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Irradiation Effects in Binary σ Phases

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The effect of fast-neutron irradiation on some binary σ phases has been studied by X-ray diffractometry. Radiation damage is evident in line broadening of the diffraction lines, relative intensity changes and anisotropic changes in lattice parameter. The fractional increase in the c parameter ($\Delta c/c$) is always greater than the fractional decrease in the a parameter ($\Delta a/a$). The observed changes are discussed in terms of the displacement and randomization of the constituent elements.

Introduction

Binary σ phases, which have a complex body-centred tetragonal structure, are generally formed from group VA and VIA metals of the periodic table with transition metals of the first, second and third long periods, and are of considerable interest theoretically and technologically. The present state of knowledge of formation and stabilization of the phase is adequately surveyed by Hall & Algie (1966). σ phases occur in steels, usually with harmful effects, owing to their extremely brittle nature, and since the phase might be present in some reactor materials, the significance of structural changes induced by neutron irradiation is important.

The crystal structure is well known and is described as a stacking of kagomé tiles by Frank & Kasper (1958), with the $A(0,0,0)$, $B(x,x,0)$, $C(x,y,0)$ and $D(x,y,0)$ atoms lying in the plane of the tile and the $E(x,x,z)$ atoms situated at intermediate positions between the pseudo-hexagonal rings of the kagomé tile. The A and D sites (coordination number 12) have the smallest volume, the B sites (coordination number 15) the largest and the C and E sites (coordination number 14) an intermediate value. The formation of the σ phase is associated with a high degree of order, in the sense that certain of the above crystallographic sites are preferred by the constituent elements. Wilson & Parselle (1965) in their work on irradiation effects on σ-MoRe, observed that this order is destroyed to some extent after irradiation. Anisotropic changes in lattice parameter were also measured, and it was postulated that these were a result of the redistribution of atoms in the lattice. The purpose of the present work was to investigate further the nature of radiation damage in additional binary σ phases. The atomic arrangement in the unirradiated state of the alloys used in the present work has already been established (Spooner & Wilson, 1964).

Experimental

Small powder samples of the following σ phases were irradiated in vacuo in aluminum cans in the reactor DIDO at the Atomic Energy Research Establishment, Harwell: MoIr28, MoOs35, NbOs40, CrRe60 and WOs67*. Integrated doses of 8×10^{19}, $1{\cdot}6\times10^{20}$ and $2{\cdot}4\times10^{20}$ fast neutrons were given to separate samples of each alloy. The integrated slow neutron dose accompanying the fast dose was approximately the same as the fast dose.

The activity induced in some of the specimens was extremely high, resulting in excessive radiation background and the necessity for remote handling. Diffractometer traces were taken at A.E.R.E. Harwell using W $L\alpha$ radiation, the specimens being prepared and mounted remotely onto the diffractometer. Monochromatization of the X-ray beam after diffraction from the specimen was achieved with a bent quartz crystal, and the subsequent detection by a proportional counter and pulse height analyser reduced the background activity to a reasonable level. The traces used in the analysis of the unirradiated specimens (Spooner & Wilson, 1964) were taken on a Hilger diffractometer using Cu $K\alpha$ radiation at Shrivenham, and in order to facilitate direct comparison with the irradiated traces, additional traces were taken of the unirradiated specimens at A.E.R.E.

Results

The diffractometer traces of all the specimens showed evidence of radiation damage in changes in width, intensity and position of the crystallographic reflexions, but, unfortunately, a combination of increased radiation damage and the increased background level prevented any quantitative measurements on traces of the most highly irradiated specimens. Measurements of changes in intensity, line displacement and line broadening were obtained for all the other alloys apart from CrRe, which did not yield any information on lattice parameters.

Lattice parameters were measured to an accuracy of about ±0·002 Å with the use of the extrapolation

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* The alloys will be presented in this way throughout this work, the first and second components being denoted X and Y respectively, the number being the atomic percentage of the Y constituent.

method of King & Massalki (1962), and these are presented in Table 1 together with the parameters before irradiation. In all cases there is an increase in the c parameter and a decrease in the a parameter, the fractional change $\Delta c/c$ always being greater than $\Delta a/a$. This is consistent with the results of Wilson & Parselle, which are also presented in Table 1 to facilitate comparison. The main difference between the two sets of results is in the volume changes of the unit cell, which in the present work show a slight decrease in many cases. In view of the relatively large changes in lattice parameter and the complexity of the structure, it is thought that these small volume changes have little real significance.

The intensity measurements of the lower angle reflexions, presented in Table 2, indicate the irregular nature of the change between the irradiated and unirradiated specimens, particularly among some of the stronger reflexions. However, the presence of order or disorder is reflected in the intensity of the weaker low angle reflexions, particularly 101 and 111, which have little or no intensity in the disordered state, and 311, which is weak in the ordered state. The results given in Table 2, normalized for each particular alloy, show the observed intensities in the irradiated and unirradiated specimens together with the calculated intensities (recomputed for W $L\alpha$ radiation) for both ordered and random distribution of atoms. The order schemes used in the intensity calculations are those determined by Spooner & Wilson (1964) for the unirradiated alloys. There is a positive indication of disorder in all the irradiated alloys as was observed by Wilson & Parselle. These authors also noted an irregular change in the intensities of σ-WRe, a surprising feature since the scattering factors of the components are so similar that order has virtually no effect on the calculated inten-

Table 1. *Lattice parameter changes in irradiated σ phases*

σ-Phase	Neutron dose (nvt)	a (Å)	$\Delta a/a$ × 10^4	c (Å)	$\Delta c/c$ × 10^4	V	$\Delta V/V$ × 10^4	Reference*
MoOs35	Unirradiated	9·615	—	4·941	—	456·8	—	(i)
MoOs35	8×10^{19}	9·602	−13·5	4·974	+54·6	458·6	+39·4	(i)
MoOs35	$1{\cdot}6\times10^{20}$	9·585	−31·2	4·994	+107·3	458·8	+43·8	(i)
MoIr28	Unirradiated	9·631	—	4·957	—	459·8	—	(i)
MoIr28	8×10^{19}	9·610	−21·8	4·971	+28·2	459·1	−15·2	(i)
MoIr28	$1{\cdot}6\times10^{20}$	9·584	−48·8	4·986	+58·5	458·0	−39·1	(i)
WOs67	Unirradiated	9·634	—	4·986	—	462·8	—	(i)
WOs67	$1{\cdot}6\times10^{20}$	9·580	−56·0	5·010	+72·2	459·8	−64·8	(i)
NbOs40	Unirradiated	9·858	—	5·063	—	492·0	—	(i)
NbOs40	8×10^{19}	9·850	−8·1	5·080	+45·4	492·9	+18·3	(i)
MoRe55	Unirradiated	9·603	—	4·983	—	459·5	—	(ii)
MoRe55	8×10^{19}	9·590	−13·0	4·998	+30·5	459·7	+4·4	(ii)
MoRe55	$1{\cdot}6\times10^{20}$	9·584	−19·6	5·005	+43·1	459·7	+3·9	(ii)
MoRe68	Unirradiated	9·572	—	4·976	—	455·9	—	(ii)
MoRe68	8×10^{19}	9·565	−7·2	4·987	+21·9	456·3	+7·1	(ii)
MoRe68	$1{\cdot}6\times10^{20}$	9·561	−10·7	4·993	+35·6	456·5	+12·2	(ii)
WRe50	Unirradiated	9·628	—	5·013	—	464·8	—	(ii)
WRe50	8×10^{19}	9·628	−0·3	5·015	+3·4	464·9	+2·8	(ii)
WRe50	$1{\cdot}6\times10^{20}$	9·621	−8·0	5·032	+37·9	465·8	+21·9	(ii)

* (i) Present work. (ii) Wilson & Parselle (1965).

Table 2. *Intensities*

I_0 = Observed unirradiated; I_1 = Observed low dose; I_2 = Observed high dose; I_c = Calculated ordered; I_r = Calculated random.

σ-Phase	MoOs35					MoIr28					NbOs40				CrRe60				WOs67		
hkl	I_0	I_1	I_2	I_c	I_r	I_0	I_1	I_2	I_c	I_r	I_0	I_1	I_c	I_r	I_0	I_1	I_c	I_r	I_0	I_2	I_r
101	21	11	—	24	2	16	—	—	16	2	35	19	33	2	1	—	1	2	3	—	2
111	6	—	—	7	—	6	—	—	5	—	11	3	9	—	—	—	—	—	—	—	—
311	—	—	3	—	6	—	—	5	—	6	—	—	—	8	14	20	14	8	5	4	8
002	29	25	16	30	24	21	21	12	22	20	32	26	31	28	29	25	29	30	25	18	29
112 410	99	98	81	93	102	78	79	128*	74	81	96	81	104	115	121	83	127	119	117	93	116
330	38	36	36	36	45	30	31	40	27	36	35	38	40	50	49	75	50	52	64	48	52
202	27	28	25	28	40	20	26	36	21	32	29	42	32	47	49	80	50	49	47	85*	47
212 420	73	129	97	70	76	62	69	85	55	61	88	88	80	86	102	95	96	91	103	97	88
411	114	135	157	119	121	133*	195*	175*	87	96	132	114	124	135	143	128	138	141	237*	231*	138
331	70	31	60	64	57	60	57	51	49	45	75	106	68	65	70	47	68	67	68	60	66
222	12	14	14	16	13	11	10	—	13	11	14	23	18	16	17	14	17	16	14	24	16
312 430	18	11	11	18	15	11	11	15	14	12	19	23	22	18	10	14	14	18	17	23	18

* Overlapping impurity lines.

sities. A similar effect was found in the present work on WOs and cannot be accounted for.

Line widths were measured at half peak height, and although there was a general broadening of reflexions, the results were somewhat irregular. However, the measurements from all the traces of the various σ phases were averaged for each kind of reflexion, and were 2·68, 1·38 and 0·41 minutes of arc for $hk2$, $hk1$ and $hk0$ reflexions respectively. The significance of these will be discussed later.

Discussion

The most significant features of radiation damage in the σ phase are the disordering of the atomic arrangement and the nature of the lattice parameter changes. These effects have been observed in simple structures and are the direct result of the displacement and replacement of atoms in the damage process. In a complex structure such as the σ phase, interpretation of the anisotropic changes in lattice parameter is complicated by the fact that they could be attributed to concentrations of defects or changes in order.

The close packed rows of E atoms in the σ structure are very favourably aligned for a focusing mechanism to operate, where the E–E interatomic distances are well below the critical value for focusing (Gibson, Goland, Milgram & Vineyard, 1960). Furthermore, the ordering forces in the plane of the kagomé tile are very strong, as emphasized by Marcinkowski & Miller (1962). Thus, the expansion of the c parameter could be attributed to an enhanced transfer of energy down the close packed rows of E atoms with the preferential location of interstitial atoms between the (002) layers of the kagomé tile. Evidence in support of this is seen in the preferential broadening of reflexions with increasing l index.

Although there are certain anomalies in the observed intensities as mentioned previously, particularly in the case of WOs, two distinct common factors emerge from the intensity results presented in Table 2. They are (i) the presence of disorder, as indicated by the weak and missing reflexions, and (ii) the excessively low intensity of the 002 reflexions, which cannot be accounted for by disorder alone. It should be pointed out that both these features are evident in the results of Wilson & Parselle (1965). The planar nature of the structure ($z=0$ and $\frac{1}{2}$) and the location of the E atoms ($z=\frac{1}{4}$ and $\frac{3}{4}$) fixes the theoretical intensity of 002 at its minimum value for a given order scheme, and this reflexion is most sensitive to changes in z. Calculations show that the intensity of 002 can be reduced considerably, without serious discrepancy amongst the other reflexions, by displacing the planar atoms from their $z=0$ and $\frac{1}{2}$ positions. This is strong evidence for the presence of distortion within the planar network of the structure, with a corresponding decrease in the a parameter similar to graphite (Woods, Bupp & Fletcher, 1956) and boron carbide (Pease, 1954; Dugdale, 1955). This distortion could be a direct result of interstitial atoms between the planar layers or of changes in order within the layers.

The relative changes in lattice parameter between the different σ phases imply that defect structure alone cannot account for the observed irradiation effects, and that the order–disorder transformation must play an integral role. In Table 3, the irradiated σ phases are listed in order of relative change in c parameter for both low and high dose rates, together with the change in occupancy of each site in going from an ordered to a disordered state. The ordering arrangement of the σ phase is a complex combination of electronic and size factors (Hall & Algie, 1966; Spor, Claus & Beck, 1966), and existing evidence on the dependence of lattice parameter and order on composition (Kasper & Waterstrat, 1956; Stüwe, 1959; Wilson, 1963) shows that increasing the X content in a given σ phase results in an increase in both a and c, which is a direct result of the introduction of larger atoms. If a is controlled by the planar occupancy, and c by the E site occupancy, as suggested by Stüwe (1959), an increase in a and a decrease in c might be expected, but the converse is observed. It is apparent from Table 3 that the parameter changes follow closely the degree of order change in the A, B and D sites, particularly the latter, where the occupancy changes are much greater than in the C and E sites. This is in contrast to unirradiated alloys, where changes in composition largely affect the C and

Table 3. *Fractional change in* X *content for various sites in the order-disorder transformation*

σ-Phase	A	B	C	D	E	$\Delta c/c \times 10^4$	$\Delta a/a \times 10^4$	Dose (nvt)
MoOs35	+0·40	−0·35	−0·287	+0·587	−0·225	+54·6	−13·5	8×10^{19}
NbOs40	+0·20	−0·40	−0·40	+0·60	−0·15	+45·4	−8·1	
MoRe55	+0·45	−0·30	−0·05	+0·262	−0·175	+30·5	−13·0	
MoIr28	+0·20	−0·275	−0·275	+0·537	−0·150	+28·2	−21·8	
MoRe68	+0·30	−0·175	−0·175	+0·325	−0·175	+21·9	−7·2	
WRe50	—	—	—	—	—	+3·4	−3·1	
MoOS35	+0·40	−0·35	−0·287	+0·587	−0·225	+107·3	−31·2	$1·6 \times 10^{20}$
WOs67	—	—	—	—	—	+72·2	−56·0	
MoIr28	+0·20	−0·275	−0·275	+0·537	−0·150	+58·5	−48·8	
MoRe55	+0·45	−0·30	−0·05	+0·262	−0·175	+43·1	−19·6	
WRe50	—	—	—	—	—	+37·9	−8·0	
MoRe68	+0·30	−0·175	−0·175	+0·325	−0·175	+35·6	−10·7	

E sites, and the lattice parameter changes follow the expected pattern. The *A*, *B* and *D* sites are the most invariant in the ordered state, *A* and *D* being occupied by Y atoms and *B* by X atoms, and must play an important role in the stability of the σ phase. They are prominent in the stacking arrangement of the structure, the *B* sites in one layer occupying positions between the *A* and *D* sites in the adjoining layers. The transformation to disorder must disturb the stable electronic configuration associated with these sites, and it is conceivable that the introduction of a large number of the larger X atoms into the 12 coordination sites is responsible for the distortion within the kagomé layers and the observed parameter changes.

The importance of the *D* site has been emphasized by the work on ternary σ phases containing silicon (Aronsson & Lundström, 1957; Stüwe, 1959; Gupta, Rajan & Beck, 1960) where an increasing silicon content in the *D* sites produces parameter changes of the same sign as those observed in irradiated σ phases. Wilson & Parselle (1965) discuss the irradiation effects in σ-MoRe in terms of order changes in the *E* site and the importance of the *E–E* bond, but Table 3 shows that the *E* site changes are relatively small and approximately the same for each alloy. In the opinion of the present author, therefore, the comparatively large changes in occupancy of the *A*, *B* and *D* sites are the most important in determining parameter changes in irradiated sigmas.

Since the theoretical knowledge of stability and ordering arrangement is so uncertain, it is impossible to conclude absolutely the reasons for the observed structural changes in irradiated binary σ phases, but it seems most likely that the destruction of order in the *A*, *B* and *D* sites, coupled with defect clusters between the (002) planes, is responsible for the distortion of these planes and the observed effects.

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On the Indexing of Powder Patterns for Polycrystalline Materials of the Orthorhombic System

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An analytical method for indexing powder patterns of polycrystalline substances having orthorhombic symmetry is discussed. The technique is an extension of Neskuchaev's method for systems of intermediate symmetry. The procedure is applied to the indexing of the powder pattern for $NiAl_3$.

Introduction

An analytical method for indexing powder patterns of the orthorhombic system was suggested by Bradley & Taylor (1937) and later developed by Hesse (1948) and Lipson (1949). Neskuchaev (1931) suggested a method for indexing powder patterns of the tetragonal, hexagonal and rhombohedral systems and mentioned the possibility of extending it to include systems of lower symmetry. The method has not been widely applied to systems of intermediate or low symmetry, and in a previous paper (Barabash & Davydov, 1967) a development of