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DEVELOPMENT OF PROCEDURES FOR THE IDENTIFICATION OF MINOR PHASES IN HEAT-RESISTANT ALLOYS BY ELECTRON DIFFRACTION

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SUMMARY

The electron diffraction studies of 16-25-6 alloy have been extended to include a series of samples aged for 1, 10, and 1000 hours at 1200°F. The principal minor phase identified in the samples aged for 10 and 100 hours was an $M_{23}C_6$ carbide. In the sample aged for 1000 hours the principal minor phase identified was an M_6C carbide. In addition, the $M_{23}C_6$ carbide was identified as the principal minor phase in samples aged for 1 hour at 1600°F and 10 hours at 1400°F.

The results from the samples aged at 1200°F support the previous hypothesis that, in the aging process, the $M_{23}C_6$ develops first and is then transformed to the M_6C carbide. Comparison of the results from samples aged at 1200°F and 1600°F shows that as the temperature of aging is increased the time required for the transformation to take place decreases.

Work to develop suitable polishing and etching procedures for preparing samples of S816 alloy for study by electron diffraction methods has been continued during this period.

DEVELOPMENT OF PROCEDURES FOR THE IDENTIFICATION OF MINOR PHASES IN HEAT-RESISTANT ALLOYS BY ELECTRON DIFFRACTION

INTRODUCTION

In the previous progress report[1], electron diffraction studies of the minor phases of several 16-25-6 alloy samples were described, and a number of experiments to find suitable polishing and etching procedures for preparing samples of S816 alloy for diffraction studies were discussed.

The results of the electron diffraction studies of 16-25-6 alloy included the identification of an $M_{23}C_6$-type carbide as the principal minor phase in a sample of the alloy aged for 1 hour at 1400°F, and the identification of an M_6C-type carbide as the principal minor phase in samples aged for 1000 hours at 1400°F and for 10 and 500 hours at 1600°F. on the basis of these results it was suggested that the $M_{23}C_6$ carbide forms during the first few hours of aging and is then transformed to the M_6C carbide as the period of aging is increased. It was evident, however, that studies of the minor phases in additional samples of the alloy aged for short periods at 1400 and 1600°F would be required to afford adequate support for this hypothesis and to provide a detailed picture of the transformation process. Therefore, the work carried out during the period of this report has been largely concerned with extending the studies of this alloy.

The general experimental procedures employed were described in detail in an earlier report[2]. Briefly, the alloy samples are electrolytically polished and etched using reagents and conditions which preferentially attack the matrix and leave the minor-phase particles protruding slightly from the etched surfaces. Electron diffraction patterns are then obtained from the minor-phase particles by passing the electron beam across the etched surfaces at a grazing angle. These patterns provide a means for identifying the minor phases of the alloy.

In the previous work, S816 alloy was found to be unusually difficult to prepare for electron diffraction examination due to the formation of films of insoluble reaction products during electrolytic polishing and etching. A variety of electrolytic polishing solutions were tried and only a very few were found that were at all satisfactory. No suitable etching solutions were found. Inasmuch as it is not possible to make a satisfactory study of this alloy until these difficulties have been overcome, work on etching the S816 alloy has been continued.

All the alloy samples used here have been furnished by Dr. J. W. Freeman and his associates of the Department of Chemical and Metallurgical Engineering of this University. Close cooperation is maintained with this group to correlate the electron diffraction results with the results of their metallurgical studies.

EXPERIMENTAL

16-25-6

In order to obtain more detailed information concerning the influence of high-temperature aging on the development of minor phases in this alloy, several additional samples were obtained for study. These were supplied by Dr. J. W. Freeman of the Department of Chemical and Metallurgical Engineering of this University. The aging treatment of each is indicated in Table I. Samples 2-F and 2-G were selected to provide a more complete series of aging treatments at 1400°F and 1600°F, while samples 2-H through 2-K provide an equivalent series aged at 1200°F.

TABLE I

16-25-6 ALLOY SAMPLES

Sample	Aging Treatment*
2-F	1 hour at 1600°F
2-G	10 hours at 1400°F
2-H	1 hour at 1200°F
2-I	10 hours at 1200°F
2-J	100 hours at 1200°F
2-K	1000 hours at 1200°F

* All samples were solution treated for 2 hours at 2050°F and water quenched before aging.

The samples to be prepared for the electron diffraction studies were first abraded with metallographic emery paper through 3/0 grade and then electrolytically polished in a solution of 700 ml of ethyl alcohol (95%), 200 ml of perchloric acid (70%), and 100 ml of glycerine, using current densities of about 5 amperes per square inch.

The samples were etched electrolytically in a hot solution (70-80°C) of 10 g. CrO_3, 12 ml water, 60 ml phosphoric acid (85%), and 15 ml sulfuric acid (96%). Depending on the response of the individual samples, current densities of 0.1 to 0.5 ampere per square inch for periods of 10 to 120 seconds were used. After etching, the samples were rinsed immediately with running tap water, then with freshly distilled water, and finally several times with a 50-50 mixture of acetone and methanol (reagent grade, redistilled), and were then allowed to drain and air-dry.

The electron diffraction results from sample 2-K, aged 1000 hours at 1200°F, indicate that the principal minor phase in this sample is a carbide of the M_6C type. A typical diffraction pattern from this sample is reproduced in Fig. 1 and a representative set of d_{hkl} values and relative intensities is included in Table II.

Of the remaining three samples aged at 1200°F, two (2-I and 2-J) have been studied. The principal minor phase identified in each case was a carbide of the $M_{23}C_6$ type. A typical pattern is reproduced in Fig. 2 and the d_{hkl} values and relative intensities are included in Table II. In several of the patterns from each of these samples, there were some additional weak rings representing interplanar spacing about 2.22, 2.09, and 1.92A. These correspond to the strongest rings of the M_6C pattern and indicate the presence of small amounts of this material in these samples.

The diffraction patterns from samples 2-F and G, aged 1 hour at 1600°F and 10 hours at 1400°F, respectively, indicated that the principal minor phase of these samples is also the $M_{23}C_6$ carbide. The interplanar spacings and relative intensities are the same as those listed for this material in Table II. A typical pattern is reproduced in Fig. 3. In several of the patterns from each of these samples there were additional rings corresponding to the strongest ones of the pattern of the M_6C carbide. Since these rings were generally very weak in the patterns from sample 2-G, it appears that only a small amount of the M_6C phase is present in this sample. However, in several of the patterns from sample 2-F they were nearly as intense as the rings from the $M_{23}C_6$ carbide, indicating a relatively larger amount of the M_6C phase in this sample. One such pattern from sample 2-F is reproduced in Fig. 4. The fact that the M_6C rings were not of the same intensity relative to the $M_{23}C_6$ rings in all the patterns from this sample suggests that the action of the etching treatment is not the same in all cases. This matter should be carefully checked by electron microscope studies of the etched surfaces in order to insure that the diffraction patterns

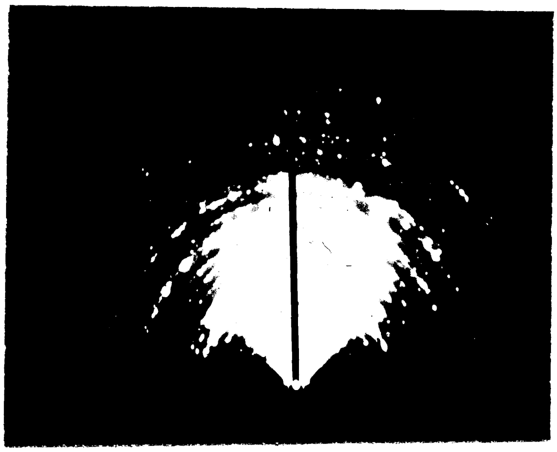

Fig. 1. Electron Diffraction Pattern of M_6C Carbide from Sample 2-K

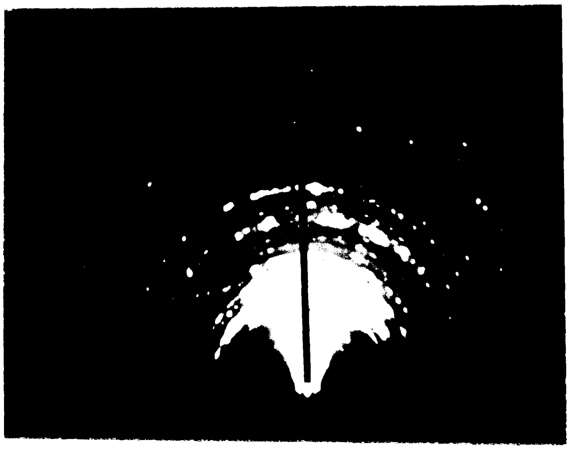

Fig. 2. Electron Diffraction Pattern of $M_{23}C_6$ Carbide from Samples 2-I and 2-J.

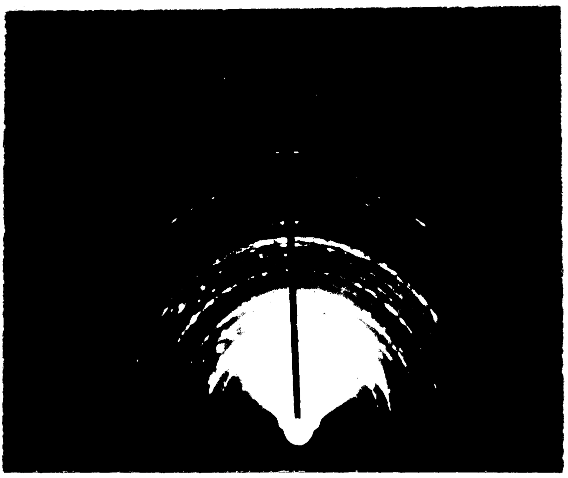

Fig. 3. Electron Diffraction Pattern of $M_{23}C_6$ Carbide from Samples 2-F and 2-G.

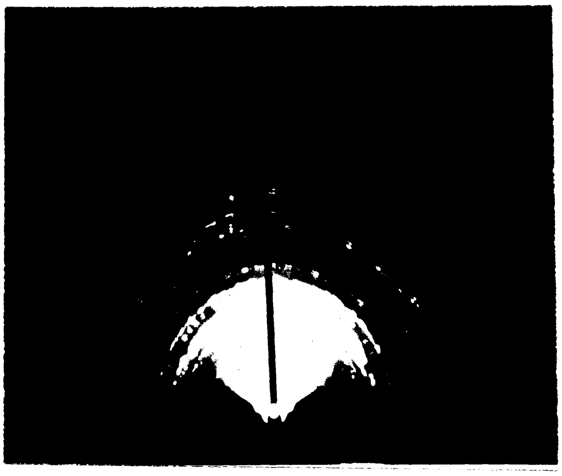

Fig. 4. Electron Diffraction Pattern of $M_{23}C_6$ and M_6C Carbides from Sample 2-F.

obtained are truly representative of the overall minor phase content of the sample.

TABLE II

INTERPLANAR SPACINGS AND RELATIVE INTENSITIES
FOR ELECTRON DIFFRACTION PATTERNS FROM 16-25-6 ALLOY

$M_{23}C_6$ Pattern from Samples 2-I and 2-J			M_6C Pattern from Sample 2-K	
d_{hkl}	I	hkl	d_{hkl}	I
6.2 Å	VW	111	6.3	W
5.4	VW	200	5.4	W
3.7	W	220	3.8	W
3.2	W	311	3.2	W
3.1	W	222	3.1	VW
		400	2.7	VW
2.46	M	331	2.49	W
2.38	MS	420	2.40	VW
2.16	S	422	2.22	S
2.05	S	511	2.10	VS
1.88	M	440	1.92	M
1.79	S	531		
		600	1.82	M
1.68	WM	620	1.72	W
1.62	W	533		
1.59	W	622	1.63	W
		444	1.56	VW
1.48	W	711	1.52	W
1.42	W	642	1.45	VW
1.38	W	731	1.41	W
1.33	VW	800	1.36	VW

S816 Alloy

Because the previous studies with S816 alloy indicated that most of the common electrolytic polishing and etching procedures would be unsatisfactory for use in preparing samples of this alloy for electron diffraction studies, it was considered important to look for other procedures which might be useful. Accordingly, three further approaches to the problem have been made.

First, a survey of the literature of the last ten years has been undertaken to look for new and different polishing and etching procedures which may be applied to this alloy. At the same time a bibliography of articles relating to other phases of the project is being compiled to provide a background of information which will be useful in interpreting the results of the research and in planning an expansion of the project.

Second, the use of immersion etchants is being considered. To date, two immersion etching solutions which are widely used in preparing stainless steels for metallographic examination have been tried. These are aqua regia and a solution consisting of 92 ml of concentrated hydrochloric acid, 5 ml of concentrated sulfuric acid, and 3 ml of concentrated nitric acid. Both these reagents produce heavy films on the S816 alloy and for that reason are not considered satisfactory for use in this work. The other commonly used immersion etching reagents will be examined in the near future.

Third, the addition of complexing agents to electrolytic polishing and etching solutions to prevent the formation of insoluble films is being investigated. Although extensive results are not available at this time, this approach does appear promising. The principal complexing agent which has been used to date is a commercial product marketed under the trade name of "Versene (Regular)" by the Bersworth Chemical Company of Framingham, Massachusetts. Chemically this material is the tetra sodium salt of ethylene diamine tetra acetic acid. It is reportedly capable of complexing any di- or trivalent ions in alkaline or acid solutions, and is stable except in strong oxidizing media such as acidic dichromate or permanganate solutions. The properties of Versene thus make it well suited for use in many electrolytic polishing and etching solutions. It has been used with some success in a 10% chromic acid solution (10 g. CrO_3 in 90 ml water). When the chromic acid solution is used as an electrolyte for etching 16-25-6 or S816 alloys, heavy films of reaction products are formed on the alloy samples, particularly those aged for long periods of time. The addition of a few per cent of Versene to the solution eliminated the film formation on 16-25-6 alloy samples and greatly reduced it on samples of S816 alloy.

DISCUSSION

The results of the electron diffraction studies of the series of 16-25-6 alloy samples aged at 1200°F provide some interesting and important information about the influence of high-temperature aging on the carbide precipitation in this alloy, particularly when compared with the results obtained from the samples aged at 1400°F and 1600°F. To facilitate such a comparison, all the results presently available for the three series of samples are combined in Table III below.

TABLE III

MINOR PHASES IDENTIFIED IN AGED SAMPLES OF 16-25-6 ALLOY***

Time of Aging (hrs)	Temperature of Aging 1200°F	1400°F	1600°F
1		($M_{23}C_6$)	$M_{23}C_6$*
10	$M_{23}C_6$*	$M_{23}C_6$*	(M_6C)**
100	$M_{23}C_6$*		
500			(M_6C)**
1000	M_6C**	(M_6C)	

* Small amounts of M_6C carbide also detected.

** Small quantities of $M_{23}C_6$ carbide also detected.

***All samples were solution treated at 2050°F for 2 hours before aging. Results enclosed in parentheses were reported and discussed in a previous report[1].

The minor phases identified in the series of samples aged at 1200°F support the conclusions reached in the last report, i.e., that, in the aging process, the $M_{23}C_6$ carbide forms first and then is transformed to the M_6C carbide as the period of aging is increased. In the samples aged for 10 and 100 hours the principal minor phase identified was the $M_{23}C_6$ carbide, while in the sample aged for the longer period of 1000 hours the principal minor phase is the M_6C carbide. This same trend is evident in the 1400°F and 1600°F series.

A comparison of the principal phases identified in the various samples of the 1200°F and 1600°F series shows that the period of aging required to produce the transformation from the $M_{23}C_6$ to the M_6C carbide decreases as the temperature of aging is increased. Thus, in the 1200°F series the $M_{23}C_6$ carbide remains the principal minor phase after 100 hours of aging, while the transformation is essentially complete in the 1600°F series after only 10 hours of aging.

The results in Table III can also be correlated with variations in the lattice parameter of the matrix phase of the alloy which are produced by the aging treatments. The lattice parameter variations shown in Fig. 5 represent part of the results of an investigation of the metallurgical

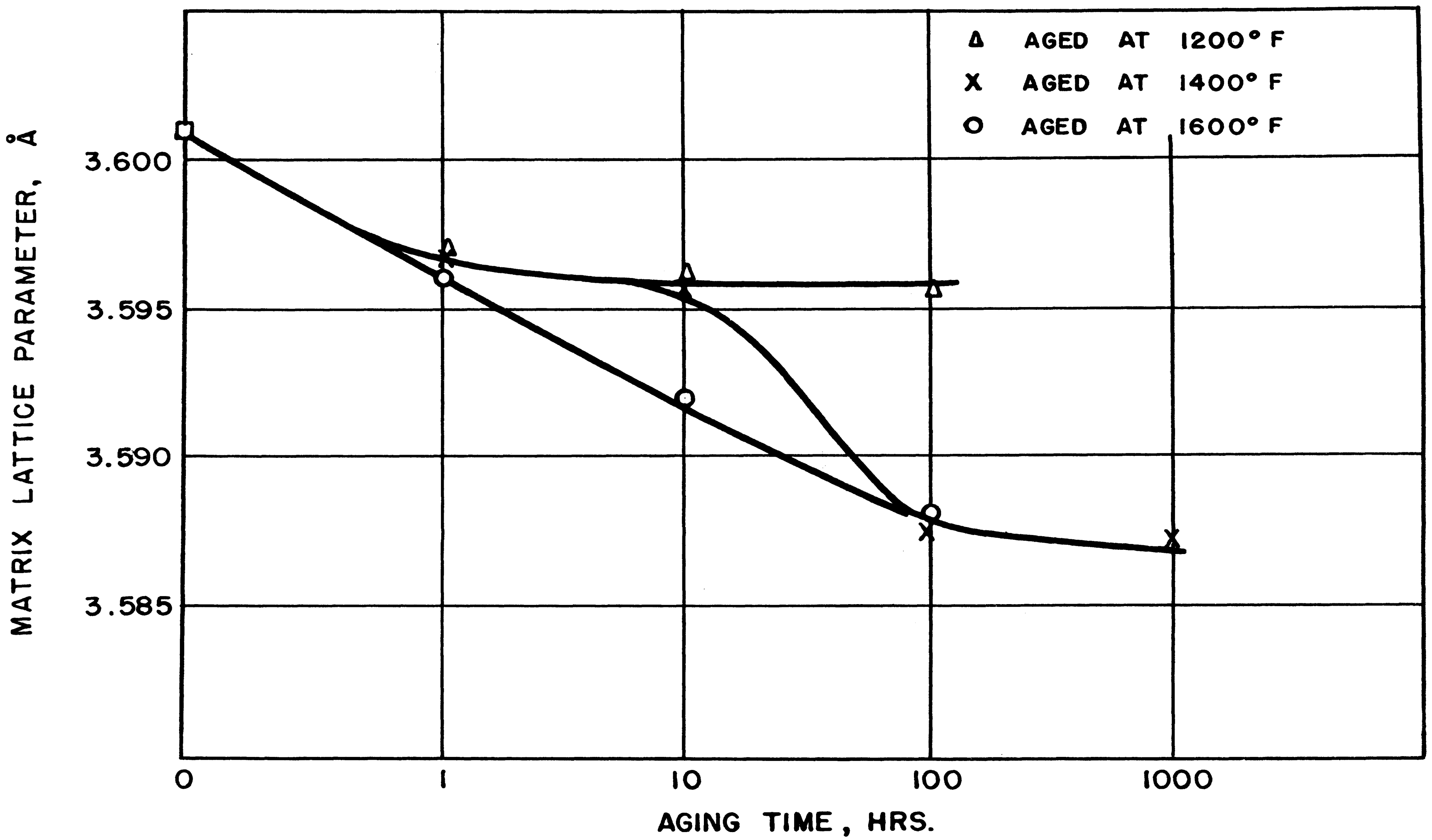

FIG. 5. INFLUENCE OF HIGH-TEMPERATURE AGING ON THE LATTICE PARAMETER OF THE MATRIX PHASE OF 16-25-6 ALLOY

properties of this alloy which was sponsored by the National Advisory Committee for Aeronautics and carried out under the direction of Dr. J. W. Freeman in the Department of Chemical and Metallurgical Engineering of this University. It will be noted that a decrease in the lattice parameter occurs during the first hour of aging at all three temperatures. In terms of the results obtained here, this decrease in lattice parameter is associated with the precipitation of the $M_{23}C_6$ carbide and may be due to the removal of large-radius atoms such as those of molybdenum from the matrix phase by the formation of the carbide. Further decreases in the matrix parameter can be related to the transformation of the $M_{23}C_6$ to the M_6C carbide. The fact that at 1200°F the matrix parameter does not show such a decrease after 100 hours of aging is in agreement with the observation that the $M_{23}C_6$ carbide remains the principal minor phase over this aging period. Since the M_6C carbide was detected in the sample aged for 1000 hours at 1200°F, the matrix parameter of this sample would be expected to be less than for the 100-hour sample. X-ray data are not available to check this point.

The general agreement of the matrix parameter data and the minor phases identified in the 1400°F and 1600°F series has been discussed in the previous report[1]. The additional minor phase data presented here for samples 2-F and 2-G of these series are in keeping with the previous conclusions.

The electron diffraction studies which have been completed to date provide identifications of the principal minor phases in representative samples of 16-25-6 alloy aged for periods up to 1000 hours at temperatures of 1200°F, 1400°F, and 1600°F. In view of the close correlation of these results with the lattice parameter studies, it does not appear necessary to include additional samples in this investigation. In continuing the examination of this alloy, there are two points which remain to be investigated: first, the extent to which all the minor phases which develop in the alloy have been detected and identified, and second, the amount, distribution, and composition of the minor-phase materials in the various samples.

Considerable information bearing on these points can be obtained from electron and optical microscopic studies of the polished and etched surfaces used in the diffraction studies. The effectiveness of the electron diffraction method in detecting the minor phases of alloy samples is largely dependent on the effectiveness of the polishing and etching techniques in exposing the minor-phase particles in the surfaces of the samples. This can be determined with the electron microscope. If it is found that the polishing and etching procedures leave essentially all the particles in the surfaces of the samples projecting above the matrix phase, then there is a reasonable basis for assuming that all the different minor phases present contributed to the diffraction patterns and therefore are subject to identification. The electron microscope studies will also permit a comparison of the size, form, and distribution of the precipitate particles in the various samples, and, when combined with optical microscope studies, may permit estimates to be made of the amounts of precipitates present. Information relative to the compositions of the minor phases may be obtained from the diffraction data, and from considerations of the elements present in the alloy and the possible effects on the lattice parameter of the matrix phase of removing small quantities of them from the matrix in forming the precipitates.

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