

UNUSUAL MAGNETIC AND STRUCTURAL PROPERTIES OF NANOCRYSTALLINE CHROMIUM

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ABSTRACT

This contribution presents a review about the crystalline and magnetic microstructure of nanocrystalline (nano-Cr) and amorphous (am-Cr) chromium. Small angle neutron scattering studies have shown fractal-type density correlations in both nano-Cr and am-Cr. The magnetic ordering in nano-Cr was studied by means of neutron powder diffraction. It is shown that the reduced crystallite size has a strong influence on the magnetic ordering of nano-Cr. The magnetic phase transitions observed in nano-Cr are also associated with anomalies of the lattice parameter.

1. INTRODUCTION

One of the most important trends in materials science is the study of nanoscale materials. The size and shape of atomic crystallites which form the material usually influence its macroscopic properties like heat conduction, mechanical stability, UV absorption, electrical resistivity, magnetic ordering etc... This influence is most pronounced when the grain sizes are of the order of 5-100 nanometers because the number of atoms on the grain surface is much larger than in a conventional, so called polycrystalline material.

The object the present study, i.e. electrodeposited nanocrystalline Chromium (nano-Cr) is an important material used by the electroplating industry. The main goal of our research was to study a material in which the small crystallite size could strongly influence its magnetic properties. Chromium [1] is very well suitable for such studies because: (i) it is an element with a simple bcc-type cubic crystal structure. (ii) the magnetic moments in Chromium form so called spin density waves (see Fig.1).

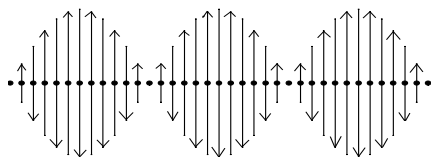


Fig.1. Schematic picture of a spin density wave in Chromium. The solid circles represent Cr atoms while the arrows represent the magnetic moments. One can see the

periodic repetition of the magnetic moments sequence.

This a key property which makes the magnetism of Cr very much unique as compared to other 3d metals like Ni, Co or Fe which have a ferromagnetic ordering. (iii) Chromium can be prepared by electrodeposition in the form of a nanocrystalline material with crystallites of the order of 25 nm. In that case each crystallite contains about 4 full spin density waves since the wavelength is of about 6.5 nm. Similar studies of nano-Cr prepared by other methods were published by Tsunoda et al. [2] for inert gas condensation and Ishibashi et al. for plasma metal reaction method [3]. The main question of the present study is: "Does the electrodeposition method and the reduced crystallite size influence the magnetic properties of nano-Cr ?"

2. MATERIALS AND METHODS

The electrodeposition process used in the preparation of the nano-Cr and amorphous (am-Cr) samples has been already described [4]. The properties of several electrodeposited nanocrystalline 3d metals like nano-Ni [5], nano-Cu [6], nano-Fe [7] and nano-Co [8] have already been studied. The electrodeposition methods have three important advantages compared to other methods frequently used in the preparation of nanocrystals like Inert Gas Condensation (IGC) or Ball Milling (BM):

- (i) they are relatively efficient (several grams per day)
- (ii) they produce materials which have densities of the order of 95%-99% of the bulk reference material
- (iii) they are relatively cheap.

The samples were compact foils with large relative densities of the order of 95 %. The crystalline microstructure was characterized by a laboratory X-ray diffraction with incident $\text{CuK}\alpha_{1/2}$ and small angle neutron scattering (SANS) measurements performed at the Swiss Neutron Source SINQ (Villigen) by using a neutron wavelength $\lambda=0.6$ nm and sample-detector distances up to 20 m. The Q range covered was: $0.03 \text{ nm}^{-1} < Q < 3.40 \text{ nm}^{-1}$, where the modulus of the scattering vector is

defined as $Q=(4\pi/\lambda)\sin\theta$, the scattering angle being 2θ . The magnetic ordering of nano-Cr and polycrystalline chromium (poly-Cr) below RT has been studied by neutron diffraction from by using the high flux neutron diffractometer D20 at Institut Laue Langevin, Grenoble. The neutron wavelength used was 0.129nm. The measurements were performed by slowly cooling and warming the sample between RT and 2 K. The neutron powder diffraction patterns were collected by the position sensitive detector ranging in $5 \text{ nm}^{-1} < Q < 72 \text{ nm}^{-1}$.

3. CRYSTALLINE MICROSTRUCTURE

The neutron and X-ray diffraction patterns show that nano-Cr has a bcc-type structure without any texture and they are free from any Cr oxide nor any other metallic impurity peaks. The neutron diffraction peaks of nano-Cr are broader than the instrumental resolution function and it was concluded that the average grain size is about $D=27 \text{ nm}$ [4]. The X-ray diffraction pattern of am-Cr shows one broad maximum which corresponds to the position of the strongest Bragg peak (110) for the bcc structure of Cr. The Full-Width at Half-Maximum (FWHM) of this broad reflection corresponds to $\Delta Q =4 \text{ nm}^{-1}$ what implies a short correlation length, $\xi= 2\pi/\Delta Q = 1.5 \text{ nm}$, in am-Cr.

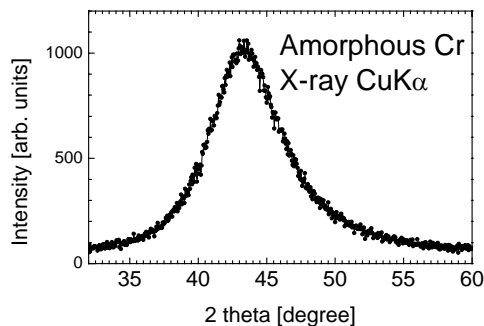


Fig. 2. X-ray powder diffraction pattern of amorphous Cr (am-Cr) measured by using CuK α radiation.

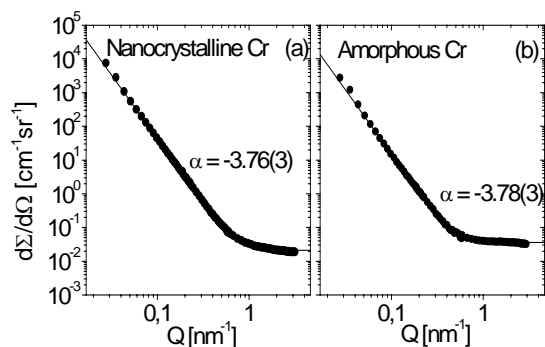


Fig.3. Radial SANS cross section measured for the nano-Cr(a) and am-Cr(b) samples (full circles). The straight lines correspond to the fitted power law function plus constant background. The resulting exponents are indicated.

The SANS cross sections measured for nano-Cr and am-Cr shown in Figs. 3a,b show a power-law $d\Sigma/d\Omega(Q) \propto Q^{-\alpha}$ with exponents $\alpha < 4$. For a system composed of scattering objects with well-defined smooth surfaces the Porod law predicts [10]: $d\Sigma/d\Omega(Q) \propto Q^{-4}$. The Porod law is not always fulfilled and there are several SAS studies where a $Q^{-\alpha}$ behavior with $\alpha < 4$ was found. These effects can be explained with the use of fractal models of microstructure [11,12]. Surface fractals with fractal dimensions $2 \leq D_S \leq 3$ contributing to SAS with exponents $3 \leq \alpha = 6 - D_S \leq 4$ were found in studies of lignite coal [13], sandstones [14] and Al/Al₂O₃ composites [15], whereas volume fractals with fractal dimensions $2 \leq D_V \leq 3$ giving exponents $2 \leq \alpha = D_V \leq 3$ were found in silica aerogels [16,17] and electrodeposited nano-Ni and nano-Co [8].

One can see that both cross sections shown in Figs 3a,b are similar: there is no saturation at low Q and the SANS signal can be fitted with a power-law dependence

$$d\Sigma/d\Omega(Q) = A \times Q^{-\alpha} + B$$

where B is the constant background due to incoherent scattering. The obtained values of the exponent α are 3.76(3) for nano-Cr and 3.78(3) for am-Cr. These results can be interpreted as a scattering on surface fractal objects with fractal dimensions of 2.24(3) for nano-Cr and 2.22(3) for am-Cr [4]. It is interesting to note that although the local atomic order probed by wide angle diffraction is very different in nano-Cr and am-Cr their large-scale microstructures probed by SANS are very similar. These fractal geometrical properties of the material can be due to specific conditions of the electrodeposition process.

4. MAGNETIC ORDERING

The magnetic ordering of Cr single crystals is of antiferromagnetic type superposed to a spin density wave (SDW) with a period of about 6.5 nm and the SDW wavevector directed parallel to the cubic [100] axis. For polycrystalline Cr above RT there is a simple antiferromagnetic ordering (AF) [1]. Between RT and 122 K the magnetic moments form the so-called transversal spin density wave (TSDW), shown schematically in Fig. 1, in which the magnetic moments are perpendicular to the SDW wavevector. At the spin-flip temperature, $T_{SF} = 122 \text{ K}$ the magnetic moments turn by 90° and they become parallel to the modulation direction forming the longitudinal (LSDW) ordering [1]. One of the best ways in which the TSDW ordering can be distinguished experimentally from the LSDW and AF

orderings is to use neutron diffraction [1]. The TSDW phase contributes to the fundamental Bragg peak (1,0,0) and also to the satellite peaks (1- δ ,0,0) and (1+ δ ,0,0), while for the LSDW and AF phases there is no intensity in the satellite peaks. The results of the powder neutron diffraction measurements on poly-Cr (fig. 4a) confirm the earlier literature reports about the spin-flip transition [1]. Down to 122 K there is clearly a TSDW ordering (satellites present) which changes by spin-flip towards the LSDW at 110 K (satellites absent).

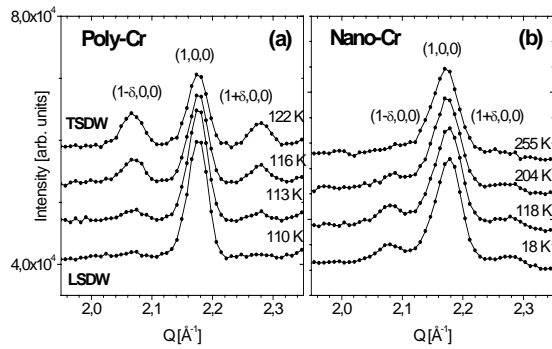


Fig.4. Temperature variation of the magnetic neutron diffraction signal of polycrystalline Cr (a) and nano-Cr(b). The central magnetic Bragg peak (1,0,0) and the satellite magnetic (1- δ ,0,0) and (1+ δ ,0,0) are marked.

The measurements for nano-Cr with a grain size of about 27 nm (fig. 3b) show a different behaviour [18]. Down to 250 K there is an AF ordering. Below 250 K some weak satellite peaks (1- δ ,0,0) and (1+ δ ,0,0) appear which are due to the TSDW phase.

There is no spin-flip transition and the satellite peaks exist down to 18 K. One can also note that the ratio of the satellite peaks intensity to the (1,0,0) peak intensity are smaller in nano-Cr as compared to the case of poly-Cr. It means that the magnetic ordering of nano-Cr below 250 K is not a pure TSDW phase but a mixture of AF, and TSDW phases [18]. The temperature dependence of the contributions of the AF and TSDW phases is shown in Fig. 5. The magnetic ordering observed at 2K has been studied by Rietveld analysis of the powder neutron diffraction data with the program FullProf [19]. The magnetic moment in the AF phase should not exceed the value of 0.42 μ_B reported for polycrystalline Cr at 4.2K by Bacon & Cowlam [20] and the amplitude of the magnetic moments in the TSDW phase should not exceed 0.62 μ_B reported in pure Cr at 4.2 K by Arrott et al. [21]. These two limitations lead to a unique solution [18] in which both phases have their maximal magnetic moments: 60% of the sample volume has the AF ordering with 0.423(13) μ_B and the remaining 40% volume has the

TSDW ordering with the amplitude of the magnetic moments 0.622(36) μ_B .

The magnetic phase transition observed near 250 K in nano-Cr is associated with a minimum of the lattice parameter of nano-Cr near 240 K. The thermal expansion of nano-Cr measured on warming shows also another minimum of the lattice constant near 210 K. Both these anomalies are associated with a jump of about 0.035% [18].

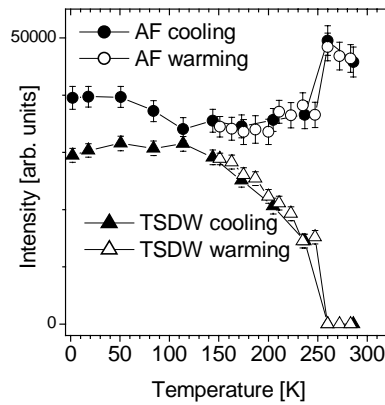


Fig. 5. Temperature dependence of the contributions of the AF and TSDW magnetic ordering in nano-Cr as determined from neutron powder diffraction data.

5. CONCLUSIONS

The magnetic ordering in nano-Cr is different as compared with conventional poly-Cr. This shows that the reduced crystallite size influences considerably the electronic and magnetic properties of chromium. It should be also noted that the magnetic properties depend strongly on the preparation method. It should be concluded that the relatively high density and fractal correlations in electrodeposited nano-Cr influence its magnetic properties. The present results should be compared with earlier neutron diffraction studies of fine Cr particles obtained by inert gas condensation by Tsunoda et al. [2] and plasma metal reaction method by Ishibashi et al. [3]. These studies were interpreted by assuming three kinds of Cr particles with different magnetic behaviour:

- smallest particles with the AF ordering below T_N .
- intermediate size particles in which the TSDW phase is stabilized below T_N (no spin flip).
- large size particles with the same ordering as Cr single crystals i.e TSDW above, and LSDW below the spin flip temperature of 123 K

The present results can be interpreted in a similar way. There is a majority of small and intermediate size particles with a little amount of large particles in the material. Above 250 K a simple AF ordering is observed as it was reported in polycrystalline Cr by Bacon & Cowlam [20]. Below 250 K the intermediate size particles become TDSW ordered, the magnitude of their ordering saturates near 110 K and remain constant down to 2 K.

6. ACKNOWLEDGEMENTS

Thanks are due to I. Sosnowska, R. Hempelmann, H. Natter, G. Rousse, P. Convert and W. Wagner. This work was supported by the E.C. Marie Curie Fellowship performed at Institut Laue Langevin, Grenoble (France) under contract HPMF-CT-2000-01002 and by the Polish Committee for Scientific Research (KBN).

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