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EVOLUTION OF THE γ/γ' INTERFACE WIDTH IN A COMMERCIAL NICKEL BASE SUPERALLOY STUDIED BY 3D ATOM PROBE (PREPRINT)

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14. ABSTRACT

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Evolution of the γ/γ' interface width in a commercial nickel base superalloy studied by 3D atom probe

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Abstract

The compositional width of the γ/γ' interface for primary and secondary γ' precipitates in the commercial nickel base superalloy, Rene 88 DT, has been characterized at sub-nanometer resolution using local electrode atom probe (LEAP) tomography. On formation during continuous cooling, the primary γ' precipitates exhibit a very sharp interface while the secondary γ' precipitates exhibit a substantially more diffuse interface. Interestingly, on subsequent isothermal aging at 760°C, the interface width increases for the primary γ' precipitates while it decreases for the secondary γ' precipitates, reaching a near equilibrium composition width for both types of interfaces after aging for 200hrs. These results imply the γ/γ' interface width is strongly dependent on temperature in these alloys.

Introduction

Rene88DT is a commercial superalloy used for turbine disk applications in aircraft jet engines. Such alloys typically exhibit excellent high temperature properties including strength, ductility, improved fracture toughness and fatigue resistance, as well as enhanced creep and oxidation resistance [1]. The microstructure of this alloy consists of a disordered *fcc* matrix γ phase with dispersed precipitates of the $L1_2$ ordered γ' phase. As key strengthening mechanisms depend upon factors such as lattice misfit between γ and γ' phases, and compositional and structural transitions across the interface, the study of these factors at the highest spatial resolutions can play a major role in understanding the

overall mechanical behavior of these superalloys [4-5]. Over the years there have been a number of reports in the literature where three dimensional atom probe (3DAP) tomography has been employed to characterize the atomic scale microstructure of the Ni based superalloys and these have been summarized in some excellent recent reviews [6-10]. In order to observe local compositional change at the interface between γ and γ' phases, integrated concentration profiles (so-called ladder diagrams) have been determined using more traditional conventional atom probe field ion microscopy (APFIM) [12]. Compared to APFIM, the more recent local electrode atom probe (LEAP) system by Imago Inc. allows for much faster data acquisition permitting data from much larger volumes to be acquired for the same time period [13], thereby giving more quantitative information of nanoscale precipitates from these large volumes. The proximity histogram (or proxigram) method, has been developed to generate concentration profiles with respect to an arbitrary surface in three dimensions, most commonly an isoconcentration surface (or isosurface for short) [14]. This analysis method gives integration of chemical information with three-dimensional position information [15]. Thus, the proxigram study is often useful to show the change in composition near the surface of interest with reducing error in quantification of chemical composition.

Initial results of 3D atom probe studies conducted on Rene 88DT have been reported in a recent paper by Hwang et. al. [Met Trans A ref]. These results discussed the partitioning of constituent alloying elements in Rene 88DT between the γ and γ' phases as a function of aging time and the resulting size and distribution of γ’ precipitates in these alloys, after rapid continuous cooling by water quenching from the high temperature single γ phase field. Faster cooling rates, such as those encountered in water quenching the alloy from the high temperature single γ phase field, typically lead to the formation of a monomodal size distribution of refined γ’ precipitates [Met Trans A ref, S.S. Babu ref]. In contrast, relatively slower cooling rates lead to the formation of γ’ precipitates of two (bimodal size distribution) or even more different size ranges [S.S. Babu ref]. During continuous cooling, nucleation events occurring at different undercoolings below the γ’ solvus temperature, typically result in the multiple size distributions of γ’ precipitates. The first burst of nucleation, occurring at lower undercoolings (or higher temperatures, just below the γ’ solvus temperature), lead to the formation of the first generation of γ’ precipitates, often referred to as primary γ’ precipitates. Similarly, a second burst of nucleation, at higher undercoolings, leads to the formation of secondary

γ’ precipitates and there might be additional bursts of nucleation at even lower temperatures [S.S. Babu ref]. In the present study, the differences in composition between γ and γ' phases is being investigated for a Rene88DT sample subjected to a super-solvus treatment in the single γ phase field, followed by slow-cooling to room temperature at an average rate of 24°C/min and subsequently aged at 760°C for different time periods. Such a heat-treatment results in the formation of multiple size ranges of γ’ precipitates and the primary focus of the present study is to investigate the γ/γ’ interfacial width associated with the primary and secondary precipitates as a function of aging time.

Experimental Procedure

The Rene 88DT alloy used in the present study contained 55.63Ni-18.02Cr-13.00Co-4.74Ti-4.45Al-2.48Mo-1.21W-0.46Nb (at%). The samples were solution treated at 1150°C for 30 min followed by slow-cooling in the furnace at an average rate of 24^0C/min. These samples were subsequently aged for 0, 50, and, 200 hours at 760°C in a large chamber vacuum furnace and air quenched. For convenience, these samples will be subsequently referred to as SC0, SC50, and, SC200 samples in the remaining part of this paper. TEM samples were prepared using conventional electro-polishing techniques followed by argon ion milling using a Gatan PIPS system, operated at 5 kV. Images were obtained using the Cr M-edge in the energy filtered transmission electron microscopy (EFTEM) mode on a FEI Tecnai F20 microscope operating at 200 KV, as described elsewhere [12]. Representative regions were imaged at different magnifications to capture the relevant secondary and/or tertiary γ' precipitates in the alloy.

Sharp needle-like specimens less 100nm tip radius for 3DAP tomography studies in the LEAP microscope were prepared using electropolishing techniques. For this purpose, samples from the different heat-treated conditions were cut into thin square rods (0.5x0.5mm square cross section) with a diamond saw. These thin rods were mechanically ground and subsequently electro-polished to tip diameters of 100nm using a commercially available Electropointer™ system. The electro-polishing was carried out in two steps, first with a 90 acetic acid + 10 perchloric acid solution using 20 V for the coarser polish and finally with a 98% butyl cellulose + 2% perchloric acid solution using 10V for the final polish. The 3DAP experiments were carried out using a LEAP 3000 local

electrode atom probe (LEAP™) system from Imago Scientific Instruments Inc. All atom probe experiments were carried out in the electric-field evaporation mode at a temperature of 60K, with the evaporation rate varying from 0.5 – 1.0 % and the pulsing voltage at 20% of the steady-state applied voltage. For the quantitative analysis for the three dimensional reconstruction, the proxigram plot has been used from isoconcentration surface using IVAS 3.0.

Results and Discussion

Fig. 1(a) shows an energy filtered transmission electron (EFTEM) image using the Cr M-edge from the SC0 sample. Two different size ranges of γ' precipitates are clearly seen in the microstructure. The coarser primary γ' precipitates exhibit irregular faceted morphologies with sizes ranging from 100 nm to 300nm while the finer scale secondary γ' precipitates exhibit more spherical-like morphologies with sizes ranging from 2-5nm. During the slow cooling, the primary γ' precipitates forming at relatively high temperatures, have a substantially longer time to grow and coarsen as compared to the secondary γ' precipitates forming at much lower temperatures. Consequently, the primary precipitates grow to the extent where strain energy effects become significant and hence they exhibit more faceted cuboidal-like morphologies [16]. In contrast, the fine scale secondary γ' precipitates nucleate and grow at relatively lower temperatures during the continuous cooling. Between primary and secondary γ' precipitates, a precipitate-free zone (PFZ) is clearly observed (refer Fig. 1(a)). From the detail three dimensional atom probe analysis using the local electrode atom probe, the primary γ’ precipitates exhibit near-equilibrium compositions, while the smaller scale secondary γ’ precipitates exhibit non-equilibrium compositions often consisting of excess Co and Cr, while being depleted in Al and Ti content. The compositions of the γ matrix near these precipitates also exhibit similar trends with the composition being closer to equilibrium near the primary precipitates as compared to the secondary precipitates. More detail analysis will be presented in other paper [11].

3DAP reconstruction of the two different SC0 samples are shown in Fig. 1b and c, and the sample from SC200 sample are presented in Fig.1d. The 14 at% Cr iso-concentration surface (isosurface), which is average concentration value between γ/γ' phase was created in red color, while Al atomic map in blue color is presented. The red region correspond to γ phase and blue region correspond to γ'

phase. Fig. 1b shows sharp interface between γ and primary γ' precipitate which is in agreement with EFTEM image. Two different γ' precipitates are observed in the second reconstruction in SC0 sample. For the SC200 sample, the primary γ' precipitate are located in the bottom of the reconstruction, as well as secondary γ' precipitates far from the primary γ' precipitate. The precipitate free zone (PFZ) are observed from both SC0 and SC200 sample, which is expected from the EFTEM image. From the EFTEM results and 3DAP reconstruction, primary γ' precipitate has very sharp interface with γ matrix. However, this is not elucidative evidence to distinguish two types of precipitates. Thus, the chemical partitioning characteristic has been investigated in this point.

The proxigram concentration profiles on the primary γ' precipitates for three different aging conditons, SC0, SC50, and SC100 are shown in Fig. 2. All the isosurface reconstruction were created with 14at.% Cr. No compositional change was observed while varying this threshold value except for shifting the reference interface line which means the zero position. Typically the average value (14 at.% Cr in this experiment) are selected to create the proxigram. This method is now well accepted for generating the proxigram study [15]. Co, Cr, and Mo are enriched in γ region while Al and Ti preferentially are enriched in γ' region. These profiles show the partitioning tendency clearly.

The compositional changes at the interface in the SC0 sample are sharp and abrupt within 0.6nm region, which corresponds approximately two atomic layers. However, the interfacial width in the SC50 and SC200 are large as 2.5 nm. This corresponds to several atomic layers of the γ or γ' phase. Interestingly, as the interface grows, the interfacial region of γ grows more compared to γ' region by consuming the Cr enriched region. The concentration of Cr in the γ region in the SC0 sample is 25.4 at.% and 26.2 for SC200, while the concentration of Al in the γ' region (11.2 at.%) does not change significantly from SC0 to SC200. In Table 1 and 2, the measured interfacial width and primary composition in the each phase are presented. This can be explained by the difference in diffusivities of elements in the γ and γ' phase. The misfit between the γ and γ' phases usually defined as $\delta = 2(a_{\gamma'} - a_{\gamma})/(a_{\gamma'} + a_{\gamma})$ where a γ' and a γ are the lattice parameters of the gamma prime and gamma phases, respectively [18]. Typically in γ' precipitate some Ni atoms are substituted by Al or Ti, and makes the lattice parameter smaller. Thus, it shows the negative misfit. Therefore, the γ region near the γ/γ' interface has compressive stress. Atoms with small atomic radius are enriched in these region to relax the elastic strain energy [12]. Cr has relatively small size of atomic radius (~ 1.28Å) compared to other elements, thus it can be enriched in this interfacial region. From the experimental results in Fig. 2, excess Cr enrichment regions are observed near the γ region. This will help to establish new

equilibrium, so this is a driving force to change the interface between γ and γ' phases. The diffusivities of the alloying elements in the γ' region are much slower than those in the γ region [17]. As aging time increases, a new equilibrium reaches by shifting and extending the interface and stop even though for a longer time aging up to 200hours.

However, the proxigram study in the secondary γ' phase shows more complex profiles across the γ/γ' interface. First, the interfacial width of as-solutionized sample has a quite large width compared to that of γ and primary γ' interface. For the fine secondary γ' precipitates have relatively small misfit even though long term aging and diffusion distance of atom for the growth of γ' phase is short which will not affect significantly on the elastic strain. Thus, no specific excess of elements were observed in the interfacial region even though long aging time up to 200 hrs (Fig.3). This will make the diffusion of elements towards both γ and γ' regions. The details should be addressed.

Conclusion

The EFTEM microstructure and 3DAP morphology, two different type of γ' precipitates were observed having precipitate free zone. An increase in the interface width of primary γ' which reached equilibrium was observed as aging time increased up to 200hrs, while the width of interface region secondary γ' precipitates decreased. Primary γ' precipitates have sharp and abrupt compositional width compared to secondary γ' precipitates.

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Heat Treatment	*Width of Primary γ'/γ*	*Width of Secondary γ'/γ*
SC 0	***0.6 nm***	***3.8 nm***
SC 50	***2.45 nm***	***2.8 nm***
SC 200	***2.5 nm***	***2.7 nm***

Table 1. The widths of primary γ’/γ and secondary γ'/γ interfaces in SC0, SC50 and SC200 samples.

Steady State Composition	***γ' region***		***γ region***	
	Cr	***Al***	***Cr***	***Al***
SC 0 Primary	***1.5***	***11***	***25.5***	***2.1***
SC 0 Secondary	***2.7***	***11.7***	***25.4***	***2.9***
SC 200 Primary	***3.1***	***11.33***	***25.8***	***2.96***
SC 200 Secondary	***2.3***	***11.6***	***23.7***	***3.5***

Table 2. The steady state compositions of Cr and Al ions in the γ' and γ regions.

Figure captions

Fig. 1 (Color online) (a) Energy-filtered TEM (EFTEM) images using the Cr M-edge from SC0 sample. (b) and (c) two different 3DAP reconstructions showing 14 at% Cr isosurface (red) and Al atoms (blue) from SC0 sample. The reconstructions show a part of primary γ' and some secondary γ' precipitates. (d) 3DAP reconstructions showing 14 at% Cr isosurface (red) and Al atoms (blue) from SC200 sample. The reconstruction shows a part of primary γ' and some secondary γ' precipitates.

Fig. 2. (Color online) Proxigrams showing the composition profiles of Co, Ti, Cr, Al and Mo atoms across primary γ'/γ interfaces for (a) SC0, (b) SC50 and (c) SC200 conditions.

Fig. 3. (Color online) Proxigrams showing the composition profiles of Co, Ti, Cr, Al and Mo atoms across secondary γ'/γ interfaces for (a) SC0, (b) SC50 and (c) SC200 conditions.

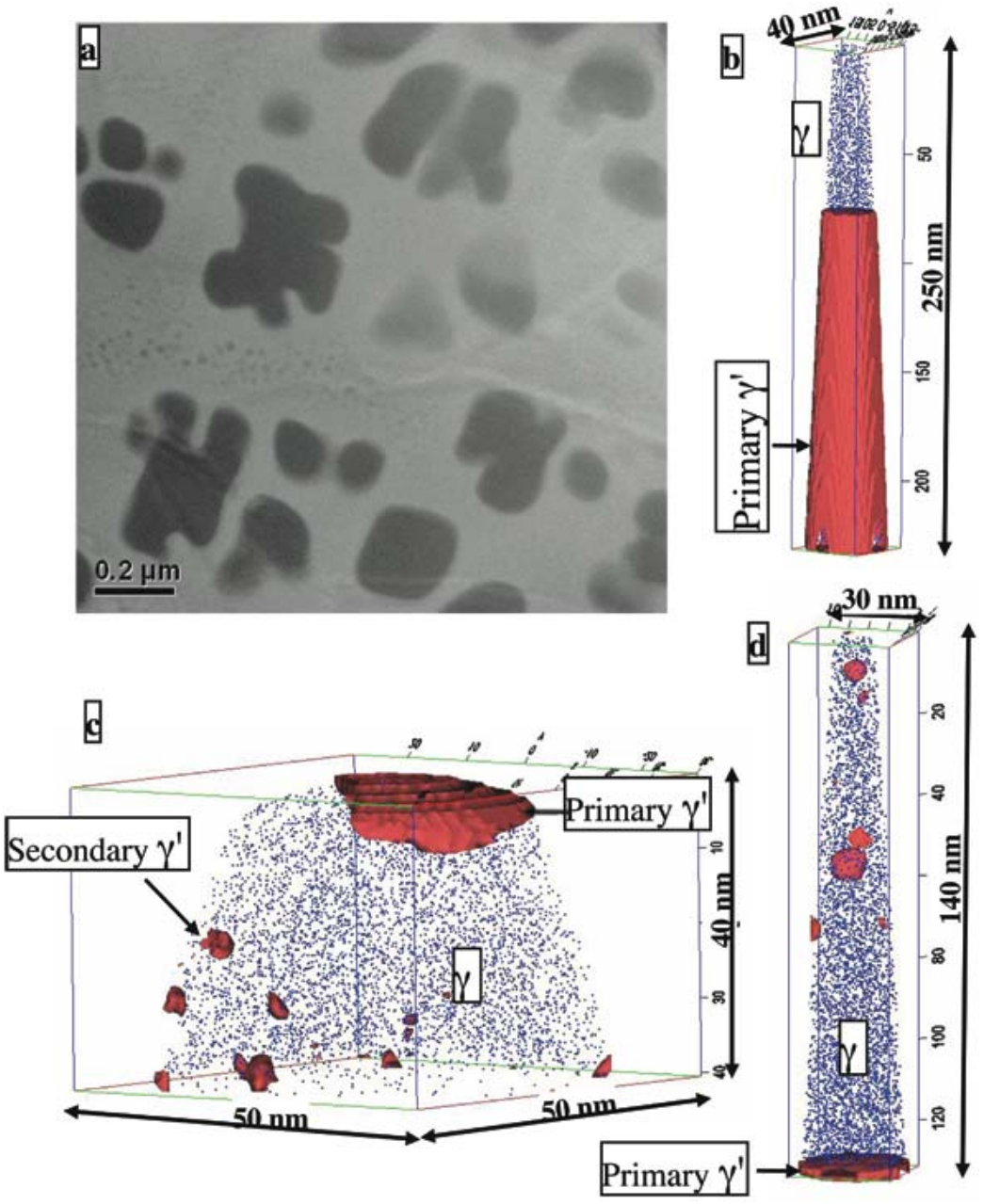
a
0.2 μm
b
40 nm
γ
250 nm
Primary γ'
c
Secondary γ'
Primary γ'
γ
40 nm
50 nm
50 nm
d
30 nm
γ
140 nm
Primary γ'

Fig. 1.

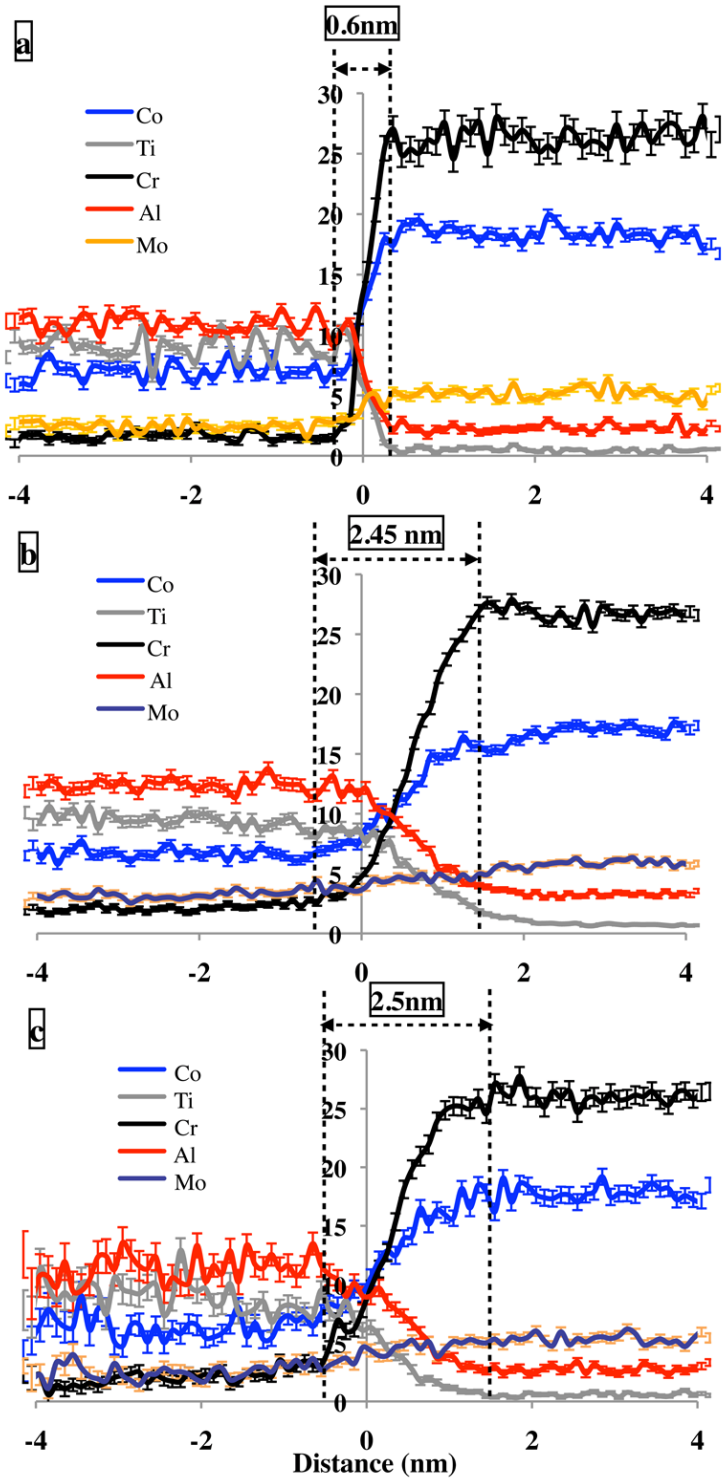

Fig. 2.

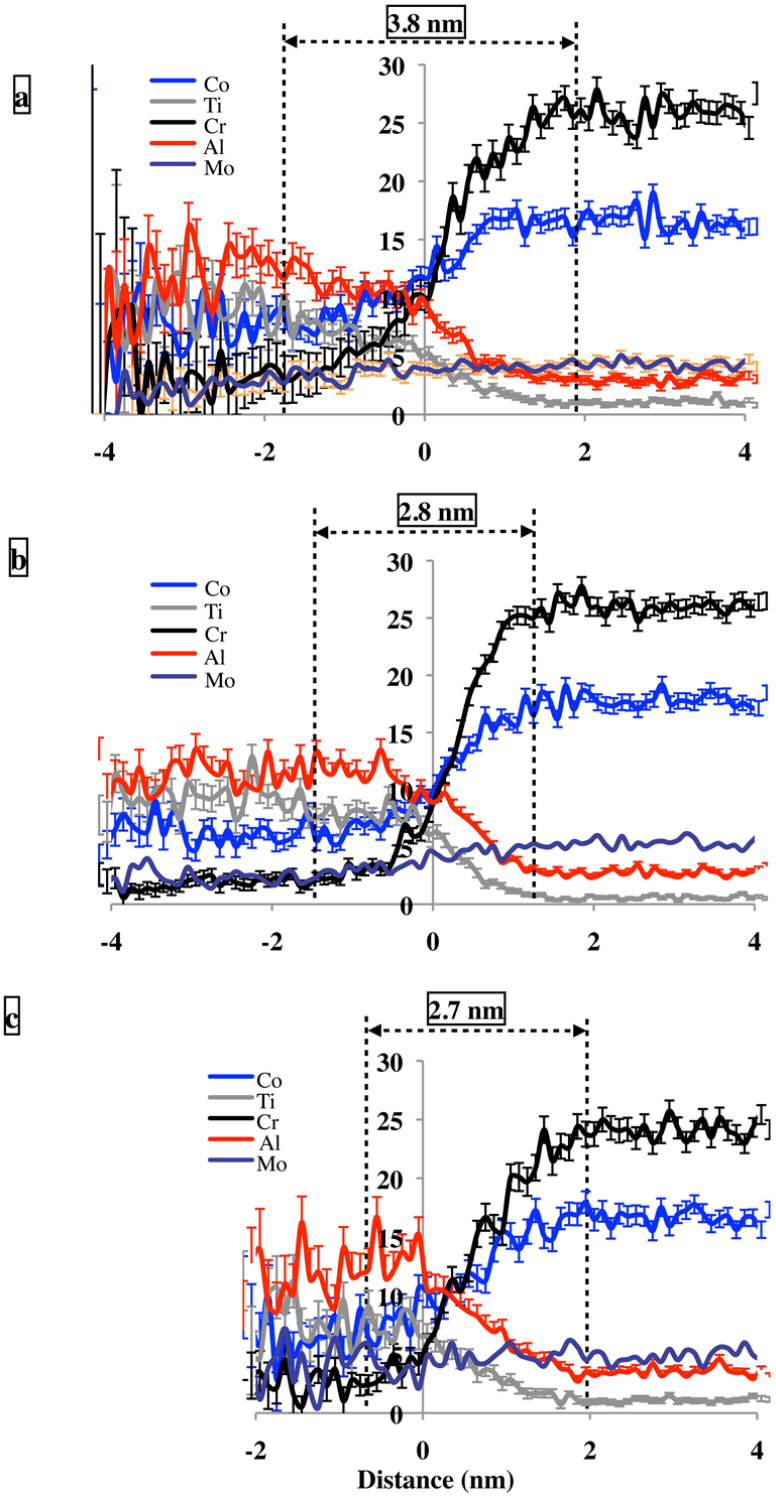
a
3.8 nm
Co
Ti
Cr
Al
Mo
30
25
20
15
10
5
0
-4
-2
0
2
4
b
2.8 nm
Co
Ti
Cr
Al
Mo
30
25
20
15
10
5
0
-4
-2
0
2
4
c
2.7 nm
Co
Ti
Cr
Al
Mo
30
25
20
15
10
5
0
-2
0
2
4
Distance (nm)

Fig. 3.