ANALYSIS OF THE SCALE FORMED ON STEEL BLOOMS DURING HEATING

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The scale formed on carbon steel blooms as a result of heating was analysed by means of light microscopy, scanning electron microscopy and X-ray diffraction. The scale consisted of wüstite, magnetite, hematite, and fayalite. The scale that dropped off onto the bottom of a pusher-type furnace was enriched with copper and nickel. The calculated average diffusion distance for liquid copper at the heating temperature of 1250℃ and heating time of 5.2 hours was 4.2 μm suggesting a very fast rate of formation ($v_1 = 0.22$ nm/s).

K e y   w o r d s: steel bloom, scale, heating, oxidation

ANALÝZA OKUJÍ VZNIKLÝCH NA POVRCHU PŘEDVALKŮ BĚHEM OHŘEVU

Okuje vzniklé na předvalcích z uhlíkové oceli v důsledku ohřevu byly analyzovány metodami optické mikroskopie, rastrovací elektronové mikroskopie a rentgenovou difrakcí. Okuje jsou složeny z wüstitu, magnetitu, hematitu a fayalitu. Okuje odpadlé na spod narážecí pece byly bohaté na měď a nikl. Vypočtená střední hloubka difuze pro taveninu mědi při teplotě ohřevu 1250℃ a při době ohřevu 5,2 hodiny byla 4,2 μm. To nasvědčuje vysoké rychlosti vzniku okují ($v_1 = 0{,}22$ nm/s).

1. Introduction

One of the most important quality shortcomings in the process of hot-rolling of steel products is the appearance of a scale during the heating of steel blooms before plastic deformation. The formation of the scale on the steel surface is strongly related to the heating conditions, i.e. heating temperature, heating time, furnace atmosphere, oxygen availability, etc. A considerable amount of research work has been carried out to aid in understanding the hot ductility of steels in the air in the

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temperature range from 700 to 1100 °C [1, 2]. Iron oxides that form at temperatures above 570 °C are known to occur in three different phases: wüstite, magnetite and hematite [3–6]. In industrial practice, oxidation of steel blooms follows a continuous heating schedule. At higher heating temperatures (e.g. 1250 °C) the mechanism of the oxidation process has not yet been fully clarified, especially when the continuous heating schedule is accompanied by changes in heating time. In order to characterize and understand the oxidation process, a detailed knowledge of the oxide microstructure as well as of the mechanism of reactions occurring at the scale/steel interface is necessary. Although several studies have been concerned with these issues, the mechanisms controlling those phenomena have not been fully understood. In an investigation of the oxide-scale structure developed on a commercial hot-rolled steel strip Chen and Yuen [7] found the thickness of the oxide scale to be the function of the finishing temperature. The distribution of tramp elements (copper, tin, nickel, etc.) plays an important role in the study of oxidation behaviour and in the understanding and control of the oxide microstructure [8–10]. Kajitani et al. [11] proposed a mechanism based on the occlusion of liquid Cu-enriched phases into the liquid eutectic phase $FeO–Fe_2SiO_4$.

Although the effects caused by change in oxidation temperature and atmosphere are known, their interactions are complex. In this work attention has been focussed on analysis of the steel scale with respect to phase composition including the scale that dropped off onto the bottom of the furnace.

2. Technique

Low-carbon (0.15wt.%C–0.6wt.%Mn–0.08wt.%Cu–0.05wt.%Ni) steel blooms (350 × 300 × 3800 mm) were heated at 1250 °C under industrial conditions in a pusher-type furnace. The furnace atmosphere was generated by combustion of natural gas, with the air factor from 1.05 to 1.10. The heating time of the steel blooms was from 5.2 to 65.2 hours. The thickness of the steel scale was measured at the end of each heating period. Specimens of the scale (10 × 5 × s, s – scale thickness) were mounted in epoxy resin and polished mechanically with silicon carbide paper (400, 600, 800 and 1000 grit), and with 0.3 μm alumina powder using doubly distilled water. They were then washed in an ultrasonic bath, rinsed with doubly distilled water, and dried. The scale samples were examined by means of light microscopy, scanning electron microscopy (SEM), and X-ray diffraction (XRD) method. Light microscopy and SEM were used to observe the oxide morphology. The distribution of the elements on the surface was investigated by SEM, and by the energy dispersive X-ray (EDX) and wave dispersive X-ray spectroscopy (WDS) analysing facilities. The XRD method served for the identification of phases in the steel scale. The counting technique and CrKα radiation were used.

3. Results and discussion

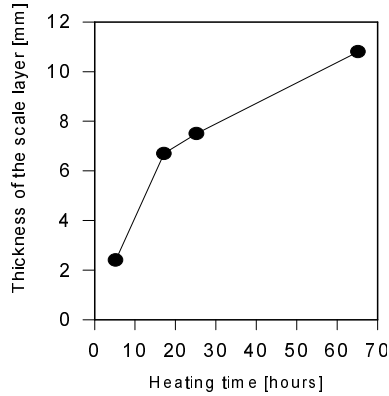Results of measurement of scale thickness clearly demonstrated that the heating time had a strong effect on the growth of the scale layer. Figure 1 shows the thickness of the steel scale as a function of the heating time. The thickness increased with the heating time and a maximum value of 10.8 mm was reached after heating for 65.2 hours. The scale that formed during that period was about five times thicker than the scale formed after 5.2 hours. The scale on the surface of steel blooms consisted of a mixture of iron oxides. At 1250 °C the scale layer was composed of wüstite (FeO), magnetite (Fe_3O_4), and hematite (Fe_2O_3), and a small content of fayalite (Fe_2SiO_4) (Figs. 2 and 3). This was confirmed by EDX analysis (Fig. 3) which showed a composition of 53wt.%Fe–39wt.%O–4wt.%Si, with a small content of carbon and manganese. Our results were in accordance with those of other authors reported in literature [3, 5].

Fig. 1. The effect of heating time of the steel blooms on the scale thickness.
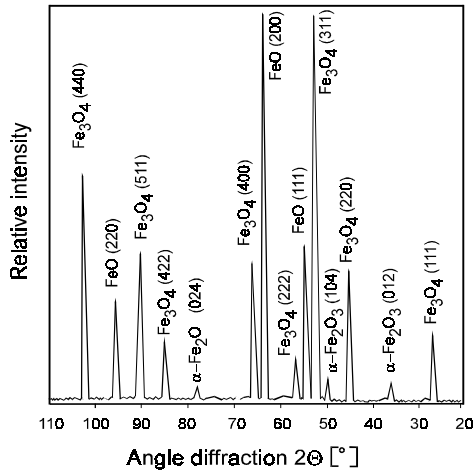

Fig. 2. X-ray diffraction spectrum of the scale layer formed on the steel blooms after heating for 5.2 hours.
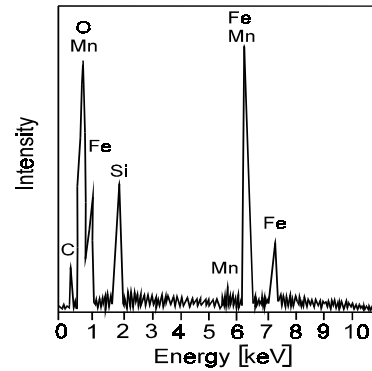

Fig. 3. Energy dispersive spectrum of the scale layer formed on the steel blooms after heating for 5.2 hours.
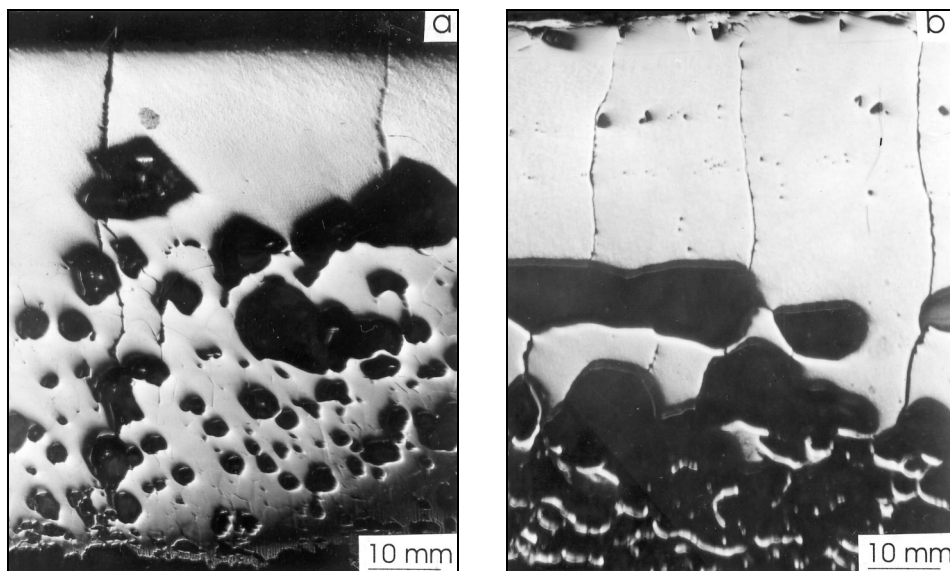
Fig. 4. Light micrographs of the scale layer formed on the steel blooms in a pusher-type furnace at different heating times: a) 17.2 hours, b) 65.2 hours.

For microstructural examination of specimens light microscopy and scanning electron microscopy were applied. Figure 4 shows the light micrographs of the scale that formed on the steel blooms as a result of heating for 17.2 and 65.2 hours. The scale consisted of grains 0.1–2 mm in size and had numerous voids in the oxide layer. The voids were taken to be the result of artifacts introduced during polishing. Figures 5a and 5b show secondary electron images (SEI) of the scale formed on the steel blooms at the heating time of 5.2 hours. At the boundaries a Si-enriched phase can be seen by means of WDS analysis (Fig. 5c).

At the temperature of 1250 °C, which is higher than the eutectic temperature of fayalite (1177 °C), the rate of steel oxidation increased because of enhanced diffusion of iron and oxygen through the molten fayalite [12]. Figures 6 and 7 show the results of testing of the scale that dropped off onto the bottom of the heating zone of a pusher-type furnace, at two different positions. The black spherical section in the secondary electron image (Fig. 6a) marks the region enriched with copper (Fig. 6b) and nickel (Fig. 6c). The composition of the Cu-phase measured by WDS analysis was 24wt.%Cu–0.4wt.%Ni–75.6wt.%Fe.

Figure 7 also shows regions where copper accumulated into the scale in the form of secondary particles. A diagram of an isothermal section of the Fe–Cu–Ni ternary system at 1200 °C is given in Fig. 8. The composition of the Cu–Ni
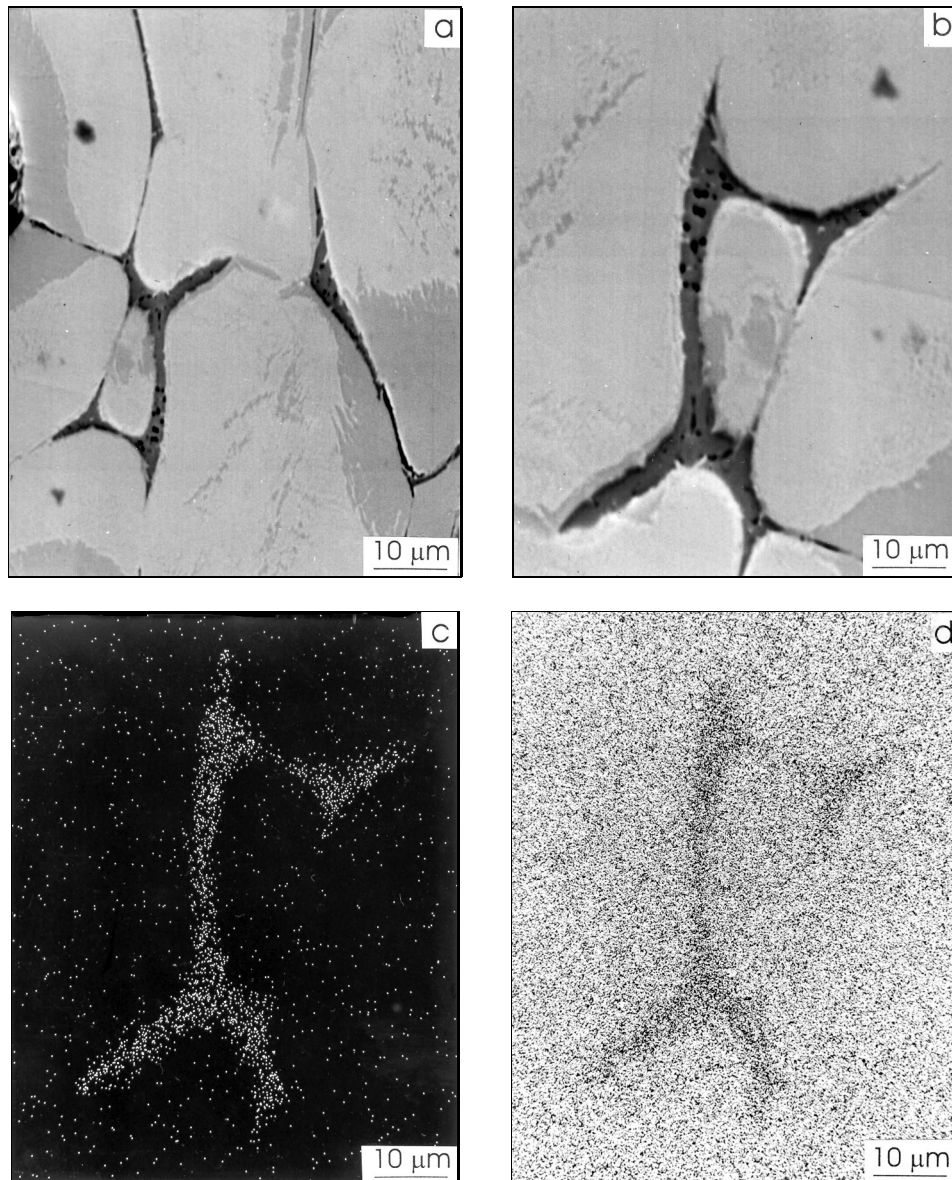
Fig. 5. SEM images (a and b) and X-ray elemental distribution of silicon (c) and iron (d) in the steel scale formed after heating for 5.2 hours.

phase in Fig. 6 (24wt.%Cu–0.4wt.%Ni–75.6wt.%Fe) shows that the Cu-rich liquid phase equilibrated with the γ + L phases in the ternary phase diagram presented
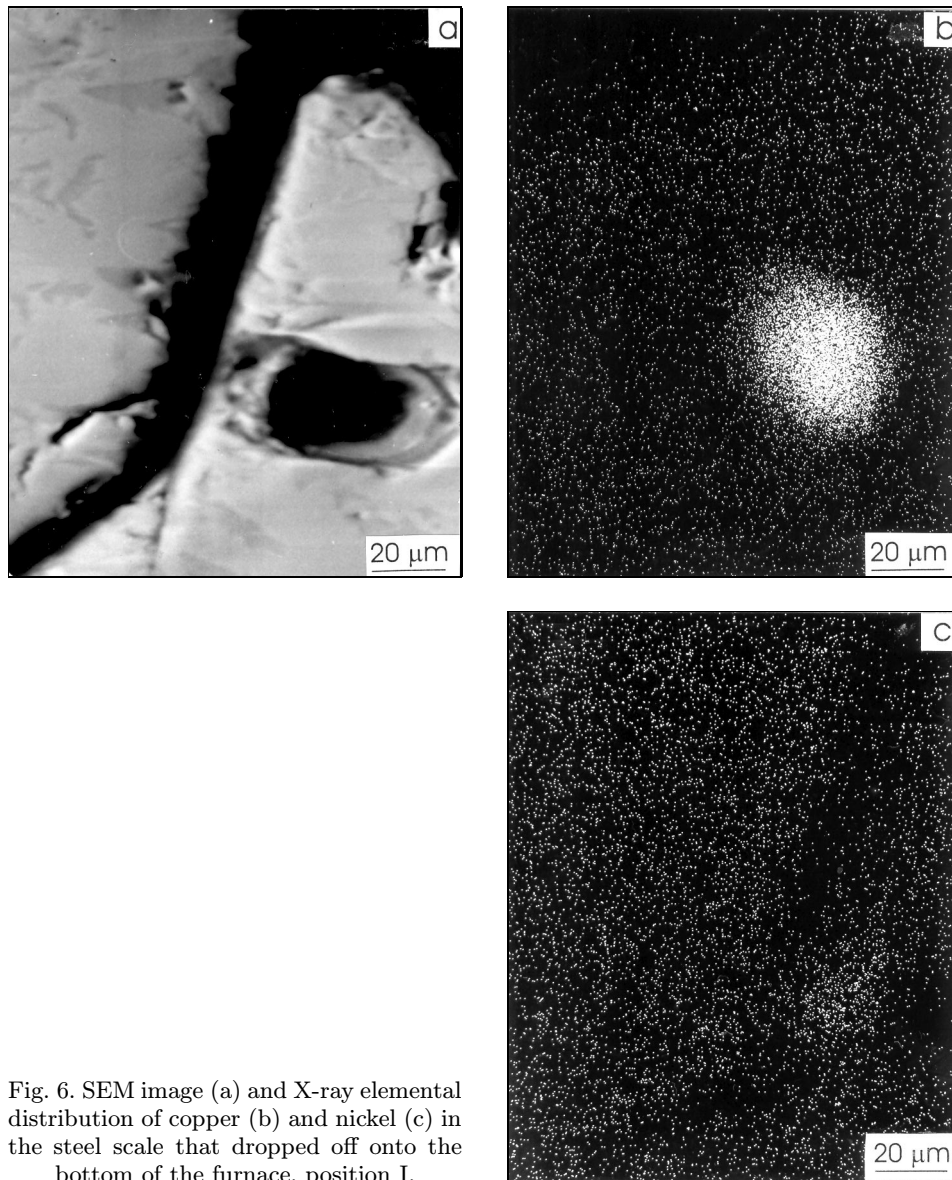
Fig. 6. SEM image (a) and X-ray elemental distribution of copper (b) and nickel (c) in the steel scale that dropped off onto the bottom of the furnace, position I.

in Fig. 9 (point A). We may speculate that liquid droplets of copper and nickel formed as a result of heavy oxidation, i.e. during long exposure of the steel blooms to a temperature of 1250 ℃ (5.2–65.2 hours).

Elemental X-ray analysis of the scale from the bottom of the furnace indicated enrichment with copper and nickel near the steel/scale interface (Figs. 6 and 7).
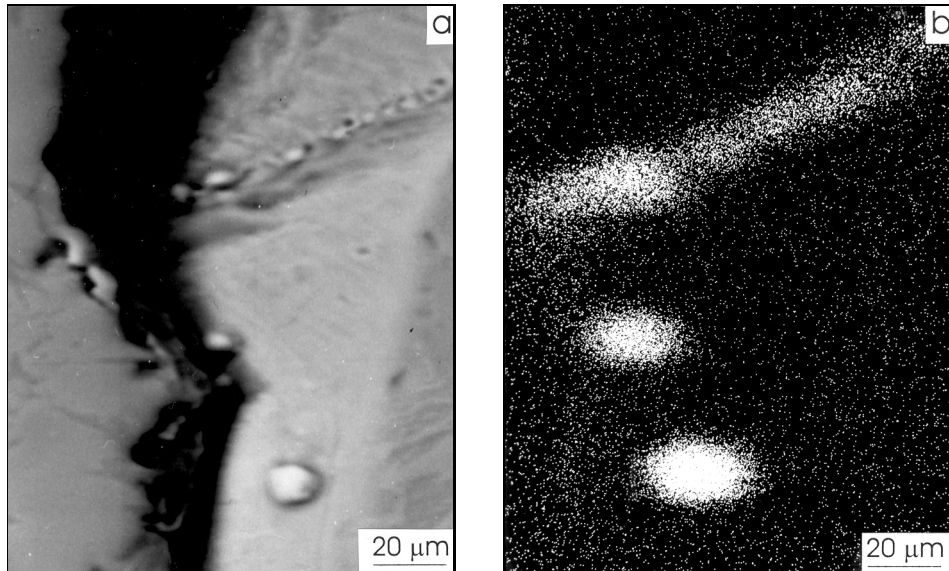
Fig. 7. SEM image (a) and X-ray elemental distribution of copper (b) in the steel scale
that dropped off onto the bottom of the furnace, position II.

Copper solubility in the scale being very limited, copper remained at the interface
between the scale and the steel matrix. The melting point of pure copper is 1085 °C.
Liquid copper can diffuse back into steel by penetrating into the austenite grain
boundaries [13] and/or take the form of liquid droplets of the Cu-enriched phase.
Assuming that the diffusion coefficient for liquid copper in austenite is 9.6×10^{-16}
m^2/s [14] the average diffusion distances for copper can be calculated by equation

$$s = (D_{\mathrm{gb}} \cdot t)^{1/2}, \tag{1}$$

where D_{gb} is the diffusion coefficient for liquid copper at the grain boundary in
solid iron

$$D_{\mathrm{gb}} = [6.5 \times 10^{-6}/\delta] \exp(-38000/RT), \tag{2}$$

where δ is the grain boundary thickness (250 nm).

The diffusion of liquid copper can be calculated by equation [15]

$$v_1 = (D_{\mathrm{gb}}/t)^{1/2}. \tag{3}$$

If the heating time value of 5.2 hours (18720 s) is inserted in equations (1)
and (3) the calculated average diffusion distance for copper at 1250 °C is 4.2 μm
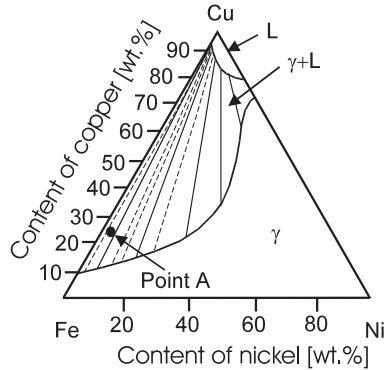
Fig. 8. Isothermal section of the Fe-Cu-Ni ternary system at 1200 °C. Point A indicates the composition of the copper- and nickel-enriched phases from Fig. 6.
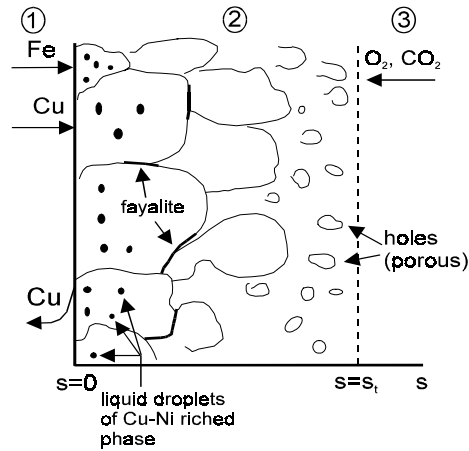
Fig. 9. Schematic illustration of the mechanism of scale formation on the steel blooms after heating in a pusher-type furnace: 1 – steel, 2 – scale, 3 – furnace atmosphere.

and the diffusion rate of liquid copper is 0.22 nm/s. Those values suggest that the rate of formation of liquid copper is very fast. Although the diffusion coefficient for tin is about ten times higher than that for copper, a liquid Sn-Fe phase was not observed in this work.

Figure 9 shows a schematic illustration of scale formation on the steel blooms. The beginning of the heating process was marked by the formation of FeO. Increase in temperature and a prolonged heating time had as a result a mixture of FeO, Fe_3O_4 and Fe_2O_3, as well as a small concentration of fayalite. As the diffusion coefficients for copper and nickel in austenite were lower than the coefficient for iron, the two metals concentrated around the internal oxides. Iron is more reactive to O_2 and CO_2 than copper and nickel. They remained in the metal form near the steel/scale interface [16]. Copper diffusion from the steel matrix to the matrix/scale interface took place at 1250 °C. With respect to the lower melting point the Cu--Ni-enriched phases at the steel/scale interface, the liquid droplets of these phases occur which dropped off to the bottom of the furnace.

4. Conclusions

From the results of analysis of the scale that formed on carbon steel blooms as a result of heating in a pusher-type furnace the following conclusions can be drawn:

1. The scale thickness increased with increase in heating time. The scale that formed after heating for 65.2 hours was about five times thicker (10.4 mm) than the scale at the end of a 5.2-hour heating period.

2. The scale on the steel blooms was composed of wüstite, magnetite, hematite and some fayalite.

3. The scale that dropped off onto the bottom of the furnace heating zone consisted of the copper- and nickel-enriched phases.

4. The calculated average diffusion distance for liquid copper at the heating temperature of 1250 ℃ and heating time of 5.2 hours was 4.2 μm, which suggests that its formation took place at a very fast rate ($v_1 = 0.22$ nm/s).

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