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## LETTER TO THE EDITOR

# A metastable Cr carbide of NaCl structure formed by carbon-ion implantation into chromium films

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**Abstract.** A metastable NaCl-structure Cr carbide was formed by 50 keV carbon-ion implantation into pure chromium metal films. The structure of the carbide phase was identified by selected-area electron diffraction to be face-centred cubic (FCC) with a lattice constant of 0.403 nm. The carbide phase was stable only up to a temperature of about 250 °C and was destabilized at higher temperature, probably because of oxidation. The formation of Cr carbide was also confirmed by Auger spectroscopy measurements. The heat of formation of the phase was calculated to be less negative than those for Ti and V carbides, i.e.  $-7 \text{ kcal mol}^{-1}$ , which reflected to some extent the metastability of the carbide formed.

Chromium is an element that may protect an alloy from oxidation and acid corrosion even at high temperature. Carbon is also a ubiquitous alloying element for iron-based alloys, and knowledge of possible chromium carbide phases is therefore of importance as regards various properties of steels and stainless steels. Many attempts have been made to form possible chromium carbide phases by various processing methods during recent years. The formation of the CrC-phase carbide is still doubtful, although there is a record of an NaCl-type CrC phase as a high-temperature compound in *Pearson's Handbook of Alloy Phases* [1]. Bloom and Grant [2] concluded in their paper that all the efforts at forming a carbide of CrC had been unsuccessful. Other sources of alloy phases, such as the *Powder Diffraction File* [3], have no entries for a CrC phase. Bloom and Grant also suggested that the next most appropriate method by which to attempt to form CrC was that of very rapid cooling, to prevent the possible transformation of the CrC phase to other phases. Ion implantation seems very promising, as the effective cooling speed available in ion beam processes has been estimated to be as high as  $10^{13}$ – $10^{14} \text{ K s}^{-1}$  [4]. Ion implantation has proved to be a powerful method for producing metastable materials. The ion beam process favours the formation of amorphous phases or phases with simple crystal structures, while phases with complicated crystalline structure have been difficult to form [5]. This has been attributed to the specific kinetic conditions in the ion beam process, which restrict the mobility of the atoms relative to that in a conventional thermal process [6]. We report, in this letter, the formation of an NaCl-type FCC CrC phase

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by carbon-ion implantation into Cr films and the thermal stability of this formed phase.

The experimental procedures were as follows. Pure chromium metal thin films were deposited onto freshly cleaved NaCl single-crystal substrates in an electron-gun evaporation system with a vacuum level of  $2 \times 10^{-6}$  Torr. The thickness of the films was about 100 nm, designed using TRIM 88 to match the 50 keV carbon-ion range plus longitudinal straggling. The as-deposited films were then implanted at room temperature. To minimize heating by ion irradiation, the target was cooled by flowing water and the ion beam current density was kept below  $1 \mu\text{A cm}^{-2}$ . After the NaCl had been dissolved in deionized water, the implanted films were analysed using a JEOL 100CX transmission electron microscope (TEM). *In situ* annealing was conducted to check the metastability of the phase studied. A Perking-Elmer Scanning Auger Electron Microscope was also employed to confirm the carbide formation as well as the elemental composition of the films.



**Figure 1.** The electron diffraction pattern of the carbide phase formed in the Cr thin films after ion implantation to a dose of  $2.5 \times 10^{17} \text{ cm}^{-2}$ . Similar patterns were also observed in the Ti and V systems.

Figure 1 shows an electron diffraction pattern observed from a Cr film that was implanted with carbon ions to a dose of  $2.5 \times 10^{17} \text{ C cm}^{-2}$ . To derive the reciprocal spacings for phase identification, pure Ni rings were interpolated in the carbide rings by putting two films together on the TEM grid to calibrate the small changes in camera length of the TEM. Calculation showed that the pattern consisted of a simple FCC structure with a lattice constant of  $a = 0.403 \text{ nm}$ . The indexing results are listed in table 1. Interestingly, the diffraction patterns obtained for Ti and V films after similar carbon-ion implantation displayed very similar ring spacings and intensity distributions. Phase identifications showed that they were also FCC carbides of NaCl-type structure. From the neighbouring location of the three elements in the transition period, it is possible for them to feature similar underlying mechanisms of carbide formation under similar ion implantation conditions. The ring spacings and the intensity distribution also favour the identification of an FCC phase of simple structure.

The carbide phase was also confirmed by the differential spectra from Auger electron spectroscopy (AES), as shown by the typical spectrum in figure 2. It has been well established that the chemical bonding state of carbon can be fingerprinted from the shape of its KLL line group [7]. For example, the shape of carbon-carbon bonding is characterized by two peaks with a certain relative intensity, while the transition-metal-carbon bonding is characterized by three peaks with specific relative intensities. The carbon KLL lineshapes shown in the figure thus definitely suggested the formation of a transition metal carbide, which in this case was of Cr carbide.

Table 1. Identification of the FCC Cr carbide phase with  $a = 0.403$  nm.

$d_{\text{observed}}$ (nm)	$d_{\text{calculated}}$ (nm)	Indexing $hkl$	Intensity (visual)
0.2330	0.2329	111	Strong
0.2017	0.2017	002	Strong
0.1427	0.1426	022	Strong
0.1218	0.1216	113	Weak
0.1166	0.1164	222	Weak
0.0901	0.0902	024	Weak
0.0820	0.0823	224	Weak

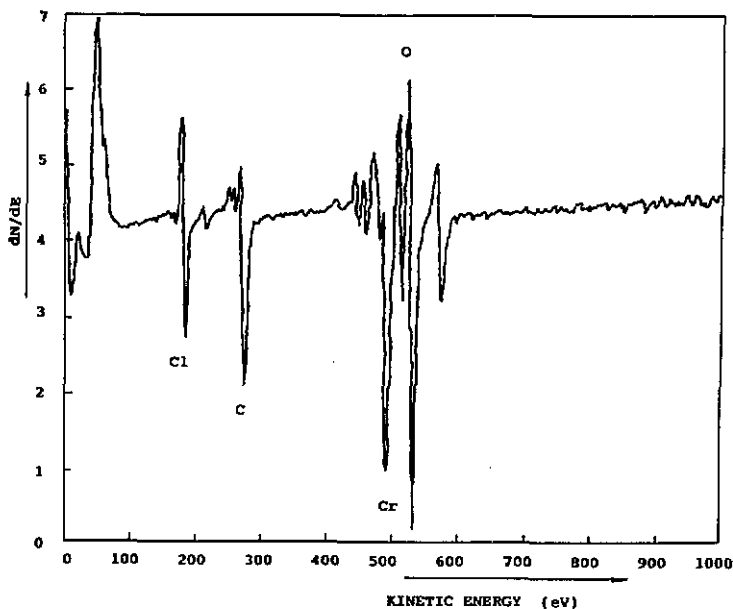


Figure 2. A typical differential Auger electron spectrum of the Cr thin films after carbon-ion implantation to doses ranging from  $2.5 \times 10^{17} \text{ cm}^{-2}$  to  $7 \times 10^{17} \text{ cm}^{-2}$ . The shape of the carbon KLL lines at about 272 eV fingerprinted the formation of transition metal carbide.

The maximum carbon concentration in the implanted films was estimated from the ion dose and the range straggling, and this led to a stoichiometry of C:Cr = 3:8 at the dose of  $2.5 \times 10^{17} \text{ C cm}^{-2}$ , which was consistent with the depth profile of the AES measurements. The carbon KLL lineshapes of the differential spectra, however, indicate that not all the implanted carbon participated in the carbide formation and that there was also some amorphous carbon [8]. A rough estimation of the percentage of carbon in the metal carbide gave an even smaller value for the effective carbon concentration necessary for forming an NaCl-type carbide with a stoichiometry of C:Cr = 1:1. The question then is why another carbide of higher Cr concentration was not formed instead. A possible interpretation is that the specific ion implantation process favours the formation of either a simple crystalline phase or an amorphous phase and is unfavourable for the formation of phases of complicated structure [5]. This led to a CrC phase of simple structure being observed. A similar phase transition

behaviour in cobalt thin films has also been observed by our group—i.e., carbon-ion implantation into cobalt films resulted in the formation of a simple hexagonal Co carbide [9].

Further evidence for the phase was obtained from the calculation of Miedema's heat of formation [10]. Generally speaking, a negative value indicates the possibility of forming a compound. The larger the absolute magnitude of the negative heat, the stronger the cohesion of the compound and the easier it is to form. The results of the calculations for TiC, VC and CrC were  $-18$ ,  $-12$  and  $-7$  kcal mol $^{-1}$ , respectively. The less negative heat of formation of the CrC phase may account, to some extent, for the relative difficulty of forming this carbide by conventional thermal processes.

To check the thermal stability of the CrC phase, an *in situ* TEM annealing investigation was conducted. At a temperature of about 250 °C, the diffraction rings of the carbide disappeared and the phase probably transformed to a chromium oxide carbide, where the oxygen in the film could be identified from the peak in the differential Auger spectra at 503 eV. It has been expected [2] that the CrC phase should be a refractory high-temperature phase, like the TiC and VC phases. However, the results were a little surprising in that they indicated such a low temperature resistance. One possible explanation is easy oxidation of the phase, which leads to instability of the phase and thus difficulty in forming it by conventional thermal processes. The source of oxygen may be the TEM column and the contamination of the films. In comparison, the electron diffraction rings for both TiC and VC remained unchanged up to the highest available temperature of the TEM, around 800 °C.

In conclusion, a metastable Cr carbide of simple FCC structure was formed for the first time by carbon-ion implantation. The phase was stable up to 250 °C and then transformed to a complex chromium oxide carbide phase. The Miedema heat of formation was calculated to be less negative, i.e.  $-7$  kcal mol $^{-1}$ . Interestingly, similar phases of TiC and VC were also observed under similar ion implantation conditions.

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## References

- [1] Villars P and Calvert L D 1985 *Pearson's Handbook of Crystallographic Data for Intermetallic Phases* vol 2 (Metals Park, OH: American Society for Metals) p 1509
- [2] Bloom D S and Grant N J 1950 *J. Met.* **41** 188
- [3] *Powder Diffraction File* 1983 JCPDS, International Center for Diffraction Data, PA, USA
- [4] Picraux S T and Choyke W J 1982 *Metastable Materials Formation by Ion Implantation* (New York: Elsevier)
- [5] Hung L S, Nastasi M, Gyulai J and Mayer J W 1983 *Appl. Phys. Lett.* **42** 672  
Nastasi M, Hung L S and Mayer J W 1983 *Appl. Phys. Lett.* **43** 831  
Hung L S and Mayer J W 1985 *Nucl. Instrum. Methods B* **7/8** 676
- [6] Johnson W L, Cheng Y T, Van Rossum M and Nicolet M A 1985 *Nucl. Instrum. Methods B* **7/8** 657
- [7] Haas T W and Grant J T 1970 *Appl. Phys. Lett.* **16** 172
- [8] Raig S C and Harding G L 1983 *Surf. Sci.* **124** 591
- [9] Liu B X, Wang J and Fang Z Z 1991 *J. Appl. Phys.* **69** 7342
- [10] Miedema A R, Dechatel P F and de Boer F R 1980 *Physica B* **100** 1