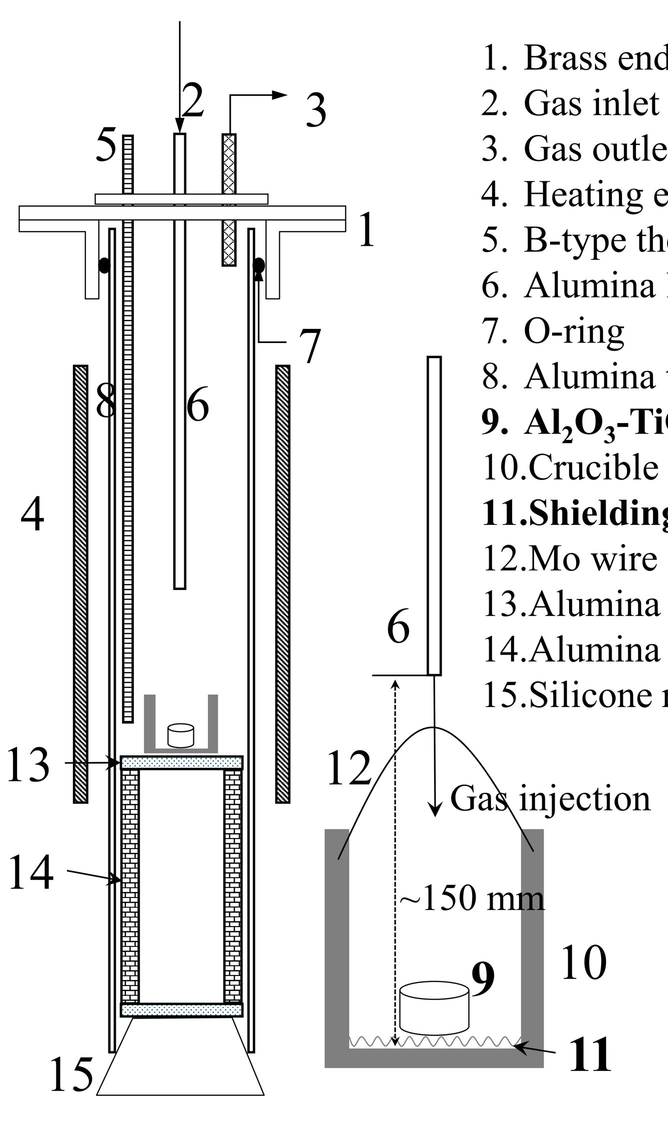
A schematic **Al_2O_3-TiO_x** phase diagram in various oxygen potential [3,4]



- Al_2TiO_5 phase which is treated as Al-Ti inclusion is stable in oxidizing atmosphere and unstable in a reducing atmosphere
- There are many literatures about Al-Ti oxide phase diagram carried out in an air condition and in a strong reducing condition
- However, there are no experimental data of mid range of oxygen partial pressure and Fe containing system matched with steelmaking conditions

2 Experimental methods

- Apparatus used in this study and experimental conditions



1. Brass endcap
2. Gas inlet
3. Gas outlet
4. Heating element($LaCrO_3$)
5. B-type thermocouple
6. Alumina lance
7. O-ring
8. Alumina tube
9. **Al_2O_3-TiO_x pellets**
10. Crucible (Alumina or Graphite)
11. **Shielding wire (Mo or Pt)**
12. Mo wire
13. Alumina plate
14. Alumina brick
15. Silicone rubber

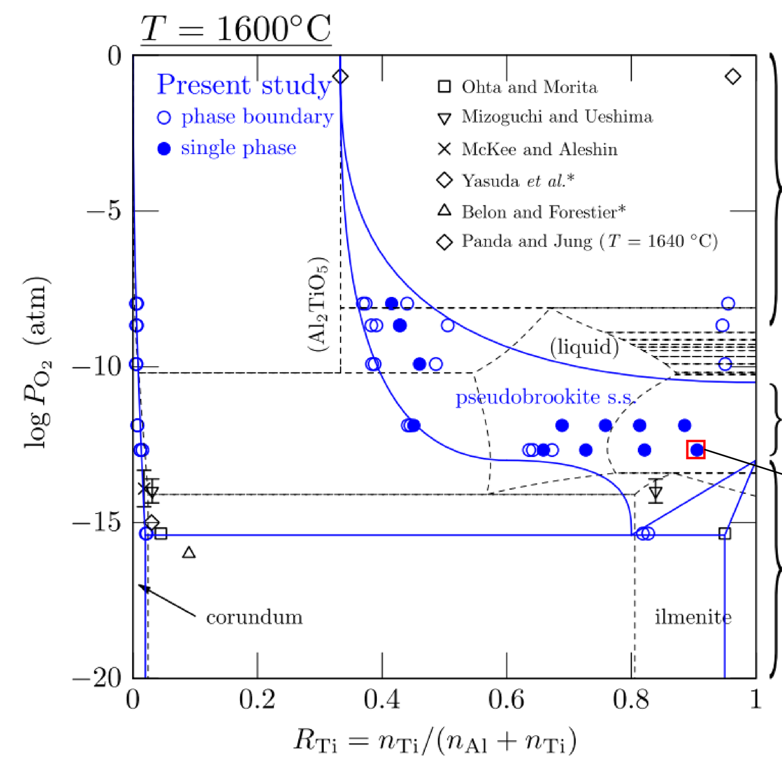
- Experimental conditions
  - Temperature: 1300 – 1600 °C
  - System: Al_2O_3-TiO_x (mixed pellets)
  - Equilibrium time : 24 ~ 48 h
  - Analysis: XRD, EPMA
- Considerations
  - Preheated at 1650 °C for 12 hours (No liquid phase)
  - ZAF correction of pure Al_2O_3, TiO_2

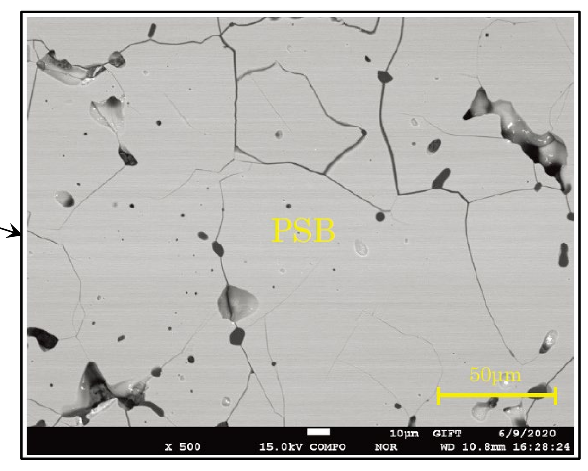
$10^{-16.6} < P_{O_2}$ (atm) $< 10^{-8.0}$

Gas mixture	Flow rate ratio ($ml \cdot min^{-1}$)
CO / CO_2	320/80, 360/40
Ar-10%H_2 / Ar-1%CO_2	200/200, 360/40
CO / Ar-1%CO_2	360/40
C (graphite) / CO	400

3 Results & Discussion

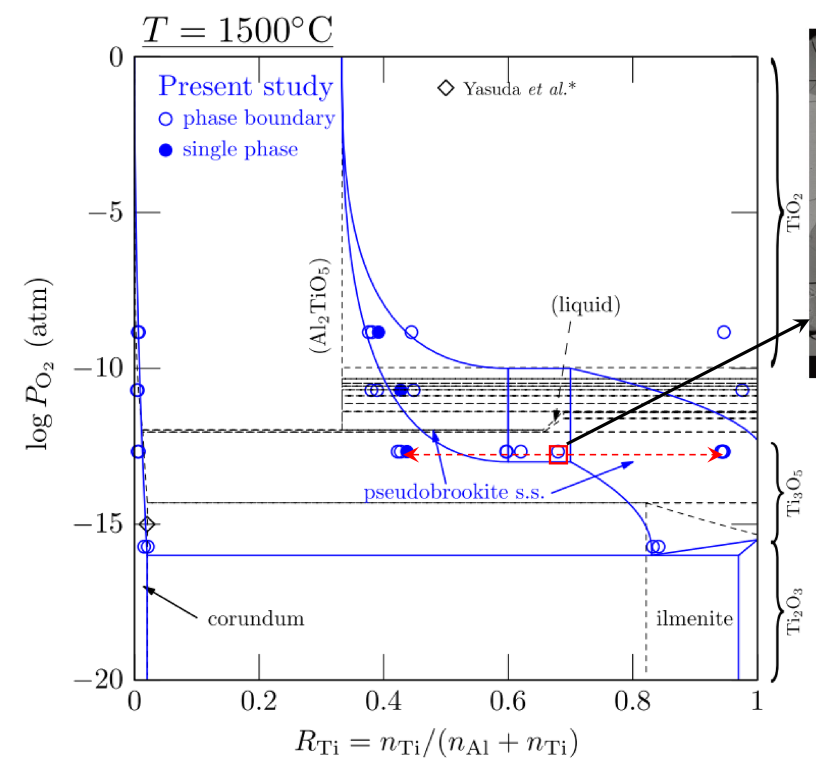
- Phase equilibria of Al_2O_3-TiO_x at 1600 °C

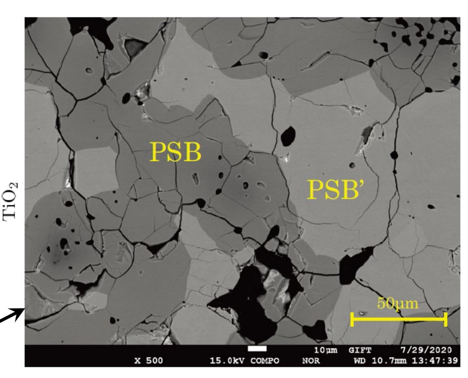




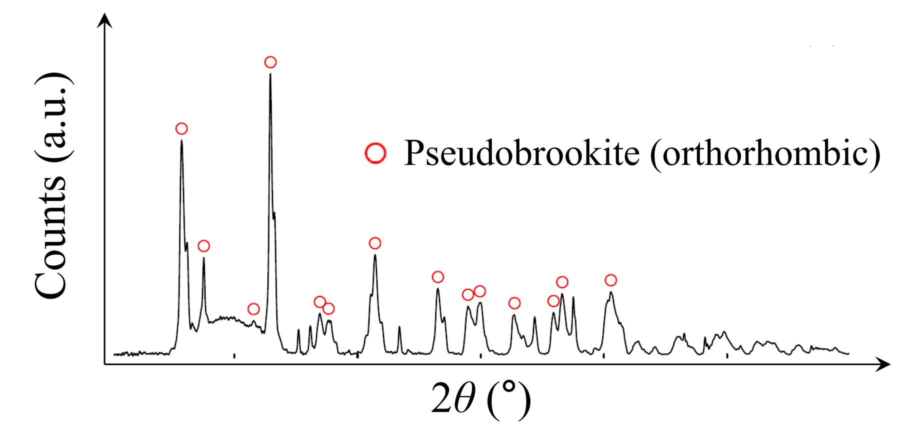
- Al_2TiO_5 is unstable in reducing conditions
- Al-Ti pseudobrookite phase is stable in wider range of P_{O_2}
- By decreasing P_{O_2}, equilibrium composition of Al-Ti pseudobrookite was changed to high Ti pseudobrookite

- Phase equilibria of Al_2O_3-TiO_x at 1500 °C

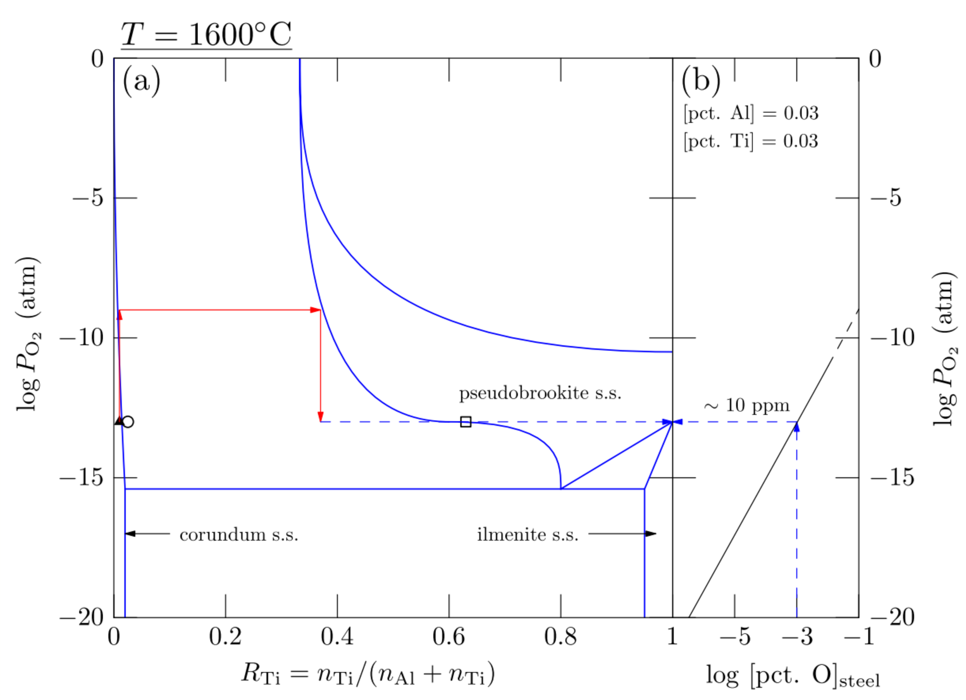




- 2-phase pseudobrookites (Al-rich + Ti-rich) were observed
- XRD results also showed only one pseudobrookite phase.



- Application to evolution of Al-Ti complex inclusion in Ti-added ULC steel production



- In steelmaking process, [pct. O] is controlled under 0.001 (<10 ppm) and this corresponds approximately to P_{O_2}=10^{-13} atm

①In these reducing condition, the main inclusions are Al_2O_3 (with few pct of Ti)
②When steel is exposed to reoxidation source,
- Ti in Al_2O_3 can be extracted and reacted with [Sol. Al] and finally form Al-Ti inclusions
③When those Al-Ti inclusions are re-trapped in the liquid steel with low P_{O_2}, decomposition reaction occurs

4 Conclusions

- Al_2TiO_5 has been treated as a major cause of the SEN clogging issue, however, stability of Al_2TiO_5 has been still ambiguous
- It was necessary to investigate the phase equilibria of Al_2O_3-TiO_x system experimentally
- As a result of the present study,
  - Al_2TiO_5 is unstable and changed to Al-Ti pseudobrookite phase with high Ti by decreasing P_{O_2}
  - This result is accompanied with following decomposition reaction occurs

$$(\mathbf{Al},\mathrm{Ti})_3O_5 \rightarrow (\mathrm{Al},\mathbf{Ti})_3O_5 + \mathbf{Al_2O_3} + \mathbf{O_2}$$

- Al-Ti complex inclusions can act as a reoxidation source in Ti-ULC steelmaking process, and cause additional **Al_2O_3** and **oxygen (O_2)** which can deteriorate steel cleanliness

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[1] Lee *et al.*, *ISIJ int.*, 59.5 (2019), 749.
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[3] Park *et al.*, *J. Europ. Ceram. Soc.*, 41 (2021), 7362.
[4] Seifert and Aldinger, *Zeit. Für Metallkd.*, 87 (1996), 841.