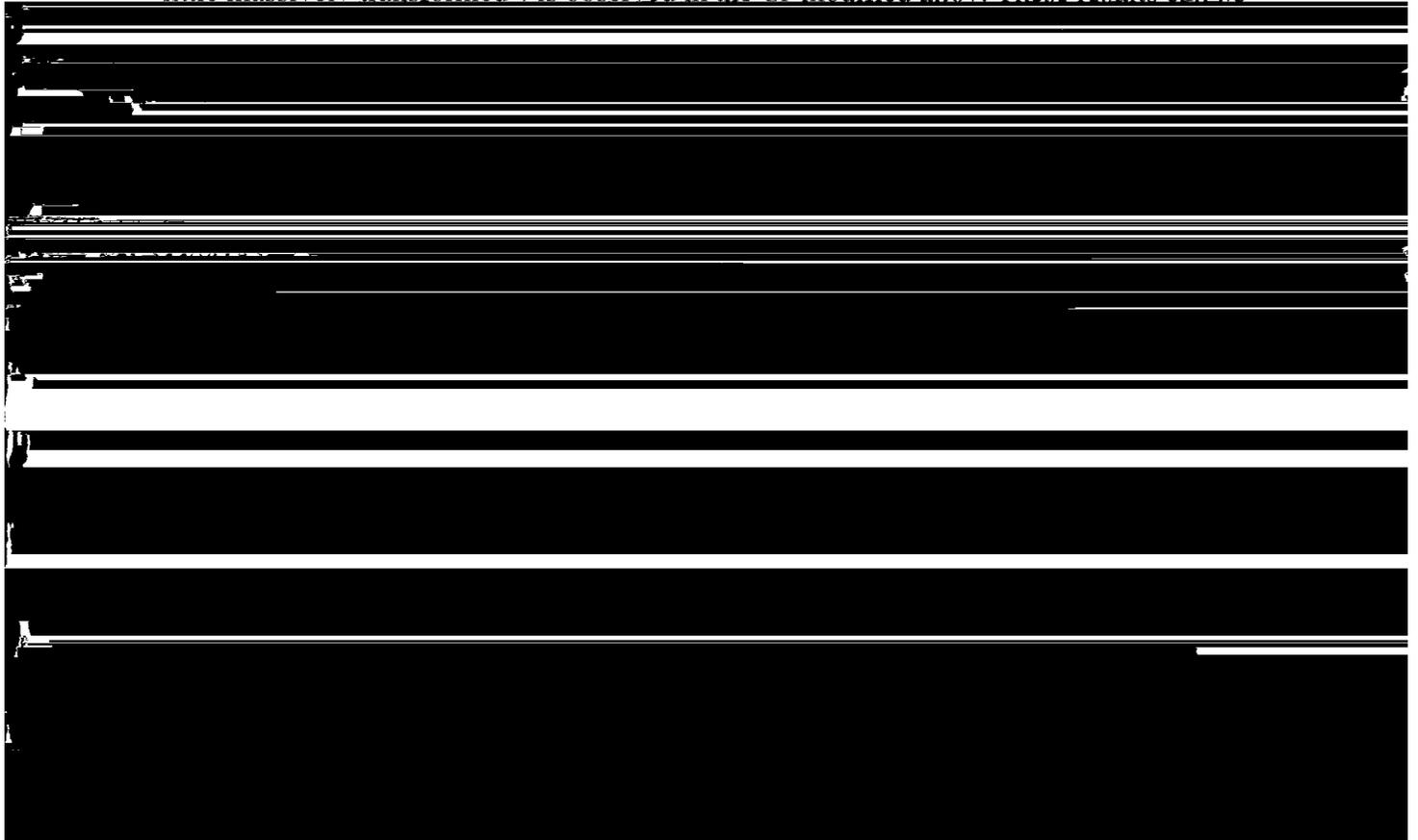


SITE OCCUPANCY DETERMINATION BY ALCHEMI OF Nb AND Cr IN γ -TiAl AND THEIR EFFECTS ON THE α TO γ MASSIVE PHASE TRANSFORMATION

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ABSTRACT

Atom location by channeling enhanced microanalysis (ALCHEMI) has been used to characterize the site distributions of Nb and Cr alloying additions in the $L1_0$ -ordered γ phase of ternary titanium aluminides. Two alloys, $Ti_{50}Al_{48}Cr_2$ and $Ti_{50}Al_{48}Nb_2$, were processed by furnace cooling from 1300°C (within the α - γ two phase field) as well as by rapid solidification using twin-anvil splat quenching of electromagnetically levitated and undercooled samples. ALCHEMI studies of furnace cooled samples yield results generally consistent with those in the published literature. Nb alloying additions are found to partition exclusively to the 'Ti' sublattice, while Cr alloying additions exhibit an 'Al' sublattice preference. However, a higher degree of disorder can be achieved with rapid solidification and high solid state cooling rates (10^5 - 10^6 K/s). Significant distribution of the ternary elements between the 'Ti' and 'Al' sublattices has been measured in the splat quenched samples, with up to 12% of the Nb atoms occupying the 'Al' sublattice and the fraction of Cr atoms on the 'Ti' sublattice doubling to ~30%. Rapid solidification of TiAl produces an equiaxed hexagonal α phase solidification structure that transforms in a massive fashion to the tetragonal γ phase. Although the amount of massively transformed γ is dependent upon the solid state cooling rate, ternary alloying additions can more strongly influence the transformation kinetics. The Nb-modified alloy exhibits significant amounts of the massively transformed γ , similar to the $Ti_{52}Al_{48}$ binary alloy, whereas little massively transformed γ is observed in the Cr-modified alloy. These results can be



increases. Samples can be levitated and splat quenched with undercoolings ranging from 0 to 160 K, which results in splat thicknesses from 140 to 400 μm . Since thicker splats experience slower solid state cooling rates, the massive transformation can be observed at various stages of the nucleation and growth process. The purpose of this investigation is to study the effect of ternary alloying additions on the solid-state phase transformations in titanium aluminides to yield a better understanding of $\alpha \rightarrow \gamma$ transformation kinetics.

EXPERIMENT

Arc cast alloys $\text{Ti}_{50}\text{Al}_{48}\text{Cr}_2$ and $\text{Ti}_{50}\text{Al}_{48}\text{Nb}_2$ with < 500 ppm (wt) oxygen were processed by heat treating in vacuum for 4 hr at 1300°C (within the α - γ two phase field) and furnace cooling at ~ 2 K/min. To induce the massive phase transformation, 500 mg spheres were electromagnetically levitated in vacuum, induction melted, and undercooled below the melting point ($\Delta T = T_m - T$) by flowing He gas over the molten sphere. Non-contact optical pyrometry measured the temperature of the undercooled droplet. At the desired ΔT , the electromagnetic field is removed and pneumatically driven twin copper anvils splat quench the falling droplet. Samples for transmission electron microscopy (TEM) were punched from the center of the splat and thinned equally from each side with final thinning by twin-jet electropolishing in 57% methanol, 37% n-butanol and 6% perchloric acid at -25°C and 21 V. The microstructures of the furnace cooled and rapidly quenched alloys were characterized by standard bright-field imaging in a Philips CM20. ALCHEMI was performed by collecting energy-dispersive spectra (EDS) at up to 16 different excitations of the (002) and (220) systematic rows of the $L1_0$ -ordered alloy. The characteristic K-series X-ray lines of each element were analyzed. For data reduction, the statistical significance for each measured characteristic intensity is weighted according to Poisson statistics. Delocalization corrected correlation coefficients were extracted from experimental parameters. These experimental methods are described in detail elsewhere [7,8].

RESULTS

Figure 1 shows the relationship between undercooling (ΔT) and splat thickness (t). Increased undercooling (ΔT) results in thicker splats with lower solid state cooling rates. For small undercooling ($\Delta T \sim 25$ K and $t \sim 150$ μm), finite element heat flow calculations estimate the solid state cooling rate at the splat center to be on the order of 10^6 K/s [9], whereas for large undercooling ($\Delta T \sim 140$ K and $t \sim 300$ μm), the cooling rate is reduced by approximately an order of magnitude to $\sim 10^5$ K/s.

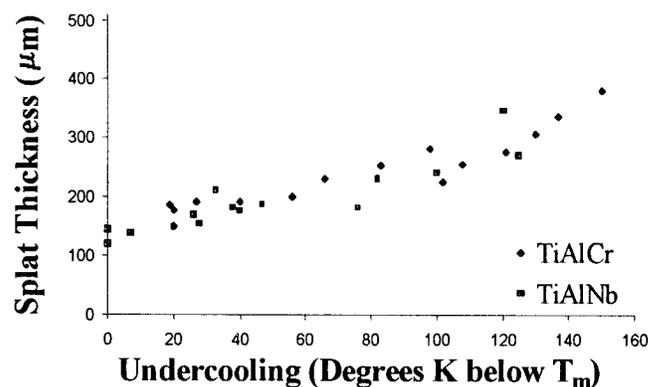


Figure 1 – Splat thickness as a function of undercooling.

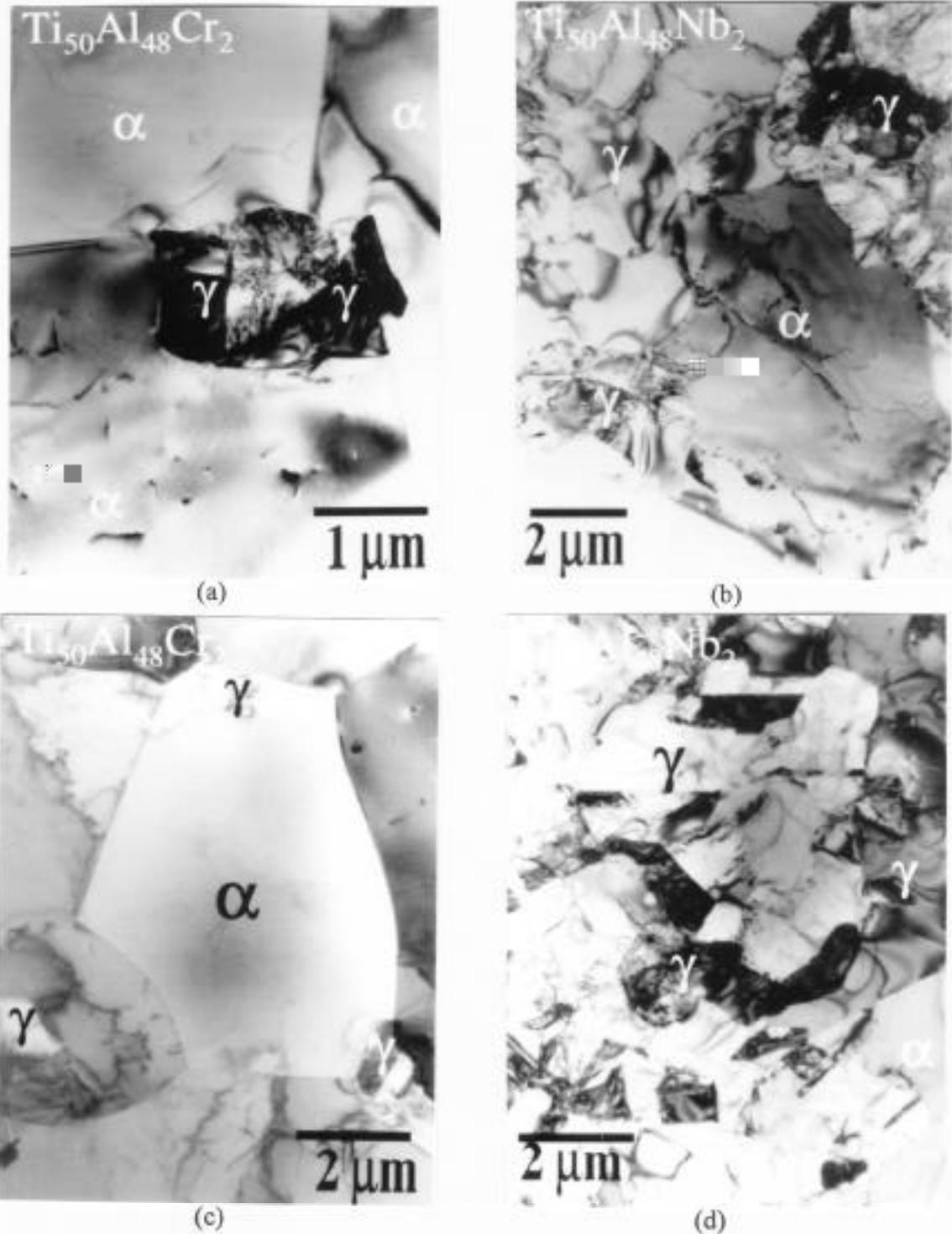


Figure 2 – The effect of ternary additions and solid state cooling rates on the massive $\alpha \rightarrow \gamma$ phase transformation. Bright field images are shown for (a,c) Cr- and (b,d) Nb-modified alloys with undercoolings ΔT of (a,b) 25 K and (c,d) 135 K. The smaller [larger] undercooling results in a splat thickness of 150 [300] μm with a solid state cooling rate at the splat center of $\sim 10^6$ [10^5] K/s. For both undercoolings, the Cr-modified alloy is mostly composed of the α phase, whereas the Nb-modified alloy is mostly composed of the massively transformed γ phase. These results suggest that ternary alloying additions can have a much greater influence than the solid state cooling rate on the $\alpha \rightarrow \gamma$ massive transformation.

Figure 2 shows the amount of the massively transformed γ phase as a function of solid state cooling rate and alloy composition. The γ phase nucleates in the Cr-modified alloy but growth of the massive phase transformation is inhibited relative to the Nb-modified alloy. Solid state cooling rates of $\sim 10^6$ K/s produce only the initial stages of γ nucleation in the Cr-modified alloy (figure 1a), whereas similar solid state cooling rates in the Nb-modified alloy (figure 1b) result in extensive γ growth. Larger undercooling produces lower solid state cooling rates, $\sim 10^5$ K/s. However, the Cr-modified alloy maintains the α solidification structure (figure 1c) whereas the $\alpha \rightarrow \gamma$ transformation is almost complete in the Nb-modified alloy (figure 1d). The Cr atoms strongly reduce the kinetics of the massive phase transformation compared to Nb. The Nb-modified alloy exhibits transformation kinetics similar to a binary $\text{Ti}_{52}\text{Al}_{48}$ alloy [9].

The site occupancies of the Cr and Nb atoms in the L_{10} -ordered structure were investigated by ALCHEMI for both the quenched and the furnace cooled alloys. Figure 3 shows data from the furnace cooled Cr-modified alloy, collected for both the (220) and (002) systematic rows of reflections. Although the (002) planes have a larger interplanar spacing, the (110) superlattice reflection produces superior 'Ti' / 'Al' site discrimination compared to the (001) superlattice reflection. In spite of the fact that the data from the (001) row have a significantly larger error bar, the two data sets yield statistically equivalent results, with $\sim 85\%$ of the Cr atoms on 'Al' sites. Figure 4 shows the ALCHEMI data from the furnace cooled Nb-modified alloy. Consistent with other studies, Nb exhibits an exclusive 'Ti' sublattice occupancy.

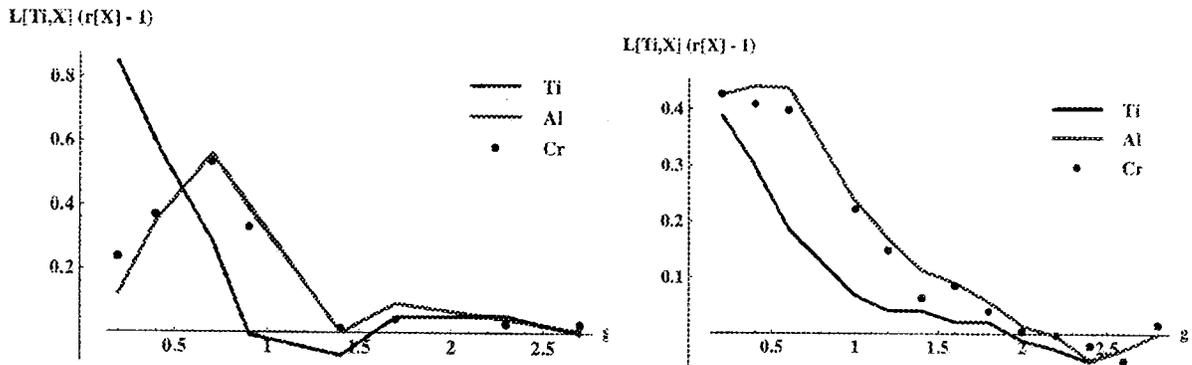


Figure 3 – Delocalization-corrected intensity ratios as a function of orientation $g = \theta / \theta_B$ [7,8], where θ_B is the Bragg angle for the fundamental (a) (220) and (b) (002) reflections, for the furnace-cooled Cr-modified alloy. Although the (220) systematic orientation exhibits better 'Ti' / 'Al' sublattice discrimination than (002), the two data sets yield statistically equivalent results, with (a) $85 \pm 3\%$ and (b) $83 \pm 8\%$ of the Cr alloying addition occupying the 'Al' sublattice.

Table I summarizes the site occupancy data for the Cr- and Nb-modified alloys in the furnace cooled (FC) and undercooled rapidly quenched (URQ) conditions. The ALCHEMI data show that Cr exhibits a pronounced ($\sim 85\%$) 'Al' sublattice preference and Nb exhibits an exclusive ($\sim 100\%$) 'Ti' sublattice occupancy in the near-equilibrium furnace cooled alloys. However, with rapid solidification and high solid state cooling rates (10^5 - 10^6 K/s), a larger degree of disorder is observed, with only $\sim 70\%$ of the Cr occupying the 'Al' sublattice and $\sim 88\%$ of the Nb occupying the 'Ti' sublattice. For both heat treatments, Nb is found to exhibit a stronger site preference than Cr. This behavior can be correlated with the characteristic radii and electronegativity data for these elements, as shown in Table II.

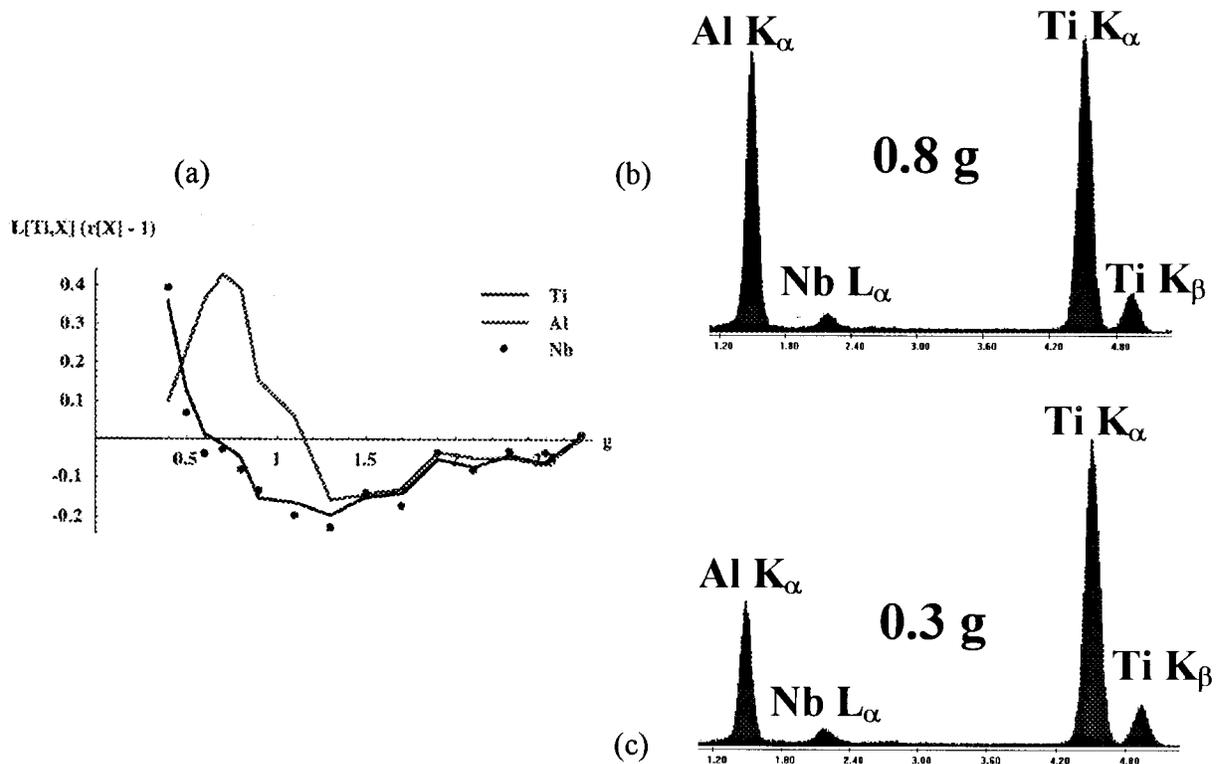


Figure 4 – ALCHEMI data for the furnace cooled Nb-modified alloy. The data in (a) show that the Nb atoms substitute for Ti atoms in the $L1_0$ structure with 100% 'Ti' sublattice occupancy. The size of the Nb L peaks remain proportionate to the Ti K peaks, in contrast to the large relative change of Al K intensity when changing the channeling conditions from (b) 0.8 g to (c) 0.3 g, with $g = \theta / \theta_{220}$.

TABLE I - ALCHEMI Data from $Ti_{50}Al_{48}Cr_2$ and $Ti_{50}Al_{48}Nb_2$

Element	Al Site Occupancy	Ti Site Occupancy
Chromium [FC]	$85 \pm 3 \%$	$15 \pm 3 \%$
Chromium [URQ]	$70 \pm 3 \%$	$30 \pm 3 \%$
Niobium [FC]	$0 \pm 5 \%$	$100 \pm 5 \%$
Niobium [URQ]	$12 \pm 3 \%$	$88 \pm 3 \%$

TABLE II - Atomic Radii and Electronegativity

Element	Atomic Radius (Å)	Covalent Radius (Å)	Electronegativity
Ti	1.48 (HCP)	1.32	1.3
Al	1.43 (FCC)	1.18	1.5
Nb	1.43 (BCC)	1.34	1.3
Cr	1.25 (BCC)	1.18	1.6

The measured sublattice preferences of the Nb and Cr alloying additions correlate strongly with the covalent rather than the atomic radii in Table II. In particular, whereas the atomic radii of Nb and Al are identical, which might suggest an 'Al' sublattice preference for Nb, there is a much closer correspondence between the covalent radii of Nb and Ti. A similar correspondence exists for the covalent radii of Cr and Al. These correlations are consistent with the strong directional bonding in L1₀-ordered γ -TiAl. Electronegativity, an indicator of solid state solubility, also predicts an affinity of Nb for 'Ti' and Cr for 'Al' sites.

CONCLUSIONS

Ternary alloying additions of Cr and Nb exhibit greater distribution between the 'Ti' and 'Al' sublattices in rapidly cooled, splat quenched TiAl alloys relative to corresponding furnace cooled alloys. A significant fraction (~12%) of the Nb alloying additions are found to occupy the 'Al' sublattice in the quenched alloys, whereas Nb has been found to occupy the 'Ti' sublattice exclusively in furnace cooled alloys. The fraction of Cr atoms occupying the 'Ti' sublattice doubles from ~15% in the furnace cooled alloys to ~30% in the quenched alloys.

Alloying additions of Cr significantly reduce the kinetics of the $\alpha \rightarrow \gamma$ massive phase transformation, whereas additions of Nb have little influence on the transformation kinetics.

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