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Quantitative analysis of carbide and intermetallic phases in Type 316 stainless steel by X-ray diffraction

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Calibration curves for quantitative analysis by X-ray diffraction of precipitates in Type 316 stainless steel have been prepared using nearly "pure" $M_{23}C_6$ carbide and sigma phase. The method was checked by an independent technique using a Quantimet 720 Image Analysing Computer. Agreement of better than ± 10% of the amount of precipitates was obtained between the two techniques.

1. Introduction

Exposure of Type 316 stainless steel and its weld metal to elevated temperatures can cause the precipitation of a number of second phases, the major ones being $M_{23}C_6$, chi, sigma and Laves phase [1, 2]. The mechanical properties of the steel, especially impact strength and creep ductility, can be markedly affected by the formation of these second-phase particles [3, 4]. Unfortunately, detailed understanding of the kinetics and mechanism of precipitation of these second phases, as well as correlation with mechanical properties has hitherto been hampered by the lack of a good technique for quantitative determination of the relative amounts of the various carbides and intermetallic phases formed in the steel during ageing.

X-ray diffraction analysis of extracted precipitates is commonly used for identification and estimation of relative amounts of phases. This straightforward technique becomes complicated, even for qualitative analysis, when several phases are simultaneously present, producing a large number of overlapping peaks. Weiss and Stickler [2], using the Debye–Scherrer photographic technique, have attempted to quantify the relative amounts of phases by visual estimation of intensities; the results obtained are necessarily very rough approximations. Spruiell and Gehlbach [5] have made substantial improvements. They installed a graphite crystal monochromator on a Philips diffractometer and used silicon single crystals as substrates for the precipitate. They also used a computer method to calculate the structure factors of the various phases and used an iterative method developed by Giamei and Freise [6] to analyse the data from a large number of peaks. Although this represents a significant improvement over Weiss and Stickler's method, it still lacks an independent check on the accuracy of the theoretical calculations.

One of the most reliable procedures for quantitative X-ray analysis of powder mixtures is the internal standard method [3]. This method, however, requires the use of pure components to prepare a calibration curve. In this investigation we are able to use the internal standard method because we have obtained nearly pure sigma phase and $M_{23}C_6$ carbide by ageing some special Type 316 alloys.

2. Basis of the method

In the internal standard method of quantitative analysis for a component in a multicomponent system, the ratio of the intensity of the ith line of a component j (I_{ij}) to the intensity of the kth line of the standard components (I_{ks}) given by [7].

$$\frac{I_{ij}}{I_{ks}} = \text{constant}\, X \frac{x_j}{x_s} \qquad (1)$$

where x_j and x_s are the weight fractions of the component j and the standard component s in the

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mixture, respectively. Since a fixed amount of the standard component is normally added to all mixtures, a plot of I_{ij}/I_{ks} against x_j should give a straight line. ZnO was used as the internal standard in the present investigation. The amount of ZnO added was 25% of the weight of the mixture. The 101 (2.473 Å) peak of ZnO was used to prepare calibration curves with the 411 (1.938 Å) peak of sigma and three peaks of $M_{23}C_6$: 531 (1.805 Å), 422 (2.178 Å) and 511 (2.051 Å). (Three peaks are required for $M_{23}C_6$ carbide because of the possibility of overlapping with peaks of sigma, chi and Laves phase; the 411 peak of sigma is usually quite free from any overlapping).

3. Experimental procedures

3.1. X-ray diffraction

A Philips PW1050 vertical diffractometer fitted with a LiF curved crystal monochromator was used to carry out the X-ray diffraction analysis. Cu*K*α radiation was used.

The samples of precipitate were mounted on a silicon single-crystal substrate which was fitted to a rotating sample holder. This silicon substrate had been oriented so that no silicon reflections were obtained [5]. This technique reduces background radiation and greatly improves peak-to-background ratios.

The peaks of interest were scanned at 0.25° 2θ min^{-1} and the intensity profile was recorded on a chart. The integrated intensity of each peak was measured with a planimeter.

3.2. Production of pure components

Nearly pure $M_{23}C_6$ carbide was produced by ageing alloy A (see Table I) for about 3000 h at 625° C. The carbide was extracted electrolytically using an open cell method similar to that used by Leitnaker and Bentley [8]. Nearly pure sigma phase was produced by ageing a low carbon Type 316 steel (alloy B, Table I) for about 20 000 h at 685° C. This alloy was cold worked by 20 to 30% prior to ageing. Attempts to produce pure chi phase by solution-treating alloy B followed by ageing at 815° C were unsuccessful. The low carbon content of this alloy appeared to be conductive to sigma formation and extended the stability range of sigma to 815° C. However, this was not a serious setback because once the relative amounts of sigma and $M_{23}C_6$ carbide have been determined, the amount of chi can usually be found by subtraction, provided that Laves phase is not present in significant quantities.

3.3. Specimen preparation

Many factors are important in affecting the reproducibility of diffractometer measurements; crystallite size, sample thickness, preferred orientation, homogeneity of mixing, surface planarity and the amount of powder irradiated [7]. The necessity of evaluating the reproducibility of the technique every time after an alteration in the procedure makes development tedious, but was found necessary in many instances. The following procedure represents the final stage in a long development series.

After weighing, the powder sample was placed in a small (2 ml) polystyrene vial containing two clear acrylic ball pestles of 3 mm diameter. The vial was closed with a polystyrene clip-on cap and shaken at high speed in a complex three-dimensional motion in a Glen Creston Analytical mixer mill. After mixing, the homogeneous powder was placed directly onto the surface of the silicon crystal substrate with a small spatula. (Ideally the powder layer should cover an area of about 1 cm^2 and should be $> 10\,\mu\text{m}$ thick). A small drop of methanol was added to help to smooth out the layer and to make the powder adhere to the surface of the silicon crystal.

4. Results and discussion

4.1. Calibration results

Figs. 1, 2 and 3 show the strip-chart records of $M_{23}C_6$ carbide, sigma phase and a sample containing both $M_{23}C_6$ and chi phase, respectively. By mixing known amounts of $M_{23}C_6$ carbide and sigma, calibration curves for these two phases were obtained. An immediate benefit of this exercise was its contribution to qualitative phase identification. Owing to the large number of overlapping peaks of $M_{23}C_6$, sigma, chi and Laves phase and

TABLE I Chemical compositions

Alloy	C	Si	Mn	P	S	Cr	Mo	Ni	B	N
A	0.071	0.46	1.36	0.011	< 0.003	16.5	2.30	13.0	0.0032	0.036
B	0.003	0.34	1.49	0.004	0.006	17.5	2.26	13.9	< 0.0005	0.016

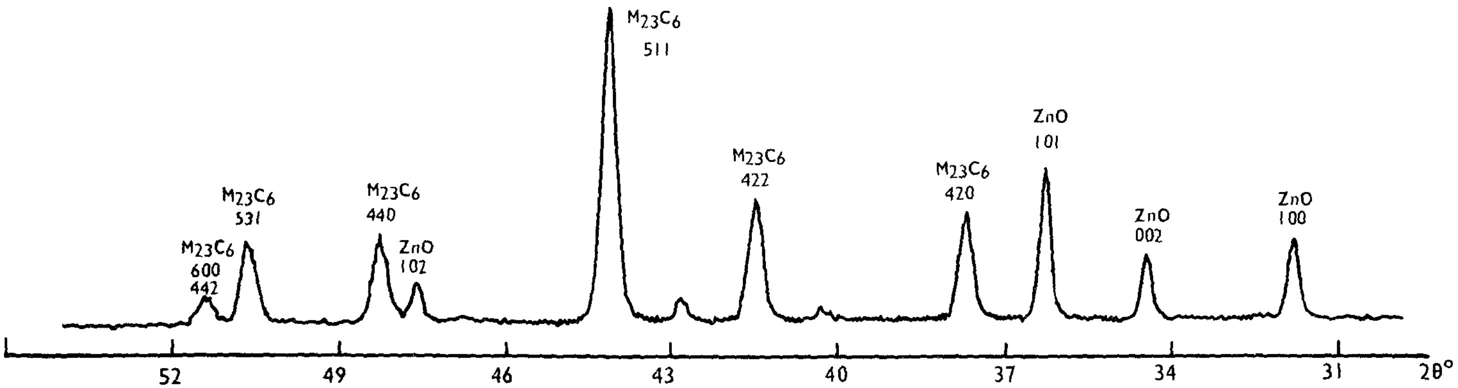

Figure 1 Diffractometer trace of $M_{23}C_6$. 0.25 g ZnO per g $M_{23}C_6$ was added as an internal standard.

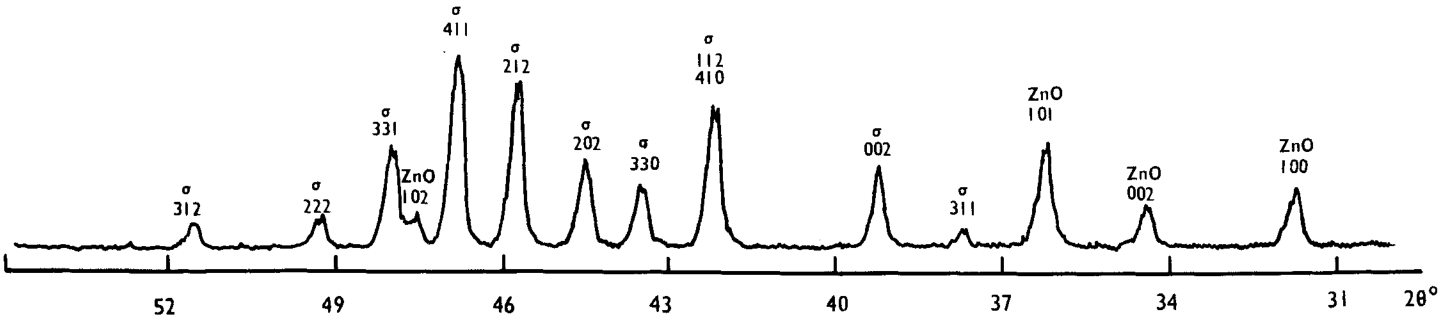

Figure 2 Diffractometer trace of σ. 0.25 g ZnO per g σ was added as an internal standard.

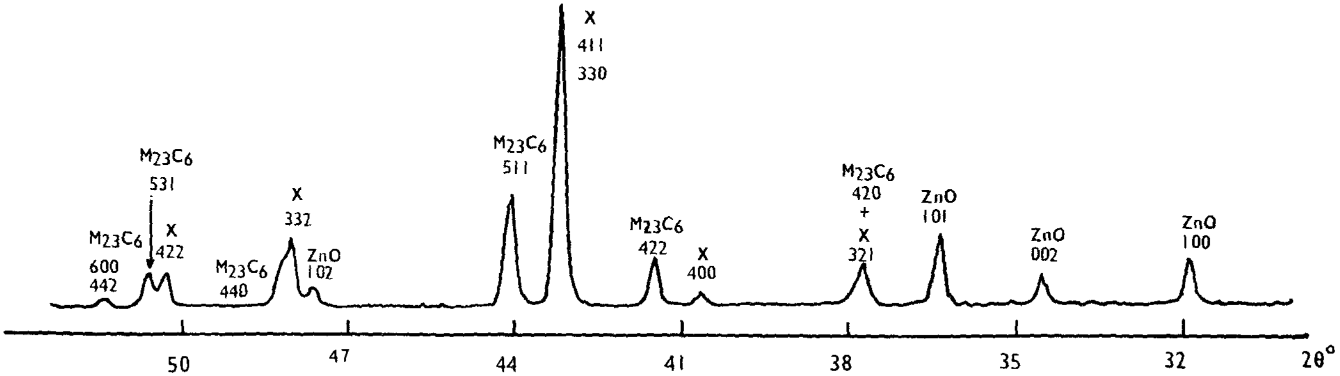

Figure 3 Diffractometer trace of alloy A, 815° C, 2932 h. A mixture of χ-phase and $M_{23}C_6$. 0.25 g ZnO per g mixture was added as an internal standard.

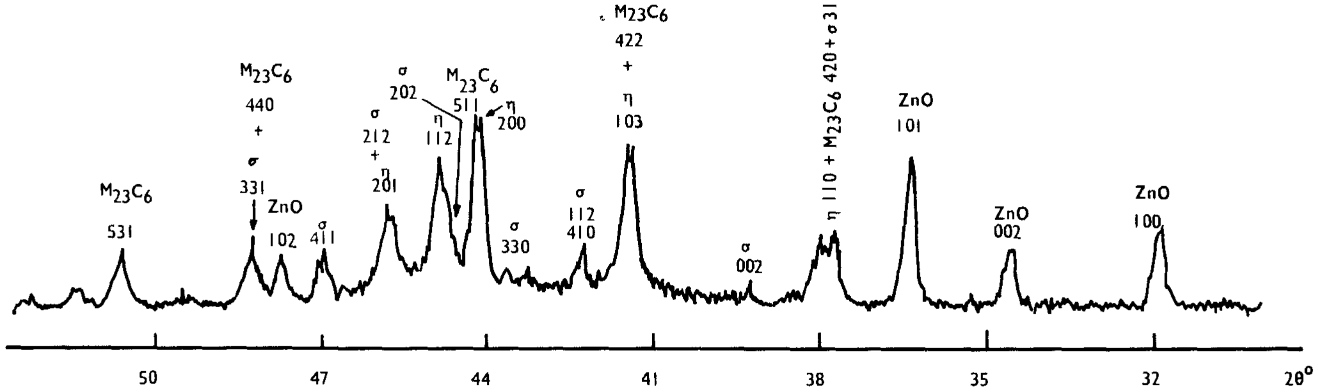

Figure 4 Diffractometer trace of alloy A, 685° C, 25445 h. A mixture of $M_{23}C_6$. σ and η phase. 0.25 g ZnO per g mixture was added as an internal standard.

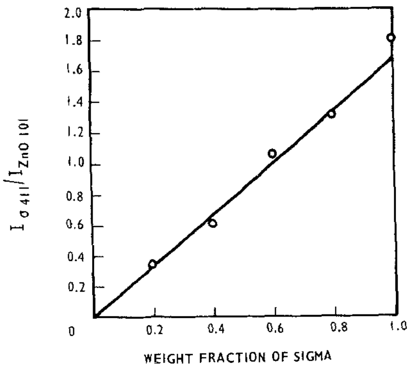

Figure 5 Calibration curve for sigma, 411 peak.

the small shifts in lattice parameters of these phases in Type 316 steel relative to those reported in the ASTM index, phase identification in Type 316 steel has up to now been very difficult. With the aid of the line profiles of the pure components, phase identification can now be performed rapidly by superimposing the pure component profiles onto the unknown profile. Fig. 4 shows a complex mixture of $M_{23}C_6$, sigma and Laves phase identified by this method.

Figs. 5, 6, 7 and 8 show the calibration curves for sigma, 411 peak and $M_{23}C_6$ 422, 511 and 531 peaks, respectively. All the points shown correspond to measurements from well-resolved peaks. Measurements from unresolved peaks are not included. It will be seen that good straight lines are obtained in all four figures.

The specimen mounting technique has the following objections: (1) it may lead to a degree of preferred orientation although rotating the sample goes some way to prevent this problem; (2) the specimen surface may not be planar. This primarily affects intensities at low 2θ angles and also leads to shifts of d-spacings from their true values. At higher angles the effect decreases rapidly.

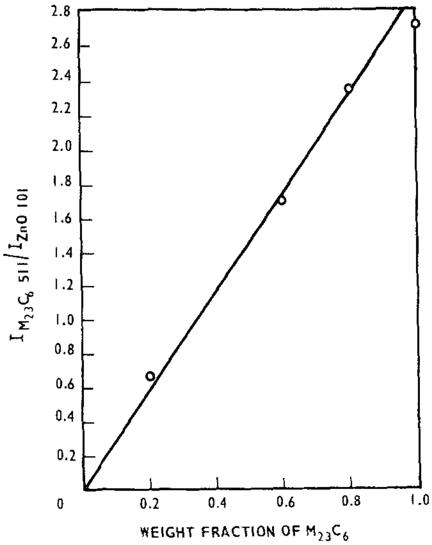

Figure 7 Calibration curve for $M_{23}C_6$, 511 peak.

For the present application, however, these disadvantages are more than offset by the simplicity of the method and the relatively small amount of powder required, especially when the supply of powder is very limited (e.g. the extracted precipitates from a creep specimen).

4.2. An independent check on the accuracy of measurement

The good straight lines obtained in Fig. 5 to 8 confirm the reproducibility of the technique and the validity of Equation 1 in the present investigation. However, the following objections may still be raised: (1) some of the precipitates may dissolve during extraction; (2) the compositions, especially the Mo content, of the $M_{23}C_6$ carbide and sigma

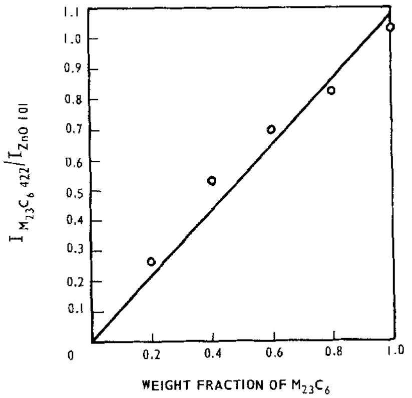

Figure 6 Calibration curve for $M_{23}C_6$, 422 peak.

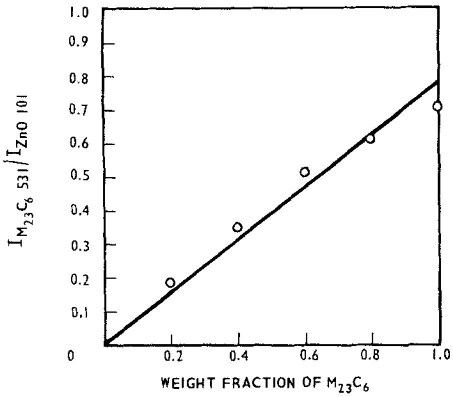

Figure 8 Calibration curve for $M_{23}C_6$, 531 peak.

phase may vary from cast to cast or may even depend on the ageing temperature, thereby causing small changes in the structure factors and consequent changes in the measured peak intensities. It is therefore necessary to have an independent check on the accuracy of this technique.

In a Type 316 steel specimen containing only two types of precipitates, i.e. $M_{23}C_6$ and chi, it is possible to measure the volume fraction of chi phase in the specimen by the Quantimet* using a selective etching technique [9]. This method can also reveal the size, distribution and morphology of the chi phase particles and has good reproducibility when the particles size is large (~ 1 μm). Lai and Meshkat [9] measured the volume fraction of chi phase as a function of ageing time at 815 and 750° C of a cast of Type 316 steel, the composition of which is given in Table I (Alloy A). These specimens contain only $M_{23}C_6$ and chi precipitates. Knowing the total weight of precipitates, the amount of $M_{23}C_6$ can be found by subtraction. The volume fraction of chi phase is approximately the same as the weight fraction, since the density of chi phase is nearly the same as that of the austenite matrix. The weight fractions of chi phase and $M_{23}C_6$ carbide determined by the Quantimet (QTM) method and by X-ray diffraction are compared in Table II. The agreement between the two methods is better than ± 10% of the amount of precipitate.

We have no independent method of checking the calibration curve for sigma and in the absence of any new information, values deduced from Fig. 5 can be taken as the best possible estimate at present.

4.3. Quantitative determination when four precipitate phases are present

We have so far obtained the calibration curves for $M_{23}C_6$ and sigma. In any three component mixture containing these two phases, the component can be found by subtraction but with three- and four-component mixtures containing Laves and chi the amounts of these two phases cannot be determined at present.

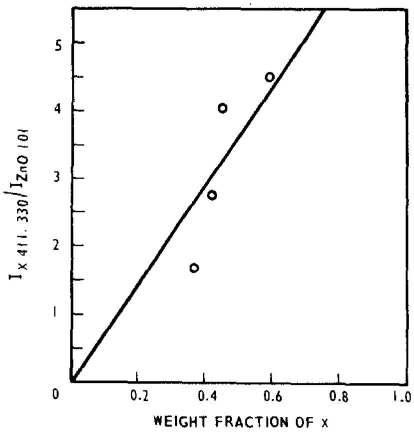

Figure 9 Calibration curve curve for χ; 411 and 330 peak.

TABLE II Comparison of QTM and X-ray results

Specimen	Wt fraction of $M_{23}C_6$ (%)		Wt fraction of χ (%)	
	QTM	X-ray	QTM	X-ray
815° C 1156 h	0.87	0.89	0.55	0.53
815° C 2000 h	0.93	1.03	0.85	0.75
815° C 2932 h	1.36	1.41	1.2	1.15
815° C 5000 h	1.27	1.21	1.69	1.75

Since we have not been able to produce "pure" chi phase (Section 3.2) we have to prepare a calibration curve for chi indirectly using the specimens listed in Table II. The strongest peak of chi at 2.09 Å (actually on overlap of the 411 and 330 peaks) was measured in each of the four specimens. Knowing the weight fraction of chi in these specimens a calibration curve for chi (Fig. 9) was prepared. The error is necessarily larger in this case because of the indirect nature of the analysis.

Another difficulty in a four component system is the large number of overlapping peaks. The sigma, 411 peak and the chi, 411 and 330 peak are usually quite free from overlap, but all the $M_{23}C_6$ peaks will have overlap to a certain extent. This is why three calibration curves for $M_{23}C_6$ are provided. The technique for dealing with line superpositions in a multicomponent system is fully described by Klug and Alexander [7].

5. Conclusion

An X-ray diffraction technique has been developed to determine the relative amounts of $M_{23}C_6$, sigma, chi and Laves phase in Type 316 stainless steel. The technique makes use of nearly "pure" $M_{23}C_6$ carbide and sigma phase to prepare calibration curves for analysis using the internal standard method. When this technique was checked by an independent method using the Quantimet, agreement of ± 10% of the amount of precipitates was obtained.

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*Quantimet 720 image analysing computer is made by Imanco Ltd.

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