Reconciling Fickian Diffusion Theory with Non-Fickian Diffusion Reality in Heat Treating Corundum

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Abstract
This paper highlights a significant discrepancy between theoretical diffusion models and empirical observations in commercial corundum (ruby/sapphire) heat treatment. While the standard Fickian diffusion model, paired with general Arrhenius equations for bulk diffusion in pure alumina, predicts processing times spanning several years (e.g., ~8.46 years), real-world experiments consistently achieve desired color modification within hours. This vast difference indicates that commercial heating processes exploit faster, non-Fickian mechanisms such as diffusion along crystal defects, grain boundaries, and surfaces. The author presents experimental data—a 1-carat flame-fusion ruby treated in 300 minutes—to contrast with the theoretical failure, advocating for empirical methodologies and alternative thermodynamic models (e.g., the solubility method using FactSage software) for practical application.

Keywords: *Corundum, Alumina, Gaseous Diffusion, Fickian Diffusion Mechanisms, Non-Fickian Transport, Materials Science, Gemology, Heat Treatment, Ruby and Sapphire*.

1. Introduction

Gemstone heat treatment relies heavily on the principles of solid-state diffusion to alter the color and clarity of rubies and sapphires. Since the 1980s, researchers have attempted to apply established Fickian diffusion models to predict optimal processing parameters, leading to the publication of many conflicting technical papers. Although improved measurement techniques such as Secondary Ion Mass Spectrometry (SIMS) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) were implemented, the results remain inconsistent. This work examines this fundamental discrepancy, comparing a Fickian theoretical calculation that predicts diffusion times over geological timescales with actual experimental results achieved within hours.

2. Diffusion Calculating Methods

Determining the diffusion coefficient is essential for calculating the diffusion time required when heating corundum during the soaking step of the process. This process can be approached using two distinct methodologies:

- **Fickian Diffusion Model:** A theoretical model based on Fick's laws of diffusion and the Arrhenius expression.
- **Non-Fickian Methods:** A practical method grounded in empirical observations and experimental data.

2.1. Fickian Diffusion Model (Theoretical)

Fick's laws provide the correct physical theoretical model for describing the physics of diffusion; however, Fick’s laws are impractical for predicting the specific diffusion time required for commercial corundum heating applications. This is because the models use diverging diffusion coefficient values, leading to considerable discrepancies.

The Fickian Diffusion Model assumes diffusion through an ideal, perfect single crystal lattice that is completely free of crystal lattice defects. This model provides results over geological time-scales (hundreds to thousands of years).

Calculating the Diffusion Time: In calculating the diffusion time of gaseous compositions (e.g., oxygen), as well as solid elements (e.g., titanium), the formulas derived from Fick’s Second Law of diffusion, in conjunction with the Arrhenius expression of the diffusion coefficient, are used depending on the conditions.

The following parameters apply to diffusion-related equations:

Paran	Description	Units
x	Depth of diffusion	m
D	Diffusion coefficient	m²/s
$D0$	Pre-exponential factor	m²/s
Ea	Activation energy	J/mol
R	Ideal gas constant	8.314 J/n
T	Absolute temperature	Kelvin (I
A	Surface area of the spec	cm²

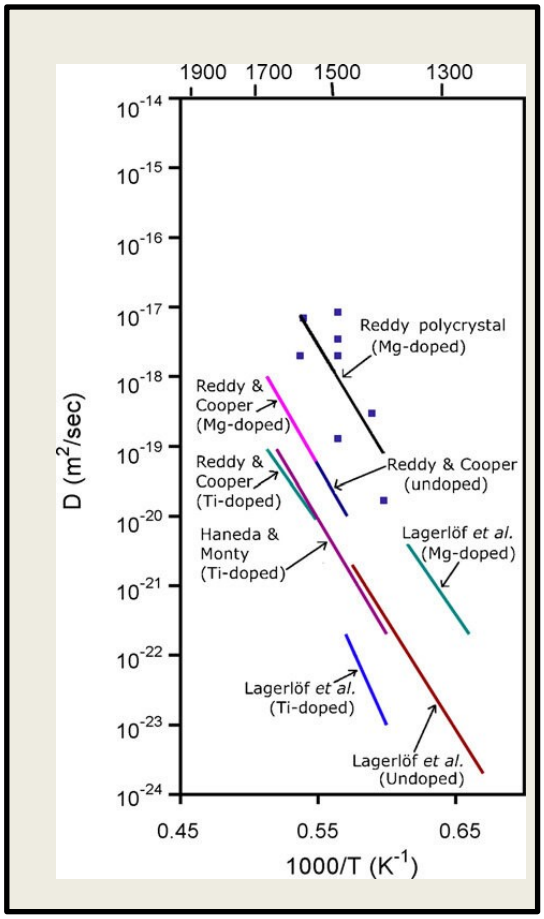
The important diffusion coefficient (D) is provided using the Arrhenius expression, which is a prerequisite to determine the diffusion time, which is the final target. The Arrhenius expression represents the diffusion mobility rate between two media (e.g., gas and corundum):

$$D=D_0\times\exp(-E_a/RT)$$

In Fick's Second Law, the depth of diffusion (x) is determined by solving the diffusion equation using the diffusion coefficient (D) and time (t), along with specific initial and boundary conditions of the system.

The depth of diffusion is not a fixed parameter within the law itself, but rather a variable (x) used in the solution to determine the concentration profile of the diffusing substance at a given time (t). The relationship is typically expressed through solutions to the Fick's Second Law of partial differential equations:

$$\partial C/\partial t = D\,((\partial^2 C)/(\partial x^2))$$



Oxygen lattice diffusion on Ti and Mg in a-Al2O3 reported by various researchers. (Heuer, 2008)

Moreover, the *error function (erf)* formula, which derives from Fick's laws, cannot be reliably applied to commercial corundum heating. The theoretical predictions are rendered useless by the inherent crystal defects of the corundum and the resulting dominance of non-Fickian diffusion dynamics.

Software applications: Solving for diffusion time (t) based on Fick's laws the calculations can be accomplished by applying the formulas using Microsoft Excel or Google Sheets. These calculations can be customized to solve specific problems. Specialized scientific software applications that are used to calculate the diffusion time (t) of elements include Mathematica, COMSOL Software, and others.

2.2. Non-Fickian Diffusion Model (Practical)

The Non-Fickian Diffusion Method is the practical approach used in commercial corundum treatment. It relies on exploiting the faster diffusion pathways provided by a crystal's natural defects. This is possible with experimental data, microscopic characterization, and empirical evidence. Decades of experience have shown that the required diffusion time is best estimated by evaluating these specific imperfections, features, and attributes inherent in the natural corundum.

3. Experiments and Observations

A heating experiment performed by the author demonstrated the reduction of a slight bluish tinge in a 1-carat flame-fusion ruby containing ~10 ppma iron (Fe) and ~2 ppma titanium (Ti). The ruby was heated in an open-loop electric muffle tube furnace at 1250∘C, purging oxygen at 200 cc/min under a 1 bar gas pressure. The bluish tinge was effectively reduced after soaking for ~300 minutes (5 hours).

In contrast, a theoretical calculation using the Fick's Law Approximation diffusion model and a general Arrhenius equation for aluminum vacancy diffusivity in bulk corundum predicts the time required for uniform diffusion across the entire ruby to be ~8.46 years. This vast difference in time indicates that the quick experimental result was likely achieved either through a much faster diffusion mechanism (e.g., along grain boundaries, dislocations, or the surface) or by only affecting a very shallow surface layer of the ruby.

Over the past decades, the author performed more than 3,000 practical experiments to determine the actual diffusion time required for removing C-H-O gases and $Ti^{4}+$ in corundum. The graphs and values published in existing literature consistently do not agree with the results obtained in these practical heating processes. Efforts to correlate established diffusion coefficient values to align with the practical experiments have, thus far, been unsuccessful.

4. Parameters Influencing Diffusion in Corundum

Diffusion in corundum is a complex process influenced by intrinsic and extrinsic factors related to its crystalline structure and defects. These factors are: Crystallographic features, anisotropy (axial orientation), physical discontinuities (parting, fracture), growth patterns and impurities (color zoning, chemical impurities), crystal lattice defects (point defects, line defects, planar defects, volume defects), and others.

5. Summary of the Distinction

Ultimately, Fickian and non-Fickian models are not alternative methods for "computing" time. Rather, they are two different physical models used to describe diffusion in different scenarios, leading to vastly different time estimates for the same process depending on the material's structural integrity.

6. Conclusion

There is no specific methodology or guidelines for accurately calculating the diffusion time for oxygen, hydrogen, and other elements in heating corundum. The user empirically determines the diffusion time based on detailed records for each heating process performed and judged case by case. On the other hand, using the solubility method calculations based on the solvent concentration and partial pressure of the gas composition at a given temperature provides a concrete, superior alternative approach for analysis using the FactSage software.

7. **Summary**:

"Despite all the work conducted over many decades, there remains a major problem in understanding diffusion in alumina," Harding, J. H., Atkinson, K. J. W., & Grimes, R. W. (2003). Experiment and theory of diffusion in alumina. *Journal of the American Ceramic Society*, 86(4), 554–559.

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