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# Revisiting the role of substrate microstructure and short-circuit diffusion in the oxidation of Ni-Cr alloys

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## 1. INTRODUCTION

The growth of a protective oxide scale on a heat-resisting alloy leads to subsurface depletion of the protective element (most commonly Cr or Al), and requires a sufficient flux of this element from the bulk to the surface (Figure 1). Selective oxidation critically depends on the alloy microstructure, as shown by Giggins and Pettit in the case of Ni-Cr alloys at 900-1100 °C [1]: in cold-worked specimens, subsurface defects generate new grain boundaries by recrystallization upon heating, which provides accelerated diffusion to the surface and favors the establishment of a Cr<sub>2</sub>O<sub>3</sub> scale.

Similar processes operate at lower temperatures, where recrystallization is absent or much slower. Depletion profiles observed in Ni-base alloys exposed to pressurized water 340-360 °C can reach dozens of nm from the surface, intergranular oxides or cracks [2]. The diffusivity of Cr is not known at these temperatures, but the extrapolation of high temperature tracer data would suggest that lattice diffusion alone cannot account for these diffusion distances. Instead, dislocations and subgrain boundaries may act as high diffusivity paths.

A difficulty in modeling these processes arises from the fact that the organization and density of 1D and 2D defects evolve during heat treatments as recovery, recrystallization and grain growth proceed. In addition, vacancy fluxes are generated in the alloy as a result of both the oxidation reaction and the Kirkendall effect. The extent to which vacancy supersaturations may develop depends on the alloy capacity for vacancy annihilation (at grain boundaries, interfaces, free surfaces or in the bulk by dislocation climb), and therefore on the density of the various types of defects. The resulting vacancy concentration will in turn affect diffusion [3].

The present work aims at better understanding the influence of the microstructure on Cr depletion and selective oxidation, in order to better integrate microstructural evolutions in oxidation kinetics modeling. It combines oxidation experiments and measurements of base diffusion data in the same temperature range, using annealed and cold-worked substrates.

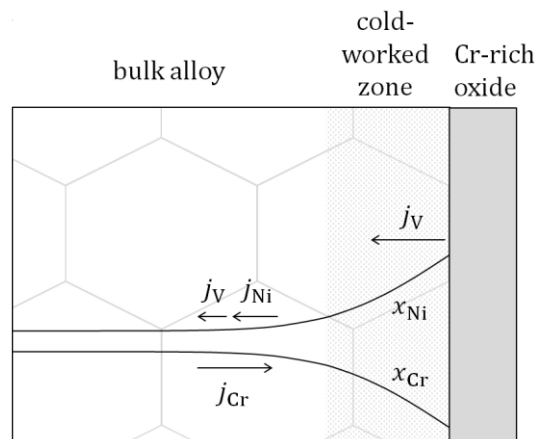


Figure 1: Concentration profiles in a binary Ni-Cr alloy during the growth of a Cr-rich oxide scale at high temperature. Fluxes of conservative species (Ni, Cr) and vacancies (V) are indicated by arrows.

## 2. EXPERIMENTAL

The diffusivity of Cr was studied via tracer experiments. Volume diffusion measurements were conducted on Ni and Ni-20Cr using  $^{52}\text{Cr}$  and  $^{54}\text{Cr}$ , respectively, as tracers. The grain boundary diffusivity was studied on Ni only, using annealed and cold-rolled substrates. Thin films (5 nm) of Cr were deposited on the substrates by sublimation. The specimens were vacuum sealed in quartz capsules diffusion heat treated at temperatures in the range 350-850 °C. The depth profiles were measured by secondary ion mass spectrometry.

Oxidation experiments were conducted in flowing dry air at 350-600 °C for times ranging from 1 to 750 h, using a Ni-30Cr alloy with two types of surface preparation: grinding and fine polishing. The subsurface microstructures were studied before and after oxidation by transmission electron microscopy (TEM).

## 3. RESULTS AND DISCUSSION

The volume diffusion coefficients were found to be in agreement with the higher temperature data reported in the literature (Figure 2a), suggesting that the volume diffusion mechanism did not change at low temperature. The diffusivities measured on individual grain boundaries of a given specimen were found to vary widely, confirming the important influence of grain boundary properties on diffusion. The general trend was also in agreement with higher temperature data measured in various Ni-base alloys (Figure 2b).

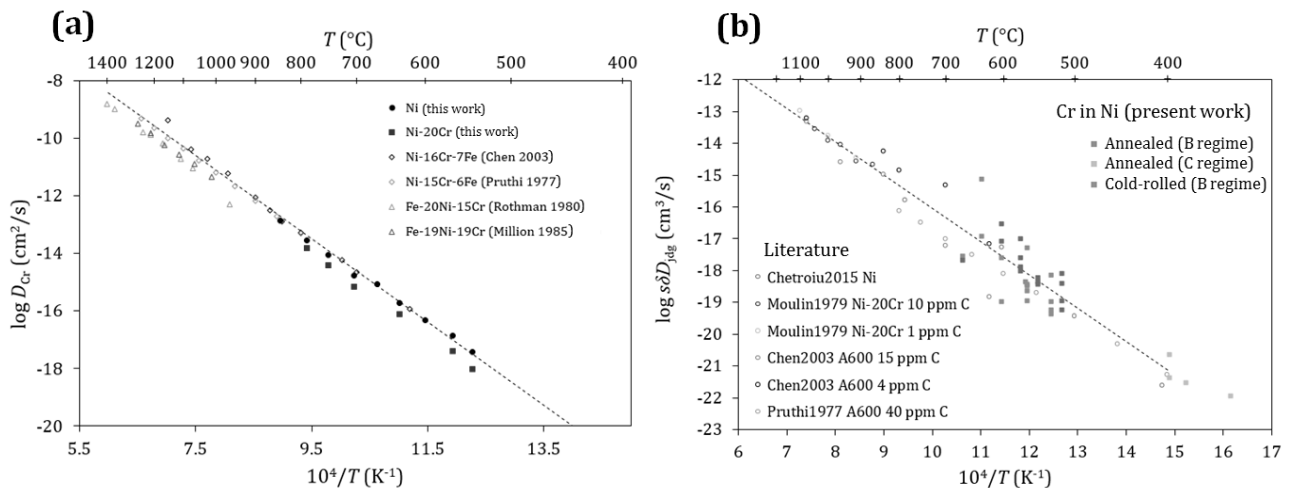


Figure 2: Tracer diffusivity data for Cr in Ni and Ni-base alloys, and comparison with literature data. (a) Volume diffusion; (b) grain boundary diffusion.

The examination of polished Ni-30Cr specimens before oxidation showed that fine polishing generated a 30-nm deep cold-worked region, with a high dislocation density and elongated grains. After 20 h oxidation at 400 °C, most of these ultra-fine grains have been consumed by the underlying  $\mu\text{m}$ -size grains. However, some are still present and retain a high dislocation density – recrystallization is not complete. Oxidation produced layers of  $\text{Cr}_2\text{O}_3$  and NiO, and pores at the metal/oxide interface. After 750 h at 550 °C, the alloy is recrystallized and pores are found within the oxide scale (Figure 3a). Concentrations profiles measured by EDS after reaction at both temperatures showed that Cr depletion was severe in some grains, and absent in others.

Grinding produced a more severely deformed region, with  $\sim 20$  nm large grains and a high dislocation density over a 500 nm depth. The high defect density favored exclusive  $\text{Cr}_2\text{O}_3$  formation, with no interfacial porosity (Figure 3b). Microstructural observations after 750 h oxidation at 550 °C, where the cold-worked region is recrystallized, show that the extent of Cr depletion is also very different from one grain to the next. A combination of depletion profiles and bright field images recorded on the same grains will be used to discuss the relationship between local diffusivity variations and microstructure during the presentation.

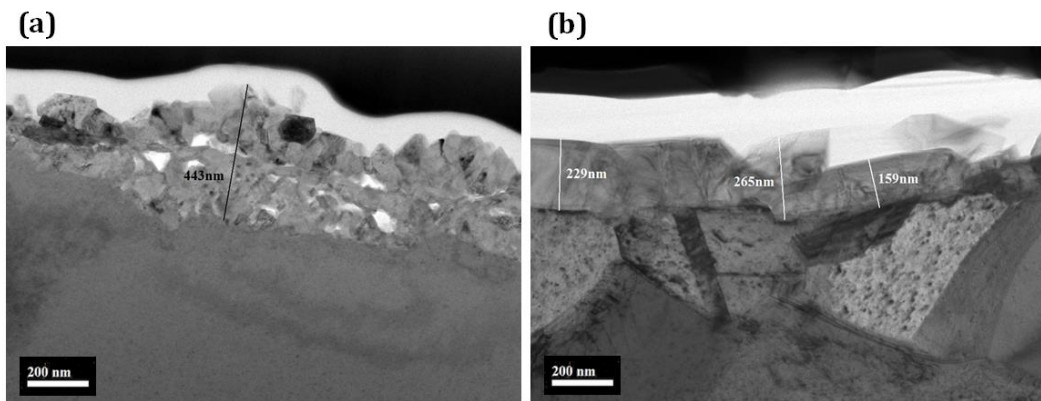


Figure 3: TEM micrographs recorded after 750 h oxidation of Ni-30Cr at 550 °C, showing (a)  $\text{Cr}_2\text{O}_3 + \text{NiO}$  formation in a polished specimen, and (b) exclusive  $\text{Cr}_2\text{O}_3$  formation in a ground specimen.

#### 4. CONCLUSIONS

The volume diffusion coefficients of Cr in Ni at 540-850 °C indicate that the mechanism of volume diffusion at these relatively low temperatures is no different from the vacancy mechanism operating at higher temperatures. Grain boundary diffusivities were measured down to 350 °C and found to vary significantly from one boundary to another. Oxidation experiments showed that Cr diffusion was locally accelerated (relative to volume diffusion) in cold-worked Ni-Cr alloys due to the high densities of dislocations and grain boundaries. Both defect density and diffusivity were subject to strong variations, which contributed to the stochastic nature of oxidation processes. The non-uniform diffusion properties were reflected in the Cr depletion profiles generated by selective oxidation, which also presented variations from one grain to another, both before and after recrystallization. The relationships between microstructural defects and Cr diffusion fluxes during oxidation will be further discussed during the presentation.

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