Isolation, identification and quantification by X-ray diffraction of carbide phases in $2\frac{1}{4}$Cr–1Mo steel

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The addition of controlled amounts of phosphorus to $2\frac{1}{4}$Cr–1Mo steel, heat treated under two different conditions, has produced microstructures containing a wide spectrum of types and amounts of individual carbide phases. X-ray diffraction analysis of carbide precipitates has been undertaken following quantitative extraction by anodic dissolution of the matrix. By combining this with selective chemical dissolution of certain carbide types, calibrations of relative weight fractions against the intensities of suitable X-ray diffraction peaks may be obtained without the need for the addition of a standard calibration powder. This has allowed the determination of the absolute amounts, within a given steel sample, of the carbide types M_6C, M_7C_3, $M_{23}C_6$ and, most importantly, the creep-strengthening M_2X phase.

1. Introduction

During a study of the effects of minor alloying and impurity elements on the creep properties of $2\frac{1}{4}$Cr–1Mo steel [1], it was found that the relative amounts of various carbide types were strongly influenced by the level of phosphorus in the steel, both in the originally heat treated condition and following elevated temperature exposure. In particular, phosphorus enhanced the formation of the molybdenum-rich, face centred cubic (fcc) M_6C phase, where M represents a fixed total of metal atoms of different kinds. Molybdenum is a major creep strengthening element in $2\frac{1}{4}$Cr–1Mo steel, both when in solid solution [2–4] and when in the form of fine hexagonal close packed (hcp) M_2X type carbides or nitrides [5]. Concentration of molybdenum in the coarse M_6C precipitates will, therefore, lead to a loss of creep strength. Thus to examine the effect of impurity elements on creep strength, there is a need to determine the relative amounts of each specific carbide type as a function of material composition, initial heat treatment and degree of thermal exposure. Such a capability would also have more widespread applications

in the assessment of the integrity of high temperature components.

Electrolytic extraction techniques for determining the overall weight fraction of carbides and other second phase precipitates in steels have been well documented [2, 3, 6–8]. The extracted samples may then be examined using X-ray diffraction procedures and quantification of the relative amounts of specific types is possible through the internal standard method [9]. This method involves comparing the intensities of X-ray diffraction peaks from phases in the sample with a peak from a standard substance (mixed with the sample in a known proportion) and has been successfully used in austenitic steels [10]. However, the method suffers from drawbacks. First, the addition of the standard substance introduces further diffraction peaks into a multicomponent system where peak overlapping may already be a problem. Secondly, it is necessary to prepare calibrations of the standard substance against each phase, which involves first obtaining pure samples of each phase in isolation. This frequently requires using different steels, or

	C	Mn	Si	Cr	Ni	Mo	S	P
Composition (wt %)	0.09 ± 0.005	0.46 ± 0.001	0.28 ± 0.01	2.29 ± 0.02	0.15 ± 0.01	1.00 ± 0.01	0.011 ± 0.002	(1) 0.005 (2) 0.021 (3) 0.039 (4) 0.077

different heat treatment procedures, to produce single-carbide systems. The resulting precipitates may therefore differ in chemical composition, and hence in intensity of X-ray diffraction peaks, from those in the material being studied.

In this paper we describe techniques for isolating various carbides from multicomponent systems obtained from $2\frac{1}{4}$Cr–1Mo steel by electrolytic extraction. Calibrations of one carbide type against another are thereby produced, allowing full quantification of the phases present and avoiding many of the disadvantages of the internal standard method.

2. Experimental techniques and results

Controlled amounts of phosphorus (in the form of iron phosphide) were added to a base melt of $2\frac{1}{4}$Cr–1Mo steel, prepared by induction melting of the constituent elements in argon atmosphere, Table I. Two different heat treatment cycles were used, producing different carbide types and designated "overaged" and "commercial". The "overaged" heat treatment was designed to produce an overaged, coarse-grained bainitic microstructure typical of that encountered within the heat affected zones of weldments and comprised a two-stage austenitizing treatment; first for 2 h at 1423 K (1150° C) then furnace cooling to 1223 K with a hold time of $\frac{1}{2}$ h, followed by air cooling to room temperature and overaging for 16 h at 983 K (710° C). The "commercial" heat treatment involved austenitizing for 1 h at 1223 K (950° C), quenching into oil and tempering for 1 h at 923 K (650° C) to produce a fine-grained bainitic microstructure which is commonly encountered in high temperature components. This microstructure was subsequently modified by isothermal ageing at 823 K (550° C).

Precipitate phases were extracted by anodic dissolution of the matrix in a 10% HCl–methanol reagent. Samples of approximate initial weight 4 g were held at 1 to 2 V relative to a platinum cathode and the extracted carbide precipitates were separated by alternate centrifuging and washing in both distilled water and methanol. For each sample, three such dissolutions were undertaken for approximately 6 h each and the weight fractions of carbides (contained within air-tight vials) were determined after thorough drying. Each dissolution resulted in the loss of 1 to 2 g of sample, giving a reproducibility of ± 0.03% for typical weight fractions of between 1 and 2%. The conditions used were based on the results of other investigators [2, 3, 6, 7] who reported consistent and reproducible results for $2\frac{1}{4}$Cr–1Mo steel, with a minimum of precipitate loss due to dissolution during extraction.

X-ray diffraction analyses of the extracted carbide residues were undertaken on a JEOL X-ray diffractometer fitted with a lithium fluoride monochromator and a rotating specimen stage, using CuKα ($\lambda = 0.1542$ nm) radiation. For the "overaged" samples this identified two principal carbide types, the f c c $M_{23}C_6$ and M_6C types with lattice parameters of 1.06 and 1.10 nm, respectively. However, it was found that the relative diffraction peak intensities from these two types varied considerably with the phosphorus level of the steel, Fig. 1. In addition, for levels of phosphorus < 0.03%, weak diffraction peaks attributable to the h c p M_2X phase, where X is carbon and/or nitrogen, were observed. Although various combinations of M and X are possible in low alloy steels, the lattice parameters measured here ($a = 0.296$ nm, $c = 0.466$ nm) correspond most closely with those of molybdenum carbide, Mo_2C [11, 12].

As the first stage in determining the relative weight fractions of the various carbide types, concentrated nitric acid was added to known weights of carbide precipitates, in glass vials, which were subjected to ultrasonic agitation for 1 min every 5 min. In the first 5 min effervescence was observed, with liberation from solution of
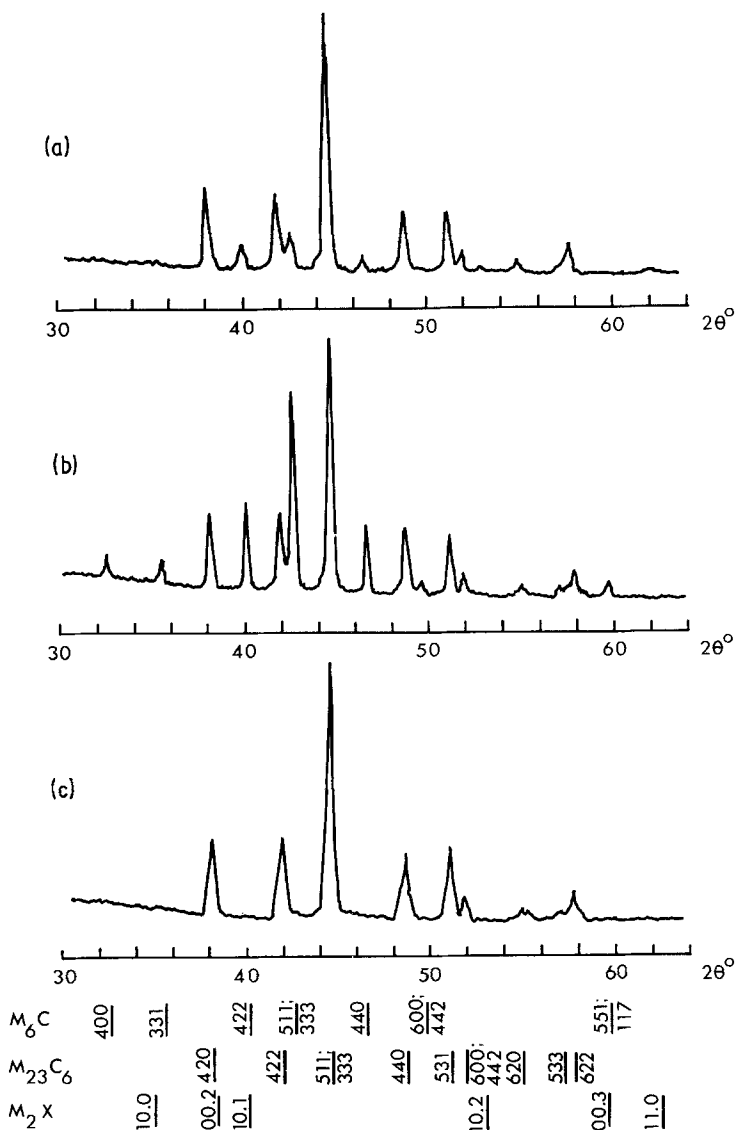
oxides of nitrogen. After 15 min the nitric acid was decanted after centrifuging and the precipitates were washed in distilled water and methanol, dried, re-weighed and re-analysed by X-ray diffraction. This showed that the M_6C and M_2X carbide types had been completely dissolved, the only diffraction peaks now observed being attributable to $M_{23}C_6$ precipitates; compare Figs. 1b and c. To ascertain whether any $M_{23}C_6$ had been dissolved, the nitric acid treatment was repeated (under the same conditions) with the remaining precipitates and the weight re-determined. This showed a further small weight loss in each case, 1.3% ± 0.3% of the remaining precipitate weights, which could be due to either limited solubility of $M_{23}C_6$ in

nitric acid, or losses during washing, or both. In either case, since the amount is small, it is reasonable to assume that a similar proportion of $M_{23}C_6$ was lost during the original dissolution and the weight estimate for M_6C precipitates was corrected accordingly. The amount of $M_{23}C_6$, and that of M_6C for phosphorus levels > 0.03%, can now be plotted as a function of phosphorus content, Fig. 2. For low phosphorus levels the method of quantifying the relative amounts of M_2X and M_6C types is described later, although the appropriate data points are included here and in Fig. 3.

The weight fraction of each precipitate type can be correlated with the relative intensities of various X-ray diffraction peaks since the two are
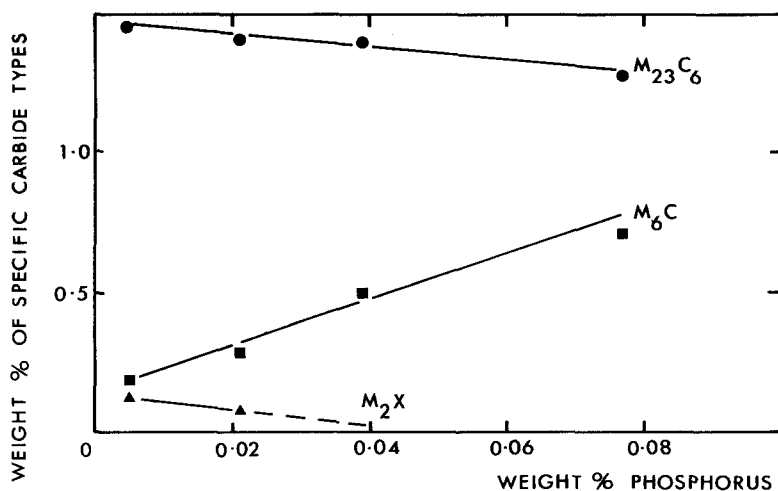
Figure 2 Proportions of various carbide types as a function of phosphorus level for "overaged" heat treatment.

proportional [9]. In theory, any non-overlapping peaks may be compared but obviously it is preferable to use the strongest when possible; the 440 M_6C peak at $2\theta \approx 46.5°$ and the $511, 333$ $M_{23}C_6$ peak at $2\theta \approx 44.5°$ provide good examples, Fig. 1. In view of the possibility of peak broadening due to variations in lattice parameter, together with additional broadening when the precipitate size is less than $\sim 0.1 \mu m$ [9], integrated peak intensities (i.e. rather than peak heights) were computed by area measurements. Intensity ratios for the $M_{23}C_6$ and M_6C carbide types are plotted as a function of weight ratio in Fig. 3. Confidence in the technique is provided by the good straight line fit through the origin, and from this graph the weight ratio of $M_{23}C_6$ to M_6C precipitates in an unknown mixture can be calculated directly from the X-ray peak intensities.

Precipitate phases were also electrolytically extracted, under the same conditions, from specimens subjected to the "commercial" heat treatment. This heat treatment produced the h c p M_7C_3 carbide ($a = 1.40$ nm, $c = 0.45$ nm) together with M_2X and a small amount of cementite (M_3C), initially with very broad peaks due to composition spreads [1] and the fineness of the precipitates [9]. Ageing at 823 K results in peak narrowing, the disappearance of M_3C and eventually the precipitation of M_6C carbides at the expense of M_2X, a process which is again strongly dependent on the phosphorus content of the steel. This is illustrated in Fig. 4, which shows a much higher level of M_6C (at the expense of Mo_2C) in the steel containing 0.04% phosphorus, compared to that containing 0.005% phosphorus, after 2000 h ageing. As before, concentrated nitric acid was added to
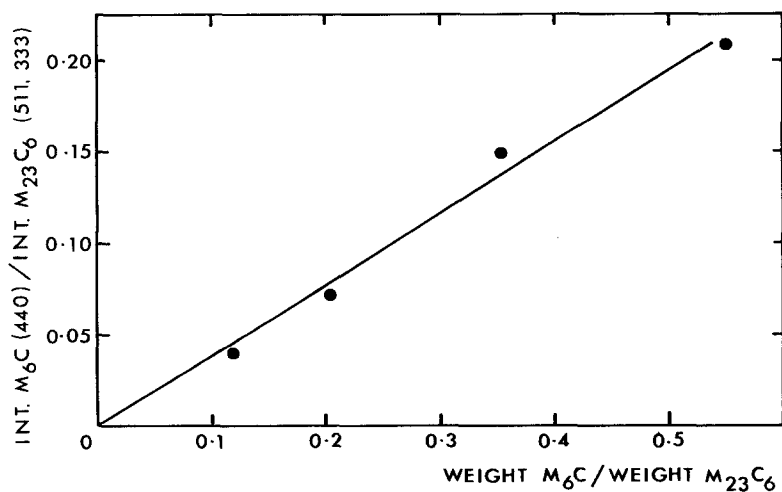

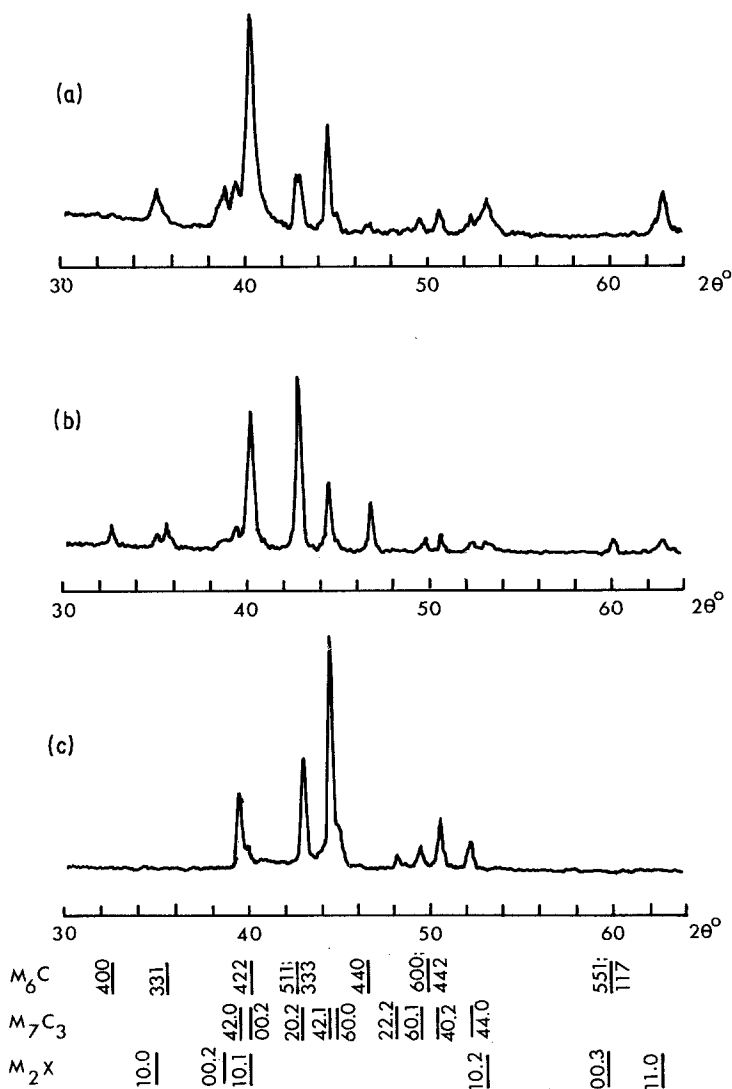*Figure 3* Intensity ratio/weight ratio calibration for M_6C and $M_{23}C_6$.

Figure 4 X-ray diffraction patterns, using Cu$K\alpha$ radiation ($\lambda = 0.1542$ nm), of carbides extracted from $2\frac{1}{4}$Cr–1Mo steel subjected to "commercial" heat treatment followed by ageing for 2000 h at 823 K: (a) 0.005% P; (b) 0.04% P; (c) as (b) but treated with nitric acid. Only the most intense M_6C and M_7C_3 peak positions are shown in the key.

known weights of precipitates which contained different ratios of these three precipitate types (M_7C_3, M_2X, M_6C) as a result of different degrees of ageing and/or phosphorus level in the steel. After washing, drying and re-weighing of the precipitates, X-ray diffraction showed that only the M_7C_3 carbide type remained, Fig. 4c, both the molybdenum-rich varieties (M_2X and M_6C) having been dissolved in the nitric acid. Re-subjecting the residue to the acid treatment resulted in a greater weight loss than previously, 3.8% $\pm$ 0.3% of the remaining weight, but this loss is still considered to be sufficiently small for a similar loss to be assumed during the first dissolution, and the relative weights were corrected accordingly.

Since M_7C_3 is now available in isolation, cali-brations of this carbide type against both M_6C and $M_{23}C_6$ may be obtained using the extracted precipitates from the "overaged" heat treatment cycle. Known weights (from the high-phosphorus steels, containing only M_6C and $M_{23}C_6$ in known proportions) were added to known weights of M_7C_3 and homogenized by subjecting to ultrasonic agitation in methanol, centrifuging and drying. A problem with this mixture is that many of the most intense M_7C_3 diffraction peaks, Fig. 4c, overlap those from M_6C and $M_{23}C_6$, Fig. 1. An exception is the 4 2 . 0 M_7C_3 peak at $2\theta \approx 39°$ which, together with the 4 2 0 $M_{23}C_6$ peak at $2\theta \approx 38°$, was used for the calibration of these two types, Fig. 5. Although this particular combination of carbides is not encountered for the heat treatment
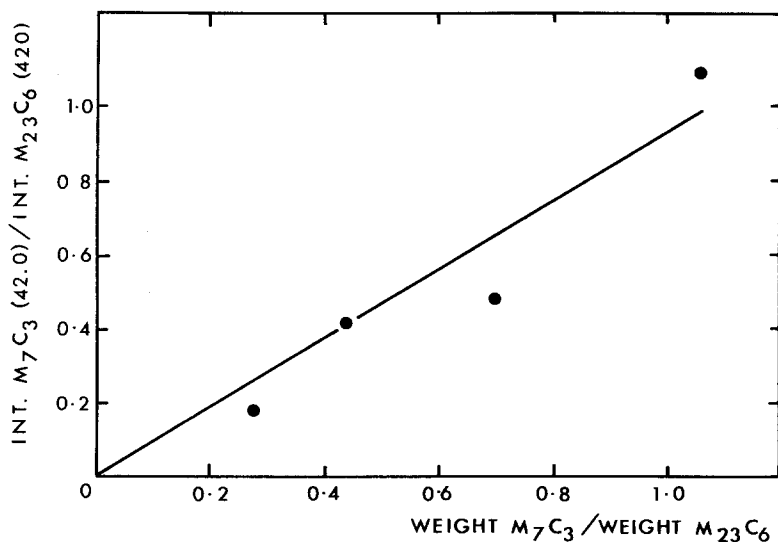
Figure 5 Intensity ratio/weight ratio calibration for M_7C_3 and $M_{23}C_6$.

cycles studies here, it is indeed possible in $2\frac{1}{4}Cr-1Mo$ steel as described by Baker and Nutting [13].

In the $M_2X/M_7C_3/M_6C$ mixture from the "commercial" heat treatment, the 42.0 M_7C_3 peak is obscured by those from M_2X but the strong group of M_7C_3 diffraction peaks (42.1, 21.2, 60.0) in the range $2\theta \approx 44$ to $45°$ is not overlapped, Fig. 4. In the $M_7C_3/M_6C/M_{23}C_6$ mixture the contribution of M_7C_3 in this angular range may be isolated by subtracting the area of the overlapping $M_{23}C_6$ ($5\,1\,1$, $3\,3\,3$) peak; this area was inferred from that of the non-overlapped $4\,2\,0$ peak, the ratio between these two peak areas (~ 3.24) being determined from pure $M_{23}C_6$, Fig. 1c. A calibraton of M_6C ($4\,4\,0$ peak) against M_7C_3, suitable for use with the carbides from the "commercial" heat treatment was thereby produced, Fig. 6. Since the weight

fraction of M_7C_3 in the mixtures subjected to nitric acid dissolution is known, it is possible to derive the weight fraction of M_6C from Fig. 6. The weight fraction of M_2X is therefore given by the difference, enabling calibrations of this precipitate type (using the 11.0 peak at $2\theta \approx 62.5°$) against M_6C and M_7C_3, Figs. 7 and 8. The relative fractions of these three precipitate types in an unknown mixture from a "commercial" heat treated specimen may now be determined directly from Figs. 6 to 8 without the need for further dissolution in nitric acid. Indeed the only binary mixture of the four precipitate types studied for which a calibration has not been presented is $M_2X + M_{23}C_6$, and this may be derived indirectly from the gradients of, for example, Figs. 3 and 7, using M_6C as a common reference for calibration. Fig. 7 was used for obtaining the data points for the lower phos-
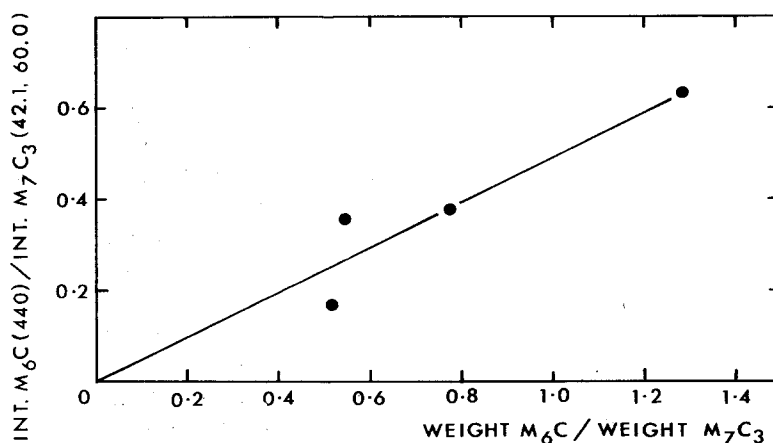

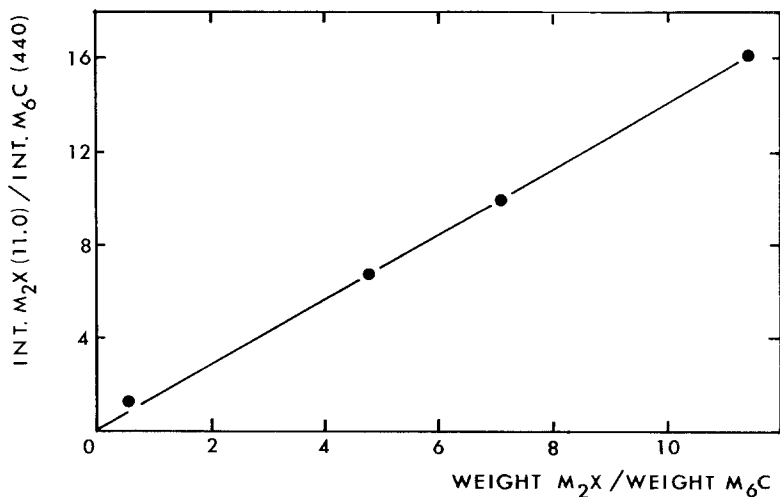*Figure 6* Intensity ratio/weight ratio calibration for M_6C and M_7C_3.

Figure 7 Intensity ratio/weight ratio calibration for M_2X and M_6C.

phorus "overaged" steels, in which small amounts of M_2X were present, Figs. 2 and 3.

3. Discussion

For many combinations of carbide types, the relative amounts may now be determined simply from the intensities of X-ray diffraction peaks from extracted residues, without the need for adding calibration powders. When overlapping of peaks is a problem, recourse may be made to the quantification of specific types by dissolution in nitric acid. For example, consider the situation where all four types, M_2X, M_6C, $M_{23}C_6$ and M_7C_3 are present. Here the main difficulty is that all the principal M_7C_3 peaks are overlapped by those of other precipitates. However, the ratio of M_6C to M_2X may be determined from Fig. 7, and dissolution of just these two types by the addition of nitric acid will give the absolute

amounts. The resulting residue of M_7C_3 and $M_{23}C_6$ may then be quantified from Fig. 5 since the 42.0 M_7C_3 reflection is no longer obscured by those from M_2X.

The carbide types studied are not specific to $2\frac{1}{4}Cr-1Mo$ and the general procedures described here may be extended to other steels. Of the carbides normally encountered in $2\frac{1}{4}Cr-1Mo$ steel, the only type not considered is the ortho-rhombic M_3C phase (cementite) [14]. This, however, is available commercially in the form Fe_3C, so calibrations against other carbide types may be produced which will be applicable to low alloy steels provided the incorporation of alloying elements into the phase does not significantly affect the structure factor. Further work is required in this area and a principal advantage of the techniques described here is that whilst minor variations in carbide compositions may
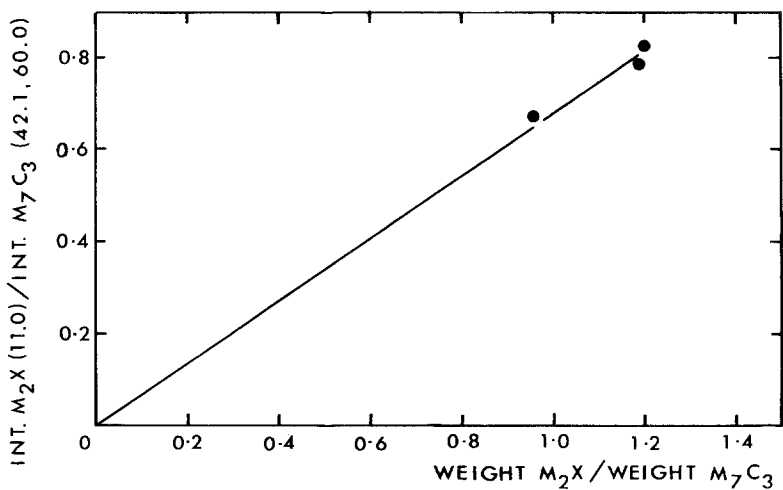

Figure 8 Intensity ratio/weight ratio calibration for M_2X and M_7C_3.

occur with heat treatment condition, impurity levels, etc., the calibrations are derived from carbides extracted from a specific steel and hence broadly characteristic of that steel in terms of composition and structure factor.

4. Conclusions

The carbides types M_2X, M_6C, $M_{23}C_6$ and M_7C_3 have been extracted from $2\frac{1}{4}Cr-1Mo$ steel by anodic dissolution. From mixtures of these types, the molybdenum-rich precipitates, M_2X and M_6C, can be preferentially dissolved by treatment with nitric acid. Advantage can be taken of this separation capability to quantify the amounts of each carbide present by X-ray diffraction analysis, without the need to add a standard calibration powder.

Acknowledgement

References

1. R. A. STEVENS and P. E. J. FLEWITT, CEGB Report No. SER/SSD/85/0020/R, *Acta Metall.* to be published.
2. R. L. KLUEH, *J. Nucl. Mater.* **68** (1977) 294.
3. *Idem, Mater. Sci. Eng.* **35** (1978) 239.
4. *Idem, Met. Trans.* **9A** (1978) 1597.
5. K. J. IRVINE, J. D. MURRAY and F. B. PICKERING, ISI Special Report No. 70 (Iron and Steel Institute, London, 1961) pp. 246–75.
6. J. M. LEITNAKER, R. L. KLUEH and W. R. LAING, *Met. Trans.* **6A** (1975) 1949.
7. R. L. KLUEH and J. M. LEITNAKER, *ibid.* **6A** (1975) 2089.
8. JIN YU and C. J. McMAHON, *ibid.* **11A** (1980) 277.
9. H. P. KLUG and L. E. ALEXANDER, "X-ray Diffraction for Polycrystalline and Amorphous Materials" (Wiley, New York, 1974).
10. J. K. L. LAI and I. F. GALBRAITH, *J. Mater. Sci.* **15** (1980) 1297.
11. K. W. ANDREWS, D. J. DYSON and S. R. KEOWN, "Interpretation of Electron Diffraction Patterns" (Adam Hilger, London, 1971) p. 203.
12. K. W. ANDREWS and H. HUGHES, *J. Iron Steel Inst.* **193** (1959) 304.
13. R. G. BAKER and J. NUTTING, *ibid.* **192** (1959) 257.
14. C. A. HIPPSLEY, *Met. Sci.* **15** (1981) 137.